# Kinetics of the Hydrodechlorination Reaction of Chlorinated Compounds on Palladium Catalysts

***by***

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## A Dissertation

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# Abstract

Hydrodechlorination is the reaction of a chlorinated organic compound (R-Cl) with hydrogen to form a carbon-hydrogen bond and HCl: R-Cl + $H_2$ = R-H + HCl. This reaction is used in refrigerant manufacturing, industrial by-product reclamation and waste management. These practical applications require in-depth understanding of hydrodechlorination reaction. In this research work, we studied four families of chlorinated compounds; $CF_3CF_{3-x}Cl_x$(x=1-3), $CH_{4-x}Cl_x$ (x=1-4), $CF_{4-x}Cl_x$ (x=1-4) and dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-), on supported palladium catalysts to create a theory capable of predicting the hydrodechlorination rate on chlorinated compounds and to explore the reaction mechanism.

A possible set of elementary reaction steps of hydrodechlorination reaction was proposed from our kinetics study of all these compounds. In this set of reaction steps, the irreversible scission of the first C-Cl bond in a chlorinated compound was proposed to be the rate-determining step; gas phase $H_2$ and HCl were suggested to be in equilibrium with surface H and Cl species; adsorbed Cl was assumed to be the most abundant surface intermediate. The overall rate of hydrodechlorination reaction could be derived from these reaction steps as $r=k'[R\text{-}Cl]/(1+K'[HCl]/[H_2]^{0.5})$. In this rate equation, k' is the product of the adsorption equilibrium constant of the chlorinated compound on catalyst surface times the rate constant for the scission of the first C-Cl bond scission step, and K' is the square root of the equilibrium constant for the equilibrium between $H_2$, HCl and their corresponding surface species: $2HCl + 2^* \leftrightarrow H_2 + 2Cl^*$.

The proposed reaction steps were examined by both isotope-exchange experiments and reaction energetics measurement. The hydrodechlorination reaction of $CF_3CFCl_2$ was performed in the presence of $H^{37}Cl$ to study the reversibility of C-Cl bond scission, and the removal of the first Cl atom from $CF_3CFCl_2$ was found to be an irreversible step. Hydrodechlorination experiments of $CF_3CFCl_2$ with $D_2$ and HCl mixture revealed that $D_2$ and HCl were in equilibrium with surface adsorbed hydrogen and chlorine during reaction. The forward rate and reverse rate of this equilibrium were at least 400 times higher than the overall hydrodechlorination rate. This result supported the assumption of equilibrium for $2HCl + 2^* \leftrightarrow H_2 + 2Cl^*$. Additionally, the activation energy for the rate determining step was extracted from hydrodechlorination reaction kinetics results of $CH_{4-x}Cl_x$ (x=1-4), $CF_{4-x}Cl_x$ (x=1-4) and dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-) compounds. It was found that for each of the series compounds, a linear relationship existed between C-Cl bond scission activation energy and gas phase C-Cl bond strength. This observation corroborates our assumption that the removal of the first Cl atom from a chlorinated compound is the rate-determining step in the hydrodechlorination reaction. Thus, all kinetic and isotope experimental results obtained from this study are consistent with the proposed reaction steps for the chlorinated compounds tested. This set of reaction steps can also be used to predict the hydrodechlorination reaction rate of a chlorinated compound, once its gas phase C-Cl bond energy is calculated and the turnover rate of a reference chlorinated compound with similar structure is known.

Some work has been done to study hydrodechlorination reaction steps and reaction intermediates beyond the rate-limiting step. Isotope tracing experiments with $D_2$ indicated that $CH_3$-, $CH_2$- groups adjacent to a C-Cl bond could undergo deuterium exchange. The study of reactions steps using *ab initio* methods, including calculation of rate constants, is also under way. Calculations for the $CH_{4-x}Cl_x$ (x=1-4) family showed that the heat of adsorption and C-Cl bond dissociation energy on a Pd surface were linearly related to their gas phase C-Cl bond strength.

Keywords: Hydrodechlorination reaction; Pd catalysts; Reaction steps; Reaction kinetics; Chlorinated compounds

# Extended Abstract

Hydrodechlorination reaction: R-Cl + $H_2$ = R-H + HCl is one important synthetic technique and has many applications. During this reaction, chlorine atoms are removed from the organic compounds as HCl and new C-H bonds are formed. This reaction can be used in refrigerant manufacturing, industrial by-product reclamation and waste management. These practical applications all require in-depth understanding of hydrodechlorination reaction.

The hydrodechlorination kinetics, such as turnover rates, selectivity and reaction orders have been presented for only a few chlorinated compounds. In addition, the hydrodechlorination reaction kinetics can vary considerably as the structure of the compound is changed. For example, the rate of hydrodechlorination for $CF_2Cl$-$CF_2Cl$ is 3000 times lower than that for the other isomer $CF_3$-$CFCl_2$. This relationship between reactant structure and hydrodechlorination reaction rate has not been fully explored. One objective of this research was then to create a theory capable of predicting the hydrodechlorination rate of chlorinated compounds and to explore the reaction mechanism. We approached this problem by studying four families of chlorinated compounds; $CF_3CF_{3-x}Cl_x$(x=1-3), $CH_{4-x}Cl_x$ (x=1-4), $CF_{4-x}Cl_x$ (x=1-4) and dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-), on supported palladium catalysts.

A possible set of elementary reaction steps of hydrodechlorination reaction was proposed from our study of all these compounds:

| | | |
|---|---|---|
| $R\text{-}Cl + * = R\text{-}Cl*$, | with an equilibrium constant $K_{CFC}$ | (1) |
| $R\text{-}Cl* \rightarrow \cdots$, | rate-determining step with a rate constant $k_0$ | (2) |
| $r = k_0K_{CFC}[R\text{-}Cl][*]$, | rate expression | (3) |
| $H_2 + 2* = 2H*$, | equilibrated step | (4) |
| $H* + Cl* = HCl + 2*$, | equilibrated step | (5) |
| $2HCl + 2* = H_2 + 2\,Cl*$, | (4) + (5), with equilibrium constant $K_0$ | (6) |
| $[*] + [Cl*] = [L]$, | site balance | (7) |
| $[*]=\dfrac{[L]}{1+\dfrac{[HCl]}{[H_2]^{0.5}}}$, | free site concentration | (8) |
| $R* + H* = RH + 2*$ | formation of hydrogenation product | (9) |

In this set of reaction steps the irreversible scission of the first C-Cl bond in a chlorinated compound was proposed to be the rate-determining step (step 2); gas phase $H_2$ and HCl were suggested to be in equilibrium with surface H and Cl species (step 6); adsorbed Cl was assumed to be the most abundant surface intermediate; hydrodechlorination products were formed by the combination of surface H and chlorinated organic compound fragments after losing Cl atoms (step 9). The overall rate of hydrodechlorination reaction could be derived from these reaction steps as $r=k'[R\text{-}Cl]/(1+K'[HCl]/[H_2]^{0.5})$. In this rate equation, k' is the product of the adsorption equilibrium constant of the chlorinated

compound on the catalyst surface (step 1) times the rate constant for the scission of the first C-Cl bond scission step (step 2), and K' is one half of the equilibrium constant for the equilibrium between $H_2$, HCl and their corresponding surface species: $2HCl + 2^* \leftrightarrow H_2 + 2Cl^*$. These steps are based on the following kinetic results: (1) It was found that for each of these four families of compounds, the rate of hydrodechlorination reaction could be related to the strength of the first C-Cl bond to be hydrogenated in chlorinated organic compounds, thus indicating that the C-Cl bond scission was involved in the rate limiting step; (2) the hydrodechlorination product HCl was found to be an inhibitor of hydrodechlorination reaction and its reaction order was negative for all the chlorinated compounds studied here, indicating adsorbed Cl was competing with chlorinated reactant for Pd active site, and this provided support for us to established the site balance [*] + [Cl*] = [L] (equation 7) (3) for a specific chlorinated organic compound, its hydrodechlorination reaction rate was found to be comparable on different types of Pd catalysts (Pd on different supports, Pd with different particle size and different Pd model catalysts, including Pd black, Pd (111), Pd (110) Pd foil), suggesting hydrodechlorination reaction might be structure insensitive and that the C-Cl bond scission might required only one Pd atom. Additionally, hydrodechlorination reaction selectivity was found to be independent of reaction conversion, suggesting that the different hydrodechlorination products were formed in parallel routes and these products were less reactive than the reactant itself.

It should be noted that this set of proposed reaction steps was deduced solely from kinetic measurement, thus we examined some of the steps by isotope-exchange experiments. The isotope experiments, to be described next, supported the proposed reaction steps. The hydrodechlorination reaction of $CF_3CFCl_2$ was performed with $H^{37}Cl$ to study the reversibility of C-Cl bond scission (step 2). Because HCl adsorbs and dissociates preferentially on the surface, the use of $HCl^{37}$ allowed the Pd surface to be saturated with $^{37}Cl$; if C-Cl bond scission is reversible then the reactant would be enriched in $^{37}Cl$. It was found that the ratio of $CF_3CFCl^{35}Cl/CF_3CFCl^{37}Cl$ in the reactant was close to 3.10, the natural $^{35}Cl/^{37}Cl$ ratio, which supported the proposed assumption that the first C-Cl bond scission step was an irreversible step. Hydrodechlorination experiments of $CF_3CFCl_2$ with $D_2$ and HCl mixture revealed that $D_2$ and HCl were in equilibrium with surface adsorbed hydrogen and chlorine during reaction. The forward rate and reverse rate of this equilibrium were at least 400 times higher than the overall hydrodechlorination rate. This result supported the assumption of equilibrium for step 6. Deuterium isotope effect in hydrodechlorination was also studied. It was found that the hydrodechlorination reaction rate with $H_2$ and with $D_2$ were similar, indicating that H or D was not involved in the rate-determining step. An experiment of $CF_3CFHCl$ with $H_2$-$D_2$ co-feed stream showed that $CF_3CFH_2$ was formed preferentially to $CF_3CFHD$ and this observation could be predicted using a combination of existing isotope effect theory and the proposed reaction steps.

The set of proposed reaction steps were also verified by studying the hydrodechlorination reaction energetics of these compounds. By definition, the activation energy of step 3 is the sum of two terms, one being the heat of adsorption of chlorinated compounds on the catalyst surface (step 1) and the other the activation energy of hydrodechlorination for the rate limiting step (step 2). We have found that the heat of adsorption on Pd surface of a chlorinated compound (step 1) is linearly related to its C-Cl bond strength using *ab initio* surface calculation technique. If the hydrodechlorination reaction rate-limiting step is indeed the removal of the first Cl from a chlorinated compound, then a Polanyi relationship should exist between the activation energy of step 2 and the C-Cl bond strength of the first C-Cl bond to break during reaction. In this way, activation energy of rate expression 3 would also show a linear dependence on C-Cl bond energy. Activation energy of rate expression 3 was calculated from hydrodechlorination reaction kinetics results of $CH_{4-x}Cl_x$ (x=1-4), $CF_{4-x}Cl_x$ (x=1-4) and dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-) compounds. It was found that for each of the three series compounds, a linear relationship did exist between C-Cl bond scission activation energy of step 3 and C-Cl bond strength. This observation indicates that our assumption that the first C-Cl bond scission step is the rate-determining step in hydrodechlorination reaction might be valid.

All the kinetic and isotope experimental results obtained from this study are consistent with the proposed reaction steps shown above (equations 1-7) for the chlorinated compounds tested. This set of reaction steps also has practical applications. For example, it can be used to predict the hydrodechlorination reaction rate of a chlorinated compound, once its C-Cl bond energy is known and the turnover rate of a reference chlorinated compound with similar structure is known.

It should be pointed out that the proposed set of reaction steps is still a simplification of the hydrodechlorination reaction network. Thus, future research of hydrodechlorination reaction kinetics should focus on studying hydrodechlorination reaction steps and reaction intermediates beyond the rate-limiting step. Some work has been done in this area during our study. Isotope tracing experiments with $D_2$ were used to examine the possible existence of C-H bond scission in H-containing chlorinated organic compounds. It was found that C-H bond scission was present in chlorinated hydrocarbons with a carbon chain greater than two carbon atoms. It was thus concluded that $CH_3$-, $CH_2$- groups adjacent to C-Cl bond could undergo C-H bond scission. The study of surface mechanism using *ab initio* methods, including calculation of rate constants, is also under way. Preliminary calculations for the $CH_{4-x}Cl_x$ (x=1-4) family showed that the heat of adsorption and C-Cl bond dissociation energy on Pd surface of these compound were linearly related to their gas phase C-Cl bond strength. Other investigations to be carried out in our group include: in situ investigation of reaction intermediates using Raman and FTIR technique, and microkinetic modeling of the hydrodechlorination reaction.

Keywords: Hydrodechlorination reaction; Pd catalysts; Reaction steps; Reaction kinetics; Chlorinated compounds

# Chapter 1

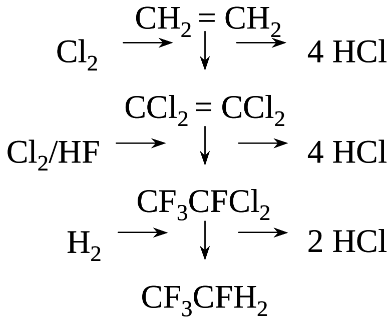
# Introduction

Hydrodechlorination reaction is the reaction between $H_2$ and an organic compound that contains C-Cl bond(s). During the reaction, chlorine is removed from the compound as HCl product and the original C-Cl bond is replaced with a new C-H bond (scheme 1).

$$\text{R-Cl} + H_2 = \text{R-H} + \text{HCl}$$

**Scheme 1: Hydrodechlorination reaction**

This reaction is applied in many syntheses that use chlorine-containing compounds as intermediates. For example, in the manufacture of $CF_3$-$CFH_2$, a widely used refrigerant, hydrodechlorination reaction is used to reduce the intimidate $CF_3$-$CFCl_2$ to the desired product (scheme 2)[1]. Hydrodechlorination reaction can also be used for the reclamation of undesired by-products into profitable commodities. One example is a Dow Chemical process in which waste 1, 2-dicholopropane is converted to reactant propylene[2]. Another example is the conversion of $CCl_4$, a by-product in many industrial chlorination processes and an potential ozone depletion agent, into valuable $CH_2Cl_2$, $CHCl_3$[3-6], which can be used as intermediates or solvents in organic synthesis. Additionally, hydrodechlorination reaction can be applied to destroy the C-Cl bond in compounds that need to be disposed of. Sometimes, this Cl removal is mandatory before a compound can be released into environment either due to the adverse effect of the chloro-containing compounds on ozone layer or due to the difficulty to naturally biodegrade these compounds. For example, hydrodechlorination reaction can be used to treat chlorinated aromatic by-products formed during petroleum refining process[7, 8]. This method has advantages over traditional incineration method that produces other harmful organic compounds during the high temperature destruction of chlorinated compounds. Another example for the application of catalytic hydrodechlorination in the area of pollution abatement is treatment of waste water that contains chlorinated compounds[9, 10].



**Scheme 2: Production of refrigerant $CF_3CFH_2$ via hydrodechlorination reaction**

There are growing interests and number of studies on the hydrodechlorination reaction of chlorine-containing compounds, especially CFCs (chlorofluorocarbons), after CFCs were scientifically linked to the depletion of the earth's ozone layer in the 1980s[1]. CFCs have many desirable properties, such as inertness, stability, and compressibility, which make them ideal choice as refrigerants. But these same properties also enable them to escape from the lower atmosphere without decomposition and contribute to stratospheric ozone depletion. In the process of searching for suitable CFC replacement compounds, it is found that HFCs (hydrofluorocarbons) have the same useful properties as CFCs and at the same time HFCs are much less harmful to the environment[11]. One of the many routes to produce HCFCs is the hydrodechlorination reaction of the CFCs catalyzed by a noble meal. This reaction can be used to transform the large amount of CFCs existing today into the more environmentally benign HFCs[1, 12].

It is thus apparent the knowledge of the nature of hydrodechlorination reaction is very important in order to tackle the current environmental problems such as the ozone depletion issue. In practice, the study of hydrodechlorination reaction can also benefit the industries that have large-scale hydrodechlorination processes and help them to determine and design the optimal reaction conditions for their hydrodechlorination reactions.

Although today there exist many hydrodechlorination reaction studies in literature, the kinetic turnover rates, selectivity and reaction orders have been presented for only a limited number of compounds, mostly CFC compounds; even less has been published to elucidate the possible reaction steps of the hydrodechlorination reaction. There are still many questions that need to be answered before one can gain a full understanding of hydrodechlorination reaction. These tasks include: a more systematic study of the hydrodechlorination reaction rates of all types of chlorinated compounds; measurement of hydrodechlorination reaction kinetics so as to provide more insight into the reaction steps; generalization of a possible mechanism that can be applied to describe the hydrodechlorination reaction of most chlorinated compounds, and more importantly, verify this reaction mechanism experimentally; to be able to predict the rate for any given chlorinated compound; and an understanding of product distribution during the reaction. Solving some of these issues will be the main focus of this research work presented here.

We will direct our efforts to the following research areas:

## 1. Study the hydrodechlorination reaction kinetics of series chlorine-containing compounds

Studying the kinetics of hydrodechlorination reaction has both theoretical and practical meaning. Firstly, the kinetic results of the hydrodechlorination reactions of different chlorinated compounds can offer clues to the possible reaction steps of this reaction. Secondly, the data obtained from the kinetic measurement can help industries that are interested in hydrodechlorination reaction in designing better and more efficient processes.

One challenge in the kinetic study of the hydrodechlorination reaction is that there exist a large number of chlorinated compounds and the reaction rates and selectivity are very dependent on the structures of the reactants. For example, ethane is the only saturated hydrocarbon with two carbons, but more than 40 saturated CFC compounds can be derived form ethane depending on the number, position and combination of hydrogen, chlorine and fluorine on the two carbons. This challenge can be also shown in the next example. Consider two isomers of $C_2F_4Cl_2$, one being $CF_2Cl$-$CF_2Cl$ while the other being $CFCl_2$-$CF_3$, due to the different position of chlorine atoms in the two molecules, the hydrodechlorination reaction rate of $CFCl_2$-$CF_3$ is almost 3000 times higher than the rate of $CF_2Cl$-$CF_2Cl$[1]. Faced with this vast diversity of chlorinated compounds and the large difference in the kinetic behaviors of these compounds, it is quite impractical to attempt to measure the reaction kinetics, such as rates, reaction orders, and selectivity of each and every chlorinated compound. A method has to be devised so that the study of a few representative chloro-containing compounds can yield the most information and help us in understanding hydrodechlorination reaction mechanism.

Our strategy will be to systematically study the hydrodechlorination kinetics of families of chlorinated compounds with varying chlorine number in their molecules. These series compounds are: two carbons CFCs, including $CF_3$-$CF_2Cl$, $CF_3$-CFHCl, $CF_3$-$CFCl_2$, $CF_3$-$CCl_3$; chlorinated hydrocarbons, including $CHCl_3$, $CH2Cl_2$, $CHCl_3$, $CCl_{4;}$ one carbon CFCs, including $CF_3Cl$, $CF_2Cl_2$, $CFCl_3$; and dichloropropanes, including 1,2-, 1,3-, 1,1-, 2,2-dichloropropane. Hydrodechlorination reaction rates, reaction orders and selectivity will be measured for all these compounds and compared with each other to investigate how the difference in molecular structure can influence the reaction kinetics. It is going to be shown that for a family of chlorinated compounds, the rate of the hydrodechlorination reaction correlates very well with the bond strength of the first C-Cl to be broken in the reaction, which we have observed in the family of $CF_3$-$CF_2Cl$, $CF_3$-CFHCl, $CF_3$-$CFCl_2$, and $CF_3$-$CCl_3$ [13]. It is also found the reaction orders for these four compounds are quite similar. For this family of compounds, if the hydrodechlorination reaction rate and reaction orders of one compound are known and the C-Cl bond energies are know for all of these compounds, then the rate and reaction orders of other compounds in the family can be predicted with satisfactory accuracy. Based on these findings, we believe the study the hydrodechlorination kinetics of families of model chlorinated compounds is an efficient way of studying the relationship between structure of chlorinated compounds and their reaction kinetics.

Kinetic data are also important in deciding which steps are important catalytic reaction steps in the hydrodechlorination reaction. For example, in the hydrodechlorination reactions of $CF_3$-$CF_2Cl$, $CF_3$-CFHCl, $CF_3$-$CFCl_2$, $CF_3$-$CCl_3$, the bond energy of the C-Cl bond to break during reaction seems to have greater influence on reaction rates and thus indicate the scission of the first C-Cl bond in a chlorinated compound might be the rate-determining step; HCl is found to be of negative reaction order in hydrodechlorination reaction and is thus an inhibitor, indicating that HCl adsorption is another important step in the hydrodechlorination reaction and Cl might be an important surface species, occupying active surface sites. To further prove these hypotheses, for each of these three series, C-Cl bond energies and reaction rates will be calculated, measured and tabulated. We will try to find out if there is any relationship between C-Cl bond energy and the turnover rate for hydrodechlorination reaction in general and quantity this relationship. The effect of HCl on hydrodechlorination reaction will continue to be examined.

It is hoped that by applying this methodology of studying series chlorinated compounds, we can learn the reaction kinetics of more chlorinated compounds and at the same time generalize in-depth knowledge about the general properties, such as reaction steps, of the hydrodechlorination reaction of other chlorinated compounds.

## 2. Investigate the possible reaction steps of hydrodechlorination reaction

Probing the reaction steps of hydrodechlorination reaction is another focus of this proposed research work. If we can assemble a set of general hydrodechlorination reaction steps which is applicable for most chlorinated compounds, it will help us in predicting of reaction rates, reaction orders and probably even selectivity of large amount of chlorinated compounds. The study of the reaction steps is thus crucial for the understanding of the hydrodechlorination reaction. The question of possible reaction steps of hydrodechlorination reaction has only been addressed by a small number of research papers. The reaction steps suggested in the literature are normally deduced from reaction kinetic measurement and have not been tested experimentally. There are still some controversies about how hydrodechlorination reaction proceeds over catalyst surface. Such questions include what is the rate-determining step; what is the most abundant surface species; which steps are reversible. This research work will try to shed some light on these issues by using a combination of kinetic study and isotope tracing technique.

Firstly, a possible reaction steps will be proposed based on generalization of the kinetic study of the series chlorinated compounds described in the previous section. Vital information about the reaction steps can be extracted from the right explanation of kinetic data. For example, comparison of relative rates for the compounds in one series can reveal which step is important in determining the rate of the reaction; studying the reaction orders of different reactants in hydrodechlorination reaction can help one to identify the important surface species during reaction; the product distribution can give us clues about the possible reaction pathways leading to different products. In the process of studying reaction kinetics of the series chlorinated compounds mentioned before, we derived a set of Langmuir-Hinshelwood type of reaction steps to describe hydrodechlorination reaction. This proposed reaction steps suggests that the rate determining step is the scission of the first C-Cl bond in a chlorinated compound; and during the reaction, $H_2$ and HCl are in equilibration with the surface H and Cl[13, 14]. It will be shown later that this proposed reaction steps can be successfully used to predict the reaction orders, and rates of the hydrodechlorination reaction of most chlorinated compounds. But one defect of this proposed reaction steps is that it is deduced solely form kinetic data. It is a simplification of the complex reaction network in reality and thus cannot predict reaction selectivity, another key reaction property, of hydrodechlorination reaction. Based on this preliminary and partially successfully proposed reaction steps, we will continue our mechanistic study and update this set of reaction steps by investigating more chlorinated compounds' hydrodechlorination reactions. For example, the hydrodechlorination reaction kinetics of other chlorinated compounds will be used to further examine the validity of this proposed reaction steps. By doing this, we hope an accurate depiction of hydrodechlorination reaction steps can be obtained from the results of this reach work.

Secondly, and more importantly, the proposed reaction steps derived from kinetic experiments, though still simple and preliminary, must be proved with results from mechanistic experiments. The information from mechanism studies will not only help us determine the validity of the current proposed reaction steps but also offer us new insight into the hydrodechlorination reaction steps and the opportunity to improve the current proposed reaction steps. Some questions still remain for the proposed hydrodechlorination reaction steps. For example, the reversibility of C-Cl scission in the hydrodechlorination reaction needs to be studied, which is important in deriving the rate expression for the hydrodechlorination reaction; the forward and reverse rates of the proposed equilibration between the gas phase $H_2$, HCl and surface H, Cl must be quantified, and this information will be essential in identifying the rate determining step in the hydrodechlorination reaction and supporting the proposed Langmuir-Hinshelwood type of reaction steps. A suitable experimental technique must be applied to investigate those questions concerning the possible reactions steps. Isotopic tracing technique is a powerful tool in elucidating the mechanisms of heterogeneous catalytic reactions since they can reveal unknown phases of the reaction[15]. For example, by using isotope species as the reactants on one side of a reversible reaction, the forward and reverse reaction can be distinguished and thus might even be quantified so as to provide more information about the reaction steps, which cannot be easily achieved by using regular unlabelled reagents. Another advantage of using isotopic tracing method properly is that during the reaction, the reaction intermediates can be labeled and thus can be followed with mass spectrometry to explore the reaction pathways. Finally, isotopic tracing method is an *in situ* technology, that is, the mechanistic information gathered using this technique is representative of the reaction steps under the actual reaction condition, which makes the reaction steps deduced from this type of isotopic experiments both very realistic and convincing. In this research work, we will apply isotopic tracing method to test the proposed reaction steps. To clarify the reversibility of the C-Cl scission step, the suggested rate-determining step, $H^{37}Cl$ will be used as one of the reactants during the hydrodechlorination reaction to label the surface with $^{37}$Cl. By observing the $^{37}$Cl distribution in the products and the starting chlorinated compound, we hope to get the Cl-Cl breakage pattern for the chlorinated compounds during hydrodechlorination reaction, especially chlorinated compounds with multiple chlorine atoms in the molecules, such as $CF_3$-$CFCl_2$. The forward and reverse rates of the proposed equilibration between the gas phase $H_2$, HCl and surface H, Cl will be quantified by replacing $H_2$ with $D_2$ as one of the reactants in the hydrodechlorination reaction. In this way, the forward and reverse reaction can be distinguished by monitoring the change of HCl and DCl concentrations. The rate of the forward and reverse reaction rates can thus be exacted from the mass spectrometry data and compared with the overall hydrodechlorination reaction to support the quasi-equilibration in the suggested Langmuir-Hinshelwood mechanism. Additionally, by comparing the overall reaction rates of hydrodechlorination reaction with $D_2$ and hydrodechlorination reaction with $H_2$, the influence of the $H_2$ adsorption step on reaction rate can be found. This can help us to know whether $H_2$ adsorption step is rate determining or not and strengthen the view that C-Cl bond scission is the RDS in the hydrodechlorination reaction. Another important concept in the isotopic tracing study is the isotope effects. Isotope effects mean that when an atom in a reactant molecule is replaced by one of its isotopes, both the reaction equilibrium constant and the rate constant are altered. Measurement of the isotopes effects in the reaction can be informative in studying the reaction steps that involve the isotope species. We also plan to study the isotope effect that might exist during the hydrodechlorination reaction when using $D_2$ as the reduction agent. Since isotope effects are solely influenced by atomic mass, for a set of reaction steps, they can be predicted using statistical mechanics theories. If the measured isotope effects for the hydrodechlorination reaction with $D_2$ match the predicted values based on the proposed reaction steps, then it will be evidence about the correctness of the proposed hydrodechlorination reaction steps. It is hoped that by conducting these isotope exchanged experiments, the obtained results can support the assumptions in the proposed reaction steps. If the proposed reaction steps are valid and can partially describe the hydrodechlorination reaction of most chlorinated compounds, it will both enhance the understanding of hydrodechlorination reaction and at the same time, serve as a solid basis for future more detailed hydrodechlorination reaction steps studies.

Finally, some efforts will be directed to the study of the hydrodechlorination reaction steps beyond the proposed Langmuir-Henshelwood mechanism. These steps are not kinetically important and thus cannot be studied by simply analyzing results from the kinetic experiments. But these steps may play important roles in determining the hydrodechlorination reaction selectivity. For example, in the compound of $CF_3$-$CFCl_2$, the C-F bond is almost 100kJ $mol^{-1}$ stronger than the C-Cl bond. By considering only the bond energy difference, one will predict that the C-F would not be broken during the hydrodechlorination process. But during the reaction, this C-F bond does break and over hydrogenated $CF_3$-$CH_3$ is produced. Since C-F bond scission happens after the rate-determining C-Cl bond scission, it is very difficult to deduce how this C-F breaks solely from the kinetics data. In order to understand the selectivity of the hydrodechlorination reaction in general, it is very important that these elementary steps beyond the rate-determining step must be identified and studied using methods other than kinetics analysis. Isotopic tracing technology can also be use for this purpose. There are actually a limited number of studies of hydrodechlorination reaction steps by means of isotope, such as Campbell and Kemball's study of $CH_3$-$CH_2Cl$ hydrodechlorination reaction with $D_2$[16]. In their experiment, the deuterium distribution in the product ethane was used to analyze the reaction steps beyond the C-Cl scission step, such as the possible C-H breakage during the hydrodechlorination reaction. We plan to apply the same isotopic tracing methodology for most of the chlorinated compounds that will be studied in this research. $D_2$ exchanged hydrodechlorination reaction will be performed for these compounds and the deuterated products' distribution would be analyzed. In this way, the bond breakage pattern beyond the C-Cl scission step could be revealed. We hope the results from the deuterated product distribution can supplement our proposed reaction steps with more elementary steps. These results can also help understand the factors that can affect the selectivity of the hydrodechlorination reaction.

### 3. Predict the rate and selectivity of the hydrodechlorination reaction

To be able to predict hydrodechlorination reaction rate for any chlorinated compound and selectivity based on the proposed reaction mechanism is another goal of this research work. If we can achieve this goal, it will be an important contribution in the process of understanding the nature of hydrodechlorination reaction, considering the vast number of chlorinated compounds and their quite different reaction kinetics. Industries who want to commercialize the hydrodechlorination reaction for a certain chlorinated compound can also benefit for this pre-knowledge that compound.

From the simplified Langmuir-Hinshelwood reaction steps deduced from the kinetics data colleted for the compounds we use here, a rate expression has been derived. It is found that this rate expression can be used to describe the hydrodechlorination reactions of most of the chlorinated compounds[17]. But, in order to be able to predict the rate, the constants, such as the rate constant of the supposed rate-determining C-Cl scission step and the equilibrium constant of the equilibration between gas phase $H_2$, HCl and surface H, Cl species in the rate expression, must be evaluated. To do this, the measured reaction kinetic data, such as rates and reaction orders, of the chlorinated compounds used in this study will be analyzed and the reaction constants will be extracted. If we can obtain the values of the rate constant and the equilibrium constant at different temperatures, the intrinsic activation energy of the first C-Cl bond scission step and the heat of reaction of the equilibration between gas phase $H_2$, HCl and surface H, Cl species can be evaluated by plotting the natural logarithm of these values against 1/T. The activation energy and heat of reaction values for all the compounds will be tabulated and compared in order to find out the relationship between compounds' reaction constants and their structures. It is found from our preliminary results on CFC compounds that the intrinsic activation energy of the C-Cl bond scission could be related to the bond strength of the first C-Cl bond to be broken in the chlorinated compound[13]; the heat of the reaction of the equilibration between gas phase $H_2$, HCl and surface H, Cl species seems to be very close for all the hydrodechlorination reaction. With this knowledge, we can predict the reaction rates and reaction orders for CFC compounds using their bond strength values. Based on this initial success, this methodology of measuring the reaction constants will be applied to other chlorinated compounds used in this research to refine our proposed rate expression. We believe that by conducting this reaction constant measurement, more knowledge can be obtained for the hydrodechlorination reaction and this knowledge can be used later to predict the reaction rates and orders of other chlorinated compounds.

Another important kinetic parameter in hydrodechlorination reaction is reaction selectivity. The ability to predict the selectivity is also desirable to the commercial hydrodechlorination processes, so that they can find out the optimal reaction conditions to increase the yield of the desired product and at the same time minimize the by-products in the reaction. But, in our preliminary study of the hydrodechlorination reaction, it is found that the prediction of reaction selectivity is a more challenging work than prediction of the reaction rate. For the prediction of the rate, only the reaction constants, such as rate constant and equilibrium constant for the kinetically important steps are needed to be known. These reaction constants can be calculated by analyzing the kinetics data of several typical chlorinated compounds, as indicated in the previous paragraph. However, if one wants to predict the reaction selectivity of the hydrodechlorination reaction, firstly, all the elementary steps for the hydrodechlorination reaction must be identified; furthermore, the reaction constants for all these steps are needed to calculate the reaction selectivity. In view of this, it is concluded analyzing only the results of kinetics measurement will not be able to reveal these reaction constant information about elementary steps beyond the kinetically important steps. In order to predict the selectivity, other techniques must be integrated with reaction kinetics analysis.

We noticed that in recent literatures, there are many examples of the application of microkinetics modeling of reaction systems to explain the experimental kinetics observations and to investigate reaction mechanisms, such as the water gas shift reaction[18-21]. In this type of study, for a certain reaction, the measured or calculated energetics of the surface species is used to calculate the rate constants or the equilibrium constants for the possible elementary steps. Then with a valid reaction mechanism composed of these elementary steps, the kinetics parameters, such as the surface coverage, reaction rate, selectivity, apparent activation energy and reaction orders can be calculated using mathematical models of the reaction. The applicability of the microkinetics modeling is not restricted to a particular type of reaction or by the actual reaction conditions of a reaction. It can also be used to check the validity of the hypothetical reaction mechanisms for reactions, if the microkinetics calculation result based on a possible reaction mechanism matches the experimental kinetics observations, the proposed reaction mechanism might be an accurate description of the real reaction steps. With the advance of computer technology and the appearance of more powerful surface calculation, microkinetics modeling software packages, this method is rapidly becoming another tool for reaction kinetics study. In view of this, we will also take advantage of this new method to address the problem of predicting the hydrodechlorination reaction selectivity. The energetics of the possible surface species for the hydrodechlorination reaction of the studied chlorinated compounds will be calculated using surface calculation methods and used to find out the reaction constants for the possible reaction steps of the hydrodechlorination reaction. Once these values are obtained, a CSTR microkinetics model can be constructed to predict the reaction rates and selectivity of these compounds using our proposed hydrodechlorination reaction steps. The calculated kinetic results will be compared with our experimental results to see whether the reaction steps are a valid representation of the true mechanism. If this is true, more microkinetics studies can be conducted for other chlorinated compound based on this valid proposed reaction steps. In this way, the prediction of the hydrodechlorination reaction selectivity of any chlorinated compound might be possible and this will also open new research ground in hydrodechlorination reaction kinetic study.

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# Chapter 2

# Literature Review and Significance of Presented Research Work

The kinetics of the hydrodechlorination reaction has been studied for some time and there are extensive research papers and reports presented in the literature. It is thus prudent to take advantage of the existing knowledge of hydrodechlorination to benefit our research work. At the same time, a review of the literature can also help us judge the value of the proposed research work and how it will contribute to and enhance the understanding of hydrodechlorination reaction.

## 2.1. Literature Review

### *2.1.1. Catalysts used for hydrodechlorination reaction*

Hydrodechlorination reaction is usually performed under the presence of noble metals. Different metals will lead to different hydrodechlorination reaction activity and selectivity. Hydrodechlorination reaction has been studied over a number of metals, including Pd[1-6], Pt[7-9], and Rh[7, 9-11]. It is found Pd usually has the highest hydrodechlorination reaction activity and is the most selective metal catalyst for this reaction[12], thus it is applied as catalyst in a large number of papers about the hydrodechlorination reaction. But there are also research works using bimetallic catalysts, such as Pt/Cu, to tailor the selectivity of the hydrodechlorination reaction. For example, there are reports using the bimetallic catalyst Pt/Cu supported on carbon to produce $CF_2{=}CF_2$ from $CF_2Cl_2$, instead of doing a complete hydrodechlorination to form $CF_2H_2$[13-17]; another example is a Dow Chemical process, in which 1,2-dichloropropane is converted to propylene using a bimetallic hydrodechlorination catalyst. In this way, by doing a partial hydrogenation, a double bond is introduced into the molecule and this will increase the value of the product[18]. For those works using Pd catalyst, most of the time they studied supported Pd catalyst. Many support materials have been used and their roles on the hydrodechlorination reaction have been studied, including carbon[19, 20], alumina[1, 21, 22] and fluorinated alumina[2, 22, 23]. While some authors suggest that the metal oxide support play a role in the reaction and sometimes would be halogenated during the reaction due to the HCl or HF formation during the hydrodechlorination reaction[24], carbon is found to be a comparatively inert support and can withstand the caustic environment during hydrodechlorination reaction[20]. To avoid the artifacts might be brought in the reaction system by oxide supports, Pd supported on carbon will be used in our research. Besides supported metal catalyst, there do exist hydrodechlorination research works dealing with model catalysts, such as evaporated films[25-27], foils[4, 5, 28] and single crystals[5, 6, 29]. There are even some studies reporting on using bulk metal powers as hydrodechlorination reaction catalysts[14, 30, 31]. A few of these papers have presented kinetics data, such as turnover rates, selectivity on different kinds of Pd catalyst[4-6, 20, 28, 29, 31]. By comparing these kinetics data, we can obtain information about several important aspects of the hydrodechlorination reaction, such as the question that whether the reaction is structure sensitive of insensitive. This kind of knowledge is also very useful in deducing the possible reaction steps for hydrodechlorination reaction.

### *2.1.2. Hydrodechlorination reaction kinetic measurements*

A variety of organic molecules has been studied for the hydrodechlorination reaction, including olefins[32], aromatics[11, 33, 34], and aliphatic[1, 4-7, 9, 14, 17, 19, 21-23, 28-32, 35-42] compounds. But one drawback in the kinetics study of hydrodechlorination reaction is that turnover rates, selectivity and reaction orders are only present for a limited number of compounds and in most of the cases, the studied compounds are mainly those compounds that have largest ozone depletion potentials, such as $CF_3$-$CFCl_2$[1, 2, 4-6, 20, 28, 31], $CF_2Cl_2$[21, 29, 42, 43] and $CCl_4$[32, 38, 44]. This problem makes it very difficult to compare the activities measured on different Pd catalysts, to compare and activity and selectivity of different chlorinated compounds and to generalize reaction steps for the hydrodechlorination reaction. Also, there are controversies about the kinetics of the hydrodechlorination reaction even within these available results. For example, while some groups, such as Campbell and Kemball[25], Coq et al.[11] and van de Sandt et al.[45] observed HCl as an inhibitor in the hydrodechlorination reaction, Ahn et al. did not find this inhibition effect[23]. Another example is that for the hydrodechlorination reaction of the same compound $CF_3$-$CFCl_2$, the reported activation energy of Karpinski et al.[1] is approximately 2 times lower than the result reported by Thompson et al. and Ribeiro et al. [4, 20]. The reason for this difference might be due to the effect of HCl. The result of Karpinski et al. suggests the reaction order of HCl to be zero, while in Ribeiro et al.'s paper, a HCl order of –1 was reported. Note that HCl inhibition is distinct form catalyst poisoning since it is reversible and is caused simply by the competition of sties between HCl and the reactant. Thus, in reporting the kinetics measurements, such as reaction rates and activation energies, HCl concentration must be specified. For example, changing the HCl concentration by 10 times will cause the reaction rate to change by 10 times correspondingly. Another consequence of not considering the inhibition of HCl is that the measured apparent activation energy would be two times lower than the correct one. It is thus crucial to establish and correct the effect of HCl for the hydrodechlorination reaction kinetics measurements. This HCl inhibition effect might explain why Karpinski et al.'s reported activation energy is lower than that reported by Ribeiro et al. The former group's omission about the HCl effect may contribute to the difference. Finally, in other cases, when turnover rates are available for the same compound in different reports, it is sometimes still hard to compare their reported rates, either due to the failure of not considering HCl effect[1, 23] or due to the problem of HCl interacting with the catalyst support and thus changing the reaction kinetics[21, 22, 24, 42]. Faced with these problems existing in the literature, in order to advance the knowledge of the hydrodechlorination reaction, more kinetic measurements have to be performed accurately to provide unambiguous raw data for the generalization of the reaction kinetics reaction steps. These works include the use of proper catalysts to avoid the artifacts caused by reactant and support interaction, the incorporation of HCl inhibition effect during the hydrodechlorination reaction kinetic measurements, and the detailed kinetics studies of chlorinated compounds other than CFC related compounds, such as $CH_2Cl_2$, which has been studied as model compounds for hydrodechlorination reaction[46, 47].

### *2.1.3. Reaction steps studies of the hydrodechlorination reaction*

Compared with the number of kinetic studies of hydrodechlorination reaction in the literature, even less has been published about the possible reaction steps. Takita et al.

suggested a mechanism for the catalytic hydrodechlorination of $CCl_2F$-$CClF_2$ on several metals. They fond that the chlorination and dechlorination of metallic surface could be the most important pathway in this reaction[48-50]. So the bond strength between chlorine the metal was thought to be one of the key factors. Gervasutti et al.[36] proposed that the dissociative adsorption of the chlorine-containing compounds as the initial reaction pathway: RCl + H$\leftrightarrow$R* + HCl. There are also studies on chlorobenzene hydrodechlorination reaction scheme, in which the scission of C-Cl bond was suggested to be an important reaction step[10, 11, 51]. Weiss et al. [32, 38]also proposed the dissociative adsorption of chlorinated compounds as the rate-determining step for $CCl_4$ hydrodechlorination. For other reaction species in the hydrodechlorination reaction, Coq and Bodnariuk[10, 11, 51] found competitive adsorption between HCl and chlorobenzene. This inhibition effect was also been observed in the hydrodechlorination reaction of $C_2H_5Cl$[25, 26], and by van de Sandt el al [30, 41]and Ribeiro et al.[4, 5, 20, 31]. Based on these previous finding and their own kinetics study of $CF_3$-$CF_2Cl_2$ on Pd single crystals and Pd foils, Ribeiro et al. suggested a possible reaction steps for the hydrodechlorination reaction of CFCs[4, 20, 31]. In the proposed Langmuir-Hinshelwood mechanism, the dissociative adsorption of CFC and the consequent C-Cl bond scission is suggested to be the rate-determining step; $H_2$ and HCl is supposed to be in equilibrium with surface adsorbed H* and Cl*; and Cl* is proposed to be the most abundant surface species. The rate expression derived from this mechanism is $r=k[CFC][H_2]^{0.5}[HCl]^{-1}$, which can be used to explain many experimental kinetic observations. This proposed reaction mechanism is similar as the one advanced by Sinfelt[52] for the hydrodechlorination of chloromethane and the rate expression is kinetically similar to the one advanced by Coq et al.[11] for the hydrodechlorination of chlorobenzene. The strong relationship between C-Cl bond strength and reaction activity has also been found for the hydrodechlorination reaction of $CF_2Cl_2$, $CF_2HCl$ and $CH_2F_2$ series compound[45, 53], indicating the assumption that C-Cl bond scission is the rate-determining step might be valid. Note that many of these reaction steps assumptions are derived mainly from kinetics observations and thus are simplification of the real reaction steps and still have defects. For example, all of them cannot be used to predict the reaction selectivity, which is an important reaction kinetics parameter. Another important issue is that some of these proposed reaction steps are still hypothetical and the validity of them is still needed to be corroborated using other experimental techniques, such as isotopic tracing.

There are also works directed to reveal more reaction steps and reaction surface intermediates of the hydrodechlorination reaction. It is found that in hydrodechlorination reaction, the product distribution is independent of the conversion during reaction[4, 20, 29, 31]. Based on this, many research groups have proposed the surface dechlorination step must be a sequential process, while gas phase products are formed in parallel routes. Examples of proposed sequential reactions are the hydrodechlorination reaction of $CCl_4$[38], $CCl_2F_2$ [22, 53], and $CF_3$-$CFCl_2$[1, 4, 5]. This property might due to the fact that the products are less reactive than the reactants. As a chlorinated molecule undergoes sequential hydrodechlorination, the remaining C-Cl bonds on the hydrogenated products become stronger. Isotopic studies are also used in the literature to study more hydrodechlorination elementary reaction steps. Campbell and Kemball studied the hydrodechlorination of $CH_3$-$CH_2Cl$ on Pd films[25, 26]. By its reaction with $D_2$, they found that the reaction mechanism might involve the formation of a carbene-like species since the product (ethane) was substantially enriched in $CH_3$-$CHD_2$. Zhou et al.[54] found that the dehalogenation step (the supposed RDS) is hemolytic. For the study of surface intermediates, Deshmukh and d'Itri [55]attempted to trap fluorocarbene species formed in the reaction of hydrodechlorination of $CCl_2F_2$ by reaction with ethylene but could not observe any fluorinated addition products. Some works were also done using FTIR technology to study the surface adsorption of $CF_3$-$CFCl_2$[56, 57]. Also, there are proposals of using Laser-Raman technique to study the surface adsorbed species during the hydrodechlorination reaction[58]. From these studies, a lot of valuable information has been obtained for the reaction steps of the hydrodechlorination reaction. But in spite of these efforts, many reaction steps issues remain to be answered. For example, in hydrodechlorination reaction, C-F bond can also be broken under hydrodechlorination reaction conditions despite the fact that C-F bond is much stronger than C-Cl bond. Another similar example is in the hydrodefluorination of $CH_3$-$CF_2H$, ethane is formed exclusively without the formation of $CH_3$-$CFH_2$[59]. To answer these questions requires that more mechanistic studies must be performed to investigate reaction steps beyond the kinetically important steps.

### *2.1.4. Reaction energetics studies*

To predict the reaction rates and selectivity, no only do we need a complete and reliable reaction steps description, the reaction energetics of each of the elementary steps in the reaction mechanism are also needed. Since many proposed reaction steps have suggested that C-Cl bond plays a central role in determining the hydrodechlorination rates, the C-Cl bond strength data of chlorinated compounds are needed. There are some studies on the gas phase C-Cl bond strengths for CFC compounds existing in the literature[60-63]. The C-Cl bond energy is either measured by experimental methods or obtained using theoretical quantum mechanical calculation methods. Group additivity method has also been used to estimate the C-Cl bond energy for chlorinated compounds[64]. These raw data can be used as parameters when predicting the reaction kinetics of hydrodechlorination reaction. We do notice that there are discrepancies among bond energy data reported by different authors. This problem can be addressed by using the more powerful and accurate modern quantum mechanical molecular calculation methods, such as the Density Functional Theory[65], to compute the C-Cl bond energy of any chlorinated compounds. This method is not only more convenient and simple than actual experimental measurements, but can also minimize errors and provide consistency for the results.

Although the gas phase bond energy data can be used as one of the parameters in the prediction, they are still evaluated in gas phase and cannot be used directly in calculating heterogeneous reaction kinetics. Some kinds of relationships are still needed to relate gas phase bond energy to surface species reactivity. Another problem with knowing only the C-Cl bond energy is that only the hydrodechlorination reaction rates can be calculated, the prediction of reaction selectivity still need the surface energetics of other kinetically unimportant steps and species. There are limited reports on the study of surface energetics of the dechlorination of chlorinated compounds. Gellman et al. experimentally studied the surface adsorption, desorption energy and the chlorine bond dissociation energy of series of chlorinated compounds on Pd single crystals[54, 66-69]. The surface energetics of 1,1,1-dichloroethylene has also been evaluated using theoretical surface calculation method[70-72]. But compared with the needs of predicting hydrodechlorination reaction rates and selectivity, these data are far from enough. The reaction energetics for the elementary steps, reaction intermediates must continue to be investigated. Theoretical surface calculation and microkinetics modeling have been successfully used to explain the water-gas shift reaction kinetics[73]. It is hoped that by using these new research tools, more detailed knowledge can be learned for hydrodechlorination reaction.

## 2.2. Significance of the Proposed Research Work

Compared with the results reported in the literature, the proposed work has the following advantages and significance.

1. The use of Pd catalyst supported on inert carbon, instead metal oxides sometimes used in the literature, in hydrodechlorination kinetic measurement can avoid any potential interference from the catalyst support. In this way, the measured data are the authentic kinetics parameters of the hydrodechlorination reaction. These unequivocal data will make the explanation and analysis of the raw data easier and thus make the generalization of the reaction steps possible.

2. The kinetics measurement of families of chlorinated compounds, such as series 1: $CF_3$-$CF_2Cl$, $CF_3$-$CFHCl$, $CF_3$-$CFCl_2$, $CF_3$-$CCl_3$; series 2: $CHCl_3$, $CH_2Cl_2$, $CHCl_3$, $CCl_4$; series 3: $CF_3Cl$, $CF_2Cl_2$, $CFCl_3$, $CCl_4$ and family 4: 1,2-dichloropropane, 1,3-dichloropropane,1,1-dichloropropane, 2,2-dichloropropane can offer more opportunities in studying the relationship between the structure of chlorinated compounds and their reaction kinetic behaviors, such as rates and selectivity in hydrodechlorination reaction. Using this method, not only can we measure the reaction kinetics of more chlorinated compound, the reaction steps, especially those kinetically important steps, can also be revealed.

3. Based on kinetic measurements, kinetically important reaction steps of hydrodechlorination of chlorinated compounds reaction the steps will be proposed. This suggested hydrodechlorination reaction steps will also be investigated and corroborated using isotopic tracing experiments. Though there are some reaction steps studies in the literature, these proposed model are mostly deduced or generalized from kinetic experimental observations and have not been thoroughly proved. We hope that from our study, a plausible reaction steps with the support of not only kinetics measurements but also isotopic tracing observations can be advanced. This will firstly provide a conclusive reaction steps for of the hydrodechlorination reaction kinetics and secondly serve as a basis for later detailed study about the reaction steps beyond these kinetically important steps. In the mean time, isotopic studies will also be applied to study

the possible reaction intermediates in the hydrodechlorination reaction and reveal more elementary steps, which are rarely available in the literature.

4. The calculation and measurement of the reaction constants and reaction energetics of kinetically important hydrodechlorination reaction elementary steps, such as gas phase C-Cl bond strength; the intrinsic activation energy of C-Cl bond scission for all the chlorinated compounds to be studied here; the heat of reaction of the equilibration between surface H, Cl and gas phase $H_2$, HCl, will help us in learning how to estimate the reaction rates of the hydrodechlorination reaction. At the same time, these data, combined with theoretical surface calculations and experimental measurements of the surface reaction energetics of other steps beyond the rate-determining step, can be used to develop a possible microkinetics model for the hydrodechlorination reaction. It is hoped that the model can be applied to predict not only the hydrodechlorination reaction rates but also the reaction selectivity for a large number of chlorinated compounds, which is highly desirable for the study of hydrodechlorination reaction.

In summary, the proposed work will address many questions that are still need to be investigated for the hydrodechlorination reaction of chlorinated compounds. When conducted properly and successfully, the obtained results will enhance the knowledge about the hydrodechlorination reaction. Compared with the existing contributions in the literature, the proposed in-depth research is both valuable and novel.

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# Chapter 3

# Research Experimental Methodology

## 3.1. Catalysts

Four types of Pd supported on carbon catalysts were used in this study. The samples consisted of palladium dispersed on a carbon support. The samples were obtained from Engelhard (0.5% Pd/C-H), DuPont (5% Pd/C-H), or Degussa (5% Pd/C-L) or prepared in house with a support from Cabot Corporation (0.5% Pd/C-L). The designation C-H and C-L on the catalysts will be used in the results report to stand for high (greater than 1000 $m^2 g^{-1}$) and low surface area supports (about 100 $m^2 g^{-1}$). The sample from Engelhard had a metal concentration of 0.5% and was supported on coconut carbon. The sample obtained from DuPont used the same support but had a concentration of Pd of 5%. The support had a total surface area of 1600 $m^2 g^{-1}$ and a pore volume of 0.7-0.8 $cm^3 g^{-1}$. The pores with a diameter greater than 2 nm accounted for a surface area of 300 $m^2 g^{-1}$ and a pore volume of 0.2 $cm^3 g^{-1}$. The pores with diameter smaller than 2 nm accounted for the remaining 1300 $m^2 g^{-1}$ of surface area and 0.5-0.6 $cm^3 g^{-1}$ of pore volume. The average particle size of the Pd particles was about 6.5 nm, which suggests that most of the Pd was in pores greater than 2 nm. A low surface area (29 $m^2 g^{-1}$) carbon black obtained from Cabot Corporation (Sterling series) was used as the support for a 0.5% Pd/C catalyst. The catalyst was prepared by the incipient wetness method using an aqueous solution of $PdCl_2$ obtained from Aldrich. For the dissolution of $PdCl_2$, 2 mol of HCl were added for every mole of salt with heating applied. From a pore size analysis, the distribution of pore size ranged from 5 to 100 nm with a total pore volume of 0.3 $cm^3 g^{-1}$. The 5% Pd/C obtained from Degussa was supported on a carbon black with serial number E 9011 XR/W 5%. It had a BET area of 107 $m^2 g^{-1}$ and a total pore volume of 1.15 $cm^3 g^{-1}$.

These samples were ground with a mortar and pestle and the fraction between 40 and 60 mesh was retained for use in the reactions. The pore size distribution and pore volume for the Cabot support and Degussa catalysts were measured with a Quantachrom Autosorb-1 volumetric sorption analyzer. The pore volume for the 0.5 and 5% Pd/C-H was measured at the DuPont Experimental Station[1].

Another Palladium supported on zirconia was also used in this study to investigate any possible support effect. The catalyst supported on zirconia was prepared by incipient wetness using an aqueous solution of $Pd(NH_3)_2(NO_2)_2$ in nitric acid obtained from Tanaka Kikinzoku Kogyo of Japan. The zirconia RC-100P was obtained from Daichi Kigenso Kagaku (DKK) of Japan. This sample was also grounded and 40/60 mesh particles were selected for use in catalytic studies.

## 3.2. Surface Area Measurements

The total surface area was measured using the BET method with $N_2$[2]. The Pd metal surface area was measured by the hydrogen-oxygen titration method according to Benson et al.[3] The experimental setup consisted of a volumetric system constructed in Pyrex and pumped by a liquid nitrogen trapped diffusion pump. The amount of gas adsorbed was determined by measuring pressure change in a pre-calibrated volume on the system with a pressure transducer (MKS model 127).

The samples were initially reduced in flowing $H_2$ (50 $cm^3 \cdot min^{-1}$) for 3 h at 300°C before the Pd surface area measurements. After the initial reduction of 3 h, subsequent hydrogen-oxygen reaction was conducted at 100°C. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression is valid under the assumption of spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms$\cdot$ $m^{-2}$ [4].

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced catalysts was also conducted. Samples for XRD analysis were reduced in a manner identical to those previously described, and then passivated with 60 Torr of $O_2$. Particle size was determined from the width of the diffraction peak using x-ray line broadening technique. The Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

### 3.3. Reactants

The two carbon CFC samples in the first series were obtained from the DuPont Experimental Station (CFC 114a $CF_3$-$CFCl_2$ and CFC 115 $CF_3$-$CF_2Cl$), Lancaster Synthesis (CFC 113a $CF_3$-$CCl_3$), and DuPont Suva Refrigerants (HCFC 124 $CF_3$-CFClH). The Chlorinated methane compounds in the second series were purchased from Sigma Chemical Company ($CH_3Cl$, CCl4) and Lancaster Synthesis (CH2Cl2, CH3Cl), The one carbon CFC series compounds were obtained from National Refrigerants Inc. (CFC13 CF3Cl), Acdel Co (CFC12 CF2Cl2, CFC11, CFCl3).

For the gases used in the experiments, the HCl mixture was obtained from Matheson. Three tanks were used during the course of experiments with 18.9%, 15.6%, and 20.7% HCl in He. This mixture was made at Matheson Gas from technical grade HCl and Matheson purity He. A mixture of $H_2$ and methane, certified as ultrahigh purity, was obtained from Matheson. This mixture contained 1033 ppm methane, used as an internal standard. The hydrogen-methane mixture was passed through a filter containing 5% Pd/C catalyst to react any oxygen in the line into water and trap it on the carbon support. The $H_2$ (BOC gases) was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was obtained from BOC gases and passed through a mass spectrometer gas trap (HP model 5182-3467).

Two types of isotope containing compounds were used in this study. The deuterium was obtained from Cambridge Isotope Laboratories. It contained 99.6% $D_2$ and 0.4% HD, and before use it was passed through the same Pd membrane purifier used for purification of $H_2$. The $H^{37}Cl$ gas was purchased from Icon Services Inc., the $H^{37}Cl$ concentration was higher than 99%.

### 3.4. Reactor Configuration (Figure 1)

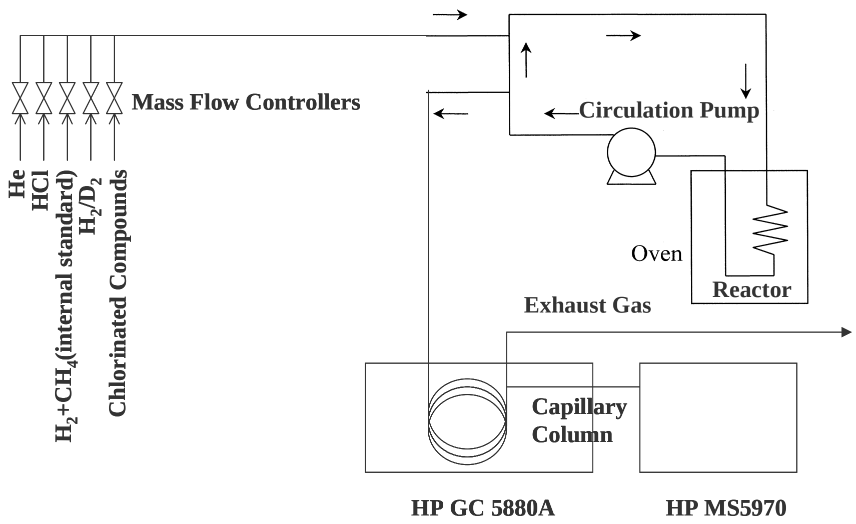

**Figure 1: Reaction system configuration used in this study**

The gas manifold was constructed of 1/8" diameter stainless steel tubing. The delivery of Gas flow was controlled with mass flow controllers (Porter Instrument Co.). Some of the chlorinated compounds used here are liquids at room temperature and was added to the reaction mixture by passing helium through the CFC in a saturator maintained at constant temperatures using a water bath. The bath temperature was controlled using a Neslab Instrument Inc. RTE-9 refrigeration / heating circulating bath. The mass flow controllers were calibrated with bubble flow meters except for the He-HCl mixture. In this case, the flow rates were determined by varying the composition of a mixture of He/HCl and $H_2/CH_4$, analyzing the mixture by gas chromatography, and observing the change in signal of the methane peak.

The reaction portion of the flow system was made of Pyrex and could be manipulated to operate in continuous or in batch mode. The reactor was made out of quartz with the catalyst held on a fritted disk. Most reaction rates were measured under the continuous stirred tank reactor (CSTR) mode with a thermocouple extending into the reactor through a thermocouple holder which was in good contact with the catalyst bed to allow precise measurement of the reaction temperature. The CSTR was equipped with a gas pump (Senior Flexonics model MB-21) for circulating the gases at a rate of about 1400 $cm^3 \cdot min^{-1}$ which allowed differential operation for the reactor and minimized heat and transport effects in the reaction. Inlet and effluent flow rates were around 100 $cm^3 \cdot min^{-1}$. CSTR is preferred in the reaction kinetics measurements because of its simple mathematical treatment and minimal heat and mass transfer limitation presence. At the same time, CSTR reactor can be operated with very low conversion, which can maintain the partial pressures of the gas species so that the reaction orders can be measured with less error[5]. The presence of heat and mass transfer limitations that might exist in the system was tested using the Madon-Boudart test[6]. From the results obtained no heat and mass transfer limitations were found, even with the highest surface area catalyst, where transport limitations would be most severe[7]. Thus, we conclude that these artifacts did not affect the results. Batch type of reaction operation is also possible for our reaction system setup by simply feeding the gas components into the reactor and then close the inlet and outlet control valves to have a closed system. Batch mode reactions are mainly applied for the study of isotopic tracing.

The exiting gas stream was sent to a gas chromatograph (GC, HP5880A) for analysis. The column used in the GC was a 5% Krytox 143AC, 60/80 Carbopack B HT 20' x 1/8" column from Supelco. The effluent from the GC column was simultaneously analyzed by a GC flame ionization detector, for quantitative analysis; and by a MS for qualitative analysis (such as in the isotopic tracing experiments). The gas was sampled into a mass selective detector (MSD, HP5970A) through a fused silica polyimide capillary (I.D. 51μm, O.D. 363μm) of 0.75m length. Each of the reactant chlorofluorocarbons and products were calibrated against the methane standard in the hydrogen-methane mixture, and response factors were then determined for each compound on the GC. After exiting the system, the gases flowed through a NaOH solution to neutralize the HCl present in the effluent stream.

### 3.5. Data Collection Procedure

From 200 to 500 milligrams of fresh catalyst was initially loaded into the reactor and reduced for 3h at 300°C with 50 $cm^3 \cdot min^{-1}$ $H_2$ to remove any possible surface impurities. For used catalyst, the catalyst was treated with 50 $cm^{3\cdot} min^{-1}$ $H_2$ for 0.5 ~ 1 h at 150°C before collecting data for the hydrodechlorination reactions.

When the reactor was operated in a CSTR mode, the inlet gas concentrations were adjusted with mass flow controllers and the temperature was controlled by a Eurotherm model 808 temperature controller. For a particular set of conditions, the reaction would be run for 30-60 minutes to get stabilized before a data point was taken. During the course of the experiments, the changes in concentration and temperature were chosen in a random order so that any variation in the system would not introduce a systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated and another data point taken. By ensuring that this last point agreed with the first point it could be shown that there was no significant deactivation of the catalyst during the time frame of the experiment. The gas mixture was sampled into the GC-MS system using an automatic valve on the GC.

For experiments performed in batch mode, the reactor was evacuated to $1\times10^{-5}$ Torr for 0.5 hour before the gas reactants were fed into it. The oven temperature was raised to the target temperature at rate of 5°C/min to prevent overheating. When the temperature of the reactor oven reached its desired level, the reactor was given 30 minutes to balance before the first point was taken. The gas mixture was taken from the reactor using a 500μl syringe through a 0.438" sol septa (From HP) mounted on a sample port on the reactor system. For each data point, 100-200μl gas mixture was transferred into the GC-MS system for analysis.

### 3.6. Error Analysis

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in reaction orders are at a maximum 10% or maximum 0.1 in 1.0 and errors in the apparent activation energies were 10 $\mathrm{kJ \cdot mol^{-1}}$. Turnover rate reproducibility was better than 90%.

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# Chapter 4

# Results and Discussions

# Paper 1

# Turnover Rates, Reaction Orders and Elementary Steps for the Hydrodechlorination of Chlorofluorocarbon Compounds on Palladium Catalysts [*] [†]

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[†] The contribution of Craig D. Thompson, Robert M. Rioux is acknowledged.

## Abstract

The rates of hydrodechlorination catalyzed by Pd supported on carbon for four chlorofluorocarbons spanned a range of 7 orders of magnitude. The rates scaled up to the bond strength of the carbon-chlorine bond for the gas-phase reactant. This finding demonstrates that the rate-determining step involves the scission of the C-Cl bond and suggests, through Polanyi and linear free-energy relationships, that rates for other compounds can be estimated if the C-Cl bond strength is known. The reaction orders for the most abundant products are approximately first-order for the chlorine-containing compound, half-order in $H_2$, and inverse first-order in HCl. The reaction steps consistent with these orders include a rate-determining step involving the adsorption of the chlorofluorocarbon to a single site (which could be a single surface palladium atom) and equilibrated steps between gas-phase $H_2$, gas-phase HCl, and adsorbed hydrogen and chlorine atoms. The rates on the supported catalysts are comparable to the ones reported before on a Pd foil, indicating that the support does not play a role in the reaction. The product distribution is independent of conversion, implying that the various products are formed from a single visit of the reactant on the surface and not from re-adsorption of gas-phase products. The four compounds studied were chloropentafluoroethane ($CF_3$-$CF_2Cl$), 2-chloro-1,1,1,2-tetrafluoroethane ($CF_3$-CFClH), 1,1-dichlorotetrafluoroethane ($CF_3$-$CFCl_2$), and 1,1,1-trichloro-2,2,2-trifluoroethane ($CF_3$-$CCl_3$).

## 1. Introduction

Hydrodechlorination involves the reaction between $H_2$ and an organic molecule containing a C-Cl bond to form HCl and a C-H bond. This reaction is quite exothermic and thus with the presence of a catalyst it can be driven to completion. The objective of this contribution is to report on the detailed kinetics of the hydrodechlorination reaction for a family of reactants and to use this information to probe the reaction steps. Knowledge of the kinetics is also important in practice to determine the optimal reaction conditions for the hydrodechlorination reaction.

Hydrodechlorination is an important step in many syntheses that use a chlorine-containing molecule as an intermediate, for example, in the manufacture of $CF_3$-$CFH_2$ (a widely used refrigerant) from $CF_3$-$CFCl_2$.[1] Another use of hydrodechlorination is for chlorine removal on a compound that needs to be disposed of. This removal is mandatory before the compounds can be released into the environment due to the adverse effect of chloro-containing molecules on the ozone layer or due to the difficulty to naturally biodegrade these compounds. Another recent application of hydrodechlorination is in the conversion of unwanted chlorinated compounds into useful ones as for example in the conversion of waste 1,2-dichloropropane into propylene.[2] The reaction of hydrodechlorination is thus very important. There are however a number of questions that need to be answered before one can take full advantage of this reaction. These include a tabulation of the rates of hydrodechlorination for any given compound, the reaction kinetic orders, the reaction steps, and a prediction of product distribution. Some of these issues will be presented here.

There are a growing number of studies on the catalysis of hydrodechlorination reactions in the literature. Palladium is the most active catalyst for this reaction[3] and one of the most studied catalysts. Many studies deal with liquid-phase reactions in the presence of a base but we will discuss only gas-phase reactions. The literature range from studies on model catalysts including evaporated films,[4-7] foils,[8] and single crystals[9] to studies on supported catalysts. These latter studies cover a variety of organic molecules including olefins,[10] aromatic,[11,12] and aliphatic compounds[13-20] with some of the molecules also containing fluorine.

One challenge in designing a hydrodechlorination process is that there are a very large number of chlorofluorocarbons and related compounds and the rates are very dependent on the structure of the reactant. For example, ethane is the only saturated hydrocarbon with two carbons, but more than 40 saturated compounds are possible by the combination of two carbons, hydrogen, chlorine, and fluorine. Since it is not practical to measure the rates for all compounds and the rates are very dependent on the structure of the reactant, a method must be devised to predict the rates. It is going to be shown that the rates of reaction for the family of four compounds $CF_3$-$CF_2Cl$, $CF_3$-$CFClH$, $CF_3$-$CFCl_2$, and $CF_3$-$CCl_3$ correlate very well with the strength of the C-Cl bond. For this family of compounds, if the rate for one compound is known and the C-Cl bond energies are known for all of them, then the rates for the other compounds can be calculated accurately. In addition, the rates of reaction on the supported catalysts and those on foils and single crystals are similar, which suggests that the reaction is not sensitive to the structure of the catalyst and that the support does not play an active role in the reaction.

Kinetic data is important in deciding what are the important catalytic reaction steps. The reaction steps proposed for the hydrodechlorination of $CF_3$-$CFCl_2$ on palladium foils[8] and single crystals of Pd[9] are:

$$\mathrm{CFC} + * \rightarrow \mathrm{CFC}*$$

This is the rate-determining step, with all the other steps for the chlorofluorocarbon (CFC) hydrodechlorination not kinetically significant. Here the asterisk represents a catalytic site. The surface is also equilibrated with $H_2$ and HCl in the gas phase.

$$H_2 + 2* = 2H*$$

$$HCl + 2* = H* + Cl*$$

Assuming that Cl* is the most abundant surface intermediate, the final rate will be[8]

$$R=K[CFC][H_2]^{0.5}/[HCl] \qquad (1)$$

This is also the kinetic expression for the hydrodechlorination of most of the products for the four compounds tested here over Pd supported on a carbon support. This reaction sequence is also virtually the same as advanced by Sinfelt[21] for the hydrodechlorination of chloromethane, and the rate equation is kinetically similar to the one advanced by Coq et al.[12] for the hydrodechlorination of chlorobenzene. These steps may be applicable in general for hydrodehalogenation reactions on noble metals. However, the rate-determining step as presented above does not show any detail except that it involves one single site. It was proposed before that because only one site is involved, the rate-determining step might involve the nondissociative adsorption of the reactant.[8] This is not a good assumption because in this case the rate should be a weak function of the structure of the reactant, contrary to the findings of this contribution. We will show that the rate-determining step consists of the scission of the carbon-chlorine bond, possibly as an oxidative addition forming a Pd-Cl and a Pd-C bond on the same Pd atom. It is suggested that the active site consists of only one Pd atom, explaining why the reaction is insensitive to the structure of the catalyst. The product distribution also gives a hint to possible reaction intermediates on the surface. We still cannot predict or explain the product distribution and this task would require a description of the reaction steps beyond the rate-determining one.

## 2. Experimental Methods

### *2.1. Catalysts*

Four catalysts were used in this study. The samples consisted of palladium dispersed on a carbon support. The samples were obtained from Engelhard (0.5% Pd/C-H), DuPont (5% Pd/C-H), or Degussa (5% Pd/C-L) or prepared in house with a support from Cabot

Corporation (0.5% Pd/C-L). The designation C-H and C-L on the catalysts stands for high (greater than 1000 $m^2\ g^{-1}$) and low surface area supports (about 100 $m^2\ g^{-1}$). The sample from Engelhard had a metal concentration of 0.5% and was supported on coconut carbon. The sample obtained from DuPont used the same support but had a concentration of Pd of 5%. The support had a total surface area of 1600 $m^2\ g^{-1}$ and a pore volume of 0.7-0.8 $cm^3\ g^{-1}$. The pores with a diameter greater than 2 nm accounted for a surface area of 300 $m^2\ g^{-1}$ and a pore volume of 0.2 $cm^3\ g^{-1}$. The pores with diameter smaller than 2 nm accounted for the remaining 1300 $m^2\ g^{-1}$ of surface area and 0.5-0.6 $cm^3\ g^{-1}$ of pore volume.[22] The average particle size of the Pd particles was about 6.5 nm, which suggests that most of the Pd is in pores greater than 2 nm. A low surface area (29 $m^2\ g^{-1}$) carbon black obtained from Cabot Corporation (Sterling series) was used as a support for a 0.5% Pd/C catalyst. The catalyst was prepared by the incipient wetness method using an aqueous solution of $PdCl_2$ obtained from Aldrich. For the dissolution of $PdCl_2$, 2 mol of HCl were added for every mole of salt with heating applied. From a pore size analysis, the distribution of pore size ranged from 5 to 100 nm with a total pore volume of 0.3 $cm^3\ g^{-1}$. The 5% Pd/C obtained from Degussa was supported on a carbon black with serial number E 9011 XR/W 5% had a BET area of 107 $m^2\ g^{-1}$ and a total pore volume of 1.15 $cm^3\ g^{-1}$. These samples were ground with a mortar and pestle and the fraction between 40 and 60 mesh was retained for use in the reactions.

The pore size distribution and pore volume for the Cabot support and Degussa catalysts were measured with a Quantachrom Autosorb-1 volumetric sorption analyzer.

The pore volume for the 0.5 and 5% Pd/C-H was measured at the DuPont Experimental Station.[22]

### 2.2. Reactants

The CFC samples were obtained from the DuPont Experimental Station (CFC 114a $CF_3$-$CFCl_2$ and CFC 115 $CF_3$-$CF_2Cl$), Lancaster Synthesis (CFC 113a $CF_3$-$CCl_3$), and DuPont Suva Refrigerants (HCFC 124-$CF_3$-CFClH). The HCl mixture was obtained from Matheson. Three tanks were used during the course of experiments with 18.9%, 15.6%, and 20.7% HCl in He. This mixture was made at Matheson Gas from technical grade HCl and Matheson purity He. A mixture of $H_2$ and methane, certified as ultrahigh purity, was obtained from Matheson. This mixture contained 1033 ppm methane, used as an internal standard. The hydrogen-methane mixture was passed through a filter containing 5% Pd/C catalyst to react any oxygen in the line into water and trap it on the carbon support. The $H_2$ (BOC gases) was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was obtained from BOC gases and passed through a mass spectrometer gas trap (HP model 5182-3467).

### 2.3. Reactor Configuration

The delivery of reaction gases was controlled by mass flow controllers (Porter Instrument Co.). CFC 113a ($CF_3$-$CCl_3$) is a liquid at room temperature and was added to the reaction mixture by passing helium through the CFC in a saturator. The mass flow controllers were calibrated with bubble flow meters except for the He-HCl mixture. In this case, the flow rates were determined by varying the composition of a mixture of He/HCl and $H_2/CH_4$, analyzing the mixture by gas chromatography, and observing the change in signal of the methane peak.

Reactions were run in a quartz continuous-stirred tank reactor (CSTR) with the catalyst supported on a fritted quartz disk within the reactor and a thermocouple well in contact with the catalyst to allow for precise measurement of the catalyst temperature. The reaction mixture was mixed with a Senior Flexonics pump model MB-21 at a flow rate of about 1400 sccm. The flow rate into the CSTR circuit from the gas delivery portion of the system and the flow rate out of the CSTR circuit were about 100 sccm. The system was kept at ambient pressure. Reaction products were analyzed with a gas chromatograph (HP 5880) and separated with a 5% Krytox 143AC, 60/80 Carbopack B HT 20' × $^{1}/_{8}$" column (Supelco, Inc.). Each of the reactant chlorofluorocarbon and products were calibrated against the methane standard in the hydrogen-methane mixture. Response factors calculated from these calibrations were used to convert the GC signal counts into relative volumetric flow rates. After exiting the system, the gases flowed through a caustic wash (NaOH) to neutralize the HCl in the stream before being vented.

### *2.4. Data Collection Procedure*

Before a new sample of catalyst was used, it was first reduced with a flow of 50 sccm $H_2$ at 300 °C for 3 h. At the start of each set of reactions, the catalyst (200-500 mg) was reduced with 50 sccm of $H_2$ at 150 °C for 30-60 min. During the course of the experiments, the changes in concentration and temperature were chosen in a random order so that any variation in the system would not introduce a systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated and another data point taken. By ensuring that this last point agreed with the first point it could be shown that there was no significant deactivation of the catalyst during the time frame of the experiment.

### *2.5. Surface Area Measurements*

The total surface area was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen-oxygen titration method according to the procedure of Benson et al.[23] with the reactor temperature held constant at 100 °C. The experimental setup consists of a static system with calibrated volumes where the amount of gas adsorbed on the catalyst can be calculated by a change in pressure measured with a pressure transducer (MKS model 127). The samples were reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 3 h at 300 °C before the Pd surface area measurements. In subsequent measurements with the same sample, it was reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 0.5 h at 100 °C. The crystallite size based on chemisorption measurements was estimated from the expression $d$ (nm) = 112/(percentage of metal exposed). This expression assumes spherical particles and a Pd surface atom density equal to an average of the low index planes of $1.27 \times 10^{19}$ atoms.[24]

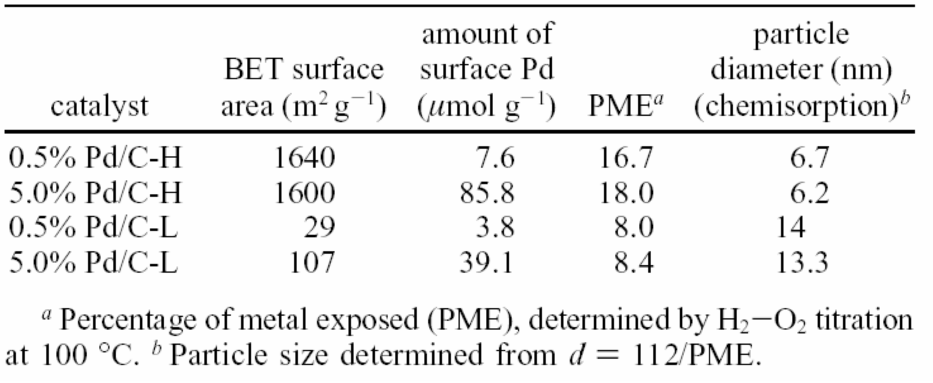
### *2.6. Error Analysis*

We have compared the data for the same experiment carried out at identical conditions to calculate the experimental error. The errors in reaction orders are at maximum 10% or maximum 0.1 in 1.0. For the apparent activation energies, the errors were about 10 kJ mol$^{-1}$. The reproducibility of turnover rate measurements were better than 10%.

## **3. Results**

### *3.1. Catalyst Properties*

Table 1 summarizes the properties of the catalysts used in this study. Four different catalysts with a loading of Pd of 0.5 and 5% and three different carbon supports were used. The high surface area support is designated C-H, and the two low surface area ones are designated C-L. The carbon supports varied in surface area but most importantly in the amount of microporosity. The low surface area supports are nonmicroporous. This property will be important since some of the reactants will condense in the micropores under reaction conditions. The data included in Table 1 are for the catalysts before reaction. Since no deactivation was observed during reaction, except in instances to be discussed below, we do not expect any significant change in the properties of the catalyst after reaction.



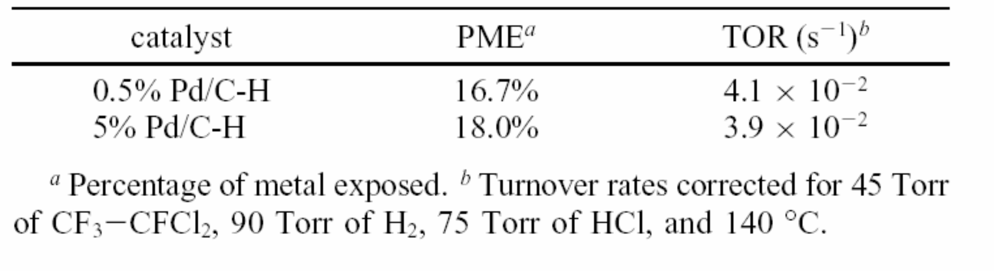
| catalyst | BET surface area ($m^2\ g^{-1}$) | amount of surface Pd ($\mu$mol $g^{-1}$) | PME[a] | particle diameter (nm) (chemisorption)[b] |
|---|---|---|---|---|
| 0.5% Pd/C-H | 1640 | 7.6 | 16.7 | 6.7 |
| 5.0% Pd/C-H | 1600 | 85.8 | 18.0 | 6.2 |
| 0.5% Pd/C-L | 29 | 3.8 | 8.0 | 14 |
| 5.0% Pd/C-L | 107 | 39.1 | 8.4 | 13.3 |

[a] Percentage of metal exposed (PME), determined by $H_2-O_2$ titration at 100 °C. [b] Particle size determined from $d = 112/\text{PME}$.

**Table 1. Catalyst Properties**

### *3.2. Test for Possible Heat and Mass Transfer Limitations*

To test for the presence of heat and mass transfer limitations, the Madon-Boudart test[25-27] was employed. The test consists of measuring reaction rates over two catalysts with different metal loading but with similar percentage of metal exposed (PME). The test was performed for the hydrodechlorination of $CF_3$-$CFCl_2$ (CFC 114a) and the catalyst with the highest surface area. The results are summarized in Table 2.



| catalyst | PME[a] | TOR ($s^{-1}$)[b] |
|---|---|---|
| 0.5% Pd/C-H | 16.7% | $4.1 \times 10^{-2}$ |
| 5% Pd/C-H | 18.0% | $3.9 \times 10^{-2}$ |

[a] Percentage of metal exposed. [b] Turnover rates corrected for 45 Torr of $CF_3-CFCl_2$, 90 Torr of $H_2$, 75 Torr of HCl, and 140 °C.

**Table 2. Test for Possible Heat and Mass Transfer Limitations**

### *3.3. Kinetic Results*

The catalytic hydrodechlorination of a family of four compounds was carried out over Pd catalysts supported on carbon. The data used to derive the reaction orders and activation energy will be presented in detail for one of the compounds ($CF_3$-$CFCl_2$). For the other three compounds, only the numerical results in tables will be presented. The range where the data was collected will be presented in the text. As will be presented below, the product distribution is given together with the turnovers rates, but it is important to emphasize that it is independent of conversion. Different catalysts were used for the experiments, from low to high total surface area, and thus with different amounts of micropores. Microporosity affected the determination of the order of reaction for the chlorofluorocarbon. Note also that the rates could not be measured at the same conditions for all the compounds since their reativities span a range of $10^7$. The reaction data will be compared at the same conditions at the end of this section. Results from the literature for a Pd foil were also included for direct comparison.

No deactivation of the samples used for kinetic tests was observed for the duration of the tests. The same sample was usually used for a number of days in the determination of kinetic parameters.

*3.3.1. $CF_3$-$CFCl_2$.* The hydrodechlorination reaction of CFC 114a ($CF_3$-$CFCl_2$) was carried over a low and a high surface area catalyst and the experimental results are summarized in Table 3. Data from the literature on a Pd foil is also shown for comparison. Three main products are formed corresponding to the hydrodehalogenation on the carbon that contains chlorine. As the number of halogens removed increases, there is a corresponding increase in the apparent activation energy for the reaction. The CFC orders (Figure 1), $H_2$ orders (Figure 2), and HCl orders (Figure 3) are close to 1, 0.5, and -1, respectively, and were determined by varying the amount of reactant under study and keeping all the other variables constant. In particular, note that because the HCl produced in the reaction inhibits the rates, excess HCl was added in all experiments (except for the HCl order determination) to minimize the number of variables. The conversion of CFC 114a was varied from 0.3% to 15% for the 0.5% Pd/C-H catalysts, with the selectivity remaining constant toward all three products. The selectivity was also constant for the other catalysts. Apparent activation energies were determined from Arrhenius plots as illustrated in Figure 4.

| | | | | | reaction order dependence | | |
|---|---|---|---|---|---|---|---|
| catalyst | product | TOR ($s^{-1}$)[a] | selectivity[b] | $E_a$ (kJ $mol^{-1}$) | CFC 114a | $H_2$ | HCl |
| 0.5% Pd/C-L | $CF_3-CH_3$ | $1.2 \times 10^{-2}$ | 4% | 100 | 0.75 | 0.30 | −0.90 |
| | $CF_3-CFH_2$ | $2.7 \times 10^{-1}$ | 84% | 100 | 0.75 | 0.35 | −0.85 |
| | $CF_3-CHFCl$ | $4.0 \times 10^{-2}$ | 12% | 75 | 0.75 | 0.55 | −0.80 |
| 0.5% Pd/C-H | $CF_3-CH_3$ | $1.9 \times 10^{-2}$ | 3.6% | 130 | 0.50 | 0.20 | −1.00 |
| | $CF_3-CFH_2$ | $4.8 \times 10^{-1}$ | 88.1% | 130 | 0.45 | 0.40 | −1.00 |
| | $CF_3-CHFCl$ | $4.5 \times 10^{-2}$ | 8.3% | 125 | 0.40 | 0.45 | −0.70 |
| Pd foil[c] | $CF_3-CH_3$ | $1.4 \times 10^{-3}$ | 2.6% | 95 | 0.90 | −0.20 | −0.70 |
| | $CF_3-CFH_2$ | $4.5 \times 10^{-2}$ | 85.5% | 110 | 0.80 | 0.45 | −1.20 |
| | $CF_3-CHFCl$ | $6.3 \times 10^{-3}$ | 12.0% | 100 | 0.90 | 0.50 | −1.00 |

[a] Turnover rates corrected for 150 Torr of $CF_3-CFCl_2$, 200 Torr of $H_2$, 20 Torr of HCl, and 150 °C. [b] The selectivity is independent of conversion. [c] Data from Ribeiro et al.[8] Reaction orders were assumed to be 1, 0.5, and −1 for CFC 114a, $H_2$, and HCl, respectively.

**Table 3. Kinetic Data for $CF_3$-$CFCl_2$ (CFC 114a) Hydrodechlorination**

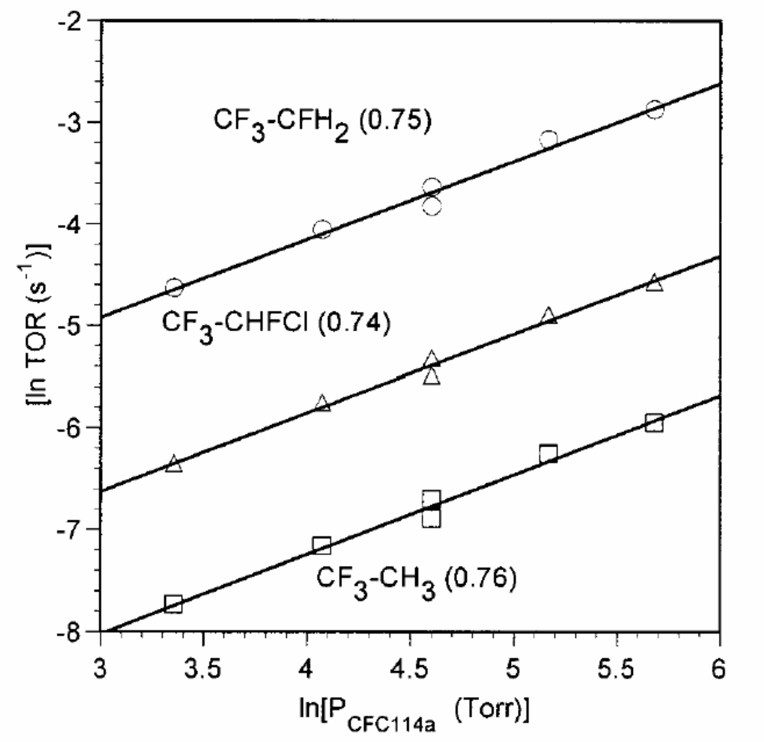


**Figure 1. Determination of reaction order in CFC 114a ($CF_3$-$CFCl_2$) on 0.5% Pd/C-L. Experiments carried out at 130 °C, 28-300 Torr of CFC 114a, 233 Torr of H2, 35 Torr of HCl. Turnover rates corrected to 200 Torr of $H_2$, 20 Torr of HCl.**

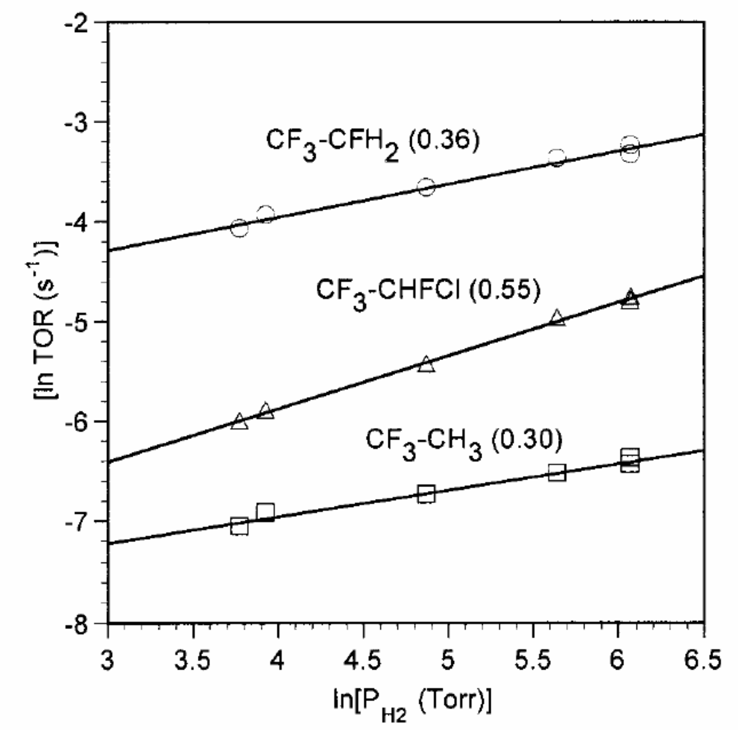


**Figure 2.** **Determination of reaction order in H2 for the reaction of CFC 114a ($CF_3$-$CFCl_2$) on 0.5% Pd/C-L. Experiments carried out at130 °C, 110 Torr of CFC 114a, 65-430 Torr of $H_2$, 42 Torr of HCl. Turnover rates corrected to 150 Torr of CFC 114a, 20 Torr of HCl.**

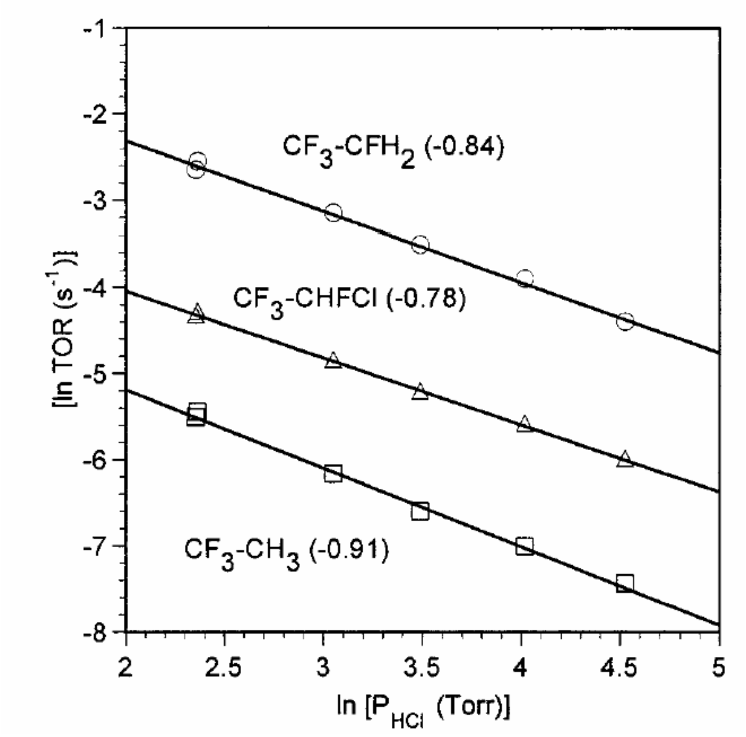


**Figure 3.** **Determination of reaction order in HCl for the reaction of CFC 114a ($CF_3$-$CFCl_2$) on 0.5% Pd/C-L. Experiments carried out at 140 °C, 95 Torr of CFC 114a, 192 Torr of $H_2$, 10-90 Torr of HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of $H_2$.**

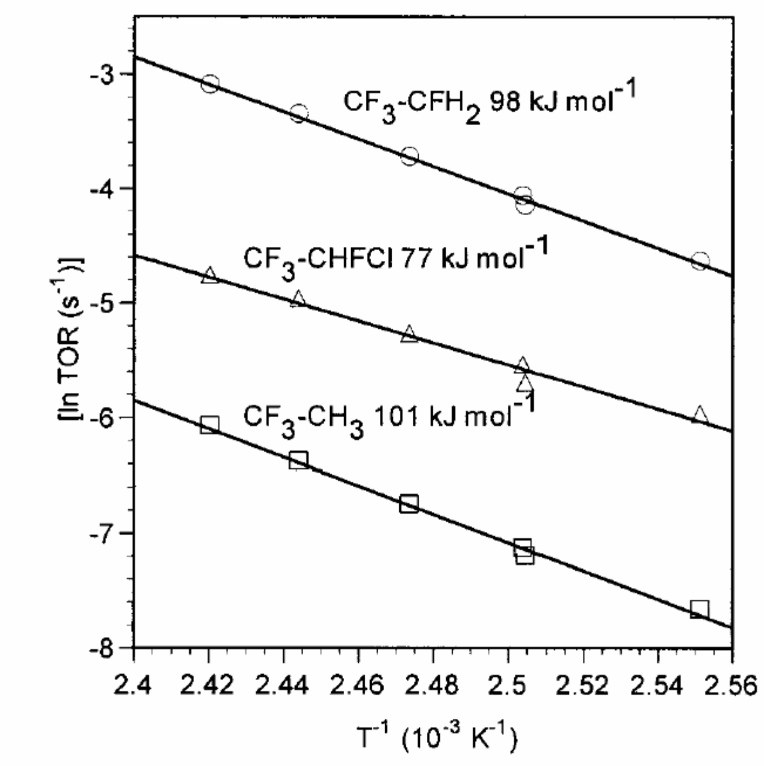
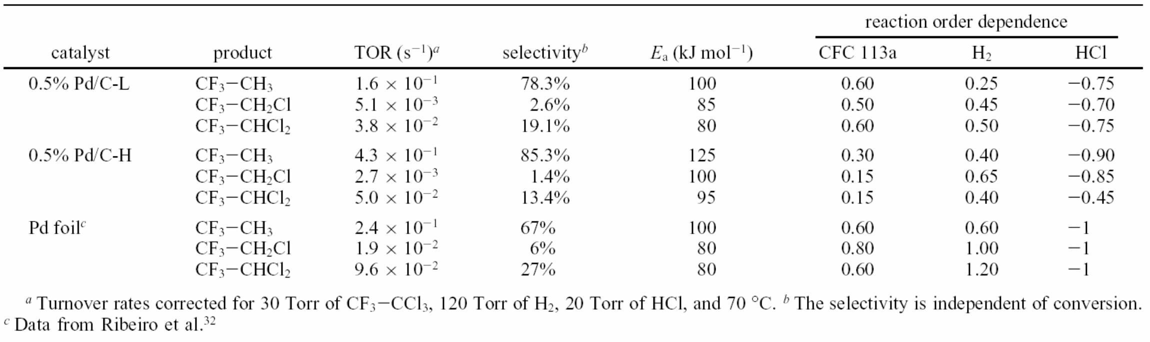


**Figure 4. Arrhenius plot for the reaction of CFC 114a ($CF_3$-$CFCl_2$) on 0.5% Pd/C-L. Experiments carried out at 110-140 °C, 168 Torr of CFC 114a, 341 Torr of $H_2$, 49 Torr of HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of $H_2$, 20 Torr of HCl.**

The conditions for the determination of apparent activation energies were 110-140 °C, 170 Torr of CFC, 340 Torr of $H_2$, and 50 Torr of HCl. For the CFC order determination, the conditions were 130 °C, 30-300 Torr of CFC, 230 Torr of $H_2$, and 35 Torr of HCl. For the $H_2$ order, the conditions were 130 °C, 120 Torr of CFC, 65-430 Torr of $H_2$, and 40 Torr of HCl. For the HCl order, the conditions were 140 °C, 95 Torr of CFC, 190 Torr of $H_2$, 10-90 Torr of HCl.

*3.3.2. $CF_3$-$CCl_3$.* The same catalysts used above were also used for the hydrodechlorination (HDCl) of $CF_3$-$CCl_3$ (CFC 113a). The kinetic parameters for the hydrodechlorination of CFC 113a are summarized in Table 4. The activation energies increase with the number of chlorine atoms removed. The product distribution is highest for the fully hydrogenated, chlorine-free product, $CF_3$-$CH_3$. The selectivity toward the monohydrogenated product, $CF_3$-$CFHCl_2$ is significant (~26%) at reaction conditions. The reaction products are much less reactive than the reactant, and the reaction observed is not in series. In fact, the reactant conversion was varied from 0.4 to 4.2% with the selectivity remaining constant toward all three products.



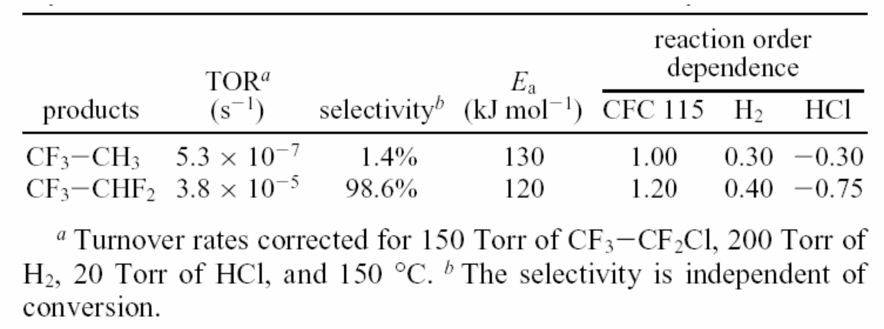
| | | | | | reaction order dependence | | |
|---|---|---|---|---|---|---|---|
| catalyst | product | TOR ($s^{-1}$)[a] | selectivity[b] | $E_a$ (kJ $mol^{-1}$) | CFC 113a | $H_2$ | HCl |
| 0.5% Pd/C-L | $CF_3-CH_3$ | $1.6 \times 10^{-1}$ | 78.3% | 100 | 0.60 | 0.25 | −0.75 |
| | $CF_3-CH_2Cl$ | $5.1 \times 10^{-3}$ | 2.6% | 85 | 0.50 | 0.45 | −0.70 |
| | $CF_3-CHCl_2$ | $3.8 \times 10^{-2}$ | 19.1% | 80 | 0.60 | 0.50 | −0.75 |
| 0.5% Pd/C-H | $CF_3-CH_3$ | $4.3 \times 10^{-1}$ | 85.3% | 125 | 0.30 | 0.40 | −0.90 |
| | $CF_3-CH_2Cl$ | $2.7 \times 10^{-3}$ | 1.4% | 100 | 0.15 | 0.65 | −0.85 |
| | $CF_3-CHCl_2$ | $5.0 \times 10^{-2}$ | 13.4% | 95 | 0.15 | 0.40 | −0.45 |
| Pd foil[c] | $CF_3-CH_3$ | $2.4 \times 10^{-1}$ | 67% | 100 | 0.60 | 0.60 | −1 |
| | $CF_3-CH_2Cl$ | $1.9 \times 10^{-2}$ | 6% | 80 | 0.80 | 1.00 | −1 |
| | $CF_3-CHCl_2$ | $9.6 \times 10^{-2}$ | 27% | 80 | 0.60 | 1.20 | −1 |

[a] Turnover rates corrected for 30 Torr of $CF_3-CCl_3$, 120 Torr of $H_2$, 20 Torr of HCl, and 70 °C. [b] The selectivity is independent of conversion. [c] Data from Ribeiro et al.[32]

**Table 4. Kinetic Data for $CF_3$-$CCl_3$ (CFC 113a) Hydrodechlorination**

The conditions for the determination of apparent activation energies were 40-65 °C, 56 Torr of CFC, 150 Torr of $H_2$, and 30 Torr of HCl. For the CFC order determination, the conditions were 45 °C, 15-50 Torr of CFC, 150 Torr of $H_2$, and 35 Torr of HCl. For the $H_2$ order, the conditions were 60 °C, 25 Torr of CFC, 35-225 Torr of $H_2$, and 20 Torr of HCl. For the HCl order the conditions were 45 °C, 16 Torr of CFC, 100 Torr of $H_2$, and 2-100 Torr of HCl.

*3.3.3 $CF_3$-$CF_2Cl$.* The results of the hydrodechlorination (HDCl) of $CF_3$-$CF_2Cl$ (CFC 115) are summarized in Table 5. The main products formed were $CF_3$-$CHF_2$ and $CF_3$-$CH_3$ with a selectivity of almost 99% to $CF_3$-$CHF_2$. Selectivity to CFC 115 products, $CF_3$-$CH_3$ and $CF_3$-$CHF_2$, remained constant with varying conversion (1.4-13.6%). Because the amount of the minor product formed is so small, we could not analyze its presence with the mass spectrometer but used the retention time in the gas chromatograph as an identification parameter. It is surprising to find that two C-F bonds are hydrogenated in this case.



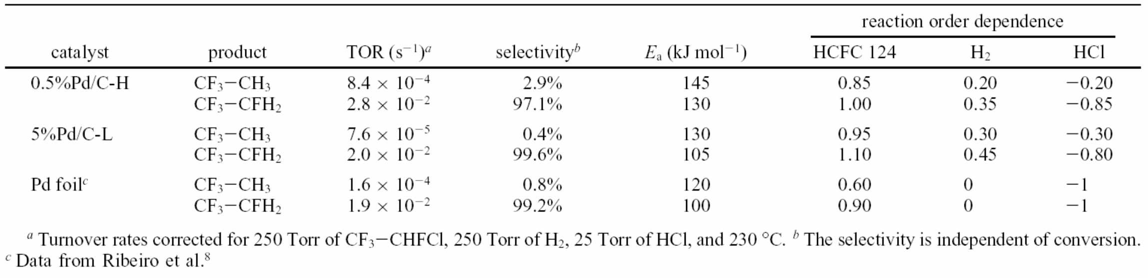
| products | TOR[a] ($s^{-1}$) | selectivity[b] | $E_a$ ($kJ\ mol^{-1}$) | reaction order dependence | | |
|---|---|---|---|---|---|---|
| | | | | CFC 115 | $H_2$ | HCl |
| $CF_3-CH_3$ | $5.3 \times 10^{-7}$ | 1.4% | 130 | 1.00 | 0.30 | −0.30 |
| $CF_3-CHF_2$ | $3.8 \times 10^{-5}$ | 98.6% | 120 | 1.20 | 0.40 | −0.75 |

[a] Turnover rates corrected for 150 Torr of $CF_3-CF_2Cl$, 200 Torr of $H_2$, 20 Torr of HCl, and 150 °C. [b] The selectivity is independent of conversion.

**Table 5. Kinetic Data for $CF_3$-$CF_2Cl$ (CFC 115) Hydrodechlorination**

The conditions for the determination of apparent activation energies were 220-295 °C, 180 Torr of CFC, 330 Torr of $H_2$, and 40 Torr of HCl. For the CFC order determination, the conditions were 260 °C, 90-340 Torr of CFC, 200 Torr of $H_2$, and 25 Torr of HCl. For the $H_2$ order, the conditions were 260 °C, 180 Torr of CFC, 30-400 Torr of $H_2$, and 30 Torr of HCl. For the HCl order the conditions were 260 °C, 145 Torr of CFC, 200 Torr of $H_2$, and 10-65 Torr of HCl.

*3.3.4. $CF_3$-CHFCl.* The last compound to be reported in this study was a hydrochlorofluorocarbon, $CF_3$-CHFCl or HCFC 124. The kinetic results of HCFC 124 are summarized in Table 6. Two products are formed, $CF_3$-$CFH_2$ and $CF_3$-$CH_3$ with a high selectivity for the formation of the HDCl product, $CF_3$-$CFH_2$. The conversion of HCFC 124 was varied from 0.2% to 2.5%, and selectivity values remained constant for both products. There is a higher amount of $CF_3$-$CH_3$ formed for the 0.5% Pd/C-H catalyst. Because the reaction temperature is the highest for this compound, deactivation was observed on one of the catalyst samples 0.5% Pd/C-L (not shown in Table 6). This catalyst deactivated and showed a lower selectivity (92%) toward the most abundant product. The reason for this deactivation was believed to be the presence of an impurity in the carbon support.



| catalyst | product | TOR ($s^{-1}$)[a] | selectivity[b] | $E_a$ (kJ $mol^{-1}$) | reaction order dependence | | |
|---|---|---|---|---|---|---|---|
| | | | | | HCFC 124 | $H_2$ | HCl |
| 0.5%Pd/C-H | $CF_3-CH_3$ | $8.4 \times 10^{-4}$ | 2.9% | 145 | 0.85 | 0.20 | −0.20 |
| | $CF_3-CFH_2$ | $2.8 \times 10^{-2}$ | 97.1% | 130 | 1.00 | 0.35 | −0.85 |
| 5%Pd/C-L | $CF_3-CH_3$ | $7.6 \times 10^{-5}$ | 0.4% | 130 | 0.95 | 0.30 | −0.30 |
| | $CF_3-CFH_2$ | $2.0 \times 10^{-2}$ | 99.6% | 105 | 1.10 | 0.45 | −0.80 |
| Pd foil[c] | $CF_3-CH_3$ | $1.6 \times 10^{-4}$ | 0.8% | 120 | 0.60 | 0 | −1 |
| | $CF_3-CFH_2$ | $1.9 \times 10^{-2}$ | 99.2% | 100 | 0.90 | 0 | −1 |

[a] Turnover rates corrected for 250 Torr of $CF_3-CHFCl$, 250 Torr of $H_2$, 25 Torr of HCl, and 230 °C. [b] The selectivity is independent of conversion. [c] Data from Ribeiro et al.[8]

**Table 6. Kinetic Data for $CF_3$-CFHCl (CFC 124) Hydrodechlorination**

The conditions for the determination of apparent activation energies were 210-240 °C, 200 Torr of CFC, 320 Torr of $H_2$, and 40 Torr of HCl. For the CFC order determination, the conditions were 220 °C, 130-300 Torr of CFC, 200 Torr of $H_2$, and 20 Torr of HCl. For the $H_2$ order, the conditions were 220 °C, 165 Torr of CFC, 30-400 Torr of $H_2$, and 30 Torr of HCl. For the HCl order, the conditions were 225 °C, 130 Torr of CFC, 200 Torr of $H_2$, and 10-70 Torr of HCl.

### *3.4. Condensation of CFC in the Pores of the Support*

On the Pd catalysts with a carbon support with an area of 1600 $m^2$ $g^{-1}$ (0.5% Pd/C-H), the reaction order on $CF_3$-$CFCl_2$ for the three reaction products is ~0.5 (Table 3), much lower than the order postulated (1.0) from the proposed mechanism discussed in the Introduction (eq 1). An explanation for this effect is that most of the surface area of the support is in the microporous regime (1300 $m^2$ $g^{-1}$), which will condense the reactant even if the reaction temperature is above its boiling point (3.6 °C), a known property of microporous solids. In addition, if the reactant is in the liquid state, the reaction order will be zero. The lower than 1.0 reaction order in CFC suggests that a fraction of the carbon support may be filled with liquid at reaction conditions. To determine if the surface is saturated with CFC 114a, adsorption isotherms at 25 °C and 100 °C were obtained. At 25 °C, the adsorption of CFC per gram of catalyst was 0.61 $cm^3$, a volume that is close to the total pore volume of 0.7-0.8 $cm^3$ $g^{-1}$ determined with $N_2$ adsorption. At 100 °C, the amount of CFC 114a adsorbed per gram of catalyst (0.4 $cm^3$ $g^{-1}$) is still substantial, suggesting that the CFC may be condensing on the catalyst micropores at reaction temperature (120 °C).

To determine if the low reaction orders were due to the saturation of the Pd pores, a support with a low surface area and virtually no microporosity was prepared. The 0.5%

Pd/C-L used a carbon support with a total pore volume of ~0.3 $cm^3$ $g^{-1}$, and with no detectable microporosity (Table 1). The reaction order in the three products of the CFC 114a reaction increased from ~0.5 to ~0.75, as shown in Table 3. The reaction orders over the low surface area catalyst are in very good agreement with the reaction orders determined over a Pd foil.

Problems with catalyst pore condensation were more severe with CFC 113a ($CF_3$-$CCl_3$) because its boiling point (45.7 °C) is close to the reaction temperature (50 °C). Thus, the reaction order in CFC 113a over the 0.5% Pd/C-H microporous catalyst in the three products range from 0.1 to 0.3 (Table 4), much lower than the proposed order of 1.0. The reaction orders over the nonmicroporous (0.5% Pd/C-L) catalyst increased to the same values found on a foil (Table 4). The reaction orders in CFC 115 ($CF_3$-$CF_2Cl$) and HCFC 124 ($CF_3$-CHFCl) were not affected by the change in catalyst support. For both catalysts, the reaction order in CFC was ~1 for the main product and ~0.9 for the minor product. Condensation is unlikely to occur on the catalyst pores for CFC 115 and HCFC 124 due to the much larger difference between boiling point (~-20 °C) and reaction temperature (~240 °C).

### *3.5. Bond Energy Calculations*

The kinetic data above allowed us to calculate the overall rates of hydrodechlorination at any reaction condition for the family of four compounds tested (Table 7). The value for the comparison of rates was chosen based on the conditions necessary for the least amount of extrapolation. Temperature was the variable that changed the rate most significantly and was adjusted to keep reaction rates at a level where they could be precisely measured. The relative turnover rate in Table 7 shows that the rates vary by 7 orders of magnitude, and thus the rate of hydrodechlorination is very dependent on the structure of the molecule. From a practical point of view it is highly desirable to be able to predict, or at least correlate, the rate of hydrodechlorination with an easily measured quantity since there is a large number of chlorofluorocarbon compounds available. We attempted to correlate the rate of hydrodechlorination with the bond dissociation energy of the C-Cl bond but could not find values in the literature for the bond energy for the four compounds used. The C-Cl bond energy however can be calculated by different methods. We believe that the easiest method is the group additivity method, which is available specifically for chlorofluorocarbons and related compounds.[28] This method may not be very precise but due to its simplicity it can be used to get a preliminary idea about the bond energies. We also used ab initio methods to calculate the C-Cl bond energies. The computer program Gaussian 94 was used to calculate the C-Cl bond dissociation energy by density functional theory (DFT), with the B3PW91/6-311+G(2d,p)//B3PW91/6-311+G(2d,p) model applied (Table 7). We checked for consistency of results by calculating the bond energy difference when the basis set was varied. The values for the bond energies as the largest basis set and theory level were approached did not vary significantly. Note that the bond dissociation is not calculated directly but by a difference of energies following the expression $E(\text{A-B}) = E(\text{A}) + E(\text{B}) - E(\text{AB})$.

Once the bond energies were available, we correlated them with the rates of reaction using known correlations in catalysis as described in detail by Boudart.[29] Starting with the relationship of Polanyi,[27] which states that for a family of similar reactions the difference in activation energy can be related to the difference of reaction enthalpy,

$$\Delta Ea=\alpha\Delta|\Delta H|$$

and from the Arrhenius equation

$$k=k_0e^{-Ea/RT}$$

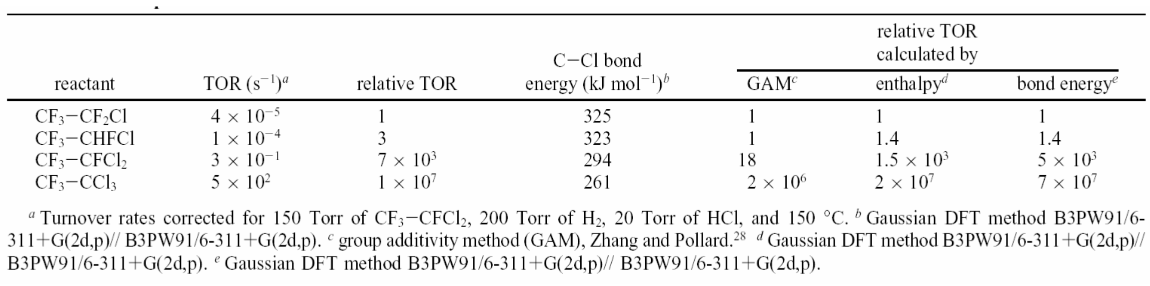
combined with the assumption that $k_0$ is identical for all the reactions in this group, the relative rates can be established for components in the family

$$k_1/k_2=e^{-\Delta Ea/RT}=e^{-\alpha\Delta|\Delta H|/RT} \qquad (2)$$

The $\Delta(\Delta H)$ in eq 2 is for the reaction R-Cl + Pd →R-Pd-Cl, where Pd represents the catalytic site. The enthalpy difference $\Delta\ (\Delta H)$ between two family members is composed of three terms, corresponding to dissociation of the R-Cl bond (R-Cl →R + Cl, $\Delta H_{\text{R-Cl}}$), formation of the R-Pd bond (R + Pd →R-Pd, $\Delta H_{\text{R-Pd}}$), and formation of Pd-Cl bond. Note that the enthalpy term for the Pd-Cl bond is common on all members and will cancel out when the difference of enthalpy is calculated. It will be shown next that using a linear free energy formalism, similar to the one in the Hammett relation used in physical-organic chemistry, one needs to calculate only the $\Delta H_{\text{R-Cl}}$ for the reaction R-Cl → R + Cl to calculate the enthalpy difference ($\Delta$ ($\Delta H$)). Suppose one has the following family of reactions with two corresponding members of each family displayed:

$$\left.\begin{array}{l}\mathrm{R{-}Pd} \rightarrow \mathrm{R} + \mathrm{Pd} \\ \mathrm{R'{-}Pd} \rightarrow \mathrm{R'} + \mathrm{Pd}\end{array}\right\}\text{family I} \quad \left.\begin{array}{l}\mathrm{R{-}Cl} \rightarrow \mathrm{R} + \mathrm{Cl} \\ \mathrm{R'{-}Cl} \rightarrow \mathrm{R'} + \mathrm{Cl}\end{array}\right\}\text{family II}$$

Family II is the reference family and family I is the one we would like to find the difference in free energy. The linear relationship between standard free energy for a family of reactions assumes that ($\Delta G^1$ - $\Delta G_0{}^1$) = $\beta$($\Delta G^2$ - $\Delta G_0{}^2$), where the superscript refers to the family in question. The constant $\beta$ depends on the substituent, Pd versus Cl, but will be the same for any two members of the families. If we assume next that entropy factors are the same for the members of the family, then $\Delta$ ($\Delta H^1$) = $\beta\Delta$ ($\Delta H^2$). The difference of enthalpy for the reaction of interest will then be $\Delta$ ($\Delta H$) = (1 -$\beta$)$\Delta$ ($\Delta H_{\text{R-Cl}}$). Substituting the value for $\Delta$ ($\Delta H$) in eq 2 allows one to calculate the turnover rate of any reaction member in the series as a function of the rate constant of a reference member if the difference in enthalpy of the dissociation reaction in the gas phase ($\Delta H_{\text{R-Cl}}$) is known. The experimental value that gives the best fit is one that corresponds to $\alpha$(1 -$\beta$) = 1. A calculation based on this method is shown in Table 7.



| reactant | TOR ($s^{-1}$)[a] | relative TOR | C−Cl bond energy (kJ $mol^{-1}$)[b] | relative TOR calculated by | | |
|---|---|---|---|---|---|---|
| | | | | GAM[c] | enthalpy[d] | bond energy[e] |
| $CF_3-CF_2Cl$ | $4 \times 10^{-5}$ | 1 | 325 | 1 | 1 | 1 |
| $CF_3-CHFCl$ | $1 \times 10^{-4}$ | 3 | 323 | 1 | 1.4 | 1.4 |
| $CF_3-CFCl_2$ | $3 \times 10^{-1}$ | $7 \times 10^3$ | 294 | 18 | $1.5 \times 10^3$ | $5 \times 10^3$ |
| $CF_3-CCl_3$ | $5 \times 10^2$ | $1 \times 10^7$ | 261 | $2 \times 10^6$ | $2 \times 10^7$ | $7 \times 10^7$ |

[a] Turnover rates corrected for 150 Torr of $CF_3-CFCl_2$, 200 Torr of $H_2$, 20 Torr of HCl, and 150 °C. [b] Gaussian DFT method B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p). [c] group additivity method (GAM), Zhang and Pollard.[28] [d] Gaussian DFT method B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p). [e] Gaussian DFT method B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p).

**Table 7. Comparison of Measured Turnover Rates to Predicted Values**

## 4. Discussion

The objective of this work was to measure the rates of hydrodechlorination and reaction orders for a family of compounds, correlate the magnitude of rates to the bond energy of the C-Cl bond, and to derive information on the reaction steps that are kinetically significant. We will start the discussion by pointing out possible artifacts that may provide incorrect results.

### *4.1. Possible Artifacts: Heat and Mass Transport, Condensation of CFC on Pores, Inhibition by HCl.*

Our first task was to show that the rates could be measured without the interference of heat and mass transport gradients, since this reaction is quite exothermic. For that purpose we used the Madon-Boudart test.[25] This test consists of measuring the rates in catalysts with the same percentage of metal exposed (same particle size) but different loading. Table 2 shows that the rates for the two catalysts are not affected by the loading, which indicates that the kinetic data is free of transport limitations for the measurement of CFC 114a ($CF_3$-$CFCl_2$). We did not apply the Madon-Boudart test for the other catalysts or for the other compounds. The catalyst tested in Table 2 is the one with the support with the highest surface area and microporosity and thus the one where transport limitations would be most severe. It is also reasonable to assume that for the other compounds the measurements will be free of transport limitations since the turnover rates were kept in the same range of values ($10^{-2}$ $s^{-1}$) by adjusting the temperature.

From the data presented on in results section 3.4, we can conclude that the lower reaction order on CFC for the support with significant microporosity was caused by condensation of CFC in the micropores. The measured value, without pore condensation, is closer to 1.0 (Table 3). Thus, the data on the microporous supports have to be interpreted carefully. Note that these data shown here only for purposes of comparison. The kinetic parameters are taken from the catalysts where no condensation was observed.

The last artifact to be discussed, and the most pervasive, is the strong inhibiting effect of HCl as observed by a reaction order of close to -1 for the four halogen-containing compounds used in this study. This effect was reported in other studies by Campbell and Kemball[4] and Coq et al.[12] Note that inhibition is distinct from poisoning since it is reversible and caused simply by competition of sites between HCl and the reactant (see mechanism discussed in the Introduction). Thus, the amount of HCl present (or conversion) should be specified when rates are reported. For example, the rate would increase by about 10 times if the concentration of HCl was decreased by 10 times. Another effect of not considering the inhibition by HCl, to be discussed below, is that "the apparent activation energy" will be 2 times lower than the correct one. It is thus critical to establish and correct the effect of HCl for hydrodechlorination reactions. Note that a more complex interaction of HCl with a Pt particle was discussed by Zhang and Beard.[30] The authors suggested that on small particles of Pt (about 0.5 nm) HCl can bind irreversibly decreasing the rate for hydrodechlorination of $CCl_4$ but on larger particles (about 6 nm) the effect is not present.

### *4.2. Reaction Orders*

The reaction orders were measured for all reaction products. There are at least two products formed when the reactants are hydrogenated, and in some cases three. The reason for the multiple products is that all halogens (including fluorine) can be substituted by a hydrogen in the carbon that contains chlorine. It is important to state again that the reaction orders in CFC on the high surface area catalyst 0.5% Pd/C-H are lower than expected due to condensation in the pores of the support. The results for the CFC order will be discussed for the catalysts where no condensation is observed.

As discussed in the Introduction, the reaction order proposed before for hydrodechlorination is first order in CFC, half order in $H_2$, and inverse first order in HCl. For the first chlorine removed, the results are close to the proposed values with the following observations. (1) The orders for the CFCs are quite similar to the values found for a foil and are slightly lower than 1.0. (2) The orders for $H_2$ and HCl are quite close to the expected value of half and inverse first order. It is important to note that the discrepancies are not a result of an error in the measurements. The cause for these discrepancies may be related to the shortcomings of our proposed kinetic mechanism, where a multi-step process is being simplified by a unique rate-determining step.

For two of the compounds tested ($CF_3$-$CFCl_2$ and $CF_3$-$CCl_3$), a second chlorine is also removed. The kinetic orders again conform to the expected rates. When a third halogen is removed to form $CF_3$-$CH_3$, the reaction order in $H_2$ and HCl however is much lower. In three of the compounds, one fluorine atom was removed, and in the fourth compound ($CF_3$-$CCl_3$) another chlorine atom was removed. Whatever the case, the reaction order in $H_2$ is lower than the expected value of 0.5 while the reaction order is also low for HCl on $CF_3$-CFHCl and $CF_3$-$CF_2$Cl. One explanation is that this is a reaction network and the assumed rate-determining step may not be a good approximation for the reaction mechanism where two very strong bonds are broken. The lower order dependence in $H_2$ for this reactant was reported before for a foil[8] and two single crystals[31] and can be seen in Tables 3 and 6 for the foil data. The hydrogen orders for $CF_3$-$CCl_3$ on the foil (Table 4) may be due to absorption of hydrogen in the Pd foil at the low reaction temperatures for that experiment.[32]

### *4.3. Reaction Selectivity*

An important feature of all four of the hydrodechlorination reactions studied is the reaction selectivity. The numbers of reaction products with varying degrees of hydrogenation were two or three depending on the reactant molecule. Experiments were conducted to determine the effect of conversion on the selectivity for each reactant. The selectivity toward the products remained constant as the conversion was varied in all catalysts tested and for all four reactants. This fact implies that the products are formed in a parallel reaction network on the surface. In other words, once the reactant adsorbs, it desorbs as a product that does not return to the surface again. This fact is supported by the observation that the reaction products are much less reactive than the reactant, and once they leave the surface of the catalyst they do not compete for adsorption with the reactant. The addition of hydrogen makes the remaining C-Cl bonds stronger. For example, as can be verified in Table 7, for the reaction of $CF_3$-$CFCl_2$ the monohydrogenated product ($CF_3$-CFHCl) is about 3000 times less active than the reactant.

Although the selectivity for a given catalyst does not change during an experiment, the selectivity of the reaction for different catalysts may change. This change in selectivity is usually associated with a deactivation. One explanation, based on the results of Table 6, is that impurities on the carbon play a role in the reaction. The catalyst 0.5% Pd/C-H (Table 6) based on a coconut support shows a lower selectivity toward the main product than a sample supported on a high purity carbon (5% Pd/C-L). It is possible that due to the higher temperature used in the hydrodechlorination of $CF_3$-CFHCl (about 250 °C), impurities on the carbon support are migrating and interacting with Pd and changing its selectivity. An even bigger change in selectivity was observed for the 0.5% Pd/C-L sample (not shown in Table 6) where the initial selectivity to $CF_3$-$CFH_2$ decreased to 92% with the sample also deactivating as a function of time. The Pd surface area decreased by a factor of 4 after reaction. This is a carbon black not purified for catalysis applications and impurities may be migrating to the Pd particles. Another example on the role of impurities on the carbon support is described by van de Sandt et al.[33] on the performance of hydrodechlorination catalysts. A more indirect effect is the interaction between the support and Pd as proposed by Coq et al.[34] to explain a large change in the selectivity for the reaction of $CF_2Cl_2$ hydrodechlorination over different supports. Another possibility is that the reaction is sensitive to the structure of the catalyst and structural changes on the Pd particles are induced by the support. However, this does not seem to be the case, as different single crystal structures of Pd did not change substantially the selectivity, but the addition of an impurity (sulfur) changed the selectivity drastically.[9] In addition to selectivity changes, Krishnankutty and Vannice[35] have proposed that the carbon support modifies the properties of the Pd catalyst for some reactions by providing interstitial and surface atoms to Pd.

### *4.4. Apparent Activation Energy*

The apparent activation energy for the various reactions varied from 80 to 145 kJ mol$^{-1}$. There is a small but definite trend of a higher apparent activation energy as more halogens are removed. This trend does not support the existence of a common rate-determining step for all reaction products since an unique rate-determining step for all of them also implies an unique activation energy value. The fact that the activation energy increases as more halogens are removed is an indication that a more complex reaction network than the one we are proposing for this reaction is necessary, in other words, that the rate determining step assumption is only an approximation.

The activation energy is quite similar between the low surface area support catalyst (0.5% Pd/C-L) and the Pd foil. However, the activation energy was always higher on the high surface area support catalyst (0.5% Pd/C-H). As discussed above, one difference with this catalyst is the microporous support which causes condensation of the CFC on the pores at reaction temperature. As will be discussed next, this condensation cannot explain a higher activation energy. We measured the "enthalpy of interaction" for $CF_3$-$CFCl_2$ between 25 and 100 °C using the Clausius-Clapeyron relation. The experimental procedure consisted of collecting adsorption isotherms at four different temperatures using the gas adsorption system described in section 2.5. At a coverage that corresponds to about 20% of a monolayer on the carbon support, the enthalpy of interaction was 40 kJ $mol^{-1}$ on the microporous support of the catalyst 0.5% Pd/C-H and 14 kJ $mol^{-1}$ on the nonmicroporous support of the catalyst 0.5% Pd/C-L. We interpret the difference in enthalpy of interaction between the two samples as an indication of the different microporous nature of the samples since the microporous structure will cause a different interaction of the molecules being adsorbed. This fact has been discussed in the literature, for example by Vernov et al.,[36] who described how the heat of adsorption and condensation is significantly higher on microporous solids. Even though the adsorption on the support should not interfere with the apparent activation energy step, in the case of the microporous support, the temperature will influence the amount of pore condensation, which in turn will influence the fraction of reaction that is occurring in the liquid versus gas phase. If the rates are dependent on the phase of the reactant, and if the rate is higher when there is condensation (note in Tables 3, 4, and 6 that the overall rates are 1.5-2.5 higher on the microporous solid Pd/C-H), then the apparent activation energy will be lower due to pore condensation, which is the opposite of the effect observed. Another possibility is an effect of the carbon support on the Pd. Krishnankutty and Vannice studied adsorption, absorption,[37] and reaction properties[35] on Pd/C catalysts and found that the turnover rates and activation energies for CO and benzene hydrogenation could be affected by the carbon support when compared with catalysts supported on other materials. For hydrodechlorination, this explanation does not seem to carry over, as the rates, apparent activation energies, and reaction orders are similar for a foil (unsupported) and a Pd/C sample.

It is important to note that the activation energies will be calculated incorrectly if the inhibiting effect of HCl is not accounted for. The activation energy is usually measured by increasing the temperature for a fixed amount of catalyst which implies that the conversion level will increase with the reaction temperature. If excess HCl is not added to the feed, as the temperature is increased the rate will not increase as fast as expected because more HCl is also being produced. It is easy to calculate that if excess HCl is not added and the rates not corrected for its effect, the "apparent activation energy" will be one-half of the actual value. Apparent activation energy results of Karpinski et al.[38] for the hydrodechlorination of CFC 114a ($CF_3$-$CFCl_2$) are approximately a factor of 2 lower than those calculated in this study. This factor may be due to the effect of HCl, although some of their data suggests that the reaction order in HCl is zero order.

### *4.5. Comparison of Rates with the Ones in the Literature*

We have attempted to compare the measured rates in this study with others in the literature. We made a direct comparison with the hydrodechlorination rates on a Pd foil[9,32] for CFC 113a ($CF_3$-$CCl_3$), HCFC 124 ($CF_3$-CFClH), and CFC 114a ($CF_3$-$CFCl_2$) as summarized in Tables 3, 4, and 6. The rates show a factor of 2-6 difference between the foil and Pd supported on carbon. The selectivity is similar for supported and unsupported catalysts. This agreement is excellent when one takes into consideration the uncertainties in measuring rates on catalysts with vastly different metal surface area. This agreement also confirms that the reaction is structure insensitive since the rates are also similar to the ones on Pd(110) and Pd(111).[9] We can also conclude that the carbon support does not play a significant role on the hydrodechlorination chemistry (except when impurities in the carbon are present, as discussed above).

Numerous studies of hydrodechlorination reactions have been conducted, but many did not report a turnover rate[15] or did not quantify the effect of HCl. Comparison of rates with the ones in the literature was thus not possible. In some other cases, the turnover rate was reported but the reaction order on HCl was different from ours, indicating a different reaction mechanism possibly by reaction of chlorine with the support.[38, 20]

Another difficulty in comparing rates in catalytic reactions in general is deactivation. Although we did not observe deactivation for the catalyst in our studies, Early et al.[20]

observed deactivation for the reaction of $CF_3$-$CFCl_2$ on non-carbon supported samples. Interestingly, the same catalysts are stable for the hydrodechlorination of $CF_2Cl_2$.[20, 39] Oxide supports may react with chlorine and fluorine produced in the reaction if the conditions of reaction are appropriate. The newly formed halogenated support may have a lower total surface area causing the metal particles to sinter.[40] For the catalysts supported on carbon, however, Wiersma et al.[19] reported that the Pd surface area actually increases with time on stream for the reaction with $CF_2Cl_2$. These catalysts still deactivated due to strong adsorption of deposits on the surface.

### *4.6. Correlating C-Cl Bond Energy with Reaction Rates*

As suggested in Table 7, the rate of reaction increases as the bond energy decreases. A quantitative comparison was made using the relationship of Polanyi as discussed above. The results of the comparison were shown in Table 7. The rates calculated using the bond strength estimated from the Group Additivity Method could not predict the rates for $CF_3$-$CFCl_2$ very well. The reason for the discrepancy is that it is an approximate method. For the comparison of bond strength with the ones in the literature, we could find the C-Cl bond energy only for $CF_3$-$CF_2Cl$ from the work of Coomber and Whittle[41] with a value of $346.0 \pm 7.1$ kJ $mol^{-1}$, a difference of 21 kJ $mol^{-1}$ or 6% from the value calculated in Table 7. Note that the values listed in Table 7 are calculated at 0 K but the one in the literature is at 298 K. Making the necessary temperature corrections using Gaussian provides a value for the bond strength at 298 K of 324.6 kJ $mol^{-1}$, an even larger difference. The temperature corrections from 0 to 298 K were 5-10 kJ $mol^{-1}$ and did not affect the relative comparisons. We kept the values at 0 K because they are easier to calculate. The comparison with the experimental rate results using the values from the ab initio calculations showed excellent matching. Note that the values calculated using the bond strength do not differ from the ones calculated using the enthalpy of reaction and that the reaction temperature chosen for the comparison in Table 7 (150 °C) was picked in the middle of the temperature range used in the experiments to minimize errors by extrapolation. Note, however, that using other reaction temperatures for the comparison in the range 50-200 °C produced similar but not identical results as the apparent activation energies are not the same.

This agreement for the rates is important in practice because it allows one to predict the rate of dechlorination for a series of compounds. It also gives important insight for the reaction steps. It strongly suggests that the rate-determining step involves the scission of the C-Cl bond. If this is the case, the relative difference in activation energies should be the same as the relative difference in bond energies. The values for the activation energies, however, show the right trend but do not provide good qualitative prediction. For example, the difference in bond energy between the extremes of the comparison, $CF_3$-$CF_2Cl$ and $CF_3$-$CCl_3$, is 63 kJ $mol^{-1}$, but the difference in the apparent activation energies for the hydrodechlorination of the first chlorine is only 22 kJ $mol^{-1}$.

The correlation between rate of dehalogenation and bond strength was also observed for the rate of hydrodefluorination. The rate of hydrogenation is higher for compounds with a lower number of fluorine atoms (lower bond strength) attached to the carbon.[42]

Note that linear free energy relationships, in the form of the Hammett equation of physical-organic chemistry, have been used before for hydrodechlorination. The rates for the hydrodechlorination of substituted chlorobenzene[43] varied by a factor of 10 and followed the Hammett relation as different substituents on the benzene ring were added. A similar Hammett relation for dehalogenation was described for aliphatic compounds by Buelow et al.[44] who found that the rate constant for dissociative adsorption decreased as more fluorine atoms were added.

### *4.7. Reaction Steps*

From the reaction kinetics, it was proposed that the rate-determining step involves the scission of the C-Cl bond, the active site may consist of one Pd atom, and that $H_2$ and HCl are in equilibrium with adsorbed H and Cl. We also know from the rate measurements that the product distribution is independent of conversion, which implies that the reactant adsorbs on the surface and reacts in a sequential manner. In other words, there is no readsorption of products for further reaction. We propose that the rate-determining step (RDS) for a generic R-Cl reactant is the oxidative addition:

$$\text{R-Cl} + \text{Pd} \rightarrow \text{R-Pd-Cl}$$

with Pd making a $\sigma$-bond with the carbon atom in the R fragment. This type of addition can be found in the organo-transition metal chemistry literature. The oxidative addition of an alkyl halide R-X on a Pd(0) species to produce a $\sigma$-alkyl metal halide complex has been reported,[45] although examples are more common when R is aryl or vinyl.[46] The latter groups are apparently more reactive. This higher reactivity has been observed on a $Pt/Al_2O_3$ catalyst where vinyl chloride was found to be much more reactive than ethyl chloride[10] for hydrodechlorination. Note again that we have no direct evidence for this step, except for the analogy with organometallic chemistry. Once the R-Pd-Cl compound is formed, hydrogen atoms on the surface may attack it forming R-H and Pd-Cl or R-Pd and HCl. In the first case, a monohydrogenated compound is formed, and in the second case, another chlorine (or fluorine) may be extracted from R forming R=Pd-Cl. We also have no information on the nature of the carbene-like species formed, and the fragment R could be bound to two Pd atoms on the surface. This complex may be attacked by a hydrogen again forming a hydrogenated species, or it may lose another halogen. The product distribution will depend on the relative rates of hydrogenation versus dehalogenation. Note that the reasoning about these reaction steps is based exclusively on the fact that the product distribution is independent of conversion and thus there must be a sequential reaction (dehalogenation/hydrogenation) on the surface. Examples of proposed sequential reactions are the hydrodechlorination of $CCl_4$,[14] $CCl_2F_2$,[18,47] and $CF_3$-$CFCl_2$.[38,8] This property is due to the fact that the products are less reactive than the reactants: as the molecule undergoes sequential hydrodechlorination, the remaining C-Cl bonds on the hydrogenated carbon become stronger.

There are other studies in the literature about the reaction steps for hydrodechlorination. Campbell and Kemball[4] studied the hydrodechlorination of $CH_3$-$CH_2Cl$ on Pd films. The reaction order in HCl and ethyl chloride were determined and were the same as reported here. Through reaction with $D_2$, they found that the reaction mechanism must involve the formation of a carbene-like species since the product (ethane) was substantially enriched in $CH_3$-$CHD_2$. Zhou et al.[48] found that the dehalogenation step (the RDS in our case) is homolytic, as also proposed here. The studies by Coq et al.[12] for the hydrodechlorination of chlorobenzene on Pd proposes a rate equation that is kinetically indistinguishable from the one presented here, and thus the rate data for chlorobenzene supports the reaction steps proposed here. Note however that the reaction steps proposed by Coq et al.[12] for hydrodechlorination of chlorobenzene differ from the ones presented here. As is well-known, different reaction steps can be constructed that will produce the same rate equation. Some of the kinetic parameters for the hydrodechlorination of $CF_2Cl_2$ have also been discussed. The inhibition by HCl is confirmed by Coq et al.[12] and van de Sandt et al.[47] but not observed by Ahn et al.[17] The reaction steps and overall rate proposed by Coq et al.[18] and Ahn et al.[17] are quite different than the ones reported here. The reaction steps may be different for this compound.

A direct experiment to verify the nature of the adsorbed intermediates is not available. Deshmukh and d'Itri[49] attempted to trap fluorocarbene species formed on the reaction of hydrodechlorination of $CCl_2F_2$ by reaction with ethylene but could not observe any fluorinated addition product. As discussed by the authors, the concentration of the fluorocarbene may be very small, which is to be expected if the rate-determining step is the first dechlorination as proposed here. Evidence that a carbene species is formed can be derived by observing the product distribution for the reaction of $CF_3$-$CFCl_2$ (Table 3) and $CF_3$-CFHCl (Table 6). The ratio of products $CF_3$-$CFH_2$ to $CF_3$-$CH_3$ is about 20 for the first compound and about 250 for the second compound. The reason for this difference is that for $CF_3$-$CFCl_2$ a carbene-like species can be formed by dechlorination but in the case of $CF_3$-CFHCl a C-H or a C-F bond, much stronger bonds than C-Cl, need to be broken for the carbene to form.

There are still a few issues that the reaction steps proposed cannot explain. One that does not seem intuitive is the tendency of hydrogenating C-F bonds on chlorofluorocarbons. These bonds are much stronger than the C-Cl bonds and should not be broken at the conditions where the C-Cl bonds are broken. For example, the C-F bond in $CF_3$-$CFCl_2$ is 100 kJ $mol^{-1}$ stronger than the C-Cl bond, and yet the C-F bond is broken in about 5% of the products. Another example is for $CF_3$-$CF_2Cl$ where $CF_3$-$CF_2H$ is the main product with $CF_3$-$CH_3$ as the minor product but $CF_3$-$CFH_2$ was not detected. A similar example in the literature is the hydrodefluorination of $CH_3$-$CF_2H$ which forms ethane almost exclusively but no $CH_3$-$CFH_2$.[42] Explaining the selectivity is still not possible and a complete reaction network with additional steps to the ones proposed here is necessary.

## 5. Summary and Conclusion

The turnover rates and reaction orders were determined for a family of four chlorofluorocarbons. The rates of hydrodechlorination span a range of 7 orders of magnitude, which shows that the rates are very dependent on the structure of the chlorofluorocarbons. Fortunately, we found out that the rates correlate very well with the strength of the C-Cl bond. Rates can be predicted within a factor of 7 in a range of $10^7$ for the four compounds tested provided that the rate for one of the members of the family is known.

The reaction steps for the reaction of hydrodechlorination were proposed based on the orders of reaction. The rate-determining step involves the C-Cl scission bond since the rates correlate with the strength of the C-Cl bond. By analogy to organometallic chemistry, we propose that this step is the oxidative addition of the reagent in one Pd atom. Surface H and Cl are in equilibrium with $H_2$ and HCl in the gas phase and the most abundant surface intermediate is chlorine. This kinetic scheme explains the strong inhibition of HCl in hydrodechlorination reactions. It is clear that these products are formed in a sequential step on the surface and not from a sequential re-adsorption of products from the gas phase. The reaction order in $H_2$ is particularly low for the product where all the halogens have undergone hydrodehalogenation (formation of $CF_3$-$CH_3$). We suggested that only one Pd atom is involved in the rate-determining step which explains why the overall rate does not change with the Pd structure. The rates for supported catalysts are comparable to the ones on a foil or a single crystal indicating that the carbon support does not play a role in the hydrodechlorination chemistry (except for impurities on the carbon). To explain the reaction selectivity remains a challenge.

There are some artifacts that need to be avoided when studying this chemistry. Microporosity is common in many carbon supports and because the boiling point of chlorofluorocarbons is close to the reaction temperature, there is the possibility for condensation on the pores of the carbon. This condensation may affect the reaction orders. Hydrogen chloride inhibits the reaction by competing for sites with the reactant. Its concentration must be specified when reporting rates and its effect accounted for when calculating the apparent activation energy.

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# Paper 2

# Hydrodechlorination of chlorofluorocarbons $CF_3$-$CFCl_2$ and $CF_3$-$CCl_3$ over Pd/carbon and Pd black catalysts* †

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## Abstract

The reaction of hydrodechlorination for the chlorofluorocarbons (CFCs) $CF_3–CFCl_2$ and $CF_3–CCl_3$ was studied over Pd supported on carbon and Pd black catalysts. The rates and selectivity were similar on all samples although Pd black samples had a higher selectivity for the more hydrogenated products. The difference in selectivity and rate for Pd black is attributed to the presence of an impurity on the surface. The reaction orders are about first order in CFC, half-order in $H_2$, and inverse first-order in HCl. These results indicate that the irreversible adsorption of CFC is the rate-determining step and that $H_2$ and HCl are equilibrated with hydrogen and chlorine on the surface. Experiments with $D_2$ on $CF_3$-CFHCl confirm that the adsorption step is irreversible.

**Keywords:** Hydrodechlorination; Chlorofluorocarbons; Pd/carbon catalyst; Pd black catalyst

## 1. Introduction

In the 1980s, halogenated chlorofluorocarbons (CFCs) were scientifically linked to the depletion of the ozone layer[1]. The stable and inert nature of CFCs is advantageous in many applications but it also enables them to escape from the lower atmosphere without decomposition, and contribute to stratospheric ozone depletion. Hydrofluorocarbons (HFCs) are much less harmful to the environment and have some of the useful properties of CFCs and may thus serve as a replacement for CFCs[2]. One of the routes to produce HFCs is the reaction between CFC and $H_2$ catalyzed by a noble metal. This reaction may also be used to transform the large amounts of CFCs that exist today into the more environmentally benign HFCs[1,3]. The transformation of CFCs into HFCs requires a knowledge of catalytic hydrodechlorination, the subject of this contribution.

Hydrodechlorination reactions have been studied over a number of metals, such as Pd[4-9], Pt [10-12], and Rh[10, 12-14], with Pd usually the most selective catalyst for this reaction. The role of the support has been studied on carbon[15-16], alumina[4] and fluorinated alumina[5]. While some authors have suggested that the support play a role in the reaction[17], we have previously reported that the support (carbon) does not influence reaction kinetics beyond condensation of CFC reactant on microporous supports[16]. While most contributions report on supported catalysts, hydrodechlorination literature does include studies on evaporated films[18-20], foils[7-8,21], and single crystals[8]. A limited number of studies have been reported on bulk metal powders[22-23]. In this publication, we will extend our previous reports on $CF_3$–$CFCl_2$ and $CF_3$–$CCl_3$ hydrodechlorination kinetics on supported Pd catalysts[16] by reporting the results on Pd black.

Turnover rates, selectivity and reaction orders have been presented for only a limited number of compounds[4-9, 17,21]. Even less has been published about possible reaction steps[13-14, 24-25]. Thompson et al.[16] suggested that the rate-determining step is the adsorption of the CFC on only one catalytic site. The rate-determining step consists of the scission of the carbon–chlorine bond, possibly as an oxidative addition, forming a Pd–Cl and Pd–C–R bond on the same catalytic site[16]. This proposed rate-determining step was deduced from the kinetics and from the fact that there is a correlation between gas-phase C–Cl bond strength and reactivity. Weiss et al.[26] also proposed dissociative adsorption of the CFC as the rate-determining step for $CCl_4$ hydrodechlorination. The reaction steps proposed are a simplification and cannot predict, for example, the reaction selectivity, which is a key property of the catalyst. It is thus necessary to learn the details of steps beyond the rate-determining one. Isotopic tracing may help to understand the hydrodechlorination reaction steps. A limited number of studies of hydrodechlorination have been conducted with isotopes. Campbell and Kemball[18] found through reaction of $CH_3$–$CH_2Cl$ on Pd films with $D_2$ that the reaction steps must proceed through a carbene like intermediate since the product (ethane) was significantly enriched with the doubly deuterated product $CH_3$–$CHD_2$. However, we will report that in the reaction of $CF_3$–CFHCl with deuterium on Pd/C, the most abundant product (98%) is the mono-deuterated product $CF_3$–CFHD. The absence of deuterium in the reactant during reaction also suggests that adsorption of CFC is irreversible.

## 2. Experimental methods

### *2.1. Catalysts*

Two palladium catalysts supported on carbon and an unsupported palladium black catalyst was used in this study. The supported catalysts differed in the total surface area or the type of carbon used. The denomination for the support, C-L, is to point out that these supports have a low surface area. A 5% Pd catalyst supported on carbon (5% Pd/C-L) was obtained from Degussa. The second carbon supported catalyst (0.5% Pd/C-L) was prepared in house via an incipient wetness procedure on a carbon support manufactured by the Cabot (Sterling Series). The incipient wetness method utilized an aqueous solution of $PdCl_2$ (Aldrich, 99.99%) with the addition of 2 mol of HCl per mole of precursor with additional heating to aid in the dissolution of $PdCl_2$. Additional information on the supported catalyst can be found elsewhere[16]. The supported samples were ground with a mortar and pestle and 40/60 mesh particles were retained for use in catalytic studies. The Pd black (Alfa Aesar, 99.9%) was used as received.

### *2.2. Reactants*

The CFC 114a ($CF_3$–$CFCl_2$) samples were obtained from DuPont, CFC 113a ($CF_3$–$CCl_3$) from Lancaster Synthesis, and HCFC 124 ($CF_3$–CFHCl) from DuPont Suva Refrigerants. The 15–20% HCl/He mixtures (three used in this study) were prepared by Matheson with technical grade HCl and Matheson purity He. The hydrogen source contained 1033 ppm of $CH_4$, which was used as an internal standard and for calibration of the gas chromatograph. The hydrogen/methane mixture was passed through a packed bed containing a 5% Pd/C catalyst to eliminate any oxygen from the $H_2$ mixture. Hydrogen was obtained from BOC gases and certified as CGA Grade D. The pure $H_2$ gas was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. The deuterium was obtained from Cambridge Isotope Laboratories. It contained 99.6% $D_2$ and 0.4% HD, and before use it was passed through a Pd membrane (Matheson hydrogen purifier model 8361).

### *2.3. Reactor configuration*

The gas manifold was constructed of 1/8 in'. diameter stainless steel tubing and flow rates were controlled with mass flow controllers (Porter Instrument). For CFC 113a ($CF_3$–$CCl_3$), a liquid at room temperature, addition to the reaction mixture was made by passing helium through the CFC in a saturator. The reaction portion of the flow system was made of Pyrex and could be manipulated to operate in continuous or in batch mode. The reactor was made out of quartz with the catalyst held on a fritted disk. Most reaction rates were measured while operating in continuous stirred tank reactor (CSTR) mode with a thermocouple extending into the reactor so that the thermocouple was well in contact with the catalyst bed. The CSTR was equipped with a gas pump (Senior Flexonics model MB-21) for circulating the gases at a rate of about 1400 $cm^3$ $min^{-1}$ which allowed differential operation and minimized heat and transport effects. Inlet and effluent flow rates were 100 $cm^3$ $min^{-1}$.

Reactions of CFC 114a ($CF_3$–$CFCl_2$) over Pd black showed a much higher selectivity to HFC 143a ($CF_3$–$CH_3$) causing a higher concentration of HF in the reactor and simultaneous deposition of an unidentified fine white powder on the glass portion of the reactor. For this reason, CFC 114a experiments over Pd black were then conducted in a stainless steel plug flow reactor (PFR). Hydrogen chloride was added to the feed to allow the reactor to operate in a differential mode, since HCl is a reaction product, which inhibits the reaction. Blank experiments were run with the stainless steel reactor to ensure that the reactor walls did not catalyze hydrodechlorination.

The exiting gas stream was sent to a gas chromatograph (GC) for analysis. The column used in the GC was a 5% Krytox$^{(TM)}$ 143AC, 60/80 Carbopack B HT 20’×1/8 inch column from Supelco. Each of the reactant CFC and products were calibrated against the methane standard in the hydrogen/methane mixture. Response factors were then determined for each compound. The distribution of deuterium in the reaction products was monitored with a Hewlett Packard mass spectrometer (MS) 5970. The MS was connected to the existing GC to allow a portion of the gases eluting the column to be directed to the MS (through a capillary tube) before entering the FID detector. In this way, signals were obtained simultaneously from the MS and the GC. After exiting the system, the gases flowed through a NaOH solution to neutralize the HCl present in the effluent stream.

### *2.4. Data collection procedure*

Two to five hundred milligrams of fresh catalyst was initially loaded into the reactor and reduced for 3 h at 300°C with 50 $cm^3$ $min^{-1}$ $H_2$. At the start of each experiment, the catalyst was reduced for 0.5–1 h at 150°C with 50 $cm^3$ $min^{-1}$ $H_2$. For a particular set of conditions, the reaction was run for 30–60 min before a data point was taken. Temperature and concentration parameters for activation energy determination and reaction orders were varied in a random fashion so that any variation in the system would not introduce a systematic error. In order to ensure that deactivation had not occurred during the duration of the experiment, the first point in the series was duplicated at the end of the experiment.

In general, reaction orders were determined by varying the partial pressure of the compound under study and maintaining all other variables (partial pressures and temperature) constant. The difficulty of delivering CFC 113a prevented the use of the standard reaction order experimental procedure. Instead of keeping each of the gas flow rates constant except CFC and helium, the CFC flow rate was held constant and the other flow rates were adjusted. By varying the total flow rate in this manner, the CFC 113a concentration is changed. The flow rate of each of the other gases was adjusted so that the same concentration of the gas was maintained in the reaction mixture.

### *2.5. Surface area measurements*

Total surface area was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen–oxygen titration method according to Benson et al.[27]. The experimental system consisted of a volumetric system constructed in Pyrex and pumped by a diffusion pump with a liquid nitrogen cooled trap. The amount of gas adsorbed was determined by measuring pressure change in the calibrated volume of the system with a pressure transducer (MKS model 127).

Both the BET method and $H_2$–$O_2$ titration method were used to determine the metal surface area of the Pd black since it is an unsupported metal. A Pd atom density, equal to an average of the low index planes, of $1.27\times10^{19}$ atoms $m^{-2}$ was assumed[28]

The samples were initially reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 3 h at 300°C before the Pd surface area measurements. After the initial reduction of 3 h, subsequent reduction was conducted at 100°C for 0.5 h. The crystallite size based on chemisorption measurements was estimated from $d$ (nm)=112/(percentage of metale xposed). This expression is valid under the assumption of spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms $m^{-2}$.

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced catalysts was also conducted. Samples for XRD analysis were reduced in a manner identical to those previously described, and then passivated with 60 Torr of $O_2$. Particle size was determined from the width of the diffraction peak using X-ray line broadening technique. The Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

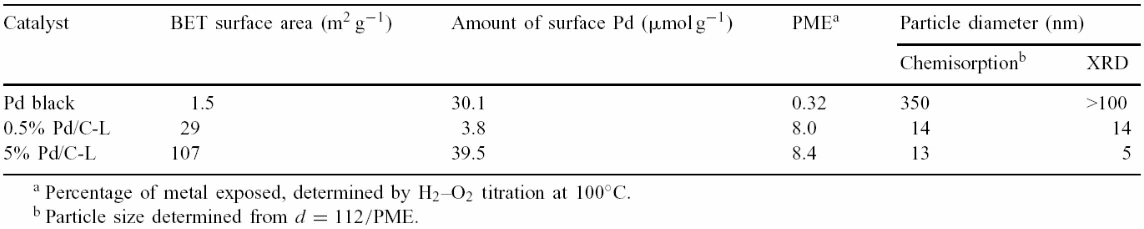
### *2.6. Error analysis*

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in reaction orders are at a maximum 10% and errors in the apparent activation energies were 10 kJ mol$^{-1}$. Turnover rate reproducibility was better than 90%.

## 3. Results and discussion

### *3.1. Catalyst properties*

The properties of the catalysts used in this study are presented in Table 1. The supported catalysts had a Pd loading of 0.5 or 5% and two different carbon supports were used. It has been shown that the carbon support plays no role in the hydrodechlorination reaction[16].



| Catalyst | BET surface area (m$^2$ g$^{-1}$) | Amount of surface Pd (μmol g$^{-1}$) | PME[a] | Particle diameter (nm) | |
|---|---|---|---|---|---|
| | | | | Chemisorption[b] | XRD |
| Pd black | 1.5 | 30.1 | 0.32 | 350 | >100 |
| 0.5% Pd/C-L | 29 | 3.8 | 8.0 | 14 | 14 |
| 5% Pd/C-L | 107 | 39.5 | 8.4 | 13 | 5 |

[a] Percentage of metal exposed, determined by $H_2$–$O_2$ titration at 100°C.

[b] Particle size determined from $d = 112/\text{PME}$.

**Table 1. Catalyst properties**

The low surface area supports (designated C-L) were non-microporous. A number of analyses were conducted on Pd black to follow the sintering behavior. The BET surface area of Pd black before reduction was 27 $m^2 g^{-1}$. Upon reduction for 1 h at 100°C the surface area decreased to 7.9 $m^2 g^{-1}$, and further reduction at 300°C for 1 h decreased the area to 1.5 $m^2 g^{-1}$. A comparison of surface area determined by BET and $H_2$–$O_2$ titration was conducted to verify whether the entire surface area of the Pd black powder consisted of palladium. Differences in surface areas determined by the two techniques would suggest that impurities (such as other metals) were present on the surface. According to the certificate of analysis, some impurities in Pd black are silicon, silver, iron, rhodium and platinum. Surface areas determined by BET and $H_2$–$O_2$ titration (assuming a Pd atom density of $1.27 \times 10^{19}$ atoms $m^{-2}$) were 1.5 and 1.2 $m^2 g^{-1}$, respectively. This result indicates that the surface may have some impurities (within the limits of the assumption of Pd atom density). Note that, however, this test will not rule out the presence of another substance on the surface that has an oxygen stoichiometry identical to Pd (e.g., another noble metal).

Particle sizes determined by XRD line broadening are also shown in Table 1. There is a good agreement between chemisorption and XRD particle sizes for the 0.5% Pd/C-L sample. On the other hand, the Pd particle size measured by XRD for the 5% Pd/C-L is about three times smaller than that determined by chemisorption, suggesting that the particles are formed by a number of smaller agglomerates.

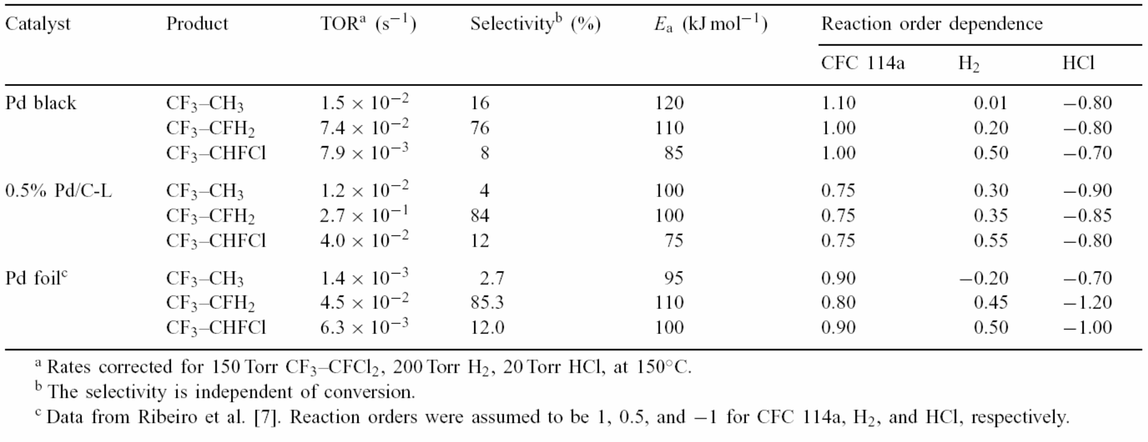
The data presented in Table 1 is representative of catalyst properties before reaction. Since no deactivation occurred during reaction, changes in catalyst properties were expected to be minor after the reaction. The stability of catalyst properties under reaction condition is supported by data for Pd black. When examined after the hydrodechlorination of CFC 113a, the PME value before reaction (after reduction) was 0.49%, while after reaction the PME value was 0.43%, a smaller value but within our experimental error.

The presence of heat and mass transfer limitations was tested using the Madon–Boudart test[29-30]. From results presented in previous work[16], heat and mass transfer limitations were non-existent with the highest surface area catalyst, where transport limitations would be most severe.

### *3.2. Kinetic measurements*

Kinetic data on an unsupported Pd powder will be presented and compared to the data on Pd/carbon and a foil for two CFCs ($CF_3$–$CFCl_2$ and $CF_3$–$CCl_3$). We would like to propose that the reaction steps to be presented also apply to other chlorine-containing compounds. If this generalization is true, it will be an important achievement as the number of organic compounds that contain chlorine is large and their properties are very dependent on molecular structure. Results on deuterium isotope substitution will also be presented to illustrate possible reaction steps.

*3.2.1. Structure sensitivity and selectivity.* In previous studies, the reaction of hydrodechlorination was studied for four compounds ($CF_3$–$CF_2Cl$, $CF_3$–$CFClH$, $CF_3$–$CFCl_2$ and $CF_3$–$CCl_3$) on palladium foils[7-8. 21], single crystals of Pd[8], and Pd supported on carbon[16]. The turnover rates for hydrodechlorination are independent of the catalyst type, suggesting the structure insensitivity of this reaction. Table 2 contains the kinetic data for Pd black, 0.5% Pd/C-L, and Pd foil. The rates for the major product, $CF_3$–$CFH_2$ are at most a factor of 6 different when the catalysts are compared. This is remarkable since there are large differences in specific surface area between the foil and the supported catalysts. These results confirm previous findings[8] that the reaction is structure insensitive for $CF_3$–$CFCl_2$ on Pd.



| Catalyst | Product | TOR[a] ($s^{-1}$) | Selectivity[b] (%) | $E_a$ ($kJ\,mol^{-1}$) | Reaction order dependence | | |
|---|---|---|---|---|---|---|---|
| | | | | | CFC 114a | $H_2$ | HCl |
| Pd black | $CF_3$–$CH_3$ | $1.5 \times 10^{-2}$ | 16 | 120 | 1.10 | 0.01 | −0.80 |
| | $CF_3$–$CFH_2$ | $7.4 \times 10^{-2}$ | 76 | 110 | 1.00 | 0.20 | −0.80 |
| | $CF_3$–CHFCl | $7.9 \times 10^{-3}$ | 8 | 85 | 1.00 | 0.50 | −0.70 |
| 0.5% Pd/C-L | $CF_3$–$CH_3$ | $1.2 \times 10^{-2}$ | 4 | 100 | 0.75 | 0.30 | −0.90 |
| | $CF_3$–$CFH_2$ | $2.7 \times 10^{-1}$ | 84 | 100 | 0.75 | 0.35 | −0.85 |
| | $CF_3$–CHFCl | $4.0 \times 10^{-2}$ | 12 | 75 | 0.75 | 0.55 | −0.80 |
| Pd foil[c] | $CF_3$–$CH_3$ | $1.4 \times 10^{-3}$ | 2.7 | 95 | 0.90 | −0.20 | −0.70 |
| | $CF_3$–$CFH_2$ | $4.5 \times 10^{-2}$ | 85.3 | 110 | 0.80 | 0.45 | −1.20 |
| | $CF_3$–CHFCl | $6.3 \times 10^{-3}$ | 12.0 | 100 | 0.90 | 0.50 | −1.00 |

[a] Rates corrected for 150 Torr $CF_3$–$CFCl_2$, 200 Torr $H_2$, 20 Torr HCl, at 150°C.

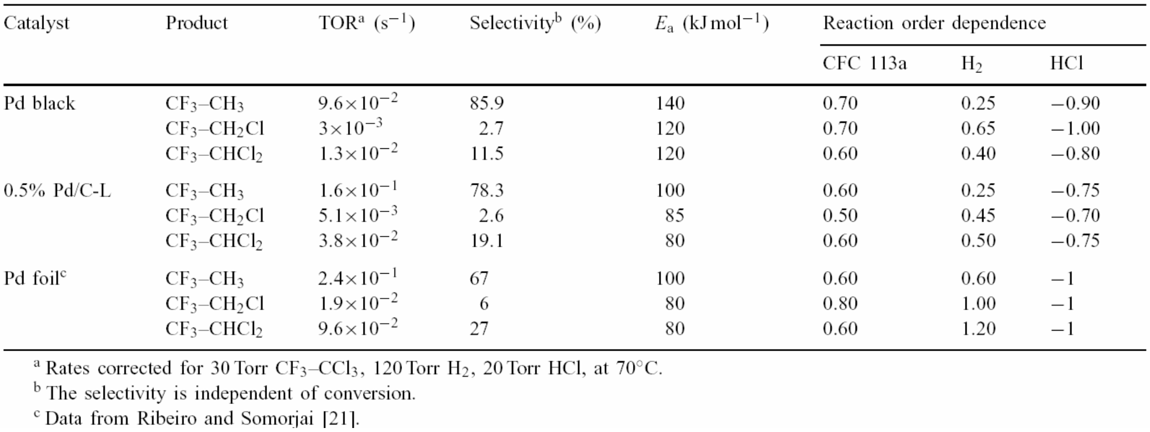
[b] The selectivity is independent of conversion.

[c] Data from Ribeiro et al. [7]. Reaction orders were assumed to be 1, 0.5, and −1 for CFC 114a, $H_2$, and HCl, respectively.

**Table 2. Kinetic data for $CF_3$–$CFCl_2$ hydrodechlorination**

There was no deactivation or change in selectivity throughout the duration of the experiment. The selectivity for the most abundant hydrodechlorination product, $CF_3$–$CFH_2$, is about 85% for the 0.5% Pd/C-L catalyst and foil, while the selectivity on the Pd black is about 75%. A lower selectivity on Pd black during a hydrodechlorination reaction has been documented before. van de Sandt et al. [22] reported selectivity to $CH_2F_2$ from $CF_2Cl_2$ of 85% for a 1 wt.% Pd/C catalyst, while the selectivity to $CH_2F_2$ was only 75% on Pd black. Our interpretation of the data is that an impurity is responsible for the lower selectivity since supported catalysts, foils and single crystals do not show appreciable variation in selectivity. From the certificate of analysis, this particular sample may have Si, Pt, Ru, Rh, and Fe at levels of about 10 ppm for each compound. Because this is a bulk sample, if these impurities migrate to the surface a substantial enrichment may be achieved.

The kinetic data for CFC 113a ($CF_3$–$CCl_3$) hydrodechlorination is summarized in Table 3. The same three catalysts used for $CF_3$–$CFCl_2$ hydrodechlorination were used for $CF_3$–$CCl_3$ hydrodechlorination. The turnover rate for the main product, $CF_3$–$CH_3$, is about $10^{-1}$ $s^{-1}$ for all three catalysts. The hydrodechlorination of CFC 113a also seems to be a structure insensitive reaction, although the average particle size is too large for a definite conclusion. Note that no kinetic data is available on single crystal surfaces for CFC 113a hydrodechlorination, as was the case for CFC 114a discussed above, or for a series of supported catalysts with particle sizes in the critical size range (1–10 nm). Thus, a definite conclusion on structure sensitivity for CFC 113a cannot be made. The selectivity on Pd black is also higher for the most hydrogenated product, $CF_3$–$CH_3$, than on the other catalysts, also suggesting that a surface impurity is playing a role.



| Catalyst | Product | TOR[a] ($s^{-1}$) | Selectivity[b] (%) | $E_a$ (kJ mol$^{-1}$) | Reaction order dependence | | |
|---|---|---|---|---|---|---|---|
| | | | | | CFC 113a | $H_2$ | HCl |
| Pd black | $CF_3$–$CH_3$ | $9.6\times10^{-2}$ | 85.9 | 140 | 0.70 | 0.25 | −0.90 |
| | $CF_3$–$CH_2Cl$ | $3\times10^{-3}$ | 2.7 | 120 | 0.70 | 0.65 | −1.00 |
| | $CF_3$–$CHCl_2$ | $1.3\times10^{-2}$ | 11.5 | 120 | 0.60 | 0.40 | −0.80 |
| 0.5% Pd/C-L | $CF_3$–$CH_3$ | $1.6\times10^{-1}$ | 78.3 | 100 | 0.60 | 0.25 | −0.75 |
| | $CF_3$–$CH_2Cl$ | $5.1\times10^{-3}$ | 2.6 | 85 | 0.50 | 0.45 | −0.70 |
| | $CF_3$–$CHCl_2$ | $3.8\times10^{-2}$ | 19.1 | 80 | 0.60 | 0.50 | −0.75 |
| Pd foil[c] | $CF_3$–$CH_3$ | $2.4\times10^{-1}$ | 67 | 100 | 0.60 | 0.60 | −1 |
| | $CF_3$–$CH_2Cl$ | $1.9\times10^{-2}$ | 6 | 80 | 0.80 | 1.00 | −1 |
| | $CF_3$–$CHCl_2$ | $9.6\times10^{-2}$ | 27 | 80 | 0.60 | 1.20 | −1 |

[a] Rates corrected for 30 Torr $CF_3$–$CCl_3$, 120 Torr $H_2$, 20 Torr HCl, at 70°C.

[b] The selectivity is independent of conversion.

[c] Data from Ribeiro and Somorjai [21].

**Table 3. Kinetic data for $CF_3$–$CCl_3$ hydrodechlorination**

*3.2.2. Reaction orders.* The reaction steps were proposed based on measured reaction orders. The reaction orders and activation energies for the hydrodechlorination reaction are summarized in Table 2 and Table 3 for $CF_3$–$CFCl_2$ and $CF_3$–$CCl_3$, respectively. The three main products formed are all derived from the sequential dehalogenation of the carbon bonded to chlorine. The CFC, $H_2$, and HCl reaction orders for the products of $CF_3$–$CFCl_2$ hydrodechlorination over Pd black are presented in Fig. 1, Fig. 2 and Fig. 3, respectively.

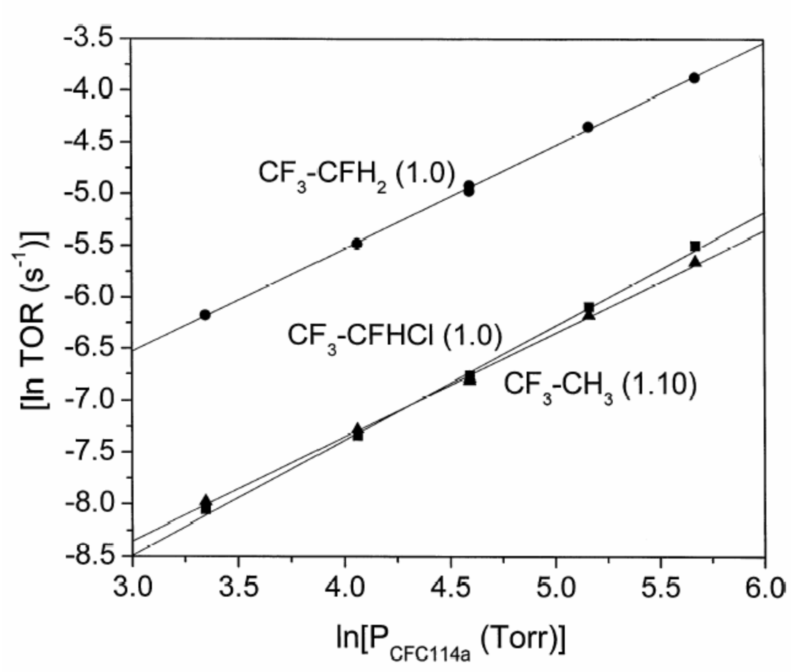


**Figure 1. Determination of reaction order in CFC 114a ($CF_3$–$CFCl_2$) on Pd black. Experiments were carried out at 125°C, 30–300 Torr CFC, 230 Torr $H_2$, and 30 Torr HCl. Turnover rates corrected to 200 Torr of $H_2$, 20 Torr of HCl.**

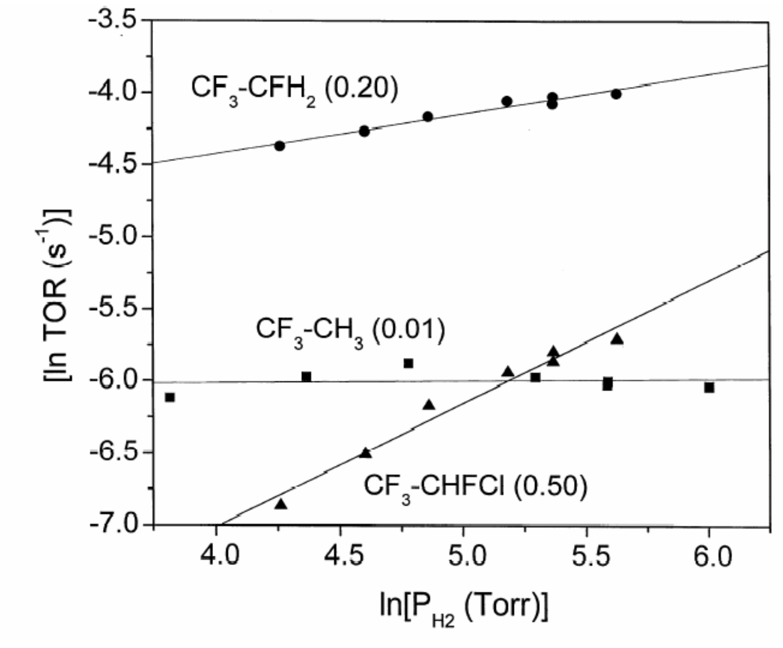


**Figure 2.** **Determination of reaction order in $H_2$ for the reaction of CFC 114a ($CF_3$–$CFCl_2$) on Pd black. Experiments were carried out at 130°C, 160 Torr CFC, 50–400 Torr $H_2$, and 30 Torr HCl. Turnover rates corrected to 150 Torr of CFC 114a, 20 Torr of HCl.**

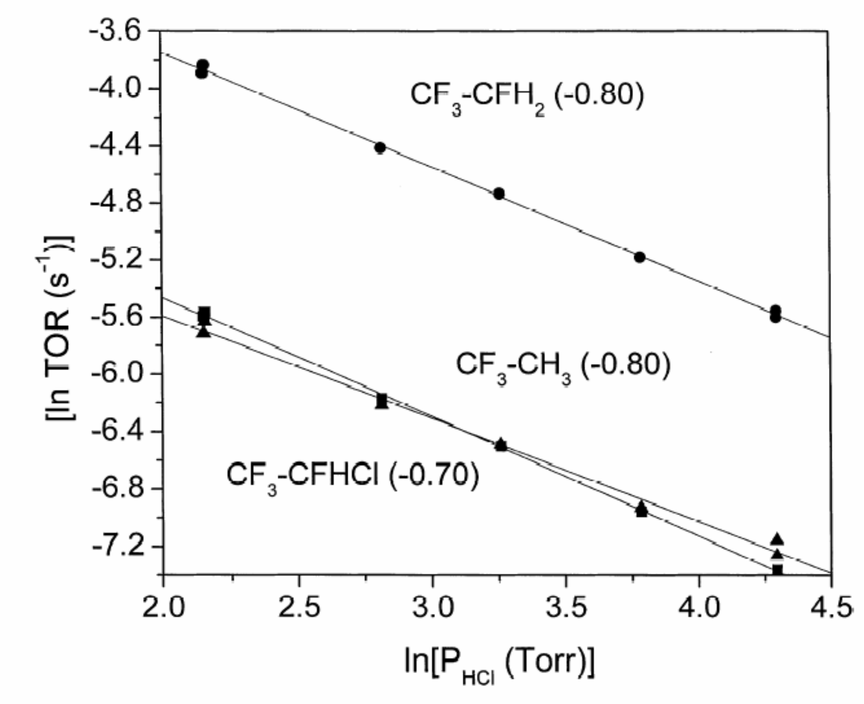


**Figure 3. Determination of reaction order in HCl for the reaction of CFC 114a ($CF_3$–$CFCl_2$) on Pd black. Experiments were carried out at 125°C, 110 Torr CFC, 190 Torr $H_2$, and 10–70 Torr HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of $H_2$.**

The reaction steps proposed before for the hydrodechlorination reaction and based on kinetic data are

$$CFC+{*}\rightarrow\cdots \tag{1}$$

The above step is the rate-determining step, with all the following steps for the CFC hydrodechlorination not kinetically significant. The symbol * represents a catalytic site. The surface is also equilibrated with $H_2$ and HCl in the gas phase:

$$H_2+2{*}=2H{*} \tag{2}$$

$$H^*+Cl^*=HCl+2^* \quad (3)$$

Making the assumption that Cl* is the most abundant surface intermediate, the final rate will be[7]:

$$r=\frac{k[CFC][H_2]^{0.5}}{[HCl]} \quad (4)$$

This expression is accurate for the most abundant product formed but it is not correct for some of the products. For example, the reaction order in $H_2$ for $CF_3$–$CH_3$ is zero when $CF_3$–$CFCl_2$ is the reactant, much lower than the expected value of 0.5. Similar to Pd foil[7] and the single crystals[8-9] results, the reaction order in $H_2$ for this product is significantly lower than the expected value, while the CFC and HCl orders are in good agreement with the expected orders. The explanation for the zero-order dependence in $H_2$ on single crystals was attributed to $H_2$ storage in the bulk of Pd[9].The authors were able to show that hydrodechlorination of $CF_3$–$CFCl_2$ occurred in the absence of gas-phase $H_2$ when solid-state hydrogen was available. A change in selectivity was noted as hydrogen was obtained from the gas phase or the solid state. Similar to the Pd black case, an increase in selectivity of $CF_3$–$CH_3$ occurred, but at the expense of the under-hydrogenated product ($CF_3$–CFHCl) rather than the hydrodechlorination product, $CF_3$–$CFH_2$.

The strong inhibition effect of HCl is apparent by the approximately inverse first-order dependence. The inhibiting effect of HCl has been accounted for in determining the apparent activation energy by reporting all the rates at the same HCl concentration (Fig. 4). This is an important consideration since the rates are a strong function of the amount of HCl (conversion).

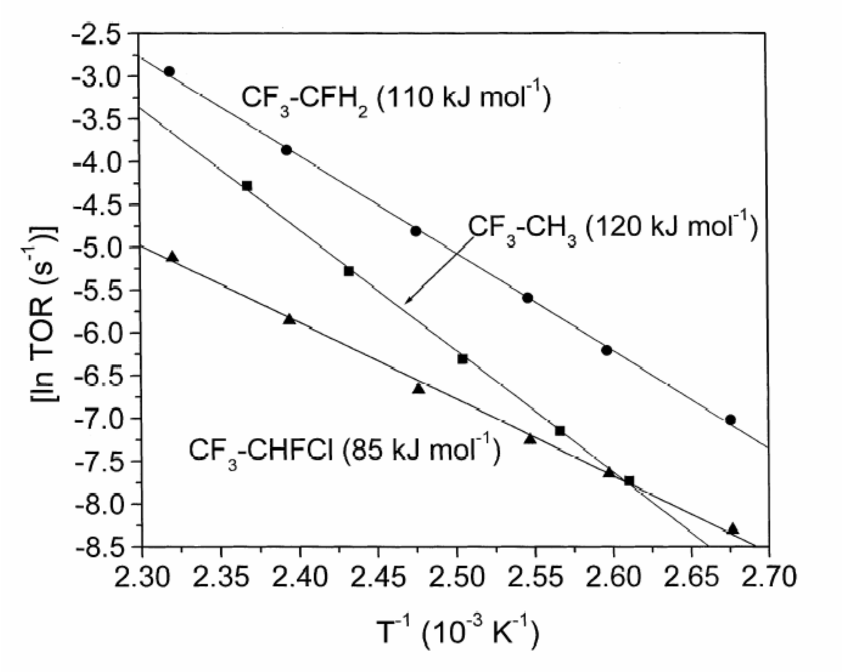


**Figure 4. Arrhenius plot for the reaction of CFC 114a ($CF_3$–$CFCl_2$) on Pd black. Experiments were carried out at 100–150°C, 170 Torr CFC, 340 Torr H2, and 40 Torr HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of $H_2$ and 20 Torr HCl.**

To construct a kinetic reaction sequence from the reaction orders, we must ensure that the measured kinetic parameters are intrinsic and have not been subjected to possible artifacts. Condensation of the CFC in the pores of microporous supports has caused reaction orders in CFC to be lower than expected[16]. On Pd black, there seems to be no apparent effect of CFC condensation, evidenced by the reaction orders of 1.0 and ~0.7 for $CF_3$–$CFCl_2$ and $CF_3$–$CCl_3$, respectively. CFC orders on Pd black are in very good agreement with Pd foil data, suggesting that condensation of $CF_3$–$CCl_3$ is minimal on Pd black.

The conclusion is that the previously proposed reaction steps are also valid on Pd black. The higher selectivity for the more hydrogenated product on Pd black may be due to a surface impurity.

*3.2.3. Rate-determining step.* The rate-determining step, Eq. (1), does not specify how the CFC binds to the surface. Because only one catalytic site is involved, Ribeiro et al[7]. proposed that this step was the non-dissociative adsorption of the CFC. A non-dissociative step would indicate a weak dependence of rates on the molecular structure. However, a study of a series of four CFC compounds showed that the turnover rate varied by a factor of $10^7$ [16] and correlated with the gas-phase C–Cl bond strength, which indicated that the rate-determining step involved the scission of the C–Cl bond. Even if only one site is available, it is in fact plausible that the scission of the C–Cl bond occurs on a single Pd atom by analogy with the oxidative addition step found in organometallic chemistry[31-32]. If only one atom is needed, it explains why this reaction appears to be insensitive to the palladium structure. As a direct analogy from organometallic chemistry, the oxidative addition of an alkyl halide satisfies C–Cl bond scission on one Pd atom. We have proposed, by analogy from organometallic chemistry, that the rate-determining step for a generic R–Cl reactant is the oxidative addition

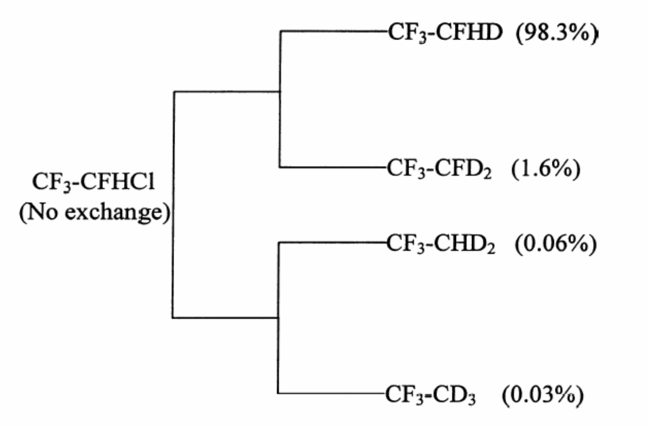
$$\text{R–Cl+Pd}^0\rightarrow\text{R–Pd–Cl}$$

Once the R–Pd–Cl compound is formed, surface hydrogen atoms can react with the R fragment forming R–H and Pd–Cl. The R–H represents a monohydrogenated product, such as $CF_3$–CFHCl or $CF_3$–$CHCl_2$.

Information on reaction intermediates was also inferred from the fact that the reaction selectivity is independent of conversion. This observation translates into the fact that once the reactant is adsorbed it follows a reaction pathway on the surface until it desorbs, never returning to the surface again. This fact is also consistent with the finding that as chlorine atoms are substituted by hydrogen atoms, the bond strength of the remaining chlorine atoms become stronger and the molecule once in the gas phase becomes much less reactive than the reactant. For example, the reactivity of $CF_3$–CFHCl is 3000 times lower than $CF_3$–$CFCl_2$ [16].

*3.2.4. Reaction steps beyond the rate-determining step.* We still cannot predict or even explain the product distribution of the hydrodechlorination reaction. Although the product distribution suggests possible reaction intermediates on the surface, prediction of product distribution can only be accomplished with a description of the reaction steps beyond the rate-determining one.

Deuterium substitution reactions were conducted to determine more details about hydrodechlorination chemistry. Learning more about the chemistry of HCFC 124 ($CF_3$–CFHCl) hydrodechlorination is possible with $D_2$ substitution. The experiments were performed by starting the reaction in a continuous-stirred tank reactor mode, with the objective to reach a steady-state value, and then switching to a batch mode, to reach a high value of conversion. The experimental procedure consisted of carrying out the reaction until the conversion reached a constant value at 16% in the continuous mode and then switching to a batch operation by turning off the inlet and outlet valves from the reactor. The conversion of HCFC 124 at time zero on the batch reactor was thus 16% and the reaction was continued to a final conversion of 54%. The selectivity for exchange on all products was independent of conversion. Note that the carbon containing the chlorine also contains a hydrogen atom. From gas-phase calculations using the Gaussian 98$^{(TM)}$ software package, the C–H bond is 100 kJ mol$^{-1}$ stronger than the C–Cl bond. Considering only the bond strength as a variable, it is expected that C–H bonds should not break at conditions where C–Cl bonds are broken. In fact, an isotope distribution (Scheme 1) verifies that in more than 98% of the products, the C–H bond remains intact. Also, because in 1.6% of the 134a ($CF_3$–$CFD_2$) product the hydrogen bond is also broken, it is reasonable to assume that if the adsorption step were reversible, some of the hydrogen atoms in the reactant would have been exchanged for deuterium ($CF_3$–CFDCl would have been detected). The exchange in the reactant was never observed, even at 54% conversion, which indicates that the adsorption step as indicated in step (1) above is irreversible.



**Scheme 1. Deuterium distribution in HCFC124($CF_3$–CFHCl) hydrodechlorination reaction. (Selectivity independent of conversion from 16% to a final**

**HCFC conversion of 54%. Reaction performed at 240°C, 516 Torr $CF_3$–CFHCl, 147 Torr D2. The catalyst was 5% Pd/C-L.) Selectivity is in parenthesis.**

The most abundant CFC reaction intermediate on the Pd surface is possibly $CF_3$–CFH–Pd, representative of a mono-hydrogenated intermediate. Less than 2% of the FC 134a ($CF_3$–$CFH_2$) that is formed loses the hydrogen bound to the carbon. The formation of the minor product FC 143a is split between $CF_3$–$CHD_2$ and $CF_3$–$CD_3$.

To illustrate the complexity and the difficulty of generalizing results with hydrodechlorination reactions, it is instructive to examine the reaction of $D_2$ exchange with chloroethane ($CH_3$–$CH_2Cl$). Campbell and Kemball[18] found that for a Pd film the most abundant deuterated ethane was $CH_3$–$CHD_2$, a result that we have reproduced on 5% Pd/C-L. This finding indicates that a carbene intermediate is formed on the surface in contrast with the reaction on $CF_3$–CFHCl described above where 98% of the time only one deuterium is exchanged, and thus almost no carbene species seem to be forming.

It is evident that explaining selectivity is still not possible. In order to explain reaction selectivity, a complete reaction network with additional steps to those proposed here are necessary.

## 4. Summary

The reaction steps for the reaction of hydrodechlorination were reviewed and deuterium isotope data was used to elucidate further details of the reaction steps. We have suggested that the rate-determining step is an oxidative addition of an alkyl halide on one Pd atom. Surface H and Cl are in equilibrium with $H_2$ and HCl in the gas phase and chlorine is the most abundant surface intermediate. Kinetic data on Pd black suggests that the proposed reaction steps are also valid on this bulk sample. The deuterium substitution experiments yielded some insight on hydrodechlorination chemistry. In the hydrodechlorination of HCFC 124 ($CF_3$-CFHCl), the adsorption is confirmed as irreversible, the C-Cl bond is broken most frequently, although a small percentage of time C-H and C-F bonds are broken. Explaining selectivity is still not possible, and a more complete reaction sequence must be assembled before the selectivity can be estimated.

## Acknowledgements

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# Paper 3

# Investigation of reaction steps for the hydrodechlorination of chlorine-containing organic compounds on Pd catalysts[*]

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## Abstract

Reaction steps for the reaction of hydrodechlorination on Pd were investigated by means of isotope-exchange experiments. The reversibility of bond scission for the two C–Cl bonds in $CF_3CFCl_2$ was investigated by following $^{37}Cl$ enrichment in the reactant and products. No enrichment of $^{37}Cl$ was observed in the reactant $CF_3CFCl_2$ but the product $CF_3CHFCl$ was enriched. Thus, the scission of the first C–Cl bond is irreversible; once the reactant loses the first chlorine it desorbs only as a product. However, after the first C–Cl bond is broken, the second chlorine may be exchanged with the pool of surface chlorine. Isotope exchange experiments between $D_2$ and HCl during hydrodechlorination of $CF_3CFCl_2$ showed that the forward rate and reverse rate for the overall reaction $H_2+2Cl^*=2HCl+2^*$ were nearly 400 times faster than the overall hydrodechlorination reaction rate. Thus, this experiment confirms that this step is in quasi-equilibrium.

**Keywords:** hydrodechlorination on Pd: reaction steps**;** hydrodechlorination on Pd: isotope exchange

## 1. Introduction

Hydrodechlorination is the reaction between $H_2$ and an organic molecule containing a C-Cl bond to form HCl and a C-H bond. Hydrodechlorination is an important step in many syntheses that use a chlorine-containing molecule as an intermediate. For example, it is used in the manufacture of $CF_3CFH_2$ (a widely used refrigerant) from $CF_3CFCl_2$[1]and $CHCl_3$ or $CH_2Cl_2$ from $CCl_4$[2]. Another recent application of dechlorination in the presence of $H_2$ is in the conversion of byproduct compounds into useful ones as for example in the conversion of 1,2-dichloropropane into propylene[3] on a bimetallic Pt-Cu catalyst.

Turnover rates, selectivity and reaction orders have been presented for a limited number of compounds[4-11]. Some studies also dealt with possible reaction steps, similar to the ones presented below[7-8, 12-17]. Ribeiro et al.[7] and Thompson et al.[4] suggested that the rate-determining step might be the scission of the carbon-chlorine bond, possibly as an oxidative addition forming a Pd-Cl and a Pd-C bond on the same catalytic site, that chlorine is the most abundant reaction intermediate, and that HCl and $H_2$ are in equilibrium with adsorbed H and Cl. An updated version of the mechanism follows. The first step is the equilibrated adsorption of the reactants with an equilrium constant $K_{CFC}$:

$$CF_3CFCl_2 + * = CF_3CFCl_2* \qquad (1)$$

This step is followed by the scission of the first C-Cl bond, which is the rate-determining step with a rate constant $k_0$ :

$$CF_3CFCl_2 * \rightarrow \cdots. \qquad (2)$$

Note that the reaction products formed after this step are not kinetically significant and thus do not need to be represented. Steps (1) and (2) above lead to the following rate expression,

$$r = k_0K_{CFC}[CF_3CFCl_2][*] \qquad (3)$$

To calculate the number of empty sites ([*]) we assume the following equilibrium for $H_2$ and HCl with the surface,

$$H_2 + 2* = 2H* \qquad (4)$$

$$H* + Cl* = HCl + 2* \qquad (5)$$

The overall reaction from (4) and (two times) (5) with equilibrium constant $K_0$ will be,

$$H_2 + 2\,Cl* = 2HCl + 2* \qquad (6)$$

Assuming that Cl* is the most abundant surface intermediate ([*] + [Cl*] = [L]) leads to the following expression for free site concentration:

$$[*] = \frac{[L]}{1 + \frac{[HCl]}{K_0^{1/2}[H_2]^{1/2}}} \qquad (7)$$

Finally, by substituting (7) into (3) with $k = k_0K_{CFC}[L]$ and $K = K_0^{-1/2}$, the rate can be calculated as:

$$r = \frac{k[CF_3CFCl_2]}{1 + K\frac{[HCl]}{[H_2]^{1/2}}} \qquad (8)$$

These reaction steps were deduced from kinetic measurements only. Another very powerful technique to study reaction steps is isotope exchange, which is the objective of this contribution. Only a limited number of isotope exchange studies have been conducted on the hydrodechlorination reaction. Campbell and Kemball[18] found that the reaction of $C_2H_5Cl$ with $D_2$ on Pd films seemed to proceed through a carbene-like intermediate since the product ethane was significantly enriched with the doubly deuterated product $CH_3CHD_2$. As described below, chlorofluorocarbons (CFCs) show some unique behavior during isotope exchange. One example is the reaction of $CF_3CFHCl$ with deuterium on Pd/C. The most abundant product was the mono-deuterated product $CF_3CFHD$, instead of the double-deuterated product as found in Campbell and Kemball's experiment. Chlorine exchange using $H^{37}Cl$ was also performed to show the irreversibility of the C-Cl bond cleavage (eq. 2), which is assumed to be the rate-determining step in the proposed reaction mechanism. Step (6) was shown to be in quasi-equilibrium by measurements using deuterium exchange.

## 2. Experimental Methods

### *2.1. Catalysts*

Two palladium catalysts supported on carbon were used in this study. The 5% Pd catalyst supported on an activated carbon (5% Pd/C) was obtained from Degussa. The second carbon supported catalyst (0.5% Pd/C) was prepared in house via an incipient wetness procedure on an activated carbon manufactured by the Cabot Corporation (Sterling Series). The incipient wetness method utilized an aqueous solution of $PdCl_2$ (Aldrich, 99.99%) with the addition of 2 moles of HCl per mole of precursor with additional heating to aid the dissolution of $PdCl_2$. More information on the carbon supported catalyst can be found in a previous publication [4]. The supported samples were ground with a mortar and pestle and 40/60 mesh particles were retained for use in catalytic studies.

### *2.2. Reactants*

The CFC-114a ($CF_3CFCl_2$) sample was obtained from DuPont, and HCFC 124 ($CF_3CFHCl$) from DuPont Suva Refrigerants. Mixtures of 15-20% HCl in He were purchased from Matheson and were made with technical grade HCl and Matheson purity He. Hydrogen gas (Matheson) contained 1033 ppm of $CH_4$, which was used as an internal standard for the calibration of the gas chromatograph. Before it was fed into the reactor system, the hydrogen-methane mixture was passed through a packed bed containing a 5% Pd/C catalyst to eliminate any oxygen from the $H_2$ mixture. The hydrogen gas used for catalyst reduction was purified with a Pd membrane hydrogen purifier (Matheson hydrogen purifier model 8361). The deuterium was obtained from Cambridge Isotope Laboratories. It contained 99.6% $D_2$ and 0.4% HD, and before use it was passed through the same Pd membrane purifier used for purification of $H_2$. The $H^{37}Cl$ gas was purchased from Icon Services Inc., the $HCl^{37}$ concentration was higher than 99%.

### *2.3. Reactor Configuration*

The gas manifold was constructed of 1/8" diameter stainless steel tubing. Gas flow was controlled with mass flow controllers (Porter Instrument Co.). The reaction portion of the flow system was made of Pyrex and could be manipulated to operate in continuous or in batch mode. The reactor was made out of quartz with the catalyst held on a fritted disk. Reaction rates were measured in a well-mixed reactor operated in batch or continuous stirred tank reactor (CSTR) mode. Temperature was measured through a thermocouple well extending to the catalyst bed. The mixing in the CSTR was provided by a bellows pump (Senior Flexonics, MB-21) with a rate of about 1400 $cm^3$ $min^{-1}$ allowing differential operation for the reactor and minimizing heat and transport effects in the reaction. Inlet and effluent flow rates were around 100 $cm^3$ $min^{-1}$.

The reaction gases were injected with a gas valve or syringe into a modified GC-MS (GC-HP 5880A, MS-HP5970A). The column used in the GC was a 5% Krytox 143AC, 60/80 Carbopack B HT 20' x 1/8" from Supelco. The effluent from the GC column was simultaneously analyzed by the GC flame ionization detector (for quantitative analysis) and by the MS (for qualitative analysis). The gas was sampled into the mass selective detector through a fused silica polyimide capillary (I.D. 51μm, O.D. 363μm) of 0.75m length. The GC response factor for all reactants and products were calibrated against methane in a hydrogen-methane calibrated mixture. After exiting the system, the gases flowed through a NaOH solution to neutralize the HCl present in the effluent stream.

### *2.4. Data Collection Procedure*

Two to five hundred milligrams of fresh catalyst was initially loaded into the reactor and reduced for 3 h at 300°C with 50 $cm^3$ $min^{-1}$ $H_2$. For repeated experiments, the catalyst was treated with 50 $cm^3$ $min^{-1}$ $H_2$ for 0.5-1 h at 150°C before the hydrodechlorination reaction.

The reactor was evacuated to $1\times10^{-5}$ Torr for 0.5 hour before the gas reactants were fed into it. The oven temperature was raised to the target temperature at a rate of 5°C $min^{-1}$. The gas mixture was taken from the reactor using a 500μl syringe through a GC septum fitted to a union mounted on the sample port of the batch reactor. For each data point, 100-200μl of the gas mixture was injected into the GC-MS for analysis.

When the reactor was operated in a CSTR mode, the inlet gas concentrations were adjusted with mass flow controllers. For a particular set of conditions, thirty to sixty minutes were allotted for the reaction to reach steady state, at which time the first data point was taken. The gas mixture was sampled into the GC-MS system using an automatic valve on the GC-MS. To ensure that deactivation had not occurred during the duration of the experiment, the reaction conditions for the first point in the series was repeated at the end of each experiment.

### *2.5. Surface Area Measurements*

The total surface area was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen-oxygen titration method according to Benson et al.[19] The experimental setup consisted of a volumetric system constructed in Pyrex and pumped by a liquid nitrogen trapped diffusion pump. The amount of gas adsorbed was determined by measuring pressure change in a pre-calibrated volume on the system with a pressure transducer (MKS model 127).

The samples were reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 3 h at 300°C before the Pd surface area measurements. After the initial reduction, subsequent hydrogen-oxygen titrations were conducted at 100°C. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression is valid under the assumption of spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms $m^{-2}$ [20].

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced and passivated catalysts was also conducted. Samples for XRD analysis were reduced in same manner as described above, and then passivated with 60 Torr of $O_2$. Particle size was determined from the width of the diffraction peak using X-ray line broadening technique. The Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

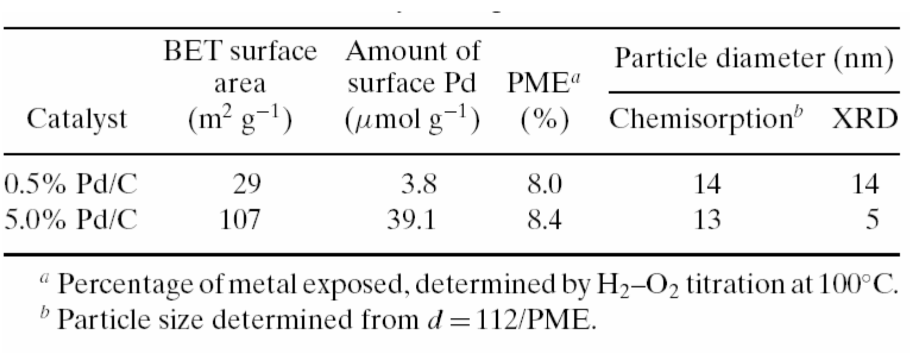
### *2.6. Error Analysis.*

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. Turnover rate reproducibility was better than 90%.

## 3. Results and discussion

### *3.1. Catalyst Properties*

Table 1 summarizes the properties of the catalysts employed. Non- microporous carbon supports were used in all experiments. Based on the results of previous research, it was found that CFC reactants may condense in the pores of microporous carbon, leading to a lower reaction order in CFC[4].



| Catalyst | BET surface area ($m^2\ g^{-1}$) | Amount of surface Pd ($\mu mol\ g^{-1}$) | PME[a] (%) | Particle diameter (nm) | |
|---|---|---|---|---|---|
| | | | | Chemisorption[b] | XRD |
| 0.5% Pd/C | 29 | 3.8 | 8.0 | 14 | 14 |
| 5.0% Pd/C | 107 | 39.1 | 8.4 | 13 | 5 |

[a] Percentage of metal exposed, determined by $H_2$–$O_2$ titration at 100°C.
[b] Particle size determined from $d = 112/\mathrm{PME}$.

**Table 1. Catalyst properties**

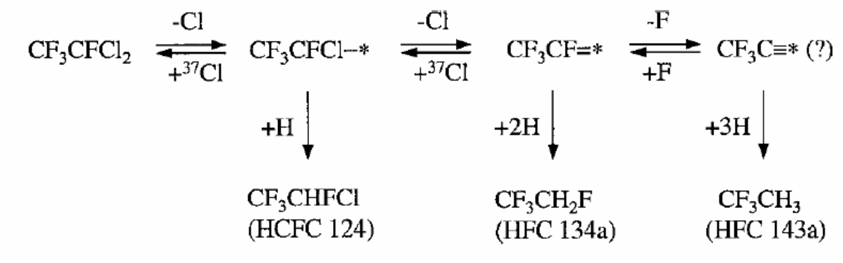
Particle size determined by XRD line broadening is also shown in Table 1. There is good agreement between chemisorption and XRD particle sizes for the 0.5% Pd/C sample. On the other hand, the Pd particle size measured by XRD for the 5.0% Pd/C catalyst is about three times smaller than that determined by chemisorption, which suggests that the particles are formed by a number of smaller agglomerates.

The parameters in Table 1 are representative of catalysts before reaction. Since no significant deactivation was observed during reaction, no significant change in the properties of the catalyst after reaction is expected.

The presence of heat and mass transfer limitations was tested using the Madon-Boudart test[21-22]. From the results presented in previous work[4], no heat and mass transfer limitations were found, even with the highest surface area catalyst, where transport limitations would be most severe. Thus, we concluded that these artifacts did not affect the results.

### *3.2. Determination of reversibility of C-Cl bond scission in* $CF_3CFCl_2$

In a previous publication[4], a correlation between the C-Cl bond energy and the rate of hydrodechlorination for a series of CFCs was observed, suggesting that the scission of the first C-Cl in the CFC is irreversible and rate determining. The objective in this section is to investigate if the C-Cl bond scission process is reversible. We have employed $CF_3CFCl_2$ for this purpose since its kinetics has been studied in detail[4,7-8,23]. As indicated in Scheme 1, two C-Cl bonds are involved. As explained next, the reversibility of the steps can be investigated using $^{37}Cl$ isotope exchange methods.



**Scheme 1. Proposed reaction network for the $CF_3CFCl_2$ hydrodechlorination reaction on a surface saturated with $^{37}Cl$.**

To investigate the reversibility of the various steps, the surface was saturated with $^{37}Cl$ from $^{37}HCl$. When a C-Cl bond in the probe molecule is broken and subsequently reformed, the molecule will show enrichment in chlorine if the chlorine from the molecule can exchange with adsorbed $^{37}Cl$ on the surface. The $^{37}Cl$ saturation on the surface can be achieved because HCl adsorbs on the surface preferentially, making Cl the most abundant reaction intermediate (mari). Also, as shown below, the rate of exchange of adsorbed chlorine with gas phase HCl (eq. 6) is 400 times faster than the hydrodechlorination rate. Thus, a high pressure of $H^{37}Cl$ in the initial mixture ensured a surface saturated with $^{37}Cl$.

For $CF_3CFCl_2$, there are two chlorine atoms that can undergo hydrodechlorination or isotope exchange. Scheme 1 shows the reactions that might happen on the surface pretreated with $H^{37}Cl$. To monitor the scission of the C-Cl bonds, the chlorine isotope distribution on the reactant $CF_3CFCl_2$ and the product $CF_3CHFCl$ (HCFC124) are analyzed. The data for the hydrodechlorination experiment of $CF_3CFCl_2$ with $H^{37}Cl$ were collected at three different $CF_3CFCl_2$ pressures (230, 136 and 52 Torr), 80 Torr of $H^{37}Cl$

and balance $H_2$ (480, 574, and 658 Torr) for a total pressure of 790 Torr. Blank experiments with unlabeled HCl were also performed under the same conditions. The turnover rate and selectivity of the experiments with $H^{37}Cl$ were comparable with the results from unlabeled HCl experiments. A total of 36 data points with $H^{37}Cl$ were collected with conversion levels as high as 20%. The chlorine isotope distribution in $CF_3CFCl_2$ was calculated using the ion at m/e 135 (and 137), which is the most intense, and corresponds to the monochlorinated species $CF_3CFCl$. Because only one chlorine is present, the ratio of intensities at m/e 135 to the one at 137 will give the isotope distribution of chlorine in $CF_3CFCl_2$ directly. The ratio of the total amount of $^{35}Cl$ to $^{37}Cl$ in $CF_3CFCl_2$ was found to be in the range 2.99±0.07, close to the natural abundance of 3.1. As an additional check, we report the relative intensities of the fragment CCl2F at m/e 105, 103 and 101, which gives the distribution of chlorine corresponding to the three compounds $CF_3CF^{37}Cl^{37}Cl$ : $CF_3CF^{35}Cl^{37}Cl$ : $CF_3CF^{35}Cl^{35}Cl$, and should occur naturally in the ratio (0.058, 0.365, 0.578). The average distribution for the $H^{37}Cl$ experiments is (0.062, 0.361, 0.577) and for unlabeled HCl is (0.063, 0.363, 0.575) with a standard deviation of 0.003 for each distribution point. Since no enrichment in the reactant was observed, this suggested that the rate of exchange was lower than our analytical detection limit. The minimum reverse reaction rate that would cause a detectable deviation in the $CF_3CFCl^{35}Cl/CF_3CFCl^{37}Cl$ ratio was calculated to be $5.1\times10^{-4}$ $s^{-1}$, while the turnover rate of the hydrodechlorination reaction at the same condition was $5–6\times10^{-2}$ $s^{-1}$, which can be taken as the forward C-Cl bond scission reaction rate. Upon comparison of these two rates, we can conclude that the first C-Cl bond scission is irreversible.

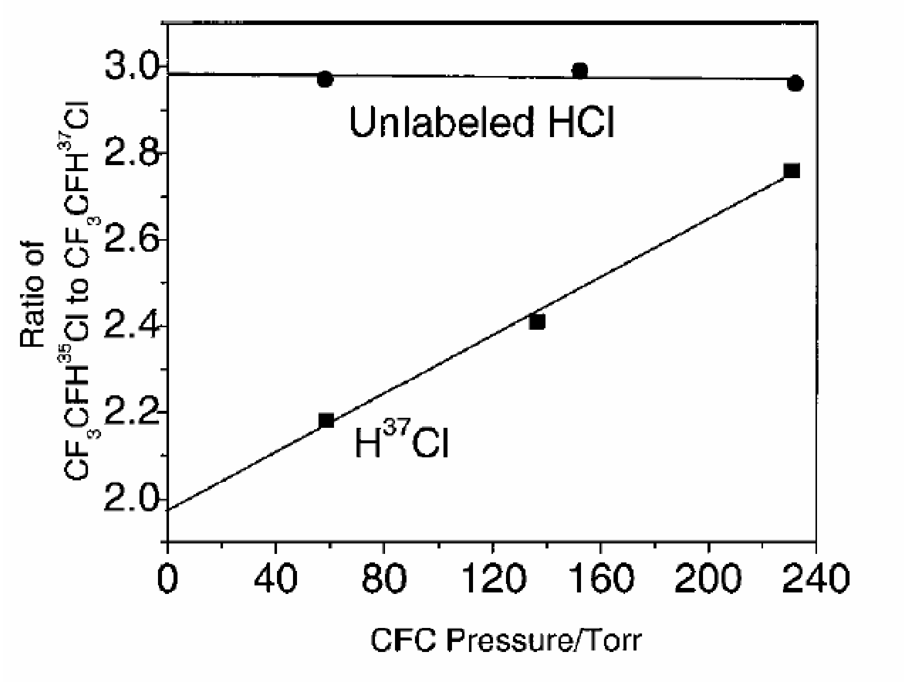


**Figure 1. Enrichment of $CF_3CFHCl$ in $^{37}Cl$ as a result of the reversibility of chlorination steps on the surface. Hydrodechlorination reaction of $CF_3CFCl_2$ carried out at the specified pressure, 480 Torr H2, 80 Torr $H^{37}Cl$, and 150°C in a batch reactor. Selectivity was independent of conversion.**

The ratio $CF_3CHF^{35}Cl/CF_3CHF^{37}Cl$ for the product $CF_3CHFCl$ was monitored to determine the reversibility of scission the second C–Cl bond. This ratio was found to be independent of conversion, less than the natural ratio of 3.1, and dependent upon initial reactant partial pressure (Fig. 1). Blank experiments with unlabeled HCl were conducted under the same $CF_3CFCl_2$ partial pressures as used in the $H^{37}Cl$ experiments to verify that no artifacts were responsible for the decrease in the ratio $CF_3CHF^{35}Cl/CF_3CHF^{37}Cl$. In all blank experiments, the ratio $CF_3CHF^{35}Cl/CF_3CHF^{37}Cl$ was close to 3.1, the natural ratio. The blank and isotope experiments confirm that switching the reactant from unlabeled HCl to $H^{37}Cl$ alone causes the ratio $CF_3CHF^{35}Cl/CF_3CHF^{37}Cl$ to change. Thus, it is concluded that for some of the C-Cl bonds the scission is reversible.

Explanations of why the ratio $CF_3CHF^{35}Cl/CF_3CHF^{37}Cl$ is a function of $CF_3CFCl_2$ and $H_2$ partial pressure and why the exchange ratio at zero pressure (infinite dilution) approaches 2.0 could not be quantitatively explained. As shown in Schemes 1, this is a multi-step reaction network with a complex dependence of rates on partial pressures. It is easy to understand however that even at infinite dilution the exchange ratio will not be zero because the $CF_3CFCl{-}*$ intermediate can be hydrogenated without ever exchanging chlorine. The possibility that $^{35}Cl$ from the reaction dilutes $^{37}Cl$ on the surface and thus decreases the exchange ratio in Fig. 1 does not seem feasible. As shown next, the rate of exchange of surface chlorine with gas phase $H^{37}Cl$ is much faster than the hydrodechlorination reaction.

### *3.3. Measurement of the forward and reverse rate for the reaction between gas phase $H_2$ and HCl and adsorbed H and Cl atoms*

In the proposed CFC hydrodechlorination reaction steps shown in Eq. 4-6, it is assumed that $H_2$ and HCl are in equilibrium with the corresponding adsorbed atomic species on the surface, and that the rate-determining step is the scission of carbon-chlorine bond in the CFC molecule. If this is true, the magnitude of the rate forward or reverse for reaction (6) should be much larger than the overall rate of reaction, and the difference between the two rates equal to the overall turnover rate. To measure the forward and reverse rates, isotope exchange was used.

Deuterium was substituted for hydrogen to measure the rate of the forward and reverse reaction in step 4. In the experiment, a mixture of 436 Torr $D_2$, 65.5 Torr unlabeled HCl, 209 Torr $CF_3CFCl_2$, and 19.2 Torr Ar (a mass spectrometer internal standard) were fed into a batch reactor pre-heated to reaction temperature (150°C).

It can be seen that because $D_2$ was used, Cl will react on the surface through reaction 5 to produce DCl instead of HCl. This can easily be distinguished from the initial HCl fed into the system with a mass spectrometer. Thus, the rate of the forward reaction can be related to formation of DCl, while the reverse reaction rate can be related to the disappearance of HCl. The ion abundance of $H^{37}Cl$ and $D^{37}Cl$ were monitored as a function of time with a mass spectrometer and then related to their respective partial pressures to quantify the forward and reverse reaction rates. In Figure 2, the variation of $H^{37}Cl$ and $D^{37}Cl$ signal was plotted as a function of time. Note that time zero in Fig. 2 is arbitrary and does not correspond to the start of reaction; data was collected before the gas stream was directed into the reactor.

Figure 2 shows that the exchange reaction was equilibrated in less than 60 seconds. From the volume of the batch reactor (0.1347 l), the $D^{37}Cl$ formation rate was found to be 7.5 $s^{-1}$, the rate of $H^{37}Cl$ consumption to be 6.4 $s^{-1}$ and the overall rate is four times higher than the rate of $H^{37}Cl$ consumption, since the other 76% of the mixture is $H^{35}Cl$, or about

30 $s^{-1}$ . The $CF_3CFCl_2$ hydrodechlorination rate measured in the same experiment was $7.4\times10^{-2}$ $s^{-1}$. From these rates, we conclude that the C-Cl bond scission process is about 400 times slower than the reaction between gas phase $H_2$, HCl and surface H, Cl atoms.

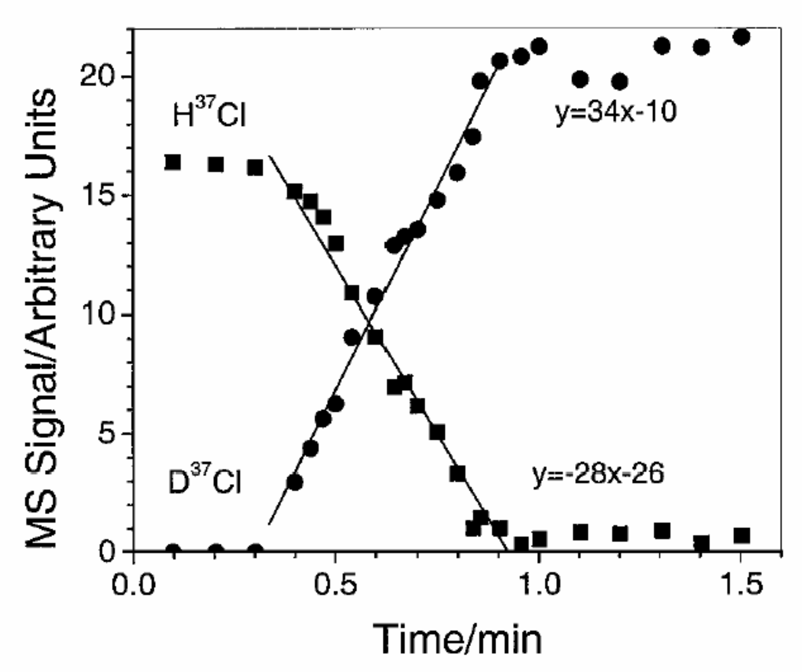


**Figure 2. Variation of $H^{37}Cl$ and $D^{37}Cl$ pressure with time during hydrodechlorination of $CF_3CFCl_2$ (209 Torr) at 150°C with 436-Torr $D_2$,65.5-Torr HCl, and 19.2-Torr Ar in a batch reactor.**

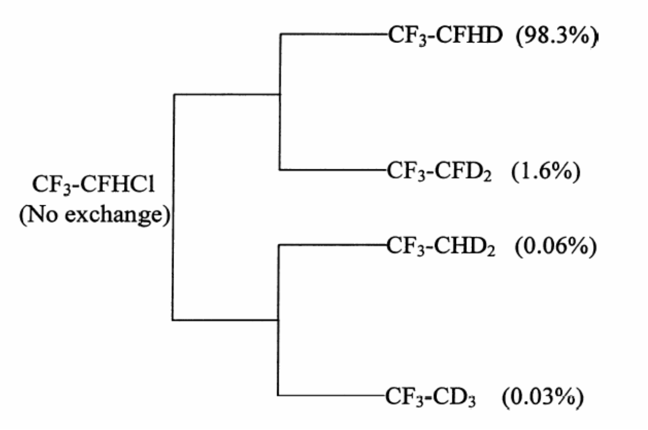
Note that for DCl and HCl in Fig. 2 the MS signal was not adjusted for the relative sensitivities. Due to the primary isotope effect, the ionized HCl molecules are much easier to undergo fragmentation than the ionized DCl molecules in the mass spectrometer. The result is that for the same amount of $D^{37}Cl$ and $H^{37}Cl$, the ion intensity of unfragmented $D^{37}Cl$ (mass 39) is higher than that for $H^{37}Cl$ (mass 38)[24]. In Fig. 2, this is the reason for a higher signal of DCl at the end than the initial signal of HCl and also a higher absolute value of the slope for DCl. To calculate the forward and reverse rates we are also assuming we are also assuming that other reactions involving these species are negligible. In conclusion, the magnitude the forward or reverse rate is about 400 times higher than the rate of hydrodechlorination. Thus, the assumption that eq. 6 is quasi-equilibrated is supported by these results.

### *3.4. Investigation of reaction steps beyond the rate determining step and possible surface intermediates.*

The proposed reaction steps in eqs. 1-8 succeeded in predicting the overall kinetics, but it cannot explain the observed product distribution. Prediction of product selectivity can only be achieved by understanding the reaction steps beyond the rate-determining step.

Deuterium substitution was used to study the hydrodechlorination of HCFC124 ($CF_3CFHCl$) as reported before for Pd black[23]. The experiment was conducted in a batch reactor, enabling a wide conversion range (16–54%) at one temperature. The selectivity of all products was found to be independent of conversion. In the $CF_3CHFCl$ molecule, the carbon containing the chlorine atom also contains a hydrogen atom. Calculations with Gaussian 98 software[25] indicated that in the gas phase the C-H bond strength is almost 100 kJ $mol^{-1}$ higher than the C-Cl bond. Considering only the bond strength as a variable, it is expected that the C-H bonds should not break at the conditions under which the C-Cl bond breaks. In fact, the product distribution is 98.3% to $CF_3CFHD$ and only

1.5% to $CF_3CFD_2$. From the isotope distribution it is believed that $CF_3CFH$-∗ should be present on the Pd surface. For the case of $CF_3CFCl_2$, it can be concluded from the product distribution that $CF_3CFCl$-* and $CF_3CF$=* species are formed on the surface (scheme 1). It is surprising however that although the C-F on the chlorine carbon is also almost 100 kJ $mol^{-1}$ stronger than the C-Cl bond, it is broken about 5% of the time. These examples illustrate the difficulty in predicting the product distribution for this reaction.



**Scheme 1. Deuterium distribution in HCFC124($CF_3$–CFHCl) hydrodechlorination reaction. (Selectivity independent of conversion from 16% to a final HCFC conversion of 54%. Reaction performed at 240°C, 516 Torr $CF_3$–CFHCl, 147 Torr D2. The catalyst was 5% Pd/C-L.) Selectivity is in parenthesis.**

## 4. Summary

Isotope exchange experiments were employed to verify the reaction steps of CFC hydrodechlorination reactions. It was found that the scission of the first C-Cl bond in

$CF_3CFCl_2$ is irreversible, while the scission of the second C-Cl bond is reversible. Thus, once the reactant adsorbs and the first C-Cl bond is broken, it can exchange other chlorine atoms but the molecule desorbs only as a product. Deuterium exchange experiments with HCl showed that adsorbed H and Cl are in equilibrium with gas phase $H_2$ and HCl, with the rate forward or reverse for the step $H_2 + 2Cl* = 2HCl + 2*$ almost 400 times higher than the overall hydrodechlorination reaction rate. The deuterium experiment with $CF_3CFHCl$ showed that most of the time only the C-Cl bond breaks. It is deduced that $CF_3CFH*$ is the major surface species. The explanation of selectivity still remains a challenge; a more complete reaction sequence beyond the rate-determining step must be assembled before selectivity can be estimated.

## Acknowledgements

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# Paper 4

# Hydrodechlorination reactions of 2-chloro-1,1,1,2-tetrafluoroethane and chloroethane in $H_2$ and $D_2$ on Pd catalysts

## Abstract

Deuterium isotope exchange was employed to investigate some of the reaction steps of the hydrodechlorination reaction of $CF_3CFHCl$ and $CH_3CH_2Cl$ on supported Pd catalysts. Reaction rates of hydrodechlorination for either chloro-organics using $D_2$ or $H_2$ were identical. It is thus concluded that H or D species are not involved in the rate-determining step of the hydrodechlorination reaction. Experiments using a combined $H_2$ and $D_2$ feed for hydrodechlorination of $CF_3CFHCl$ show that $CF_3CFH_2$ was preferentially formed over $CF_3CFHD$. This experimental observation can be explained by considering isotope effects and is consistent with gas phase $H_2$ being in equilibrium with surface adsorbed H and a reaction step consisting of the combination of surface adsorbed $CF_3$-CFH-* species with H*. Deuterated product distributions of $CF_3CFHCl$ and $CH_3CH_2Cl$ hydrodechlorination experiments with $D_2$ were analyzed to explore the reaction steps beyond the kinetically relevant steps. The main product of $CF_3CFHCl$ hydrodechlorination was $CF_3CFHD$, showing that the C-Cl bond is preferentially broken. In the case of $CH_3CH_2Cl$ however substantial C–H bond breaking accompanies the initial C–Cl scission. Deuterium exchange experiments with ethane on Pd/C and Pd/$ZrO_2$ were investigated to understand the kinetics of H/D exchange. The results indicate the $CH_3CH_2Cl$ product distribution is not caused by the re-adsorption and subsequent exchange reaction of ethane.

**Keywords**: Hydrodechlorination on Pd; Isotope effects; Reaction Steps; Deuterium.

## 1. Introduction

Hydrodechlorination reaction is the reaction where the chlorine in an organic molecule is substituted by hydrogen. The hydrodechlorination reaction has found applications in many areas. For example, it is used in the production of $CF_3CFH_2$ (a widely used refrigerant) from $CF_3CFCl_2$ [1]. In addition, hydrodechlorination reaction can be used as a way to address environmental issues, such as waste water treatment [2, 3]. Hydrodechlorination is also used to convert chlorofluorocarbons (CFCs), which have been linked to the earth's ozone layer depletion [1], into hydrofluorocarbons (HFCs). These HFC compounds are much less harmful to the environment, at the same time, they retain some of the useful properties of CFCs and can serve as replacements for CFCs [4]. Due to the wide practical application of this reaction, there has been a growing interest in its study.

Hydrodechlorination reactions have been studied over a number of metals, such as Pd [5-12], Pt [13-15], and Rh [13, 15-17], with Pd usually the most reactive and selective catalyst for this reaction [18]. In this contribution, a Pd catalyst supported on carbon will be used for the experiments. The role of the support has been studied on carbon [12, 19], alumina [5, 20-22] and fluorinated alumina [6, 22]. While some authors suggested that the support might play a role in hydrodechlorination reactions [23], we have previously reported that the support (carbon) does not influence reaction kinetics beyond the possible condensation of some CFC reactants in the pores of microporous supports [12]. Hydrodechlorination literature also includes studies on model catalysts, such as evaporated films [24-26], foils [8, 9, 27], and single crystals [28]. A limited number of studies also reported hydrodechlorination reactions on bulk metal powders [11, 29, 30]. However, turnover rates, selectivity and reaction orders of hydrodechlorination reaction have been measured for only a limited number of compounds [5, 6, 8, 9, 11, 12, 23, 27, 28], with most of them being chlorofluorocarbons. Recently, there have been some studies using chlorinate compounds other than chlorofluorocarbons as model compounds to gain more knowledge of hydrodechlorination reaction kinetics, such as the research papers of $CH_2Cl_2$ [31, 32].

Many literature reports also tried to elucidate the possible reaction steps [8, 9, 11, 12, 16, 17, 33-37] of hydrodechlorination. From the study of a series of four CFC compounds, Thompson *et al.* proposed a set of reaction steps to describe this reaction. The first step is the equilibrated adsorption of chlorinated reactants with equilibrium constant $K_{CFC}$:

$$\text{R-Cl} + * = \text{R-Cl}* \qquad (1)$$

This step is followed by the irreversible scission of the C-Cl bond, proposed as the rate-determining step (rds) with rate constant $k_{0.}$

$$\text{R-Cl}\,* \rightarrow \cdots \qquad (2)$$

This step was confirmed by the finding that the rate of hydrodechlorination correlates with gas phase bond strength for the first C–Cl bond to break during reaction. Note that the reaction products formed after this step are not kinetically significant and thus do not need to be represented. Steps (1) and (2) above lead to the following rate expression,

$$r = k_0 K_{CFC}[\text{R-Cl}][*] \qquad (3)$$

To calculate the number of empty sites ([*]), it is assumed that reactions (4) and (5) below are in equilibrium

$H_2 + 2^* = 2H^*$ (4)

$H^* + Cl^* = HCl + 2^*$ (5)

The overall reaction from (4) and two times (5) is equation (6), and its equilibrium constant is denoted $K_{0.}$

$H_2 + 2\ Cl^* = 2HCl + 2^*$ (6)

Assuming that Cl* is the most abundant surface intermediate ([*] + [Cl*] = [L], with [L] the total site concentration) leads to the following expression for the free site concentration:

$$[*] = \frac{[L]}{1 + \frac{[HCl]}{K_0^{1/2}[H_2]^{1/2}}} \qquad (7)$$

By substituting (7) into (3), and defining $k = k_0 K_{CFC}[L]$ and $K = K_0^{-1/2}$, the hydrodechlorination reaction rate can be expressed as:

$r=k[R\text{-}Cl]/\{1+K[HCl]/[H_2]^{0.5}\}$ (8)

And finally, hydrodechlorination products are formed by the combination of fragments of chlorinated compounds and surface adsorbed hydrogen.

$R^* + H^* \rightarrow RH + 2^*$ (9)

It should be pointed out that these reaction steps were deduced from hydrodechlorination reaction kinetics measurements only, and further support by other experimental methods would lend support to the proposed steps. Isotope tracing is a powerful tool to probe reaction kinetics and selectivity. A limited number of isotope exchange studies have been conducted on hydrodechlorination reactions [11, 24, 34]. The reaction steps proposed by Thompson *et al.* was examined using isotopic tracing experiments by Chen *et al.* [34], and they have concluded that the proposed reaction steps are valid for describing CFC hydrodechlorination reaction kinetics. Exchange experiments with $H^{37}Cl$ have demonstrated that the proposed hydrodechlorination rds, C-Cl bond scission, is irreversible [34]. Experiments utilizing $D_2$ exchange showed that, steps (4) and (5) above are in equilibrium. The only other previous report in the literature on $D_2$ exchange by Campbell *et al.* [24] show that the reaction of $CH_3CH_2Cl$ on a Pd film most likely proceeds through a carbene like intermediate since the reaction product ethane was significantly enriched with the doubly deuterated product $CH_3{-}CHD_2$, showing the presence of C-H bond scission. However, we have reported that in the reaction of $CF_3{-}CFHCl$ with deuterium on Pd/C [11], the most abundant product (98%) is the mono-deuterated product $CF_3{-}CFHD$ and thus only the C-Cl bond breaks during the $CF_3{-}CFHCl$ hydrodechlorination reaction.

In this article, we will continue to explore hydrodechlorination reaction steps using $D_2$. One focus of this study is the deuterium isotope effect. We will be investigating the isotope effect on both the reaction equilibrium constants and the rate constants of reaction [38]. One possible application of isotope effect is to identify the rate determining step of a reaction. For example, if the observed overall rate of a reaction is changed by a switch from $H_2$ to $D_2$, then the rate-determining step must involve H (or D). We plan to study the overall hydrodechlorination rates of $CF_3$-CFHCl and $CH_3$-$CH_2$Cl with $D_2$ or $H_2$ on palladium catalysts. By comparing their rates with different hydrogen isotopes, it is hoped we can reveal the role of hydrogen in the rate determining step. In addition, when $D_2$ is used in hydrodechlorination reaction, step 4, 5 and 9 in the proposed reaction steps may also be affected by deuterium isotope effect. This effect will also be monitored and analyzed to provide evidence for the existence of these elementary steps. Another parameter to be investigated using deuterium is the C-H bond scission during the hydrodechlorination reaction. We will show that the deuterium substitution of a C-H bond on the carbon containing chlorine changes significantly with the structure of the reactant, for example for $CF_3$-CFHCl and $CH_3$-$CH_2Cl$. Additionally, results for the ethane exchange reaction with $D_2$ will be shown to provide more insight into the C-H bond scission pathway in hydrocarbon compounds on the Pd surface.

## 2. Experimental Methods

### *2.1. Catalysts*

Two palladium catalysts on different supports (carbon and zirconia) were used in this study. The 5% Pd catalyst supported on activated carbon (5% Pd/C) was obtained from Degussa with serial number E 9011 XR/W 5%. It had a BET area of 107 $m^2$ $g^{-1}$ and a total pore volume of 1.15 $cm^3$ $g^{-1}$. The pore size distribution and pore volume of the Degussa catalyst were measured with a Quantachrome Autosorb-1 volumetric sorption analyzer. The Pd catalyst supported on zirconia was prepared by incipient wetness method using an aqueous solution of $Pd(NH_3)_2(NO_2)_2$ in nitric acid obtained from Tanaka Kikinzoku Kogyo of Japan. The zirconia RC-100P was from Daichi Kigenso Kagaku (DKK) of Japan. The original catalyst samples were ground with a mortar and pestle and the fraction between 40 and 60 mesh size was retained for use in hydrodechlorination reactions.

### *2.2. Reactants*

The $CF_3$-CFHCl (HCFC 124) was from DuPont Suva Refrigerants. The 99.7% $CH_3CH_2Cl$ and 99.9% $C_2H_6$ samples were purchased from Aldrich Chemical Company. The $H_2$ used for catalytic reactions was a mixture of $H_2$ and methane, certified as ultrahigh purity from the Matheson Gas Company. The mixture contained 1033 ppm methane, used as an internal standard for GC measurements. The hydrogen-methane mixture was passed through a purifier containing 5% Pd/C catalyst before entering the reaction system to remove any oxygen from the $H_2/CH_4$ transfer line. The $H_2$ used for catalyst reduction (BOC Gases) was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was obtained from BOC gases and purified through a gas trap (HP model 5182-3467). The deuterium used in this study was obtained from Cambridge Isotope Laboratories. It contains 99.6% $D_2$ and 0.4% HD, and before use it was purified in the same Pd membrane used for purification of $H_2$.

### *2.3. Reactor Configuration*

The gas manifold was constructed of 1/8" diameter stainless steel tubing. Gas flows were controlled with mass flow controllers (Porter Instrument Co.). The volumetric gas flow rates from the mass flow controllers had been calibrated with a bubble flow meter. The reaction portion of the flow system was made of Pyrex glass and the reactor was made out of quartz with the catalyst held on a fritted disk. Reactions could be carried out in the well-mixed reaction system either in continuous stirred tank reactor (CSTR) or batch mode. Heating of the reactor was provided by a VWR 21100 tube furnace controlled by a Eurothem model 808 temperature controller. The reaction temperature inside the reactor was measured through a thermocouple well extending into the catalyst bed. The inlet and outlet flow rates of the CSTR were ~100 $cm^3$ $min^{-1}$.

Mixing in the CSTR was provided by a bellows pump (Senior Flexonics, MB-21) with a circulation rate of 1400 $cm^3$ $min^{-1}$. The high flow allowed differential reactor operation and minimized transport effects. The absence of heat and mass transfer limitations were confirmed by the Madon-Boudart test [39]. From results presented in previous work [12], heat and mass transfer limitations were absent on the highest surface area catalyst used, where transport limitations would be most severe.

The reaction mixture was injected into a modified GC-MS (GC-HP 5880A and MS-HP5970A). The column used in the GC was a 5% Krytox 143AC, 60/80 Carbopack B HT 20' x 1/8"column from Supelco. The effluent from the GC column was simultaneously analyzed by a flame ionization detector for quantitative analysis by mass spectroscopy for qualitative analysis. The gas was sampled into the mass selective detector through a fused silica polyimide capillary column (51μm I.D., 363μm O.D., 0.75 m). The GC response factors for all the reactants and products were calibrated against methane using the hydrogen-methane mixute. Prior to venting, the gas effluent was passed through a NaOH solution to neutralize the HCl present in the stream.

### *2.4. Data Collection Procedure*

Two to five hundred milligrams of fresh Pd/C catalyst was initially loaded into the reactor and reduced for 3 hrs at 300°C with 50 $cm^3$ $min^{-1}$ $H_2$. For repeated reactions, the catalyst was treated with 50 $cm^3$ $min^{-1}$ $H_2$ for 0.5-1 h at 150°C before the hydrodechlorination experiments.

When the reactor was operated in batch mode, the reactor was evacuated to $1\times10^{-5}$ Torr for 0.5 hour before gas reactants were introduced. The oven temperature was raised to the reaction temperature at a rate of 5K $min^{-1}$. For each data point, 100-200μl of gas mixture was injected with a syringe into the GC-MS for analysis.

When the reactor was operated in the CSTR mode, mass flow controllers regulated the inlet gas concentrations. For a particular set of conditions, the reaction would be carried out for 30-60 minutes before the first data point was taken. The gas mixture was sampled into the GC-MS using an automatic valve in the GC. During the course of the experiments, the changes in concentration or temperature were chosen in random order to eliminate potential systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated. By comparing the first and last points, the amount of deactivation could be calculated.

### *2.5. Surface Area Measurements*

The total surface area of the catalysts was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen-oxygen titration method described by Benson *et al.* [40]. The experimental setup consisted of a volumetric system constructed in Pyrex glass and pumped by a liquid nitrogen trapped diffusion pump. The amount of gas adsorbed was determined by monitoring the pressure change in a pre-calibrated volume on the reaction system with a pressure transducer (MKS model 127).

The Pd/C or the Pd/$ZrO_2$ catalyst sample was reduced in flowing $H_2$ (50 $cm^3\ min^{-1}$) for 3 hrs at 573K before Pd surface area measurements. After the initial reduction, hydrogen-oxygen titration was conducted at 373K. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression assumes spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms $m^{-2}$ [41].

X-ray diffraction (using Rigaku Geigerflex diffractometer) of reduced and then passivated Pd/C catalyst was also conducted. The sample for XRD analysis was reduced by the previously mentioned procedure, and then passivated with 60 Torr of $O_2$. The Scherrer equation was used to calculate the Pd particle size with appropriate correction for instrumental line broadening.

### *2.6. Error Analysis*

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in the experiments were at most 10%.

## 3. Results

### *3.1. Catalyst Properties*

The properties of the catalysts are displayed in Table 1. The carbon support for this catalyst is a non-microporous sample. Non-microporous carbon support was chosen in this research work because in our previous research [12], we found that certain CFC reactants condense in the micropores of carbon during reaction, and thus lower the apparent reaction order of CFC. The carbon support itself plays no role in the hydrodechlorination reaction beyond the previously discussed condensation effect [11]. Metal oxide supports, such as alumina or zirconia can react with chlorine and fluorine and in addition the modified support can catalyze halogen [5, 23] thus potentially altering the reaction kinetics. Comparison of used Pd/$ZrO_2$ samples by XRD with fresh samples verified that $ZrO_2$ was unchanged with no indication on the formation of chlorinated or fluorinated zirconium compounds. The Pd dispersion, including particle size determined by XRD line broadening, are also shown in Table 1. The property parameters in Table 1 are representative of catalyst before reaction. Since no significant deactivation was observed during reaction, we do not expect any significant changes in the properties of the catalyst during reaction.

| Catalyst | BET surface area ($m^2\ g^{-1}$) | Amount of Surface Pd ($\mu mol\ g^{-1}$) | PME[a] (%) | Particle Diameter (nm) | |
|---|---|---|---|---|---|
| | | | | Chemisorption[b] | XRD |
| 5.0% Pd/C | 107 | 39.1 | 8.4 | 13 | 5 |
| 10%Pd/$ZrO_2$ | 130 | 37.6 | 4.0 | 28 | N/A |

[a] Percentage of metal exposed, determined by $H_2$-$O_2$ titration at 373K.
[b] Particle size determined from d=112/PME.

**Table 1. Catalyst Properties**

*3.2. Overall $CF_3$-CFHCl hydrodechlorination rates with $H_2$ and $D_2$*

By comparing the rate of hydrodechlorination in $D_2$ and $H_2$, the extent of H involvement in the rate-determining step can be determined [42]. The results and conditions of $CF_3CFHCl$ and $CH_3CH_2Cl$ hydrodechlorination in either $H_2$ or $D_2$ on Pd/C catalyst are shown in Table 2. At similar reaction conditions, $CF_3CFHCl$ and $C_2H_5Cl$ hydrodechlorination rates in $H_2$ were essentially the same as those in $D_2$.

| Reactant | Reaction | Reaction Conditions | Corrected TOR ($s^{-1}$)* |
|---|---|---|---|
| $CF_3CHFCl$ | With $H_2$ | $H_2$: 108 Torr<br>HCFC124: 526Torr<br>Temperature: 306 °C | $2.16\times10^{-4}$ |
| | With $D_2$ | $D_2$: 112 Torr<br>HCFC124: 524Torr<br>Temperature: 306 °C | $2.13\times10^{-4}$ |
| $CH_3CH_2Cl$ | With $H_2$ | $H_2$: 258 Torr<br>$CH_3CH_2Cl$: 151 Torr<br>Temperature: 227 °C | $3.15\times10^{-4}$ |
| | With $D_2$ | $D_2$: 246 Torr<br>$CH_3CH_2Cl$: 125 Torr<br>Temperature: 227 °C | $3.05\times10^{-4}$ |

* Rates and selectivity corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$ or $D_2$, 20 Torr HCl, and 150°C.

**Table 2. Comparison of $CF_3CFHCl$ and $CH_3CH_2Cl$ hydrodechlorination rates with $H_2$ or $D_2$ on Pd/C.**

### *3.3. Hydrodechlorination of $CF_3CFHCl$ with $H_2$–$D_2$ co-feed on Pd/C*

When $D_2$ is used in the hydrodechlorination of $CF_3$-CFHCl, for those steps involving hydrogen ((4), (5) and (9)), deuterium isotope effects are expected to occur. Equilibrium isotope effect may change the equilibrium constants of (4) and (5), while a kinetic isotope effect may alter the rate constant of (9). However, since none of these three steps are rate determining, it is not possible to observe isotope effects from the overall kinetics parameters. An isotopic tracing experiment was designed in which $H_2$–$D_2$ were co-fed with $CF_3CFHCl$ and the ratio of concentrations [$CF_3CFH_2$]/[$CF_3CFHD$] was measured. The H and D reaction pathways could be followed simultaneously.

The hydrodechlorination of $CF_3CFHCl$ with a $H_2$-$D_2$ mixture was conducted at 553K in a CSTR. The $H_2$ and $D_2$ total pressure was maintained at 420 Torr and the $H_2/D_2$ ratio was varied by changing their respective flow rates. The concentration of $CF_3$-$CFH_2$ and $CF_3$-CFHD were quantified by mass spectrometry by the –$CFH_2$ (m/z 33) and –CFHD (m/z 34) fragments, respectively. The $[CF_3CFH_2]/[CF_3CFHD]$ ratio was measured as a function of the $H_2/D_2$ ratio and as plotted in Figure 1 show a linear relation. The line also shows $[CF_3CFH_2]/[CF_3CFHD]$ ratio is always higher than the initial $[H_2]/[D_2]$ ratio, implying that $CF_3CFH_2$ is produced preferentially on the Pd surface.

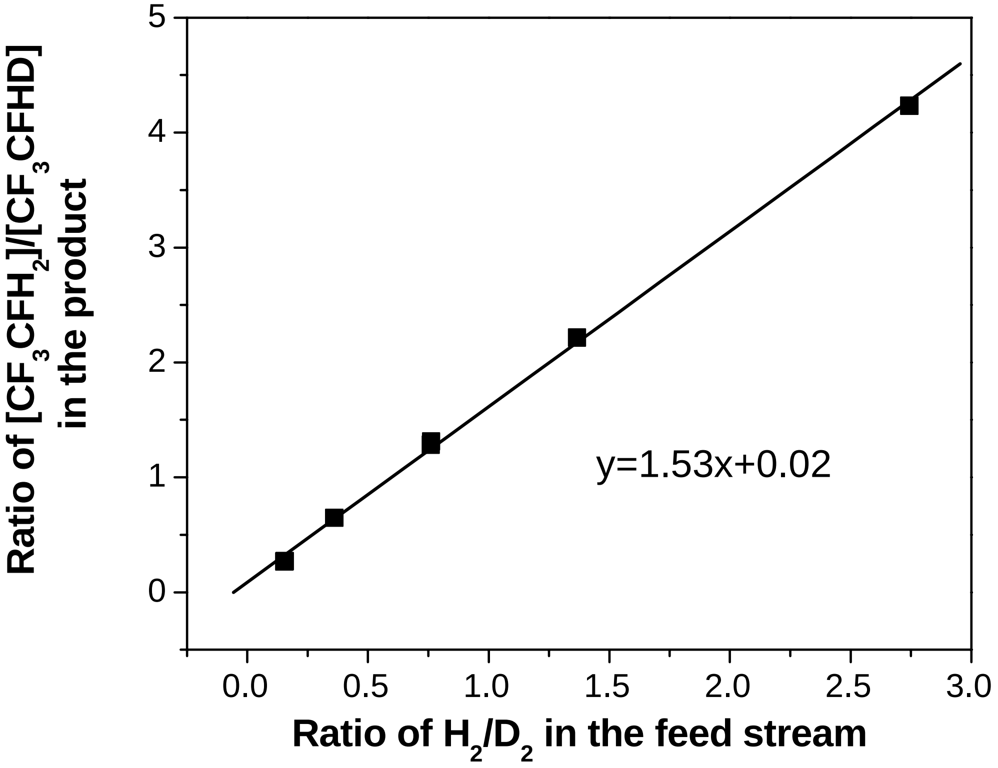


**Figure 1. Relationship between the ratio of $CF_3CFH_2/CF_3CFHD$ in the product and the ratio of $H_2/D_2$ in the feed stream in the hydrodechlorination reaction of $CF_3CFHCl$ with a $D_2$-$H_2$ co-feed. Reaction conducted at 553K in the**

**CSTR reactor, with 330 Torr $CF_3CFHCl$ and 420 Torr $H_2$+$D_2$ total pressure**

*3.4. Product distribution of $CF_3CFHCl$ and $CH_3CH_2Cl$ hydrodechlorination with $D_2$ on Pd/C and Pd/$ZrO_2$*

The proposed reaction steps shown in steps (1)-(9) only contain elementary steps related to the hydrodechlorination product formed after one chlorine is removed. For compounds with more than one chlorine one would like to know what determines the observed hydrodechlorination reaction selectivity. The prediction of product distribution requires a detailed set of reaction steps, including the elementary steps beyond the rate-determining step. One such step is C-H bond scission, and it can be studied by analyzing deuterated product distribution from $D_2$ exchanged hydrodechlorination reaction.

We have studied C-H bond scission in deuterium substituted hydrodechlorination of $CF_3CFHCl$ on Pd catalysts and the result has been reported before in a separate publication [11] and is shown in Figure 2. The deuterated product distribution of $CF_3CFHCl$ is 98.3% towards $CF_3CFHD$, indicating that the C-Cl bond breaks preferentially.

In this study, $CH_3CH_2Cl$ hydrodechlorination with $D_2$ was performed on Pd/C and Pd/$ZrO_2$. The reaction on Pd/C catalyst was carried out at 443K, with 171 Torr $C_2H_5Cl$ and 654 Torr $D_2$ in a batch reactor. The reaction on Pd/$ZrO_2$ was carried out at 363K with 114 Torr $C_2H_5Cl$ and 641 Torr $D_2$. The concentration of each possible deuterated ethane product in the mixture was calculated in an algorithm that takes into account the multiple fragments and interference of the isotopomers upon fragmentation; fragments from heavier deuterated ethanes formed by C-H or C-D bond fragmentation contribute to ion peaks of lighter deuterated ethanes in a mixture of ethanes with different deuterium content [43, 44]. The corrected ethane product distributions from the two experiments on Pd/C and Pd/$ZrO_2$ are shown in Figure 3. The extent of deuteration was independent on the conversion. The batch reactor ranged from 1–29%, but the product distribution remained the same during $C_2H_5Cl$ hydrodechlorination reaction with $D_2$.

Singly deuterated ethane is the main product for both catalysts. Both catalysts display similar selectivity, but differ markedly in their overall turnover rate. Activities for hydrodechlorination with $D_2$ are summarized in Table 3. The corrected $CH_3CH_2Cl$ hydrodechlorination turnover rate obtained on Pd/$ZrO_2$ catalyst is significantly higher than the rate measured on the carbon based catalyst. The rate on Pd/$ZrO_2$ is comparable to the rate previously measured on a Pd film catalyst [24]. Rates of $CF_3CFHCl$ hydrodechlorination are also presented in Table 3. Unlike $C_2H_5Cl$, $CF_3CFHCl$ hydrodechlorination rate on Pd/$ZrO_2$ is comparable to the rate on Pd/C catalyst. It should be pointed out that during reaction on Pd/$ZrO_2$ the selectivity of $CF_3CFHCl$ showed a change with reaction time. This is probably to due to fact that metal oxide support can cause dismutation reaction of CFC compounds and thus change reaction selectivity [45, 46]. To make comparisons possible, all the rates reported here have been corrected to standard conditions of 150 Torr $CH_3CH_2Cl$ or $CF_3$-CFHCl, 200 Torr $D_2$, 20 Torr of HCl and 423K.

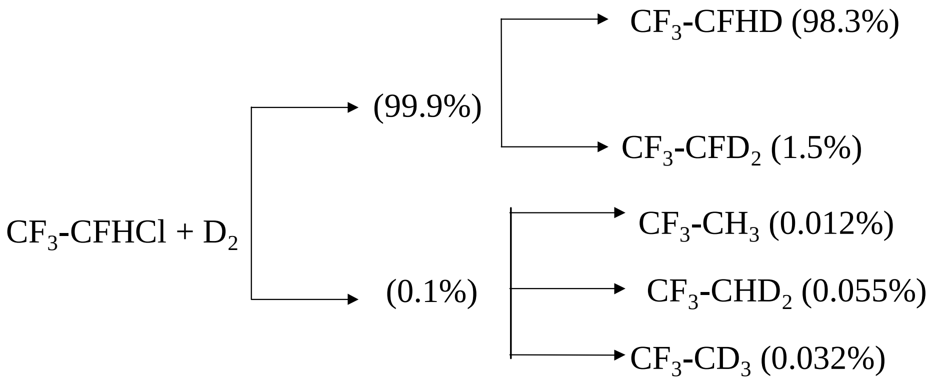


**Figure 2.** **Deuterated product distribution in HCFC-124 ($CF_3$–CFHCl) hydrodechlorination reaction. Selectivity is independent of conversion from 16% to a final HCFC conversion of 54%. Reaction performed at 240°C, 516 Torr $CF_3$–CFHCl, 147 Torr $D_2$ on Pd/C catalyst. Selectivity is in parenthesis.**

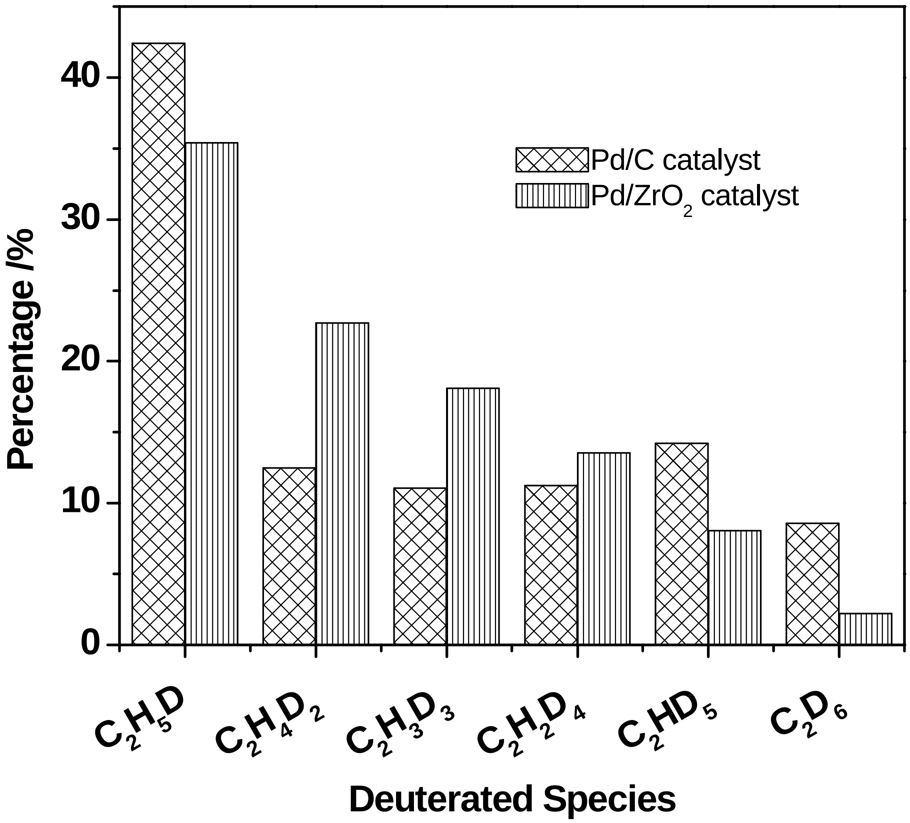


**Figure 3. Product distribution of $C_2H_5Cl$ hydrodechlorination with $D_2$ in a batch reactor. Reaction conditions for Pd/C were 443 K, 171 Torr $C_2H_5Cl$ and 654 Torr $D_2$. $Pd/ZrO_2$ reaction conditions were 363 K with 114 Torr $C_2H_5Cl$ and 641 Torr $D_2$. Selectivity was independent of conversion.**

| **Reactant** | **Catalyst** | **Corrected TOR ($s^{-1}$) [a]** |
|---|---|---|
| $CH_3CH_2Cl$ | Pd/C | $3.2\times10^{-4}$ |
| | $Pd/ZrO_2$ | $4\times10^{-2}$ |
| | Pd film [b] | $9\times10^{-2}$ [b] |
| $CF_3CHFCl$ | Pd/C | $1.22\times10^{-4}$ |
| | $Pd/ZrO_2$ | $1.28\times10^{-4}$ |

[a] Rates and selectivity corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl, and 150°C.

[b] Result reported by Campbell and Kemball [24] assuming CFC order=1, $H_2$ order=0.5 and HCl order=-1

**Table 3. Comparison of $CF_3CFHCl$ and $CH_3CH_2Cl$ overall hydrodechlorination turnover rates on Pd catalysts.**

### *3.5. Product distribution of $C_2H_6$ deuterium exchange on Pd/C and $Pd/ZrO_2$*

During the hydrodechlorination of $CH_3CH_2Cl$ with $D_2$, one major concern was that the observed product distribution might be caused by re-adsorption of ethane and further deuterium exchange. To verify whether deuterium exchange on ethane was contributing to the product distribution in Figure 3, $C_2H_6$ exchange experiments with $D_2$ were also conducted on the Pd/C and $Pd/ZrO_2$ catalysts in batch mode. It was found that no significant amount of deuterium exchanged ethane was detected on Pd/C catalyst until the temperature was increased above 673 K while $C_2H_6$ exchange on $Pd/ZrO_2$ was measurable above 473 K. Note that the batch reaction of $CH_3CH_2Cl$ hydrodechlorination with $D_2$ was conducted on the Pd/C and $Pd/ZrO_2$ catalyst at 443 K and 363 K, respectively, conditions where the rate of ethane exchange with deuterium would be negligible.

The deuterated species distribution from the ethane-deuterium exchange reaction is different from $CH_3CH_2Cl$ hydrodechlorination reaction with $D_2$. Ethane with higher deuterium content is formed in ethane-deuterium exchange experiment. For example, on the Pd/C catalyst, the mean number of deuterium entering ethane in ethane-deuterium exchange is 3.2, compared with 2.6 for the chloroethane-deuterium exchange.

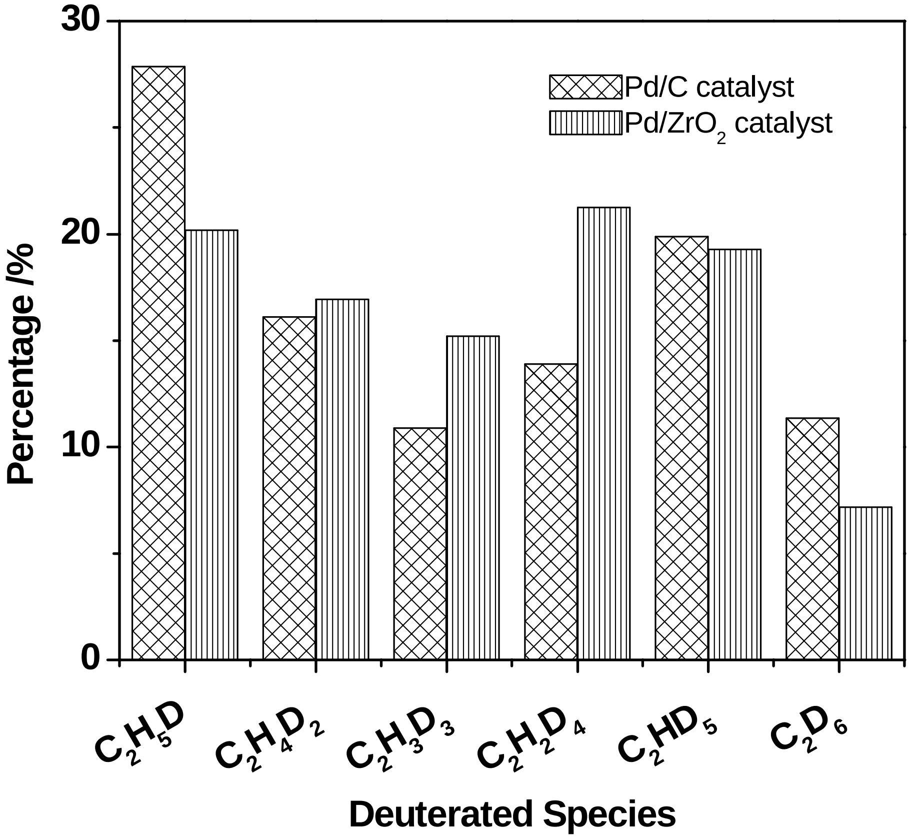


**Figure4. Product distribution for $C_2H_6$ deuterium exchange reaction in a batch reactor. Reaction conditions on Pd/C were 731 K, 168 Torr $C_2H_6$ and 671 Torr $D_2$. Reaction conditions on Pd/$ZrO_2$ were 486 K, 156 Torr $C_2H_6$ and 644 Torr $D_2$. Selectivity was independent on conversion.**

## 4. Discussion

### *4.1. Rate determining step in hydrodechlorination reaction*

Nearly identical rates were measured for $CF_3$-CFHCl and $C_2H_5Cl$ hydrodechlorination reaction with $H_2$ or $D_2$. We have proposed that the rate–determining step for a series of $CF_3CF_{3-x}Cl_x$(x =1-3) chlorinated compounds involves C–Cl bond cleavage [11, 12]. For each of the CFC compounds in this series, there is a correlation between the hydrodechlorination rate and the bond energy of the first C-Cl bond to be broken [12]. This observation suggests that C–Cl bond breaking is rate–determining and the present results showing the same rates in $H_2$ or $D_2$ confirms that the rds does not involve hydrogen.

There are examples in the literature showing that when $H_2$ adsorption or C-H (or C-D) bond scission or formation is the rate determining step, such as hydrocarbon exchange reaction with $D_2$ [47, 48] and ethylene hydrogenation reaction [49-52], the reaction rate with $H_2$ is at least two times faster than the reaction rate with $D_2$. The results presented in Table 2 on rate comparisons with $H_2$ or $D_2$ exclude any H (or D) involving steps (4,5,9) as rate-determining.

### *4.2. Isotope Effects in $CF_3CFHCl$ hydrodechlorination with $H_2$-$D_2$ co-feed*

Two interesting observations are made when $CF_3CFHCl$ hydrodechlorination is conducted with both $H_2$ and $D_2$ in the gas phase. First, the ratio of $[CF_3CFH_2]/[CF_3CFHD]$ in hydrodechlorination product is linearly related to the initial $[H_2]/[D_2]$ ratio in feed stream. Second, the slope of the line in Figure 1 shows that if the $[H_2]/[D_2]$ ratio in feed stream is 1:1, more $CF_3CFH_2$ is produced than $CF_3CFHD$, indicating the presence of isotope effects. In the following discussion, these two observations will be explained, which will further validate the proposed reaction steps.

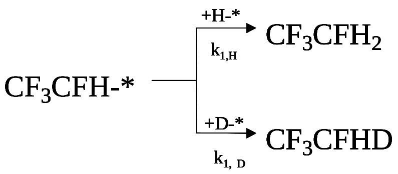
### *4.2.1. Relationship between $[CF_3CFH_2]/[CF_3CFHD]$ ratio to the initial $[H_2]/[D_2]$ ratio.*

We have shown that equilibrium between gas phase $D_2$, $H_2$ and surface H, D will exist during CFC hydrodechlorination [34]. The Pd surface will thus have both H and D atoms adsorbed on it. As a result, when $CF_3$-CFHCl molecule adsorbs on the Pd surface and breaks its C-Cl bond to form the surface intermediate $CF_3CFH$-*, this surface species can either take up a H atom to form $CF_3$-$CFH_2$ or take up a D atom to form $CF_3$-CFHD. Due to isotope effects, $H_2$ and $D_2$ may have different equilibrium constants on the Pd surface (denoted as $K_{H2}$ and $K_{D2}$, respectively); while the combination of $CF_3CFH$-* with adsorbed H (rate constant denoted by $k_{1,H}$) or adsorbed D (rate constant denoted by $k_{1,D}$) may be different. The previous discussion can be illustrated by the scheme shown below, note that HD can also be formed by the combination of surface H* and D*.

$H_2 + 2^* = 2H^*$, with equilibrium constant $K_{H2}$ (4a)

$D_2 + 2^* = 2D^*$, with equilibrium constant $K_{D2}$ (4b)

$HD + 2^* = H^* + D^*$, with equilibrium constant $K_{HD}$ (4c)



(modified step 9)

**Scheme 1**

It is apparent from scheme 1 that the formation of $CF_3$-$CFH_2$ and $CF_3$-CFHD occurs in parallel. So the ratio of $CF_3$-$CFH_2$/$CF_3$-CFHD in product can be expressed using their respective formation rates:

$$ratio = \frac{CF_3CFH_2}{CF_3CFHD} = \frac{k_{1,H}[CF_3CFH-*][H*]}{k_{1,D}[CF_3CFH-*][D*]} = \frac{k_{1,H}[H*]}{k_{1,D}[D*]} \tag{10}$$

From equation. (10), the $CF_3CFH_2$/$CF_3$CFHD ratio is related linearly to the surface concentration ratio, [H*]/[D*]. However, this surface term can be related to gas phase [$H_2$] and [$D_2$] if one considers the equilibrated step (4a) and (4b) in scheme 1. The equilibrium relationships are written as:

$$K_{D_2} = \frac{[D*]^2}{[D_2][*]^2} \tag{11}$$

and

$$K_{H_2} = \frac{[H*]^2}{[H_2][*]^2} \tag{12}$$

Solving for the surface concentrations and dividing equation (11) by (12), the following equation is obtained:

$$\frac{[H*]}{[D*]} = \frac{K_{H_2}{}^{0.5}[H_2]^{0.5}}{K_{D_2}{}^{0.5}[D_2]^{0.5}} \tag{13}$$

Substituting equation (13) into equation (10), the relationship between the $H_2$, $D_2$ concentration in the gas phase and the $CF_3$-$CFH_2$/$CF_3$-CFHD ratio in the product is

$$\frac{CF_3CFH_2}{CF_3CFHD} = K''\frac{[H_2]^{0.5}}{[D_2]^{0.5}} \tag{14}$$

$$\text{where } K'' = \frac{k_{1,H}K_{H_2}{}^{0.5}}{k_{1,D}K_{D_2}{}^{0.5}}$$

The coefficient K'' is constant at a constant temperature because it is composed of only rate and equilibrium constants. This implies that for the steps listed in scheme 1, the $CF_3$-$CFH_2$/$CF_3$-CFHD ratio in the product is linearly related to the term $[H_2]^{0.5}/[D_2]^{0.5}$ at constant temperature. But, it should be noted that the $H_2$ and $D_2$ concentration in equation (14) is the $H_2$ and $D_2$ concentration under reaction conditions after the equilibrium in equation (4a)-(4c) are established, and not the initial $H_2$ and $D_2$ concentration in the feed stream. In the real experiment, the inlet gases $H_2$ and $D_2$ equilibrate as a mixture $H_2$, $D_2$ and newly formed HD as shown in scheme 1. It is desirable to relate this $[H_2]^{0.5}/[D_2]^{0.5}$ ratio under reaction condition to the initial $H_2$ and $D_2$ concentration in feed stream, which are easily measured. This calculation is possible by considering the equilibrium in equation (4a)-(4c) and a mass balance in the system, as shown in the following analysis.

The equilibrium from 4a to 4c can be written as one overall reaction:

$H_2 + D_2 = 2HD$, with equilibrium constant $K_{overall}$ (15)

This equilibrium has been studied before [53] and is represented as (temperature in Kelvin):

$$\mathrm{K}_{\text{overall}} = \frac{[\mathrm{HD}]^2}{[\mathrm{D}_2][\mathrm{H}_2]} = 4.24 \times e^{-79/T} \tag{16}$$

At 553K, the temperature of $CF_3CFHCl$ hydrodechlorination experiments:

$$\mathrm{K}_{\text{overall}} = \frac{[\mathrm{HD}]^2}{[\mathrm{D}_2][\mathrm{H}_2]} = 3.67 \text{, and } [\mathrm{HD}] = 1.92\sqrt{[\mathrm{H}_2][\mathrm{D}_2]} \tag{17}$$

A mass balance for H and D yields two equations:

$$2[H_2] + [HD] \approx 2[H_2]_0 \tag{18}$$

$$2[D_2] + [HD] \approx 2[D_2]_0 \tag{19}$$

where the subscript “0” denotes initial concentration. A complete H and D mass balance would also include steps (6) and (9). Since the conversion is low (< 7%), the concentrations of HCl and DCl are small and the change in gas phase D or H concentration is not significant, and the mass balance can be approximated by equations (18) and (19). Substitution of equation (17) into equations (18)-(19), one obtains:

$$2[\mathrm{H}_2] + 1.92\sqrt{[\mathrm{H}_2][\mathrm{D}_2]} \approx 2[\mathrm{H}_2]_0,$$

which equals $\sqrt{[\mathrm{H}_2]}(\sqrt{[\mathrm{H}_2]} + 0.96\sqrt{[\mathrm{D}_2]}) \approx [\mathrm{H}_2]_0$ (20)

and,

$$2[\mathrm{D}_2] + 1.92\sqrt{[\mathrm{H}_2][\mathrm{D}_2]} \approx 2[\mathrm{D}_2]_0,$$

which equals $\sqrt{[\mathrm{D}_2]}(\sqrt{[\mathrm{D}_2]} + 0.96\sqrt{[\mathrm{H}_2]}) \approx [\mathrm{D}_2]_0$ (21)

Dividing equation 20 by equation 21, we have,

$$\frac{\sqrt{[\mathrm{H}_2]}(\sqrt{[\mathrm{H}_2]} + 0.96\sqrt{[\mathrm{D}_2]})}{\sqrt{[\mathrm{D}_2]}(\sqrt{[\mathrm{D}_2]} + 0.96\sqrt{[\mathrm{H}_2]})} \approx \frac{[\mathrm{H}_2]_0}{[\mathrm{D}_2]_0} \tag{22}$$

We have noticed that the ratio term $\frac{(\sqrt{[H_2]}+0.96\sqrt{[D_2]}))}{(\sqrt{[D_2]}+0.96\sqrt{[H_2]})}$ is very close to 1 in our experiment (it varies from 0.98 to 1.03 in the $[H_2]_0/[D_2]_0$ range we explored in Figure 1). Eqn. (22) can be further simplified to obtain the following relationship between the $H_2$, $D_2$ concentration under the reaction conditions and the initial $H_2$ and $D_2$ concentration:

$$\frac{\sqrt{[H_2]}}{\sqrt{[D_2]}} \approx \frac{[H_2]_0}{[D_2]_0} \tag{23}$$

With this analysis, eqn. (14) can now be written as:

$$\frac{CF_3CFH_2}{CF_3CFHD} = K''\frac{[H_2]_0}{[D_2]_0} \tag{24}$$

where $K'' = \frac{k_{1,H}K_{H_2}{}^{0.5}}{k_{1,D}K_{D_2}{}^{0.5}}$

At a constant temperature, the ratio of hydrogenated species to deuterated species is linearly related to the ratio of initial $H_2$ concentration to initial $D_2$ concentration in the feed stream.

*4.2.2. Preferential formation of $CF_3CFH_2$ during $CF_3CFHCl/H_2/D_2$ reaction.* The slope of the line in Figure 1 is not unity, which means that the hydrogenated species is formed at a higher rate than the deuterated species. This experimental observation can be qualitatively explained by considering isotope effects (both equilibrium isotope effect and kinetics isotope effect) affecting steps (4) and (9) in scheme 1, by which the product $CF_3CFH_2$ and $CF_3CFHD$ are formed. The Pd surface has a higher "affinity" towards $H_2$ than to $D_2$ because of an equilibrium isotope effect [54, 55] resulting in $K_{H2} > K_{D2}$ in step 4.

Additionally, for step 9, the C-H (or C-D) bond formation step will be affected by a kinetic isotope effect, since the zero point energy of C-H bond is 1.1 kJ mol$^{-1}$ higher than a C-D bond [56]. Absolute reaction rate theory [42], predicts that under the same reaction conditions, C-H bond formation rate constant ($k_{1,H}$) will be higher than C-D bond formation rate constant ($k_{1,D}$) [52, 57, 58]. As a result of the combination of these two factors, the term K'' from equation (24) is greater than 1. This prediction agrees with the results shown in Figure 1, where the slope of the straight line is 1.53. With this analysis, it is now clear why $CF_3CFH_2$ is produced preferentially over $CF_3CFHD$ on the Pd surface.

In conclusion, the preferential $CF_3CFH_2$ formation under a $H_2$-$D_2$ co-feed is consistent with the proposed reaction steps shown in the introductory part of this contribution.

### *4.3. C-H bond scission in the hydrodechlorination reaction of $CH_3CH_2Cl$*

Our finding from $CH_3CH_2Cl$ hydrodechlorination with $D_2$ showing that singly deuterated ethane is the predominant species indicates that the reaction on Pd/C and Pd/$ZrO_2$ proceeds through $CH_3CH_2$-*, similarly to $CF_3CFH$-* from $CF_3$-CFHCl hydrodechlorination. However, there are also ethane species with higher deuterium content (fig. 3), indicating that multiple C–H bonds are broken and other surface intermediates besides $CH_3CH_2$-* may be on the surface. In this sense, the $CH_3CH_2Cl$ hydrodechlorination differs from $CF_3CFHCl$ hydrodechlorination in which C-H bond scission is insignificant (Figure 2). We believe the increased level of C-H bond scission in $CH_3CH_2Cl$ hydrodechlorination is due to the presence of C–H bonds in the β-carbon. Another support for this view is our results with other chlorinated compounds. We found from $D_2$ exchanged hydrodechlorination of $CH_3Cl$, which has no β-carbon, 98% of the methane product was $CH_3D$; while 1,3- and 1,2-dichloropropane hydrodechlorination with $D_2$ show propanes with multiple deuterium substitution were formed due to the presence of β-carbon. It should be noted that this deuterated product distribution was solely caused by $CH_3CH_2Cl$ hydrodechlorination reaction and not by the re-adsorption and subsequent exchange reaction of its product $C_2H_6$. We have shown that product distribution patterns, as well as the reaction temperatures presented were very different for $C_2H_5Cl/D_2$ hydrodechlorination reaction and $C_2H_6/D_2$ exchange reaction (figure 3 and figure 4).

Hydrodechlorination of $CH_3CH_2Cl$ with $D_2$ hydrodechlorination produced a different product distribution than reported before by Campbell and Kemball [24]. In our product distribution, singly deuterated ethane is the main product while doubly deuterated ethane is the predominant product in the work of Campbell and Kemball. The reason might be due to the difference in the Pd catalysts used in these studies. Unlike our supported catalysts, the Pd film used by Campbell and Kemball was polycrystalline which contained higher amount of kinks and edges due to their film preparation method [59]. These defects might behave differently towards the C-H bond scission steps [60].

We have also compared our ethane deuterium exchange results with those of other research groups. Anderson and Kemball [61] found on a Pd film that the major product from ethane exchange with deuterium was the perdeuterated species ($C_2D_6$), while Guczi and Karpinski [60] found single- and double-deuterated species to be the major products on their Pd film. Sarkany *et al.* [62] studied the ethane deuterium exchange reaction on a Pd black catalyst and found similar product distribution as reported on a Pd film by Guczi and Karpinski. These literature results are all different from what we observed on supported catalysts shown in Figure 4. The explanation for this discrepancy seems to be the dependence of ethane exchange reaction on the structure of Pd. When comparing their result with Anderson and Kemball's result [61], Guczi and Karpinski [60] suggested that the difference in preparation method for the two Pd films might be the reason for the discrepancy of the product distribution. The Pd film used by Guczi and Karpinski was annealed at high temperature (773K) after deposition and was highly sintered while the film used by Anderson and Kemball was not subjected to this treatment. Guzci and Karpinski proposed that the heavily sintered Pd film had less surface imperfections and sites of low coordination which were supposedly more active for multiple ethane-deuterium exchange [60]. Kemball *et al.* [61] also proposed that the ethane exchange reaction might need multiple Pd sites to proceed and this reaction might be structure sensitive.

In the results presented in section 3.5 and section 3.6, it has been shown that the rates of $CH_3CH_2Cl$/deuterium hydrodechlorination and ethane/deuterium exchange reactions on different Pd catalysts are quite different. But the reasons behind rate difference of these two reactions are quite different. Here we would analyze them one by one.

For ethane/deuterium exchange reaction, this rate difference can be understood by considering the structure sensitivity of this reaction. Ethane deuterium exchange reaction has been proposed to proceed via multiple Pd sites [61], thus, the reaction rates of C-H scission steps might not be the same on Pd catalysts with different surface structure. To explain why the reaction rates obtained on Pd/C are significantly lower than the rates on other types of Pd catalysts, we used a model for Pd supported on carbon advanced by Krisnankutty and Vannice [63] showing that carbon is added to the Pd lattice and also to the surface. According to this model, as the surface is subdivided by carbon, reaction rate will thus be reduced for reactions that need multiple sites, such as the reaction between ethane and deuterium studied here.

The interpretation of rate difference of $C_2H_5Cl/D_2$ hydrodechlorination reaction on Pd/C and Pd/$ZrO_2$ is more complicated. Unlike the situation in $C_2H_5Cl$, in $CF_3CFHCl$ hydrodechlorination reaction, the rates were found to be similar on Pd/$ZrO_2$ catalyst and Pd/C. Our pervious CFC hydrodechlorination results and some literature study of hydrodechlorination reactions on Pd model catalysts all suggest that this reaction should be structure insensitive [8, 11, 12, 27, 28]. Thus this new result from $C_2H_5Cl/D_2$ experiment should not be explained by structure sensitivity of hydrodechlorination reaction and the data is somewhat puzzling at a first sight. Some research groups also found hydrodechlorination reaction turnover rates were dependent on Pd particle size, that is, hydrodechlorination reaction rate increased with larger Pd clusters [5, 20, 22, 64, 65]. However, it is improper to reach the conclusion that hydrodechlorination reaction is structure sensitive base on these reports. Some of these data were often compromised by artifacts, such as metal-support interaction [20, 22], change of Pd surface by carbiding process [20], ignoring the inhibition effect of HCl [5, 20]or conducting surface structure sensitivity far beyond the proper 1-10nm size range as suggested by Boudart *et al.* [66] (For example, Karpinski *et al.* [5] reported $CF_3CF_2Cl$ hydrodechlorination was structure sensitive to Pd size from 11nm to even as large as 53nm). We believe the answer to the observed different $C_2H_5Cl/D_2$ rates on Pd/C and $Pd/ZrO_2$ is the absence of excessive HCl during reaction. Aramendia *et al.* [64], when explaining their different chlorobenzene hydrodechlorination rates on Pd catalysts with varying particle size, proposed that Cl formed during reaction could migrate into catalyst bulk and thus smaller Pd particles with higher $Pd_{surface}/Pd_{bulk}$ ratio would be rapidly saturated with Cl, which in turn would poison the surface and lead to low activity. In our $C_2H_5Cl/D_2$, because apparently we could not use H-containing HCl, our results suffered from this Cl poisoning effect and the reaction rate was found to be high on $Pd/ZrO_2$ (size: 28nm) and low on Pd/C (size: 5nm). However, when excessive HCl is present during reaction, smaller and larger Pd particles alike would have similar Cl coverage. In this way, the turnover rates measured would be close, as we found in $CF_3CFHCl$ case, whose turnover rates were measured with excessive HCl used as a feed stream (reaction conditions shown in reference [12]). The results shown in table 3 stress the importance of considering HCl inhibition effect during hydrodechlorination reaction, which point has also been voiced before in literature [8, 9, 11, 12, 27, 28].

Deuterium substituted reaction results show that the two molecules, $CH_3CH_2Cl$ and $CF_3CFHCl$, both of which have C-Cl bond and C-H bond, behave differently during hydrodechlorination reaction. Although $CH_3CH_2Cl$ and $CF_3CFHCl$ have similar kinetically relevant reaction steps, the detailed reaction steps of these two chlorinated compounds are different. This illustrates the difficulty in generalizing a universal reaction mechanism for the hydrodechlorination reaction.

## 5. Conclusion

The hydrodechlorination rates of $CF_3CFHCl$ and $CH_3CH_2Cl$ have been measured in $D_2$ and $H_2$ on Pd catalysts to further elucidate the mechanism of hydrodechlorination. The two rates are essentially the same, indicating that H (or D) is not involved in the rate-determining step. Previous results suggest that the hydrodechlorination rate is correlated with the strength of the C-Cl bond which is broken upon adsorption. New results presented in this contribution provides further support for the proposed rate-determining step.

Hydrodechlorination of $CF_3CFHCl$ with a $H_2$-$D_2$ co-feed has been performed to investigate the elementary steps that follow the rate-determining step. The hydrogenated product is formed preferentially over the deuterated one and it is concluded that there are isotope effects in some of the elementary steps that occur after the rate determining step. The experimental observations were explained qualitatively using the proposed hydrodechlorination reaction steps and isotope effect theory. This result is also consistent with the existence of the following elementary steps in the hydrodechlorination reaction: the equilibrium between gas phase hydrogen and surface adsorbed H; the combination of surface adsorbed $CF_3$-CFH-* species and surface H to form the hydrodechlorination reaction product.

The deuterated product distributions from the hydrodechlorination experiments of $CF_3CFHCl$ and $CH_3CH_2Cl$ with $D_2$ have also been analyzed to provide more information about reaction steps beyond the rate determining step. It is found that for the $CF_3CFHCl$ hydrodechlorination reaction, most of the time only the C-Cl bond breaks and $CF_3CFH*$ is the major surface species. In the case of $CH_3CH_2Cl$, C-Cl bond scission is accompanied by C-H bond scission. By comparing deuterium exchanged hydrodechlorination reaction of $CH_3CH_2Cl$ with other chlorinated compounds, such as $CH_3Cl$ and dichloropropanes, it is believed that the $CH_3$- group adjacent to the C-Cl bond can trigger C-H bond scission in the hydrodechlorination reaction. It is also found that the H/D exchange may be structure sensitive. H/D exchange in ethane suggests that the rate and the deuterated species distribution of this reaction are dependent on the structure of Pd catalyst. Although the isotopic studies reported in this contribution have yielded more evidence for the proposed hydrodechlorination reaction mechanism containing only kinetically important steps, the different deuterated product distribution of $CF_3CFHCl$ and $CH_3CH_2Cl$ hydrodechlorination suggests that the reaction steps which determine selectivity are dependent upon reactant molecular structure.

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# Paper 5

# Kinetic Study of the Hydrodechlorination Reaction of $CH_{4-x}Cl_x$ (x=1-4) Compounds on Palladium Catalysts

## Abstract

The hydrodechlorination reaction kinetics on a group of $CH_{4-x}Cl_x$ (x=1-4) compounds was measured on Pd/carbon catalysts. It was found that the hydrodechlorination reaction rates correlated with the strength of the gas phase C-Cl bond energy. It was thus concluded that the first C-Cl bond scission on the surface is the rate determining step of the hydrodechlorination reaction. The observed hydrodechlorination reaction kinetics of $CH_{4-x}Cl_x$ (x=1-4) compounds supports a previously proposed Langmuir-Hinshelwood type of hydrodechlorination reaction mechanism. That is, (1) gas phase $H_2$ and HCl are in equilibrium with surface H and Cl; (2) adsorbed Cl is the most abundant surface intermediate and (3) irreversible scission of the first C-Cl bond is the rate-determining step. The overall hydrodechlorination reaction rate for these series of compounds can be written as $r=k'[CFC]/(1+K'[HCl]/[H_2]^{0.5}$. Based on this model, the activation energy of the hydrodechlorination rate determining step for these compounds was calculated and it was found out they were linearly related to the bond strength of the first C-Cl bond to break during reaction. It was also found that hydrodechlorination reaction kinetics was comparable on different catalyst supports, suggesting the support did not play a role in hydrodechlorination reaction. During hydrodechlorination with $D_2$ on $CH_{4-x}Cl_x$ (x=1-3), the C-H bond scission could be followed and it occurred with a small selectivity It was noticed that for the rate-liming first C-Cl bond scission process, only 2%, 6% and 9% of hydrodechlorination products were enriched in $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$.

**Key words:** $CH_{4-x}Cl_x$ (x=1-4) compounds, hydrodechlorination reaction, reaction kinetics, reaction steps, palladium

## 1. Introduction

Hydrodechlorination is the reaction between $H_2$ and an organic molecule containing C-Cl bond(s). During hydrodechlorination reaction process, Cl is removed from the molecule and replaced with H. This is an important synthetic reaction and has found use in many areas. For example, it is used in the manufacture of $CF_3CFH_2$ (a widely used refrigerant) from $CF_3CFCl_2$ [1]. It can also be used in by-product reclamation, one example like this is the conversion of 1,2-dichloropropane into propylene on a bimetallic Pt-Cu catalyst [2], and another example is the production of $CHCl_3$ or $CH_2Cl_2$ from $CCl_4$ [3, 4]. Hydrodechlorination reaction can also be used as a way to address environmental issues, such as waste water treatment [5, 6]. Hydrodechlorination reaction may also be used to transform large amounts of CFCs that exist today into the more environmentally benign HFCs [1, 7]. In the 1980s, chlorofluorocarbons (CFCs) were scientifically connected to the depletion of the ozone layer [1]. At the same time, it was found that hydrofluorocarbons (HFCs), which can be produced by the hydrodechlorination of CFCs, are much less harmful to the environment and have some of the useful properties of CFCs and can thus serve as a replacement for CFCs [8]. All these practical applications require an in-depth understanding of the hydrodechlorination reaction.

Hydrodechlorination reaction is usually performed under the presence of noble catalysts. A number of metals, such as Pd [9-16], Pt [17-19], and Rh [17, 19-21] have been studied as hydrodechlorination catalysts, with Pd being the most active and selective catalyst for this reaction [22]. Supported catalysts are often used and the role of the support has been studied for carbon [16, 23], alumina [9, 24, 25] and fluorinated alumina [10, 24]. While some authors have suggested that catalyst support plays a role in the reaction [26], we have previously reported that the support (carbon) does not influence reaction kinetics beyond condensation of CFC reactant on microporous supports [16]. While most contributions report on supported catalysts, hydrodechlorination reaction has also been studied on model catalyst, such as evaporated films [27-29], foils [12, 13, 30], and single crystals [13, 31]. A limited number of studies have been reported on bulk metal powders [15, 32, 33]. In this contribution, we will continue to use Pd supported on carbon. At the same time another Pd/$ZrO_2$ sample will be used to further study the effect of catalyst support on hydrodechlorination reaction.

Unfortunately, turnover rates, selectivity and reaction orders have been presented for only a limited number of compounds [9, 10, 12, 13, 15, 16, 26, 30, 31], with most of them being chlorofluorocarbons. Recently, there have been some hydrodechlorination reaction kinetics studies using chlorinate compounds other than chlorofluorocarbons as model compounds, such as $CH_2Cl_2$ [34, 35]. One important question is the possible reaction steps for this reaction. A general set of reactions steps that can describe hydrodechlorination reaction in general would be useful.

Previous work has addressed possible reaction steps [12, 13, 15, 16, 20, 21, 36-38]. Based on their study hydrodechlorination reactions on a series CFCs, Thompson *et al.* [16] suggested that the rate-determining step consisted of the irreversible scission of C-Cl bond; other gas phase species, $H_2$ and HCl were in equilibrium with surface adsorbed H and Cl. This proposed rate-determining step was deduced from the reaction kinetic measurements and from the fact that there was a correlation between gas-phase C–Cl bond strength and rates. The reaction steps proposed by Thompson *et al.* were confirmed using isotopic tracing experiments by Chen *et al.* [38]. This set of proposed reaction steps is summarized in scheme 1:

$R\text{-}Cl + * = R\text{-}Cl*$, with an equilibrium constant $K_{CFC}$ (1)

$R\text{-}Cl* \rightarrow \cdots$, rate-determining step with a rate constant $k_0$ (2)

$r = k_0 K_{CFC}[R\text{-}Cl][*]$, rate expression (3)

$H_2 + 2* = 2H*$, equilibrated (4)

$H* + Cl* = HCl + 2*$, equilibrated (5)

$2HCl + 2* = H_2 + 2\,Cl*$, (4) + (5), with equilibrium constant $K_0$ (6)

$[*] + [Cl*] = [L]$, site balance (7)

$$[*] = \frac{[L]}{1 + K_0^{1/2}\dfrac{[HCl]}{[H_2]^{0.5}}}, \quad \text{free site concentration} \tag{8}$$

and the overall rate can be derived as:

$$r = \frac{k'[R\text{-}Cl]}{1 + K'\dfrac{[HCl]}{[H_2]^{0.5}}}, \quad \text{with } k' = k_0 K_{CFC}[L] \text{ and } K' = K_0^{1/2} \tag{9}$$

**Scheme 1. Possible hydrodechlorination reaction steps**

Hydrodechlorination experiments with $D_2$ were also conducted to explore the hydrodechlorination reaction steps beyond C-Cl bond scission, such as the possible presence of C-H bond scission [15, 27].

In our previous publications, we have noticed that studying hydrodechlorination reaction kinetics of a series of chlorinated compounds is an ideal way of investigating reaction steps. In this contribution, we will extend our kinetic study of the hydrodechlorination reaction to the series of chloromethanes; $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$ and $CCl_4$. The hydrodechlorination kinetics for these compounds is reported and compared with the existing data for CFC compounds. It would be demonstrated that the hydrodechlorination reaction kinetics of these four compounds can also be described by the proposed reaction steps in scheme 1. The hydrodechlorination in presence of $D_2$ will also be performed for these compounds to study whether C-H bond scission exists during reaction. It was found that no more than 9% of the hydrodechlorination products formed by the scission of the first C-Cl bond of $CH_{4-x}Cl_x$ (1-4) compounds were enriched with deuterium.

## 2. Experimental Methods

### *2.1. Catalysts*

Two types of supported Palladium catalyst were used in this study. The 5% Pd catalyst supported on activated carbon was obtained from Degussa. Another Palladium sample supported on zirconia was also used in this study to investigate any possible support effect. The $Pd/ZrO_2$ was prepared by incipient wetness method using an aqueous solution of $Pd(NH_3)_2(NO_2)_2$ in nitric acid obtained from Tanaka Kikinzoku Kogyo of Japan. The zirconia RC-100P was from Daichi Kigenso Kagaku (DKK) of Japan. All the supported samples were ground with a mortar and pestle and 40/60 mesh particles were retained for use in catalytic studies.

### *2.2. Reactants*

The Chlorinated methane compounds were purchased from Sigma Chemical Company ($CH_3Cl$, $CCl_4$) and Lancaster Synthesis ($CH_2Cl_2$, $CH_3Cl$). The mixture of 15-20% HCl in He was obtained from Matheson and was made with technical grade HCl and Matheson purity He. The $H_2$ (BOC gases) was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was also obtained from BOC gases. For the helium used as GC carrier gas, it was passed through a mass spectrometer gas trap (HP model 5182-3467) before feeding into the system. The deuterium used in this study was obtained from Cambridge Isotope Laboratories. It contained 99.6% $D_2$ and 0.4% HD, and before use it was also passed through the same Pd membrane purifier used for the purification of $H_2$.

### *2.3. Reactor Configuration*

The gas manifold was constructed of 1/8" diameter stainless steel tubing. The gas flow of different gas components was controlled with mass flow controllers (Porter Instrument Co.). Some of the chlorinated compounds used here are liquids at room temperature and was added to the reaction mixture by passing helium through the liquid in a saturator maintained at constant temperatures using a water bath. The bath temperature was controlled using a Neslab Instrument Inc. RTE-9 refrigeration/ heating circulating bath. The mass flow controllers were calibrated with a bubble flow meter except for the He-HCl mixture. For this mixture, the flow rates were determined by varying the composition of a mixture of He/HCl and $H_2/CH_4$ (from Matheson Gases, a mixture of $H_2$ and 1003ppm $CH_4$ as internal standard), then analyzing the mixture by gas chromatography, and observing the change in signal of the methane peak.

The reaction portion of the flow system was made of Pyrex and could be manipulated to operate in continuous or in batch mode. The reactor was made out of quartz with the catalyst held on a fritted disk. The reaction temperature was measured through a thermocouple well extending to the catalyst bed. The mixing in the reactor was provided by a bellows pump (Senior Flexonics, MB-21) with a rate of about 1400 $cm^3$ $min^{-1}$, allowing differential operation for the reactor and minimizing heat and transport effects in the reaction. The presence of heat and mass transfer limitations that might exist in the reaction system had been tested using the Madon-Boudart test [39]. From the results presented in a previous work [16], heat and mass transfer limitations were not found even with the a Pd/C catalyst supported on high surface area carbon, where transport limitations would be most severe. Thus, we can conclude that our results from the experiments are not affected by heat and mass transfer limitations artifacts.

The reaction gases were analyzed with a modified GC-MS (GC-HP 5880A, MS-HP5970A) system. The column used in the GC was a 5% Krytox 143AC, 60/80

Carbopack B HT 20' x 1/8" from Supelco. The effluent from the GC column was simultaneously analyzed by the GC flame ionization detector (for quantitative analysis) and by the MS (for qualitative analysis). The gas was sampled into the mass selective detector through a fused silica polyimide capillary (I.D. 51µm, O.D. 363µm, Length 0.75m). The GC response factors for all reactants and products were calibrated against methane in a hydrogen-methane calibrated mixture. After exiting the system, the reaction gas mixture flowed through a NaOH solution to neutralize the HCl present in the effluent stream before venting.

### *2.4. Data Collection Procedure*

Two to five hundred milligrams of fresh catalyst was initially loaded into the reactor and reduced for 3 h at 300°C with 50 $cm^3$ $min^{-1}$ $H_2$. For repeated experiments, the catalyst was treated with 50 $cm^3$ $min^{-1}$ $H_2$ for 0.5-1 h at 150°C before the consequent hydrodechlorination reactions.

When the reactor was operated in CSTR mode, such as rate or reaction order measurement, the total inlet and effluent flow rates were around 100 $cm^3$ $min^{-1}$. The inlet gas concentrations were adjusted with mass flow controllers and reaction temperature was controlled by a Eurotherm model 808 temperature controller. For a particular set of conditions, the reaction would be run for 30-60 minutes to get stabilized before a data point was taken. During the course of the experiments, the changes in concentration and temperature were chosen in a random order so that any variation in the system would not introduce a systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated and another data point was taken. By ensuring that this last point agreed with the first point it could be shown that there was no significant deactivation of the catalyst during the time frame of the experiment. The gas mixture was sampled into the GC-MS system using the automatic gas valve on the GC.

Apparent activation energy was determined by measuring the reaction rate at different temperatures while keeping the reactant concentrations constant, and then using an Arrhenius plot. Reaction orders were determined by varying the amount of reactant to be studied while keeping all the other variables constant. The reaction conversion during reaction was kept low (<5%) to maintain the concentration of reaction gases constant so as to simplify the mathematical treatment. Due to the different reactivity of these compounds, the reaction conditions such as reaction temperature used for measuring their kinetic had to be different in order to achieve low conversion. These conditions are listed below. HCl were added in all the reactions to further minimize the variable in reaction system since HCl is an inhibitor of hydrodechlorination reaction.

For $CH_3Cl$ reactions on Pd/C catalyst, the conditions for the determination of apparent activation energies were 227-261 °C, 220 Torr of $CH_3Cl$, 181 Torr of $H_2$, and 74 Torr of HCl. For $CH_3Cl$ order determination, the conditions were 227 °C, 46-193 Torr of $CH_3Cl$, 159 Torr of $H_2$, and 64 Torr of HCl. For $H_2$ order, the conditions were 224 °C, 145 Torr of $CH_3Cl$, 82-306 Torr of $H_2$, and 48 Torr of HCl. For HCl order, the conditions were 227 °C, 193 Torr of $CH_3Cl$, 159 Torr of $H_2$, 10-64 Torr of HCl.

Additionally, for the study of reaction energetics, HCl reaction order measurements were conducted at 213, 237 and 244 °C. $CH_3Cl$ reaction kinetic measurements were also carried out on $Pd/ZrO_2$ catalyst at 205 °C. For $CH_2Cl_2$ compound, the conditions for the determination of apparent activation energies were 187-229 °C, 22 Torr of CFC, 196 Torr of $H_2$, and 38 Torr of HCl. For $CH_2Cl_2$ order determination, the conditions were 201°C, 21-43 Torr of $CH_2Cl_2$, 199 Torr of $H_2$, and 38 Torr of HCl. For $H_2$ order, the conditions were 198°C, 25 Torr of $CH_2Cl_2$, 108-379 Torr of $H_2$, and 37 Torr of HCl. For HCl order, the conditions were 199°C, 25 Torr of $CH_2Cl_2$, 127 Torr of $H_2$, 22-64 Torr of HCl. HCl reaction order experiment was repeated at another three different temperature: 188, 210, and 220 °C. $CH_3Cl$ reaction kinetic measurements were also carried out on $Pd/ZrO_2$ catalyst at 156 °C. For $CHCl_3$, the conditions for the determination of apparent activation energies were 92-143 °C, 14 Torr of $CHCl_3$, 235 Torr of $H_2$, and 48 Torr of HCl. For $CHCl_3$ order determination, the conditions were 114 °C, 15-40 Torr of $CHCl_3$, 237 Torr of $H_2$, and 49 Torr of HCl. For $H_2$ order, the conditions were 114 °C, 18 Torr of $CHCl_3$, 183-399 Torr of $H_2$, and 48 Torr of HCl. For HCl order, the conditions were 115 °C, 20 Torr of $CHCl_3$, 155 Torr of $H_2$, 20-64 Torr of HCl. The three other temperatures under which HCl reaction order experiment was repeated were: 91,100 and 124 °C. To find out the effect of reaction temperature on $CHCl_3$ reaction order, $CHCl_3$ order measurement was also conducted at 100 and 135 °C. For $CCl_4$, the conditions for the determination of apparent activation energies were 48-92 °C, 10 Torr of $CCl_4$, 155 Torr of $H_2$, and 58 Torr of HCl. For $CCl_4$ order determination, the conditions were 61 °C, 9-16 Torr of $CCl_4$, 173 Torr of $H_2$, and 45 Torr of HCl. For $H_2$ order, the conditions were 114 °C, 16 Torr of $CCl_4$, 129-256 Torr of $H_2$, and 50 Torr of HCl. For HCl order, the conditions were 115

°C, 17 Torr of $CCl_4$, 173Torr of $H_2$, 17-50 Torr of HCl. The three other temperatures under which HCl reaction order experiment was repeated were: 41, 51 and 70 °C. For comparison, we also repeated HCl reaction order measurement of $CF_3CFHCl$ at four different temperatures, the reaction conditions were 132 Torr CFC, 211 Torr $H_2$ and 11-41 Torr HCl. The temperatures selected were 216, 226, 236 and 247 °C.

Most of the $D_2$ exchanged experiments were conducted in batch mode. The reactor was evacuated to $1\times10^{-5}$ Torr with diffusion vacuum pump and then kept at this vacuum level for 0.5 hour before the gas reactants were fed into it. The oven temperature was raised to the target temperature at a rate of 5°C $min^{-1}$. The gas mixture was taken from the reactor using a 500μl syringe through a GC septum fitted to a union mounted on the sample port of the batch reactor. For each data point, 100-200μl of the gas mixture was injected into the GC-MS for analysis. The reaction of $CH_3Cl$ with $D_2$ was performed at 205 °C, with 416 Torr $CH_3Cl$ and 434 Torr $D_2$. The reaction of $CH_2Cl_2$ with $D_2$ was performed at 184 °C, with 30 Torr $CH_2Cl_2$ and 261 Torr $D_2$. The reaction of $CHCl_3$ with $D_2$ was performed at 95 °C, with 18 Torr $CH_2Cl_2$ and 328 Torr $D_2$.

### *2.5. Surface Area Measurement*

The total surface area was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen-oxygen titration method according to Benson *et al.* [40] The experimental setup consisted of a volumetric system constructed in Pyrex and pumped by a liquid nitrogen trapped diffusion pump. The amount of gas adsorbed was determined by measuring pressure change in a pre-calibrated volume on the system with a pressure transducer (MKS model 127).

The samples were reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 3 h at 300°C before the Pd surface area measurements. After the initial reduction, subsequent hydrogen-oxygen titration was conducted at 100°C. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression is valid under the assumption of spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms $m^{-2}$ [41].

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced and passivated catalysts was also conducted. Samples for XRD analysis were reduced in same manner as described above, and then passivated with 60 Torr of $O_2$. Particle size was determined from the width of the diffraction peak using X-ray line broadening technique. The Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

### *2.6. Error Analysis*

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in reaction orders are at a maximum 10% or maximum 0.1 in 1.0 and errors in the apparent activation energies were 10 kJ $mol^{-1}$. Turnover rate reproducibility was better than 90%.

## 3. Results

### 3.1. Catalyst Properties

Table 1 summarizes the properties of the two kinds of catalysts we used in this research. The carbon support of the Pd/C catalyst we used was a non-microporous type of carbon with BET surface area of 107 $m^2 g^{-1}$. The Pd particle size determined by $H_2$-$O_2$ titration and XRD line broadening for this Pd/C sample is also shown in table 1.

The parameters in table 1 are representative of catalysts before the hydrodechlorination reaction. For most of the chlorinated hydrocarbons used in this research, no significant deactivation was observed during the reaction, thus we do not expect any significant change in the properties of the catalyst after reaction. The only exception was $CCl_4$ hydrodechlorination reaction, in which significant deactivation was observed. We believe that this deactivation was caused by coke formation during $CCl_4$ hydrodechlorination reaction. This problem will be discussed in more detail below.

| catalysts | BET Surface Area ($m^2g^{-1}$) | PME | Particle Diameter (nm) | |
|---|---|---|---|---|
| | | | chemisorption[a] | XRD |
| 5.0% Pd/C (Degussa) | 107 | 8.4 | 13.3 | 5 |
| 10% Pd/$ZrO_2$ | 130 | 4.0 | 28.0 | N/A |

[a]Percentage of metal exposed, determined by $H_2$-$O_2$ titration @ 100°C.
[b]Particle size determined from d=1.12/PME.

**Table 1. Catalyst Properties**

### *3.2. Hydrodechlorination Reaction Kinetics of $CH_{4-x}Cl_x$ (x=1-4)*

Table 2 summarizes the hydrodechlorination reaction kinetics, including apparent activation energy, apparent reaction orders, selectivity and reaction rate, of $CH_{4-x}Cl_x$ (x=1-4) compounds on Pd catalysts. Most of the kinetic measurements were performed with Pd/C catalyst. Additionally, reaction kinetics of $CH_3Cl$ and $CH_2Cl_2$ were also collected on Pd/$ZrO_2$ to study the effect of different catalyst support. As indicated in the experimental section, the reaction conditions used for the kinetic measurements of each compound was very different due to their different reactivity. To allow comparison, the reaction rates were corrected to a standard condition, which is 150 Torr of chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl and 150 °C.

| **Reactant** | **Catalyst** | **Reaction Temperature** | **Products** | **TOR[a] ($s^{-1}$) (Selectivity[b])** | **$E_a$ (kJ $mol^{-1}$)** | **Reaction Order Dependence** | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | **chlorinated hydrocarbon** | **$H_2$** | **HCl** |
| $CH_3Cl$ | Pd/C | 227°C | $CH_4$ | $1.5\times10^{-4}$ (100) | 82 | 1.16 | 0.37 | -0.46 |
| | $Pd/ZrO_2$ | 205°C | | $5.8\times10^{-4}$ (100) | 101 | | | |
| $CH_2Cl_2$ | Pd/C | 201°C | $CH_4$ | $1.34\times10^{-2}$ (62) | 93 | 1.04 | 0.44 | -0.6 |
| | | | $CH_3Cl$ | $8.38\times10^{-3}$ (38) | 80 | 1.08 | 0.68 | -0.6 |
| | $Pd/ZrO_2$ | 156°C | $CH_4$ | $9.1\times10^{-3}$ (70) | 114 | 0.75 | 0.41 | -0.91 |
| | | | $CH_3Cl$ | $3.9\times10^{3}$ (30) | 84 | 0.58 | 0.82 | -0.92 |
| $CHCl_3$ | Pd/C | 114°C | $CH_4$ | $2.17\times10^{-1}$ (82) | 86 | 0.44 | 0.81 | -0.54 |
| | | | $CH_3Cl$ | $1.07\times10^{-2}$ (4) | 76 | 0.26 | 0.65 | -0.32 |
| | | | $CH_2Cl_2$ | $3.57\times10^{-2}$ (14) | 90 | 0.7 | -0.26 | -0.61 |
| $CCl_4$* | Pd/C | 61°C | $CH_4$ | $3.66\times10^{-1}$ (31) | 56 | 0.26 | 0.55 | -0.55 |
| | | | $CH_3Cl$ | $1.74\times10^{-1}$ (15) | 72 | 0.71 | 0.32 | -0.5 |
| | | | $CH_2Cl_2$ | $6.87\times10^{-2}$ (6) | 40 | 0.49 | 0.25 | -0.43 |
| | | | $CHCl_3$ | $5.77\times10^{-1}$ (49) | 52 | 0.34 | 0.16 | -0.4 |

[a] Rates corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl, and 150°C.
[b] The selectivity is independent of conversion
* Hydrocarbon by-products were also detected: $C_2H_4/C_2H_6$, $C_3H_6/C_3H_8$, $C_4H_8/C_4H_{10}$, $C_5H_{10}/C_5H_{12}$

**Table 2. Kinetics Data for chlorinated hydrocarbons $CH_{4-x}Cl_x$(X=1-4)**

From table 2, it can be seen that the reaction rates of the four chlorinated methanes are in the following order, $CH_3Cl<CH_2Cl_2<CHCl_3<CCl_4$. That is, the hydrodechlorination reaction rate increases with the number of chlorine atoms in the compound. Similar trend was also observed for the series $CF_3CF_{3-x}Cl_x$ (x=1-3) [16]. For $CH_3Cl$ and $CH_2Cl_2$ compounds, the hydrodechlorination reaction rates on Pd/C catalyst were comparable with the rates on $Pd/ZrO_2$ catalyst. With the exception of $CH_3Cl$, all the other chlorinated methane compounds had multiple products, corresponding to different degree of chlorine removal. The selectivity towards these products was found to be independent of reaction conversion in the conversion range we explored. For example, in one experiment, the conversion of $CH_2Cl_2$ was varied from 2-25%, but the selectivity remained at 65% towards $CH_4$ and 25% towards $CH_3Cl$. Similarly, the selectivity was

constant for $CHCl_3$ in a conversion range of 2-21% and $CCl_4$ in a conversion range of 5-15%. It should be pointed out that in the reaction of $CCl_4$, hydrocarbons such as $C_2H_4/C_2H_6$, $C_3H_6/C_3H_8$, $C_4H_8/C_4H_{10}$, $C_5H_{10}/C_5H_{12}$, were also detected.

We compared the reaction kinetic parameters of chlorinated methane compounds with those of CFC compounds we had studied in a separate paper. The hydrodechlorination reaction kinetics of $CF_3CFHCl$ is shown in table 3 as a reference. It was found that the apparent HCl reaction orders of chlorinated methanes on Pd/C catalyst were all less negative than HCl order of $CF_3CFHCl$. Table 4 shows another comparison of HCl orders of $CH_3Cl$ and $CF_3CFHCl$ at different temperatures.

| **Reactant** | **Reaction Temperature** | **Products** | **TOR[a] ($s^{-1}$) (Selectivity[b])** | **$E_a$ (kJ $mol^{-1}$)** | **Reaction Order Dependence** | | |
|---|---|---|---|---|---|---|---|
| | | | | | **CFC** | **$H_2$** | **HCl** |
| $CF_3$-CFHCl | 223°C | $CF_3$-$CH_2F$ | $1.59\times10^{-4}$ (99.9) | 93 | 1.1 | 0.43 | -0.8 |
| | | $CF_3$-$CH_3$ | $1.98\times10^{-7}$ (0.1) | 80 | 0.95 | 0.27 | -0.3 |

[a] Rates corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl, and 150°C.
[b] The selectivity is independent of conversion

**Table 3. Kinetics Data for $CF_3$-CFHCl (HCFC124)**

| **Reactant** | **Kinetics Parameter** | **HCl Order Measurement Temperature (°C)** | | | |
|---|---|---|---|---|---|
| | | 213 | 225 | 237 | 244 |
| $CH_3Cl$ | HCl order | -0.55 | -0.52 | -0.49 | -0.47 |
| $CF_3$-CHFCl | HCl order | -0.89 | -0.82 | -0.81 | -0.79 |

**Table 4. Comparison between apparent HCl reaction orders of $CH_3Cl$ and $CF_3$-CHFCl at different temperatures**

The effect of the reaction temperature on $CHCl_3$ reaction order was studied and presented in table 5. It shows that when temperature went up, $CHCl_3$ reaction order deviated even far away from 1, the chloromethane order found for $CH_3Cl$, $CH_2Cl_2$ and $CF_3CFHCl$.

| **Reactant** | **Temperature for Order Measurement (°C)** | **$CHCl_3$ Order for Main Product $CH_4$** |
|---|---|---|
| $CHCl_3$ | 135 | 0.1 |
| | 114 | 0.34 |
| | 100 | 0.48 |

**Table 5. $CHCl_3$ order dependence on temperature**

### *3.3. Extracting Reaction Constants k', K' from Kinetic Results and Fitting Kinetic Results to Rate Expression 9*

There are two constants in rate equation (9). We found that these two constants could be extracted from hydrodechlorination kinetic measurements. The method we used to calculate these constants using kinetic data is to linearize expression (9) into the following equation:

$$\frac{1}{r} = \frac{1}{k'[R-Cl]} + \frac{K'}{k'[R-Cl]} \times \frac{[HCl]}{[H_2]^{0.5}} \qquad (10)$$

By keeping the partial pressure of R-Cl compound constant and changing the value of $[HCl]/[H_2]^{1/2}$, a plot of 1/r against $[HCl]/[H_2]^{1/2}$ will generate a straight line. The rate constant (k') and equilibrium constant (K') can be calculated from the intercept and slope of the straight line. The independent variable $[HCl]/[H_2]^{1/2}$ was varied by changing the HCl or $H_2$ partial pressure. Figure 1 shows one example of using the data from HCl reaction order experiment of $CH_3Cl$ and equation 10 to find out the two reaction constants.

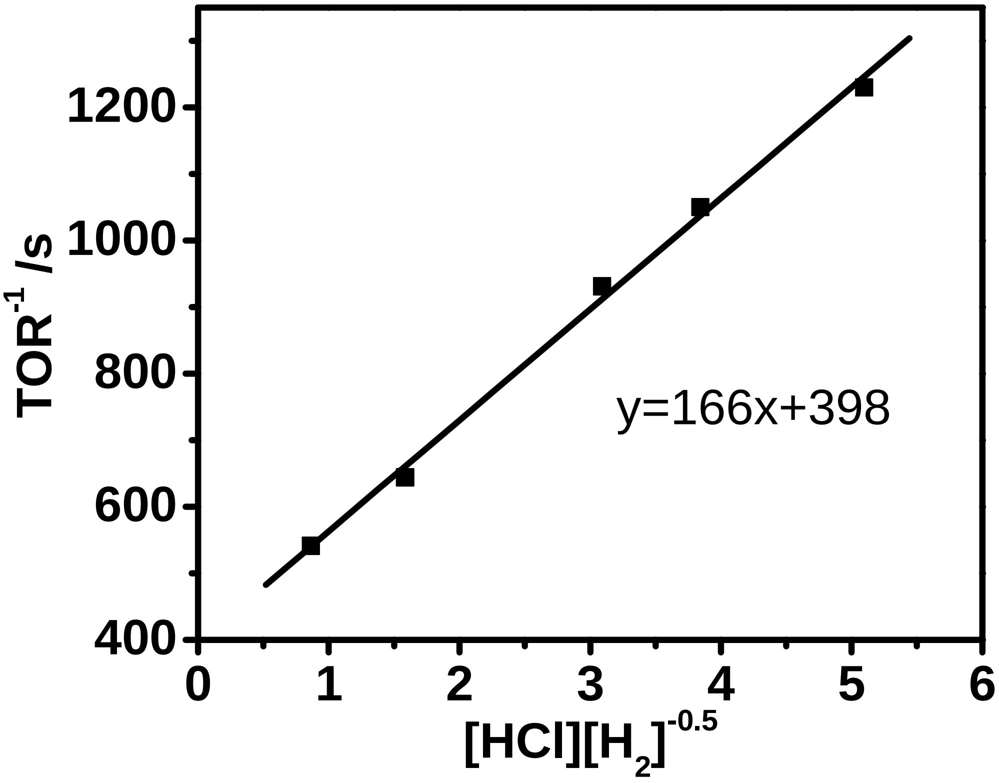

**Figure 1. Calculating k' and K' from Turnover rate data of HCl reaction order measurement experiments**

Once we have the two reaction constants at a certain temperature, we can use them and equation 9 to predict hydrodechlorination reaction rate of a chlorinated compound at a given reaction condition. We calculated hydrodechlorination reaction rate of $CH_3Cl$ at

227 °C using the conditions listed in experimental section and compared the predicted rates with measured rates. This comparison is shown in figure 2.

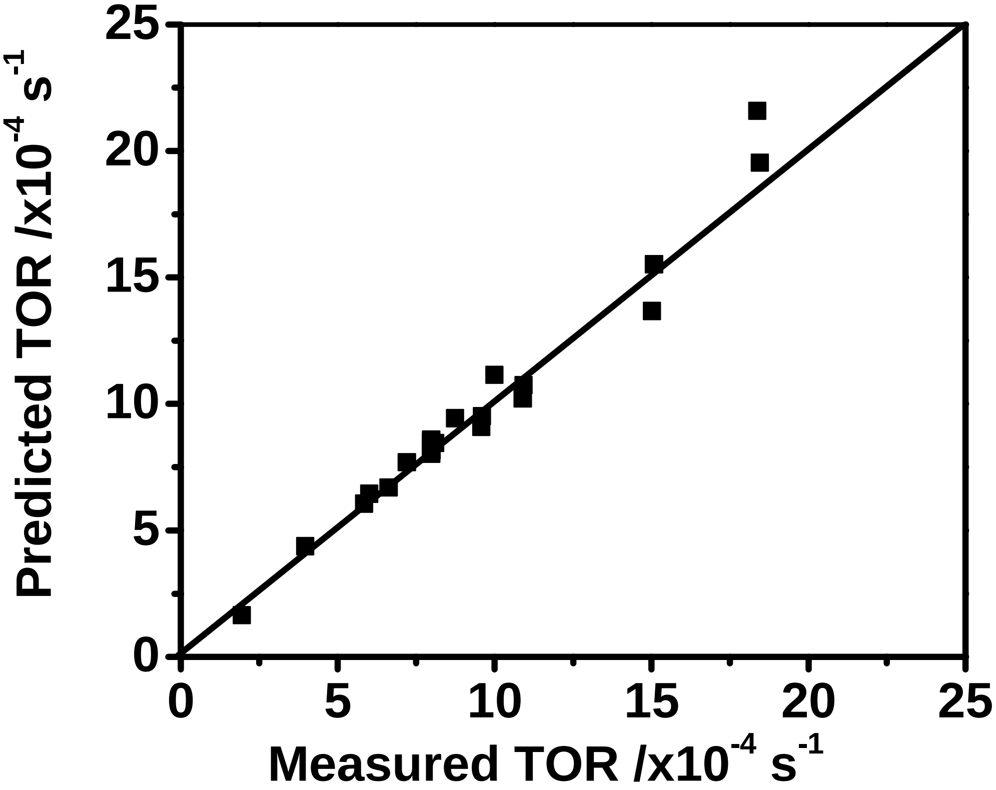

**Figure 2. Comparison between measured hydrodechlorination reaction rate and prediction rate using equation 9 of $CH_3Cl$ compound**

*3.4. Calculating Reaction Energetics of Elementary Steps*

Constant k' and K' contain information about reaction energetics. Note from equation 9 that the rate constant k' is the product of two terms, the equilibrium constant of adsorption of the chlorinated organic compound on Pd and the other the rate constant of rate-determining step 2 in the proposed reaction steps. Thus the activation energy of step 3 (defined as “intrinsic activation energy” of hydrodechlorination reaction in this contribution to distinguish it from apparent activation energy listed in table 2) is in fact the sum of a heat of reaction of step 1 and activation energy of step 2. The term K’ can be used to evaluate the heat of reaction of the equilibrium of $H_2$ and HCl in reaction system (equation 6). We found that these two reaction energetics could also be extracted for our kinetic results.

For each of the chlorinated organic compounds used, their k’ and K’ values were extracted at four different temperatures using the method discussed in section 3.4. Then, the activation energy and heat of reaction were calculated from the slope of the logarithm of k’ or K’ against 1/T. The results for $CH_{4-x}Cl_x$ (x=1-4) are summarized in two graphs, one for the calculation of intrinsic activation energy (k’) of rate equation 3 (figure 3); the other for the calculation of ΔH (K’) of equilibrated step 6 (figure 4). Note that in Figure 4, the result of $CF_3CFHCl$ is also shown for later comparison. The intrinsic Ea of equation 3 was closely related to the reactivity of different chlorinated methane compounds, for example, the most reactive compound $CCl_4$ had the lowest intrinsic activation energy. For the reaction energetics ΔH values shown in figure 4, although they were all negative, the magnitude of ΔH was different for each compound.

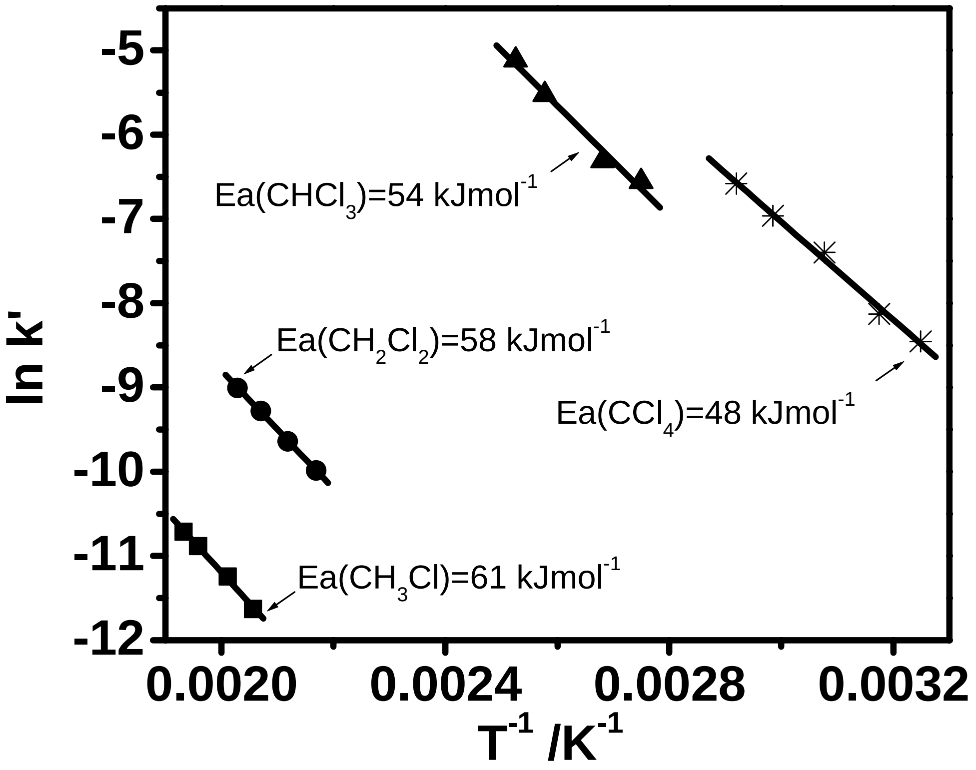

**Figure 3. Intrinsic Ea of $CH_{4-x}Cl_x$ (x=1-4) compounds**

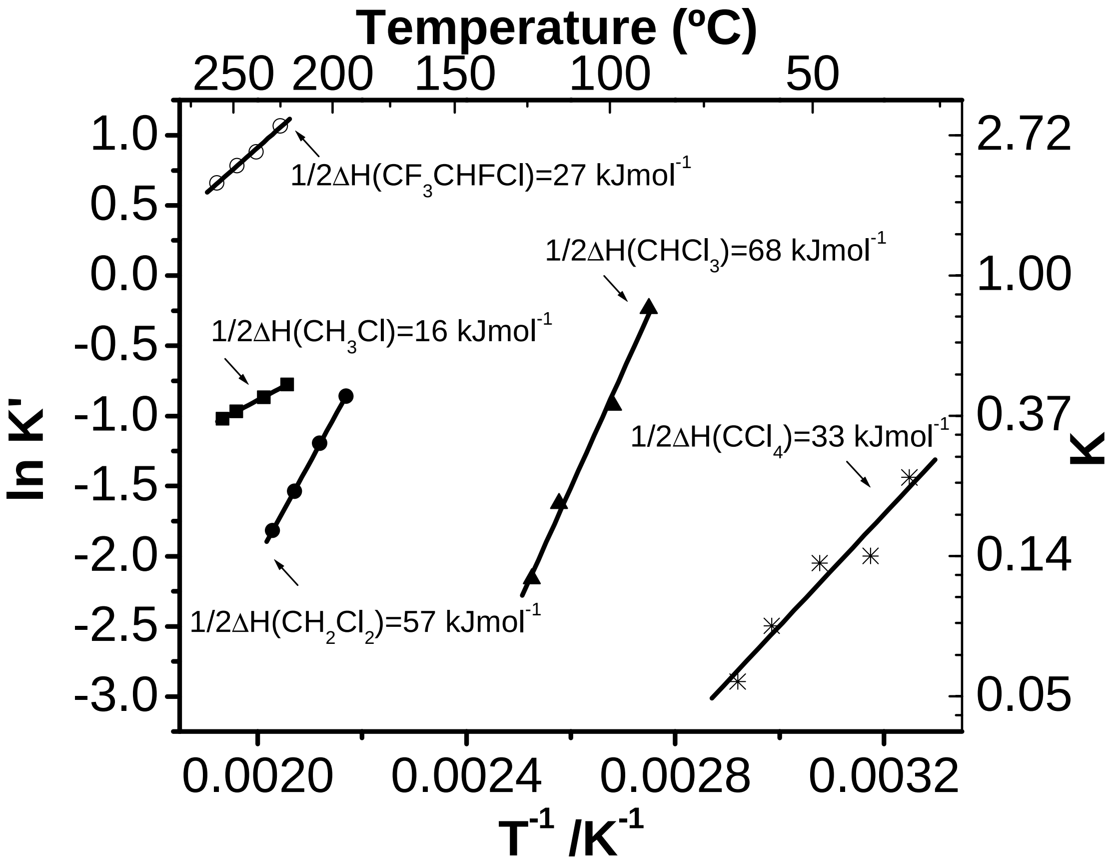

**Figure 4. Heat of reaction for the equilibrium between gas phase $H_2$, HCl and surface H, Cl species. (eq.6) of $CH_{4-x}Cl_x$ (x=1-4) compounds and HCFC124**

### *3.5. C-Cl Bond Energy Calculation and Prediction of Relative Hydrodechlorination Reaction Rates of $CH_{4-x}Cl_x$ (x=1-4) Compounds*

In our previous publication [16], we noticed that there was a correlation between the relative turnover rate of $CF_3CF_{3-x}Cl_x$ (x=1-3) compounds and the bond energy of the first C-Cl bond to break during hydrodechlorination reaction. In this section, we want to investigate whether this relationship between turnover rate and C-Cl bond strength also exists for $CH_{4-x}Cl_x$ (x=1-4) compounds.

The C-Cl bond energy of these chlorinated methane compounds were calculated using a quantum chemistry calculation software package Gaussian 98 [42]. The model used was B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(2d,p), essentially a DFT (Density Functional Theory) method. Bond energy was found out by taking the energy difference of the molecule as a whole and its fragments, that is, E(A-B)=E(A)+E(B)-E(AB). These bond energy values can then be used to estimate the relative hydrodechlorination turnover rates of $CH_{4-x}Cl_x$ (x=1-4) using a method which has been devised in our previous publication [16]. This method is mainly based on Polanyi [43] relationship, which states that for a family of similar reactions, the difference in activation energy is linearly related to the difference in reaction enthalpy; and linear free energy formalism, similar to the one in the Hammett relation used in physical-organic chemistry, which can be used to correlate ΔH of surface C-Cl bond scission to equation gas phase C-Cl bond strength $\Delta H_{R\text{-}Cl}$. After this treatment, the ratio of rate constant of different chlorinated methane compounds can be expressed as a function of the difference of their gas phase C-Cl bond energy, as shown in equation 11. A more detailed derivation of this equation is shown in reference 16.

$$\frac{k_1}{k_2} = e^{-\Delta Ea/RT} = e^{-\alpha(1-\beta)\Delta\left|\Delta H_{R-Cl}\right|/RT} \qquad (11)$$

This new equation allows one to calculate the relative turnover rate of any member in the series as a function of the rate constant of a reference member if the difference in enthalpy of the dissociation reaction in the gas phase $\Delta H_{\text{R-Cl}}$ and reaction conditions are known. In equation 11, $\alpha$ is a constant from Polanyi relationship, while $\beta$ is a constant from linear free energy treatment. The experimental value that gives the best fit is one that corresponds to $\alpha(1-\beta) = 0.5$. The values of calculated C-Cl bond energy, relative hydrodechlorination rates and experimental relative rates are summarized in table 6. The agreement between predicted relative hydrodechlorination rates and experimental relative rates is good except $CCl_4$.

| **Compound** | **C-Cl Bond Energy (kJ/mol)**[a] | **Overall Turnover Rate ($s^{-1}$)**[b] | **Relative Turnover Rate** | **Predicted Relative Turnover Rate** |
|---|---|---|---|---|
| $CH_3Cl$ | 346 | $1.5\times10^{-4}$ | 1 | 1 |
| $CH_2Cl_2$ | 318 | $2.18\times10^{-2}$ | $1.45\times10^{2}$ | $1.2\times10^{2}$ |
| $CHCl_3$ | 288 | 0.58 | $3.87\times10^{3}$ | $3.3\times10^{3}$ |
| $CCl_4$ | 250 | 1.7 | $1.13\times10^{4}$ | $8.46\times10^{5}$ |

[a] Values calculated using Gaussian94 program, the method used is B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p)

[b] Rates corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl, and 150°C.

**Table 6. C-Cl bond strength of $CH_{4-x}Cl_x$ (X=1-4) compounds, comparison between measured turnover rate and predicted rate using equation 11**

### *3.6. Relationship between C-Cl Bond Energy and Intrinsic Activation Energy of $CH_{4-x}Cl_x$ (x=1-4) Compounds*

We also studied the relationship between different reaction energetics in hydrodechlorination reaction. When the intrinsic activation energy values of $CH_{4-x}Cl_x$ (x=1-4) compounds were plotted against their calculated CFC C-Cl bond strength values in figure 4, a linear relationship between these two parameters was observed, as shown in figure 5. In fact, this is a Polanyi relationship which we just discussed in section 3.4, that is, for a family of reactions, $Ea=Ea_0-\alpha\Delta H$, where Ea is the activation energy of a reaction, $\Delta H$ is the heat of reaction of this reaction, $Ea_0$ and $\alpha$ are linear equation constants.

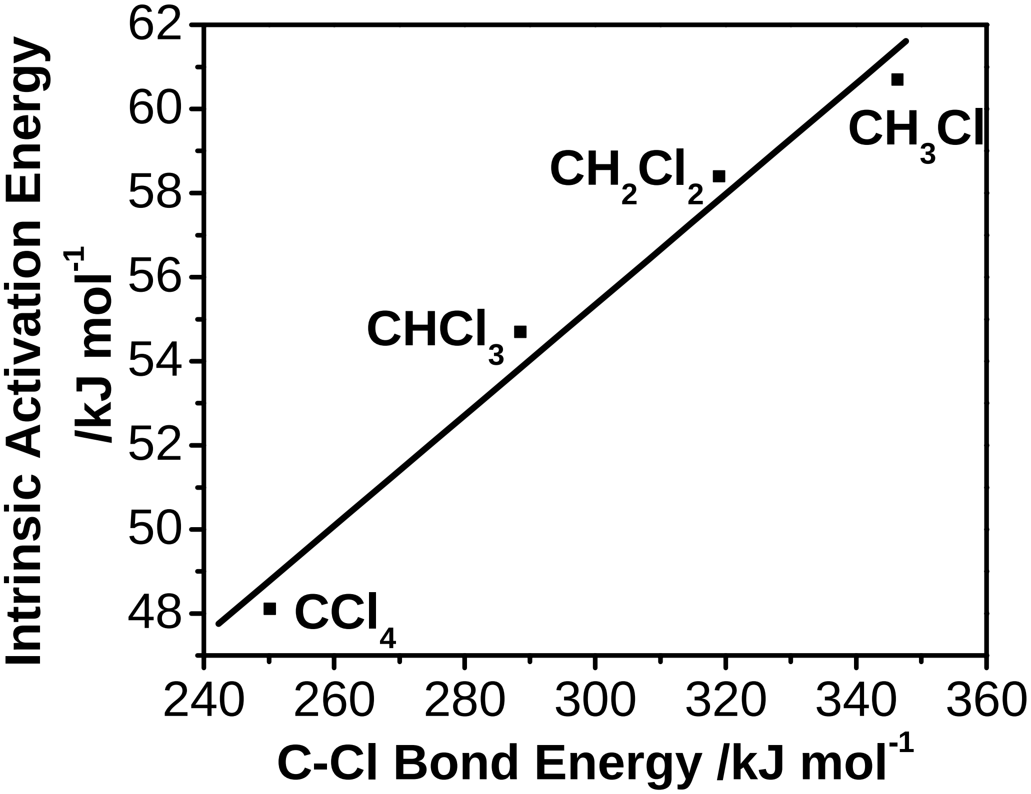

**Figure 5. Relationship between C-Cl bond strength and intrinsic activation energy of $CH_{4-x}Cl_x$ (x=1-4) compounds**

### *3.7. Product Distribution of Deuterium Exchanged Hydrodechlorination Reaction of $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$*

For the hydrodechlorination reactions $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ compounds with $D_2$, the reaction mixture was analyzed by GC-MS and the percentage of different deuterated products was calculated. By looking at the deuterium distribution, we can also find out if the C-H bond is broken during reaction. These results are summarized in figures 6-8.

Figure 6 shows the deuterated methane distribution of $CH_3Cl$ during reaction with $D_2$. About 96% of the product was singly deuterated methane, indicating that C-H bond scission was insignificant during reaction. Figure 7 shows the deuterated product distribution of $CH_2Cl_2$. Since there were two products in the hydrodechlorination reaction of $CH_2Cl_2$, the product distributions of both products were examined. For chloromethane, formed by the first C-Cl bond scission step during reaction, the dominant species was still singly deuterated species $CH_2DCl$ (94%) and only 6% of chloromethane had more than one deuterium. However, for methane, formed by removal of both two chlorines, more C-H bond was exchanged to C-D bond and nearly 35% of methane had more than two deuteriums. A similar trend, that is, increased C-D bond formation with the removal of more Cl from a chlorinated compound, was also noticed in $CHCl_3$ hydrodechlorination with $D_2$. For example, the fully deuterated product percentage in the three product dichloromethane, chloromethane and methane was 8.5%, 17.8% and 37.8% respectively.

Another trend was found by comparing the deuterated product distribution of different chlorinated methanes. We noticed that more C-H can be exchanged to C-D bond in a chlorinated methane compound with more chlorine in its molecule. Take the example of first C-Cl bond scission process of these chlorinated methanes. In $CH_3Cl$, the percentage of product methane with more than one deuterium was only 2%; while in chloromethane formed by removal of first C-Cl bond in $CH_2Cl_2$, the number increased to 6%; and in $CHCl_3$ reaction with $D_2$, 8.5% of dichloromethane product had more than one deuterium.

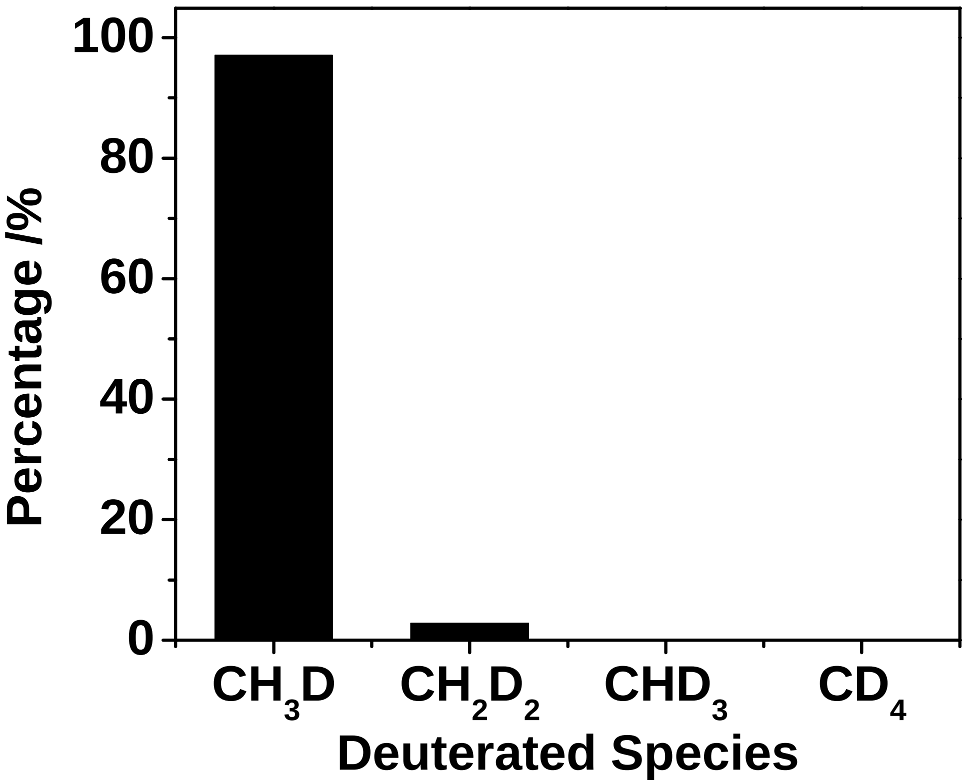

**Figure 6. Product distribution in $CH_3Cl$ reaction with $D_2$. Reaction was conducted in Batch reactor, With 416 Torr CH3Cl, 434 Torr $D_2$, at 205°C. Conversion was from 3.2% to 13.6%. The distribution is independent of conversion**

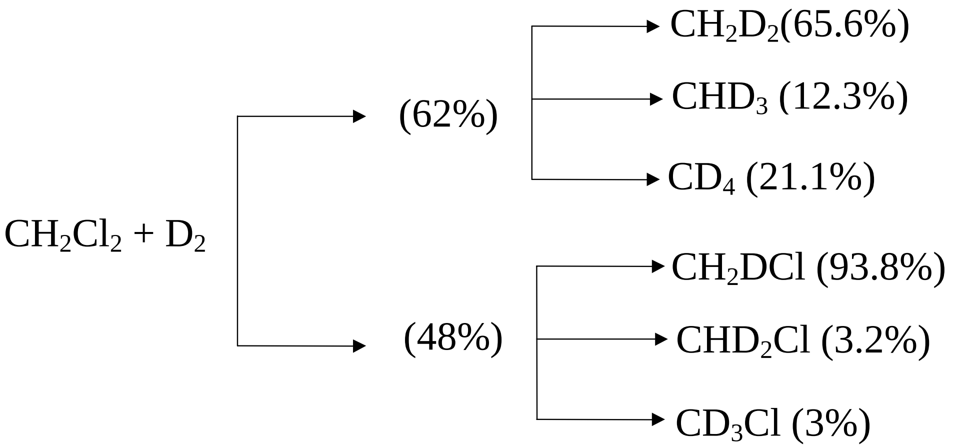

**Figure 7. Product distribution in $CH_2Cl_2$ reaction with $D_2$. Reaction was conducted in batch reactor, with 30 Torr of $CH_2Cl_2$, 200 Torr of $D_2$. Reaction temperature was from 184-235°C. Conversion was from 7-21%. The product distribution is independent of conversion.**

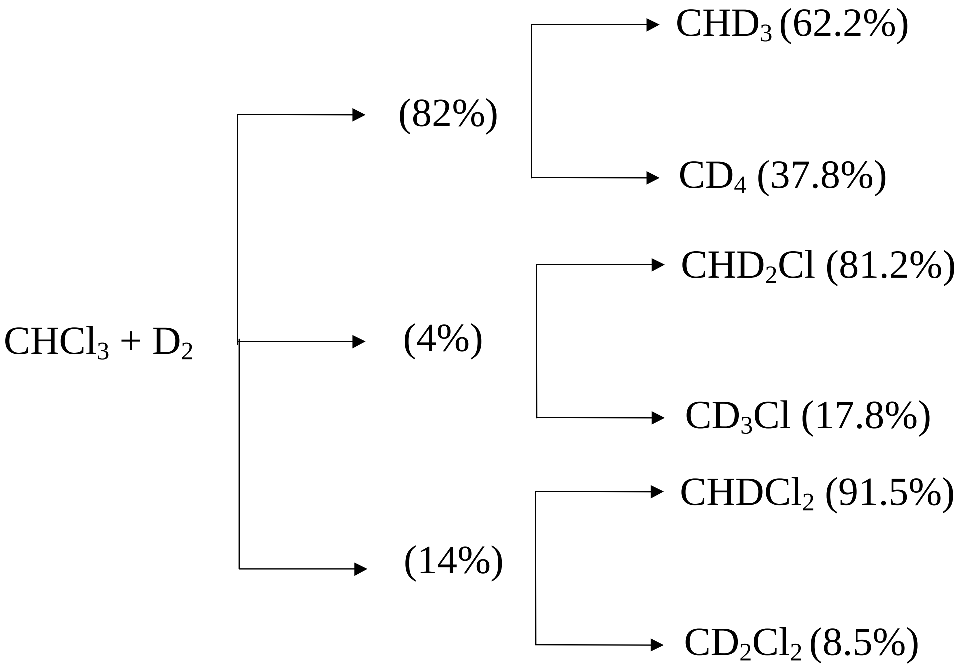

**Figure 8. Product distribution in $CHCl_3$ reaction with $D_2$. Reaction was conducted in batch reactor. The reaction was 95 °C, with 18 Torr $CH_2Cl_2$ and 328 Torr $D_2$.**

## 4. Discussion

### *4.1. Reaction Steps of $CH_{4-x}Cl_x$ (x=1-4) Compounds*

The collected hydrodechlorination kinetic results of $CH_{4-x}Cl_x$ (x=1-4) compounds, such as their rates and reaction energetics can provide insight into possible hydrodechlorination reaction steps. The generalized reaction steps will be compared with steps listed in scheme 1, which was derived from CFC hydrodechlorination reaction [12, 15, 16]. One question is whether the proposed reaction steps in scheme 1 can also be applied on these chlorinated methane compounds.

We will first examine which step is the rate limiting step of hydrodechlorination reactions of dichloropropane compounds. In a previous publication [16], we found that for the group $CF_3CF_{4-x}Cl_x$ (x=1-3), the relative hydrodechlorination rate correlated very well with the bond energy of the first C-Cl bond to break in the hydrodechlorination reaction. In fact, based on this finding, we proposed that the first C-Cl bond scission should be the rate limiting for these compounds. A similar correlation was also found for $CH_{4-x}Cl_x$ (x=1-4) compounds studied here. The agreement between experimental data and predicted values in table 4 is acceptable if one considers the fact that the reactivity of these compounds varies by a factor of $10^4$, while using C-Cl bond energy as the only parameter for prediction of relative turnover rate of each compound, the maximum error we made is at most a factor of 3 (except for $CCl_4$, and the reason will be addressed later) It should be noted that in the prediction of relative rate of these compounds from their bond energy values, the equation we used (equation 11) has one adjustable parameter with it, that is, $\alpha(1-\beta)$. A value of 0.5 was found to give the best prediction of hydrodechlorination reaction rate. Even with an adjustable parameter, we can clearly observation the dependence of rate on C-Cl bond strength. This agreement suggests that the first C-Cl bond scission step is the rate limiting step in the hydrodechlorination reactions of $CH_{4-x}Cl_x$ (x=1-4) compounds, similarly to what is suggested by scheme 1. Another support for C-Cl bond scission being the rate limiting step is the Polanyi correlation between intrinsic activation energy and gas phase C-Cl bond strength of these compounds result (figure 5). We have pointed out that in the proposed reaction steps, intrinsic activation energy of equation 3 is a linear summation of the heat of adsorption of the chlorinated compound on Pd (step 1) and the activation energy of the proposed reaction step (step 2). With C-Cl bond scission being the rate limiting step and its activation energy is in a linear relationship with gas phase C-Cl bond strength (we have demonstrated that the enthalpy of surface C-Cl bond scission is linearly related to gas phase bond dissociation energy of C-Cl bond in a chlorinated compound using a linear free energy relationship [12, 43]), intrinsic activation energy should show a linearly dependence on C-Cl bond strength. In fact, this is what figure 5 shows. From this analysis of kinetic results, we can further conclude that the first C-Cl bond scission step on Pd surface is the rate determining step of hydrodechlorination reaction, as we have proposed before

The finding that the rate limiting step is the same for the families $CH_{4-x}Cl_x$ (x=1-4) and $CF_3CF_{4-x}Cl_x$ (x=1-3) suggests that the proposed reaction steps for the latter family in scheme 1 might also be applicable to the former family. The results shown in figure 2 further supports this view. It shows the rate expression derived from scheme 1 can give out accurate prediction of hydrodechlorination reaction rate of a chlorinated compound.

In summary, the newly obtained kinetic results of hydrodechlorination reactions of chlorinated methane compounds also support the proposed hydrodechlorination reaction steps as shown in scheme 1. It suggests that scheme 1 is a general set of reaction steps and can be used to describe the hydrodechlorination reaction kinetics for other chlorinated compounds. Considering the large number of existing chlorinated compounds and their diverse hydrodechlorination reaction behavior, a universal set of hydrodechlorination reaction steps is very desirable for practical applications, such as prediction of their reaction rates.

### *4.2. Reaction Orders*

*4.2.1. Comparison between apparent HCl reaction orders of chlorinated methanes and CFCs*. One noticeable difference between the kinetic parameters of chlorinated methanes (table 2) and CFC compounds, such as $CF_3$-CFHCl (HCF124) shown in table 3, is that the measured apparent HCl reaction orders for chlorinated methanes were less negative than the HCl orders for CFCs. This difference can be addressed by the examining the reaction expression.

The apparent reaction order is defined as the coefficient "c" in the power rate law $r=k''[CFC]^a[H_2]^b[HCl]^c$. However, we have show that the rate expression that best describes this reaction is $r=k'[CFC]/\{1+ K'[HCl]/[H_2]^{1/2}\}$. This expression can be simplified into a power rate law if the magnitude of $K'[HCl]/[H_2]^{1/2}$ in the denominator is large compared to 1. When this assumption is true, the power-rate law HCl reaction order will be -1. The value of "c" will thus depend on the magnitude of K' and can vary between -1 and 0. The magnitude of K' values (figure 4), for $CF_3CFHCl$ were higher than those for $CH_{4-x}Cl_x$ (x=1-4) compounds under the same reaction conditions and thus the less negative apparent HCl reaction orders. It remains to be explained why the K' values for different chlorinated hydrocarbons are different since reaction (6) is independent of the chlorinated hydrocarbon undergoing reaction.

Additionally, Table 4 shows that the apparent HCl order of a chlorinated compound gets closer to -1 when the temperature increases. As pointed out before, the constant K' in the rate expression 9 is related to the equilibrium constant of reaction 6. Figure 4 shows that the heat of reaction of this step is negative, thus reaction (6) is exothermic and the value of K' will become larger as the temperature is increased. From the discussion from last paragraph, we can notice that when K' value increase, rate expression 9 can be better approximated by a power law rate expression, and the measured apparent HCl reaction order will get closer to -1.

*4.2.2. Chlorinated organic compound reaction orders of $CHCl_3$ and $CCl_4$.* For the hydrodechlorination reaction of $CH_3Cl$ and $CH_2Cl_2$, the reaction orders of the chlorinated organic species were close to 1, similar to the value for the CFC reaction $CF_3$-CHFCl listed and as predicted by the proposed mechanism. But for the other two chlorinated methanes studied here, $CHCl_3$ and $CCl_4$, the reaction orders of the chlorinated species are lower than 1. The proposed mechanism predicts a reaction order of 1 seems to be contradictory against the proposed reaction steps; however, we believe this was caused by an artifact, that is, condensation of organic chlorinated compounds in the pores of carbon support.

In a previous publication [16], we also found the CFC reaction order of $CF_3$-$CHCl_2$ was also lower than 1, and the adsorption isotherms of $CF_3CFCl_2$ on the high surface area carbon showed that a substantial amount of the carbon support pores might be filled with condensed $CF_3CFCl_2$ (b.p. 3.6 °C) even at 100°C. If a reactant is in liquid phase, it will not respond to the change of its gas phase concentration and the reaction order will be zero. Thus when a portion of hydrodechlorination is in gas phase and a portion in liquid phase, the apparent order of chlorinated organic compound would be between 0 and 1. Because the boiling points of $CHCl_3$ and $CCl_4$ (60 and 77 °C, respectively) is close to their reaction temperature (114, and 61 °C respectively). it can be seen that the difference was not large and thus condensation of reactants was possible during hydrodechlorination reaction of these two compounds. As a result, lower chlorinated organic compound orders were obtained from experiments.

Other factors that can lead to $CHCl_3$ reaction order deviation is its high reactivity and high Cl content. It should be noted that on the $CHCl_3$ structure, there are 3 chlorine atoms, and they can all be substituted by H atoms during the hydrodechlorination, compared to other compounds like $CH_3Cl$ and $CH_2Cl_2$, more Cl atoms will generated on the surface from the $CHCl_3$ compound. At the same time, because of the comparatively low temperature under which (due to the high reactivity of $CHCl_3$) we were running the $CHCl_3$ hydrodechlorination reactions, the forward and reverse rates for the equilibration reaction 6 were decreased. These facts, combined with the higher reactivity of $CHCl_3$ as shown in table 2, make the Cl generated from $CHCl_3$ become a competitive factor with the Cl coming from HCl we added in the system. So in constructing site balance for this specific compound, another term accounts for these Cl from $CHCl_3$ must be added when one wants to do a surface site balance, and this term is apparently related to $CHCl_3$ concentration. In this case, this inhibition factor will be related both to the input $CHCl_3$ concentration and input HCl concentration. Thus, in measuring the apparent $CHCl_3$ reaction order, the reaction order will also have Cl inhibition caused by $CHCl_3$ itself, and the apparent order will be lower than 1. This hypothesis can is also supported by the results presented in table 6, which shows that $CHCl_3$ reaction order responded to the temperature change and it deviated even far away from 1 at high reaction temperature. In fact, when the reaction temperature goes down, the rate of the $CHCl_3$ hydrodechlorination will be lower and thus will not generate a large amount of Cl on the surface. Thus the inhibition factor from $CHCl_3$ hydrodechlorination will be less significant, and $CHCl_3$ order will be expected to get close to 1.

### *4.3. Reaction Selectivity*

Another important kinetic parameter (it is not kinetics parameter, it is kinetic parameter) of the hydrodechlorination reaction for all the four compounds studied here is the reaction selectivity. The number of hydrodechlorination reaction products varies from only one in $CH_3Cl$ to a maximum of four for $CCl_4$, depending on the degree of hydrogenation. One feature of their selectivity towards different products is that it remained constant as the conversion was varied during reaction (shown in section 3.2). This finding implies that once a hydrodechlorination product is formed, it does react again. This is due to the fact that the hydrodechlorination reaction products are much less reactive than the reactant. For example, for $CH_2Cl_2$ its product $CH_3Cl$ is 100 time less reactive that the reactant. Thus, under the reaction conditions for $CH_2Cl_2$ hydrodechlorination used in our kinetic experiments, the $CHCl_3$ hydrodechlorination reaction does not affect the selectivity of $CH_2Cl_2$. This finding of parallel pathways towards different hydrodechlorination reaction products can be useful is another important information in the study of reaction steps.

In $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ hydrodechlorination reaction, only the products formed through C-Cl bond scission process were detected. But in $CCl_4$, besides hydrodechlorination products, some $C_2$-$C_5$ hydrocarbon species produced by C-C bond formation were also detected during its hydrodechlorination reaction. Previous hydrodechlorination studies of $CCl_4$ also reported the formation of longer chain hydrocarbons [44, 45]. The reason for this coupling reaction is due to the higher reactivity of $CCl_4$ and its structure. All of the four chlorine atoms in $CCl_4$ molecules can be removed, and carbon atom will be formed on the surface. These carbon species may not be very stable, so some of them can combine with each other to form the skeletons of other longer chain hydrocarbons, and surface H can be added to the skeletons to produce hydrocarbons with higher carbon number [44].

### *4.4. Hydrodechlorination reaction rate of $CCl_4$*

One problem of $CCl_4$ hydrodechlorination reaction is that the measured rate is lower than its predicted rate. In table 6, a prediction about turnover rate based on C-Cl bond strength suggests $CCl_4$ should react about 80 times faster than what we actually measured in the experiments. We think this discrepancy can be explained by the deactivation problem we observed for $CCl_4$. Unlike the other three compounds, significant deactivation was found in the hydrodechlorination reaction of $CCl_4$. This problem has also been noticed in previous literature reports [45-47]. As already pointed out in section 4.3, during the hydrodechlorination reaction of $CCl_4$, when all four chlorines are removed for its molecule, carbon species can be formed. Besides combing with each other to produce hydrocarbons with longer chains, these carbon species can also be a source of coke formation. When coke is present in the reaction system, a portion of the active Pd sites would be buried and not accessible to reactant $CCl_4$, and thus a lower reaction rate is resulted. In fact, developing durable $CCl_4$ hydrodechlorination catalyst is another important research subject [46, 47]. It is thus concluded that this low rate of $CCl_4$ is caused by an artifact and it does not affect the validity of the propose reaction steps

### *4.5. The Effect of Catalyst Support on Hydrodechlorination Reaction Kinetics*

In a previous study, we reported that for palladium catalyst supported on carbon, carbon did not affect the hydrodechlorination reaction kinetics except for the fact that chlorinated compounds with higher boiling point might condense in the pores of this support and lower the CFC reaction order in the hydrodechlorination reaction [15, 16]. In this study, a palladium catalyst supported on zirconia was used to further investigate the effect of support. From the results shown in table 2, it can be seen that the hydrodechlorination reaction rates and selectivity of $CH_3Cl$ and $CH_2Cl_2$ were comparable on the two catalysts. Previous studies in the literature reported that a metal oxide support, such as alumina, might change the hydrodechlorination reaction selectivity of CFC compounds by introducing a fluorine-chlorine exchange pathway [24, 48, 49]. However, since we do not have fluorine present, this exchange reaction is not relevant. This comparison sustains our previous statement that the catalyst support does not participate in the reaction.

### *4.6. Reaction Steps beyond Rate-determining Step C-Cl Bond Scission*

It should be noted that the reaction steps in scheme 1 does not have enough details to explain the product distribution in the hydrodechlorination reaction. The prediction of product distribution can only be achieved with a more detailed set of reaction steps with the inclusion of the reaction steps beyond the rate-determining step. One such step is C-H bond scission. Campbell and Kemball [27] reported in $D_2$ exchanged $CH_3CH_2Cl$ hydrodechlorination reaction that the doubly deuterated product $CH_3CHD_2$ was the most abundant one. Thus they concluded that in the hydrodechlorination reaction of $CH_3CH_2Cl$, both the C-Cl bond a C-H bond in the same carbon was broken. However, our $D_2$ exchanged experiments of $CF_3$-CHFCl indicated that in the hydrodechlorination reaction for this compound, only the C-Cl bond was broken and 98% of the product was $CF_3$-CFHD[15].

The deuterated product distribution results of $CH_{4-x}Cl_x$ (x=1-3) compounds in figures 5-7 shows that no significant C-H bond scission accompanies the first C-Cl bond scission process, similarly to what we found for the $CF_3CHFCl$ compound. Our results on deuterium exchanged hydrodechlorination reaction of $CH_3CH_2Cl$, confirmed that C-H bond could be broken during reaction, and 58% of product ethane had more than one deuterium in the molecule. I will By comparing the structure $CH_{4-x}Cl_x$ (x=1-3), $CF_3CFHCl$, and $CH_3CH_2Cl$, it is believed $CH_3$- or $CH_2$- groups adjacent to the C-Cl bond can undergo C-H bond scission and lead to products with higher deuterium content. As for the scission of the second and third C-Cl bond in $CH_2Cl_2$ and $CHCl_3$ (figure 7 and 8), C-H bond scission starts to become important. With the degree of dechlorination, more hydrogen can be exchanged by surface deuterium atoms.

## 5. Conclusion

The hydrodechlorination reaction kinetics of a series chlorinated hydrocarbons, $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$ and $CCl_4$ was studied and compared with the previously obtained kinetics for CFC compounds. It is found that the hydrodechlorination reaction rates of these chlorinated hydrocarbons are dependent on the strength of the first C-Cl bond to break in these compounds. Additionally, a linear Polanyi relationship exists between the activation energy of the first C-Cl bond scission and the C-Cl bond energy. These results show that the first C-Cl bond scission step is the rate-determining step in the hydrodechlorination reactions of these chlorinated hydrocarbons. The reaction kinetics of these compounds can be described by a rate expression $r=k'[R\text{-}Cl]/\{1+K'[HCl]/[H2]^{0.5}\}$. It is also found the reaction steps of $CH_{4-x}Cl_x$ (x=1-3) compounds are similar to a previously proposed set of reaction steps based on the study of the hydrodechlorination reaction of CFC compounds, indicating these reaction steps might be generally valid for describing the reaction kinetics of hydrodechlorination reaction. The hydrodechlorination reaction steps beyond the rate-determining C-Cl bond scission step have also probed for $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ using $D_2$ isotopic tracing techniques. No significant C-H bond scission has been found to accompany the first C-Cl bond scission, which is similar to the result obtained for $CF_3$-CFHCl isotopic tracing experiment with $D_2$. It is believed that $CH_3$- or $CH_2$- groups adjacent to the C-Cl bond can undergo C-H bond scission and lead to products with higher deuterium content.

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# Paper 6

## Kinetic Study of the Hydrodechlorination Reaction for $CF_{4-x}Cl_x$ (x=1-3) Compounds on Pd/Carbon Catalyst

## Abstract

The hydrodechlorination reaction kinetics of a group of $CF_{3-x}Cl_x$ (x=1-3) compounds was measured on Pd/Carbon catalysts. It was also found that the activation energy of the rate determining step for this series of CFC compounds varied linearly with the strength of the first C-Cl bond to break during hydrodechlorination reaction. The C-Cl bond energy was also used to predict the relative hydrodechlorination reaction rates of these compounds. Hydrodechlorination kinetics results of $CF_2Cl_2$ obtained on Pd/Carbon catalyst agreed with those obtained on Pd model catalysts in literature (model catalysts data). These kinetic results support a previously proposed Langmuir-Hinshelwood type of hydrodechlorination reaction mechanism. The steps are, (1) gas phase $H_2$ and HCl are in equilibrium with surface H and Cl; (2) adsorbed Cl is the most abundant surface intermediate and (3) irreversible scission of the first C-Cl bond is the rate-determining step. From the reaction steps, the overall rate of hydrodechlorination reaction can be derived as $r=k'[CFC]/(1+K'[HCl]/[H_2]^{0.5}$.

**Key words**: hydrodechlorination, reaction kinetics, reaction steps, palladium, $CF_{3-x}Cl_x$ (x=1-3) compounds

## 1. Introduction

Hydrodechlorination is the reaction between hydrogen and an organic compound that contains C-Cl bond(s). During reaction, Cl atom is removed from the molecule and replaced with a hydrogen atom. This reaction is often used in syntheses that use chlorinated molecules as intermediates, for example, the production of $CF_3CFH_2$ (a widely used refrigerant) from $CF_3CFCl_2$ [1]. This is also one example of converting chlorofluorocarbons (CFCs), which have been linked to global ozone layer depletion [1], into more environmentally friendly hydrofluorocarbons (HFCs), which can serve as replacements for CFC refrigerants [2]. Another example of using this reaction to address environmental issues is the possibility of using the hydrodechlorination reaction as a way of waste water pollutant abatement [3, 4]. Recently, there are reports of another type of reaction based on hydrodechlorination, called hydrogen assisted dechlorination, which can be use a means of by-product reclamation. One example like this is the a commercialized Dow Chemical process, in which of 1,2-dichloropropane is converted into propylene on a bimetallic Pt-Cu catalyst and then recycled [5]. With its wide applications, there is a growing interest in catalytic the study of catalytic hydrodechlorination reactions.

One of CFC compounds which received a lot of attention is $CF_2Cl_2$, since there are suggestions of using its hydrodechlorination reaction product $CF_2H_2$ as a heavy duty cooling agent, which poses less adverse environmental effects than the currently used $CF_3CH_2F$ and $CF_2Cl_2$ [6-8]. Many research groups have published reports about the hydrodechlorination reaction kinetics of this compound. A number of metals, including

Pd [6-19], Pt [6, 20], and Rh [20, 21] and Ru [22] have been applied as the hydrodechlorination catalysts, with Pd usually the most reactive and selective catalyst for this reaction [23]. Since supported metal catalysts are typically used in $CF_2Cl_2$ hydrodechlorination reaction, the role of the support in the reaction is also a subject of many studies. There are reports about the role of several supports, for example, carbon [8, 19], alumina [8, 12, 13] and fluorinated alumina [7-9]. While some authors have suggested that oxide supports might play a role in hydrodechlorination reaction [24], we have previously reported that the support (carbon) does not influence reaction kinetics beyond the possible condensation of some low boiling point CFC reactants in the pores of microporous supports [25, 26]. In this report, we plan to use Pd/C as the catalyst in this contribution to take advantage of the inertness of the carbon support and at the same time the reactivity of Pd. Besides supported catalyst, there are also $CF_2Cl_2$ hydrodechlorination literature concerning model catalysts, such as single crystals [27], with limited number of studies have reported hydrodechlorination reactions on bulk metal powders [28, 29]. Most of the previous publications are more concerned with the hydrodechlorination reaction catalyst selection and selectivity control [6-8, 19, 30], but more and more papers now have reported the other important hydrodechlorination reaction kinetic parameters, such as turnover rates, selectivity and reaction orders of the $CF_2Cl_2$ [9, 12, 13, 24-27, 31]. These quantitative kinetics results can be helpful in obtaining in-depth understanding of hydrodechlorination reaction of this compound. However, for other commonly used CFCs with only one carbon atom, such as $CFCl_3$ and $CF_3Cl$, few reports exist for their hydrodechlorination reactions [32]. To fill this gap, in this publication, we will conduct a systematic study the hydrodechlorination reaction kinetics of this series of $CF_{4-x}Cl_x$ (x=1-3) compounds.

More importantly, the kinetics of these compounds will be used to further explore hydrodechlorination reaction steps. Several research articles have addressed the possible reaction steps of this reaction and many approaches have been taken, including generalization of kinetics results, isotopic tracing techniques, and surface science studies [10, 21, 25, 26, 31, 33-38]. From our previous work [26], we have concluded that studying hydrodechlorination reaction kinetics of series of chlorinated compounds with similar structure, such as $CF_{4-x}Cl_x$ (x=1-3) compounds to be investigated here, is an ideal way to understand hydrodechlorination reaction mechanism. A set of Langmuir-Hinshelwood type of hydrodechlorination reaction steps was proposed form the kinetic study of a series of $CF_3CF_{3-x}Cl_x$ (x=1-3) compounds. The irreversible C-Cl scission bond is proposed to be the rate-determining step in this reaction, since it is found that there is a correlation between a CFC compound's hydrodechlorination rate and its first C-Cl bond strength. For the other reaction species, $H_2$ and HCl, they are supposed to be in equilibrium with surface adsorbed H* and Cl* during reaction. Cl* is assumed to be the most abundant surface intermediate since it is found the reaction order of HCl is always negative during hydrodechlorination, indicating the inhibition effect of Cl* species. These reaction steps are summarized in scheme 1.

R-Cl + * = R-Cl*, with an equilibrium constant $K_{CFC}$ (1)

R-Cl* $\rightarrow \cdots$, rate-determining step with a rate constant $k_0$ (2)

$r=k_0K_{CFC}[R\text{-}Cl][*]$, rate expression (3)

$H_2 + 2^* = 2H^*$, equilibrated (4)

H* + Cl* = HCl + 2*, equilibrated (5)

$2HCl + 2^* = H_2 + 2 Cl^*$, (4) + (5), with equilibrium constant $K_0$ (6)

$[^*] + [Cl^*] = [L]$, site balance (7)

$$[^*]=\frac{[L]}{1+K_0^{0.5}\frac{[HCl]}{[H_2]^{0.5}}},$$ free site concentration (8)

**Scheme 1. Possible hydrodechlorination reaction steps**

Form this set of reaction steps, the overall hydrodechlorination rate is derived as:

$r=k'[R\text{-}Cl]/\{1+K'[HCl]/[H_2]^{0.5}\}$, with $k' = k_0K_{CFC}[L]$ and $K' = K_0^{1/2}$ (9)

In this article, we will examine whether the kinetics data of $CF_{4-x}Cl_x$ (x=1-3) support the proposed reaction steps based on the study of $CF_3CF_{3-x}Cl_x$ (x=1-3) compound. If this is true, then it implies this set of reaction steps can be used to describe the hydrodechlorination reaction of other chlorinated compounds in general. Considering the vast number of existing chlorinate compounds and their diverse hydrodechlorination behavior, a universal set of reaction step that can be applied to predict their reaction kinetics is highly desirable.

## 2. Experimental Methods

### *2.1. Catalyst*

The catalyst used in this study is a 5% Pd catalyst supported on activated carbon, which was obtained from Degussa with serial number E 9011 XR/W 5%. It has a BET area of 107 $m^2$ $g^{-1}$ and a total pore volume of 1.15 $cm^3$ $g^{-1}$. The pore size distribution and pore volume of the Degussa catalysts were measured with a Quantachrom Autosorb-1 volumetric sorption analyzer. This catalyst sample was grounded with a mortar before use, and pestle and the fraction between 40 and 60 mesh was retained for hydrodechlorination reaction.

### *2.2. Reactants*

$CF_3Cl$ was obtained from National Refrigerants, Inc. $CF_2Cl_2$ and $CFCl_3$ were purchased from Acdelco Company. The mixture of 15-20% HCl in He were manufactured by Matheson Gas Products, Inc. and was made with technical grade HCl and Matheson purity He. The $H_2$ used for catalytic reactions (from BOC Gases) was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was also obtained from BOC gases. For the He used as GC-MS system carrier gas, it was passed through a mass spectrometer gas trap (HP model 5182-3467) before feeding into the GC column.

### *2.3. Reactor Configuration*

The gas manifold was constructed of 1/8" diameter stainless steel tubing. Gas flow was controlled with mass flow controllers (Porter Instrument Co.). For $CFCl_3$, which is liquid at room temperature, it was added to the reaction mixture by passing helium through the reactant in a saturator maintained at constant temperatures using a water bath.

The bath temperature was controlled using a Neslab Instrument Inc. RTE-9 refrigeration/heating circulating bath. The mass flow controllers had been calibrated with bubble flow meters except for the He/HCl mixture. In this case, the flow rates were determined by varying the composition of a mixture of the He/HCl and a $H_2/CH_4$ gas (Matheson Gas, 1033ppm methane in $H_2$), then analyzing the mixture by gas chromatography, and observing the change in signal of the methane peak.

The reaction portion of the flow system was made of Pyrex glass and the reactor was made out of quartz with the catalyst held on a fritted disk. Kinetic measurement experiments were a continuous stirred tank reactor (CSTR) mode. Temperature was measured through a thermocouple well extending to the catalyst bed. The mixing in the CSTR was achieved by a bellows pump (Senior Flexonics, MB-21) with a rate of about 1400 $cm^3$ $min^{-1}$ allowing differential operation for the reactor and minimizing heat and transport limitation effects in the reaction. The presence of heat and mass transfer limitations in this system was tested using the Madon-Boudart test [39]. From the results presented in a previously published report [26], heat and mass transfer limitations were not detected even with another type of Pd catalyst supported on carbon with a higher surface area, where transport limitations would be expected to be most severe. Inlet and effluent flow rates were around 100 $cm^3$ $min^{-1}$ in normal experiments.

The reaction gases were analyzed with a modified GC-MS (GC-HP 5880A, MS-HP5970A) system. The column used in the GC was a 5% Krytox 143AC, 60/80 Carbopack B HT 20' x 1/8" from Supelco. The effluent from the GC column was simultaneously analyzed by a flame ionization detector on GC (for quantitative analysis) and by the MS (for qualitative analysis). The gas was sampled into the mass selective detector through a fused silica polyimide capillary (I.D. 51μm, O.D. 363μm, length 0.75m). GC response factors of all reactants and products had already been calibrated against methane using the $H_2/CH_4$ calibrated mixture. After exiting the system, the gases flowed through a NaOH solution to neutralize HCl present in the effluent stream.

### *2.4. Data Collection Procedure and reaction conditions*

Two to five hundred milligrams of fresh Pd/C catalyst was initially loaded into the reactor and reduced for 3 h at 300°C with 50 $cm^3$ $min^{-1}$ $H_2$. For repeated experiments, the catalyst was treated with 50 $cm^3$ $min^{-1}$ $H_2$ for 0.5-1 h at 150°C before the following hydrodechlorination reactions.

For the kinetics measurement experiments conducted in CSTR mode, the inlet gas concentrations were adjusted with mass flow controllers and the reaction temperature was controlled by a Eurotherm model 808 temperature controller. For a particular set of conditions, the reaction would be let run for 30-60 minutes to get stabilized before a data point was taken. During the course of the experiments, the changes in concentration and temperature were chosen in a random order so that any variation in the system would not introduce a systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated and another data point was taken. By ensuring that this last point agreed with the first point it could be shown that there was no significant deactivation of the catalyst during the time frame of the experiment. The gas mixture was sampled into the GC-MS system using an automatic valve on the GC.

In measuring the hydrodechlorination reactions kinetics of $CF_{4-x}Cl_x$ (x=1-3) compounds, we kept the reaction conversion low (<5%) to maintain the concentration of reaction gases constant so as to simplify mathematical treatment. In order to achieve low conversion and due to the different reactivity of these compounds, the reaction conditions, for example, reaction temperature, used for measuring their kinetic had to be different. These conditions are listed below. It should also be noted HCl were added during all the reactions to further minimize the variable in reaction system. This is due to the fact that HCl is an inhibitor of hydrodechlorination reaction. Apparent activation energy was determined by measuring the reaction rate at different temperatures while keeping the reactant concentrations constant, and then using an Arrhenius plot. Reaction orders were determined by varying the amount of reactant to be studied while keeping all the other variables constant.

For $CF_3Cl$ compound, the conditions for apparent activation energy determination were 310-365 °C, 205 Torr of CFC, 229 Torr of $H_2$, and 35 Torr of HCl. For CFC order determination, the conditions were 321°C, 105-329 Torr of CFC, 230 Torr of $H_2$, and 35 Torr of HCl. For $H_2$ order measurement, the conditions were 320°C, 191 Torr of CFC, 88-329 Torr of $H_2$, and 32 Torr of HCl. For HCl order measurement, the conditions were 320°C, 210 Torr of CFC, 231 Torr of $H_2$, 19-53 Torr of HCl. Additionally, for the study of reaction energetics to be discussed in section 3.3, HCl reaction order experiment was repeated at three different temperatures: 277, 302, and 339 °C.

For $CH_2Cl_2$, The conditions for apparent activation energy measurement were 181-220 °C, 278 Torr of CFC, 225 Torr of $H_2$, and 55 Torr of HCl.  For CFC order determination, the conditions were 193 °C, 148-438 Torr of CFC, 130 Torr of $H_2$, and 28 Torr of HCl.  The conditions used for $H_2$ order determination were 193 °C, 222 Torr of CFC, 78-282 Torr of $H_2$, and 28 Torr of HCl.  For HCl order measurement, the conditions were 194 °C, 214 Torr of CFC, 173 Torr of $H_2$, 21-65 Torr of HCl.  The three other temperatures under which HCl reaction order experiment was repeated were: 213,235 and 252 °C

Finally, for $CF_3Cl$, the conditions for the determination of apparent activation energy were 75-114 °C, 245 Torr of CFC, 110 Torr of $H_2$, and 30 Torr of HCl.  For CFC order determination, the conditions were 96 °C, 60-219 Torr of CFC, 120 Torr of $H_2$, and 35 Torr of HCl.  For $H_2$ order measurement, the conditions were 95 °C, 161 Torr of CFC, 34-208 Torr of $H_2$, and 36 Torr of HCl. For HCl order measurement, the conditions were 96 °C, 234 Torr of CFC, 113 Torr of $H_2$, 17-66 Torr of HCl.  HCl reaction order measurements were also conducted at 87, 107 and 117 °C.

### *2.5. Surface Area Measurements*

The total surface area of the catalysts was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen-oxygen titration method according to Benson *et al.* [40]. The experimental setup consisted of a volumetric system constructed in Pyrex glass and pumped by a liquid nitrogen trapped diffusion pump. The amount of gas adsorbed was determined by measuring pressure change in a pre-calibrated volume on the system with a pressure transducer (MKS model 127).

The Pd/C catalyst sample was reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 3 h at 300°C before the Pd surface area measurement. After the initial reduction, subsequent hydrogen-oxygen titration was conducted at 100°C. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression is valid under the assumption of spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms $m^{-2}$ [41].

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced and then passivated Pd/C catalyst was also conducted. The sample for XRD analysis was reduced in same manner as described above, and then passivated with 60 Torr of $O_2$. Particle size was determined from the width of the diffraction peak using X-ray line broadening technique. Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

### *2.6. Error Analysis*

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in the reaction order measurements were at maximum 10% or maximum 0.1 in 1.0 and errors in activation energy were 10 kJ mol$^{-1}$. Turnover rate experimental reproducibility was better than 90%.

## 3. Results

### 3.1. Catalyst Properties

The carbon support for the 5% Pd/C catalyst used in this research had a BET surface area of 107 m$^2$ g$^{-1}$ and was non-microporous in nature. This type of carbon support was chosen in this study because our previous results [25, 26] indicated that some CFC reactants with high boiling point could condense in the pores of microporous carbon supports during the hydrodechlorination reaction thus decreasing the reaction order for CFC. Beyond this condensation effect for some of the CFC species, it was found that the carbon support itself was inert and played no significant role in hydrodechlorination reaction. The percentage of metal exposed (PME) measured by the $H_2$-$O_2$ titration method was 8.4%. Based on this information, the Pd particle size was calculated to be 13.3 nm (d=1.12/PME). However, the Pd particle size determined by XRD line broadening method was 5 nm, suggesting that the Pd particles were formed by a number of smaller agglomerates. These property parameters shown here are representative of the catalyst before reaction. Since no significant deactivation was observed during reaction, we do not expect any significant changes in the properties of the catalyst after reaction. It was also concluded that this type of carbon supported Pd catalyst was stable under hydrodechlorination reaction conditions.

### *3.2. Kinetic Results of Hydrodechlorination Reaction of $CF_{4-x}Cl_x$ (x=1-3) Compounds*

The apparent activation energy, reaction orders, selectivity and reaction rate, for the hydrodechlorination of $CF_{4-x}Cl_x$ (x=1-3) on Pd/C catalyst are summarized in table 1. These kinetic results will also be analyzed and compared with the kinetics of some other CFC compounds, such as $CF_3CF_{3-x}Cl_x$ (x=1-3) and $CF_{4-x}Cl_x$ (x=1-4) compounds. We have studied before to further examine the proposed reaction steps. Note that the reaction rates reported in table 1 are corrected to a standard condition of 150 Torr of chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl and 150 °C so as to make the comparison of the reactivity of these compounds possible.

From the results, it can be noticed that $CF_3Cl$ had the lowest reactivity of all three compounds. This is also why the kinetic measurements of its hydrodechlorination reaction of $CF_3Cl$ were carried out at a higher temperature. Only one product, $CF_3H$ was present during $CF_3Cl$ hydrodechlorination reaction. There were no products formed through C-F bond scission, unlike the other two products $CF_2Cl_2$ and $CFCl_3$. The CFC reaction order was close to 1, a similar value to what observed for some other CFC compounds, such as $CF_3CF_2Cl$ and $CF_3CFHCl$ [26]. The HCl reaction order of $CF_3Cl$ was negative, as also found before. However, compared with the HCl order of $CF_3CF_2Cl$ and $CF_3CFHCl$ compounds studied before, the HCl order of $CF_3Cl$ was less negative. We will offer an explanation for this observation in the discussion section.

For $CF_2Cl_2$ hydrodechlorination reaction, there were two products, $CF_2H_2$ and $CH_4$. It is noticeable that the under-hydrogenated species $CF_2HCl$ was not formed. However, for $CF_3CFCl_2$ with also contains a $–CCl_2$ group, $CF_3CFHCl$ could be produced with nearly 10% selectivity [26]. Another issue for $CF_2Cl_2$ hydrodechlorination reaction is that the fully hydrogenated product ($CH_4$) was produced in significant amounts (~15%), indicating C-F bond scission. The selectivity towards $CF_2H_2$ and $CH_4$ was found to be independent of the $CF_2Cl_2$ reaction conversion (conversion range explored was from 0.1% to 1.2%). The reaction orders of $CF_2Cl_2$ were comparable to the ones measured for $CF_3CF_{3-x}Cl_x$ (x=1-3) compounds, that is, CFC order, $H_2$ orders, and HCl order are close to 1, 0.5, and -1, respectively.

$CFCl_3$ was the most reactive of all three compounds studied here. Similar to the case of $CF_2Cl_2$, only two products, $CFH_3$ and $CH_4$ were detected and under-hydrogenated products $CFHCl_2$ or $CFH_2Cl$ were not present. The selectivity towards the two products was again found to be independent of reaction conversion (conversion range: 0.08%-1.1%). As for the reaction orders of $CFCl_3$, the most noticeable difference from $CF_3Cl$ and $CF_2Cl_2$ is that its CFC reaction order was lower than 1. The CFC order has been studied before for chlorinated compounds with higher chlorine content, such as $CF_3$-$CCl_3$ compound reported in a separate publication [26], which also showed a CFC reaction order smaller than 1.

Beside the trend in reaction rates, other trends can also be noticed. For example, the apparent activation energy of these three compounds decreased as the number of chlorines in the molecule increases. Additionally, for $CF_2Cl_2$ and $CFCl_3$, the activation energy of different product increases with the degree of dehalogenation.

| Reactant | Temperature of reaction order measurements | Products | TOR[a] ($s^{-1}$) (Selectivity[b]) | $E_a$ (kJ $mol^{-1}$) | Reaction Order Dependence | | |
|---|---|---|---|---|---|---|---|
| | | | | | CFC | $H_2$ | HCl |
| $CF_3Cl$ | 320°C | $CF_3H$ | $2.49\times10^{-7}$ (100) | 117 | 0.99 | 0.25 | -0.52 |
| $CF_2Cl_2$ | 193°C | $CF_2H_2$ | $7.69\times10^{-4}$ (88) | 94 | 0.77 | 0.39 | -0.85 |
| | | $CH_4$ | $1.08\times10^{-4}$ (12) | 96 | 0.71 | 0.32 | -0.82 |
| $CFCl_3$ | 96°C | $CFH_3$ | $1.81\times10^{-1}$ (72) | 73 | 0.47 | 0.31 | -0.71 |
| | | $CH_4$ | $7.02\times10^{-2}$ (28) | 80 | 0.45 | 0.32 | -0.36 |

[a] Rates corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl, and 150°C.
[b] The selectivity is independent of conversion

**Table 1. Kinetic Data for $CF_{4-x}Cl_x$ (x=1-3) Compounds**

### *3.3. Extraction of constants k', K' from hydrodechlorination rate expression and calculation of reaction energetics of elementary steps*

There are two constants in the reaction expression $r=k'[R\text{-}Cl]/\{1+ K'[HCl]/[H_2]^{1/2}\}$. k' is a product of two terms, one being the equilibrium constant of CFC adsorption on Pd surface, the other being the rate constant of the rate-determining step in the proposed reaction steps. The value of K' is square root of the equilibrium constant between for step 6: $HCl + 2^* = H_2 + 2Cl^*$. These two constants contain information about reaction energetics. The energy term associated with k' is the sum of heat of adsorption of CFC species and the activation energy of the rate limiting step. This energy term is also the activation energy of rate equation 3, which will be called “intrinsic activation energy” of hydrodechlorination reaction to distinguish it from the apparent activation energy listed in table 1. The energy term that determines K’ is in fact one half of heat of reaction of step 6. We will demonstrate that k’ and K’ constants can be extracted from hydrodechlorination kinetic measurements and in turn the intrinsic activation energy and heat of reaction of step 6 can be calculated by measuring these two constants at different temperatures.

*3.3.1. Extracting reaction constants k’, K’ from kinetic measurement.* One way to calculate these constants using kinetic data is to linearize the rate expression (9) to the following equation:

$$\frac{1}{r} = \frac{1}{k'[R-Cl]} + \frac{K'}{k'[R-Cl]} \times \frac{[HCl]}{[H_2]^{0.5}} \tag{10}$$

If we keep the partial pressure of CFC constant and change the value of $[HCl]/[H_2]^{1/2}$, then a plot of 1/r against $[HCl]/[H_2]^{1/2}$ will produce a straight line and the rate constant k’ and equilibrium constant K’ can be calculated from the intercept and slope of the line. The value of $[HCl]/[H_2]^{1/2}$ can be altered by varying either the HCl partial pressure or $H_2$ pressure during reaction. With this analysis, it can be seen that the turnover rate data from HCl reaction order measurement or $H_2$ order measurement can be processed using equation 11 to calculate k’ and K’. In practice, we chose the results from HCl reaction order measurements instead of $H_2$ order measurements because the term $[HCl]/[H_2]^{0.5}$ is more sensitive to the variation in HCl concentration than the variation in $H_2$ concentration. Figure 1 shows one example of using the data from $CF_2Cl_2$ HCl reaction order experiment and equation 10 to find out the two reaction constants.

Another way to calculate k’ and K’ from kinetics results is to use non-linear parameter fitting method. We also explored this method using commercially available data processing software packages. The results from non-linear fitting method were comparable with the results from the graphical method. In the calculation of the k’ and K’ values of these $CF_{4-x}Cl_x$ (x=1-3) compounds, we used the graphical method due to its simplicity.

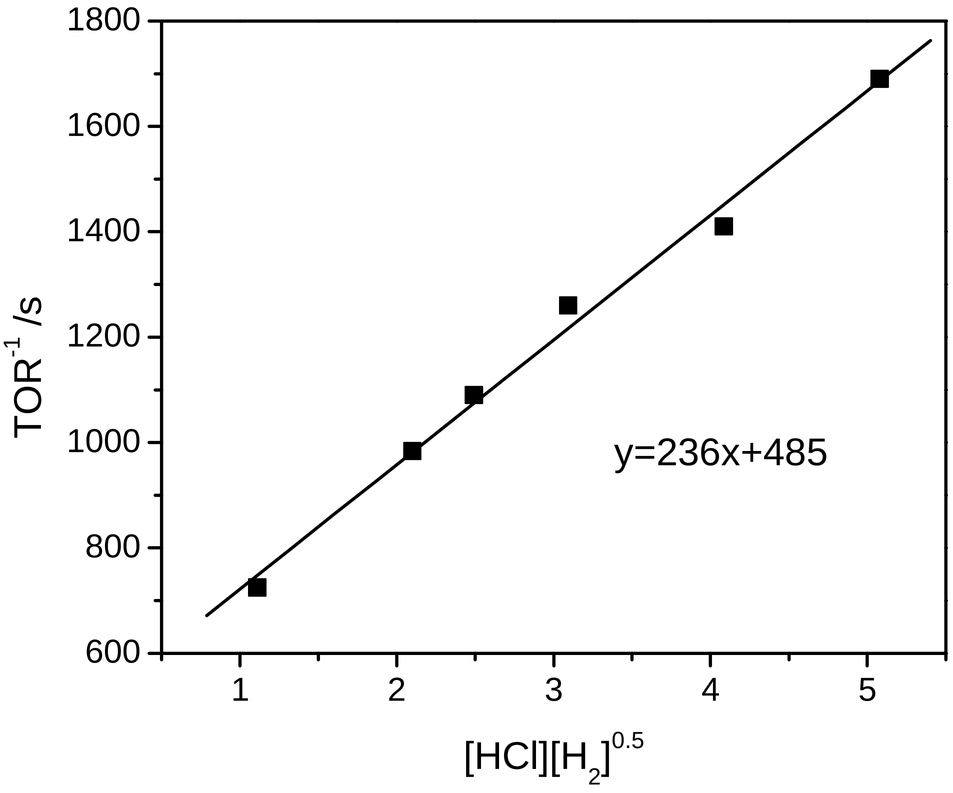

**Figure 1.** **Rate constant k’ and equilibrium constant K’ for $CF_2Cl_2$. Reaction was performed with the 214 Torr of CFC, 173 Torr of $H_2$, 21-65 Torr of HCl, and reaction temperature 235°C.**

*3.3.2. Calculating Reaction Energetics associated with k' and K'.* To calculate the reaction energetics of interest, for each CFC compounds used here, HCl reaction order measurement experiments were performed at four different temperatures, and their k' and K' values were extracted using the method discussed in section 3.3.1. These results are summarized in two graphs. Figure 2 is for the calculation of intrinsic activation energy using an Arrhenius plot, and figure 3 is for the calculation of ΔH of equilibrated step 6: $HCl + 2^* = H_2 + 2Cl^*$. Intrinsic Ea seems to be closely related to the reactivity of different CFC compounds. For example, the most reactive compound $CFCl_3$ had the lowest intrinsic activation energy. For ΔH values of these compounds, they were all around –60kJ $mol^{-1}$, further suggesting they were linked to the same step. We also noticed a trend in apparent HCl orders which were measured by approximating equation 9 into a power law rate expression. When reaction temperature went up, HCl reaction order deviated even further from -1. Take the example of $CF_3Cl$, at 277, 302, 320, 339 °C, the obtained apparent HCl reaction order was: 0.63, 0.58, 0.48, 0.33 respectively.

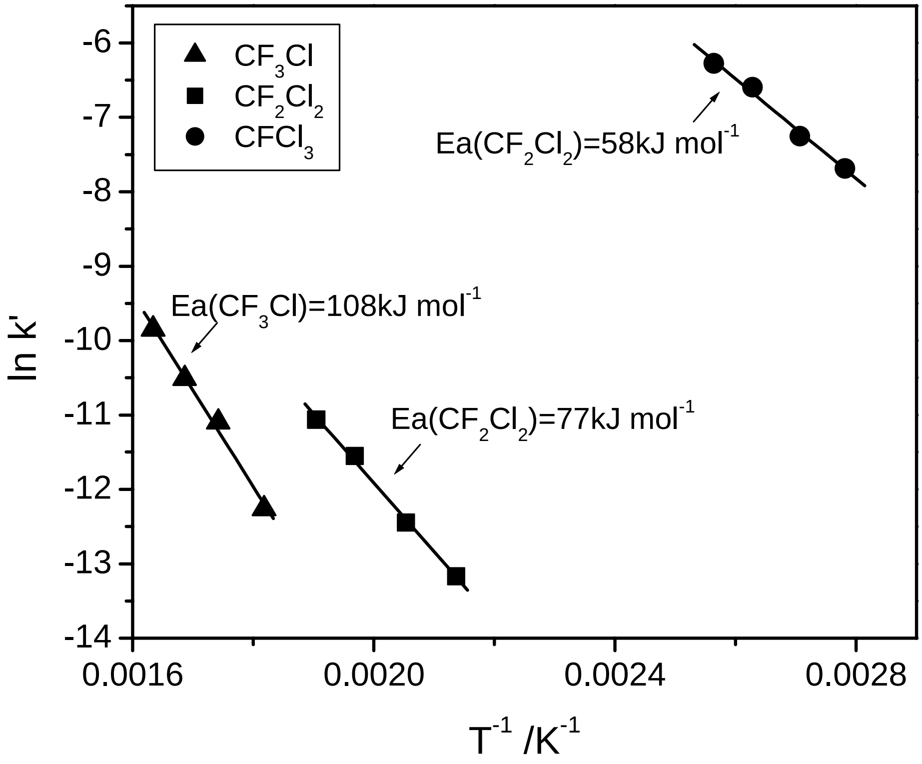

**Figure 2.** **Intrinsic activation energy (sum of activation energy of rate limiting step 2 and heat of adsorption energy of step 2) of the equation 3 in scheme 1 for $CF_{4-x}Cl_x$ (x=1-3) compounds**

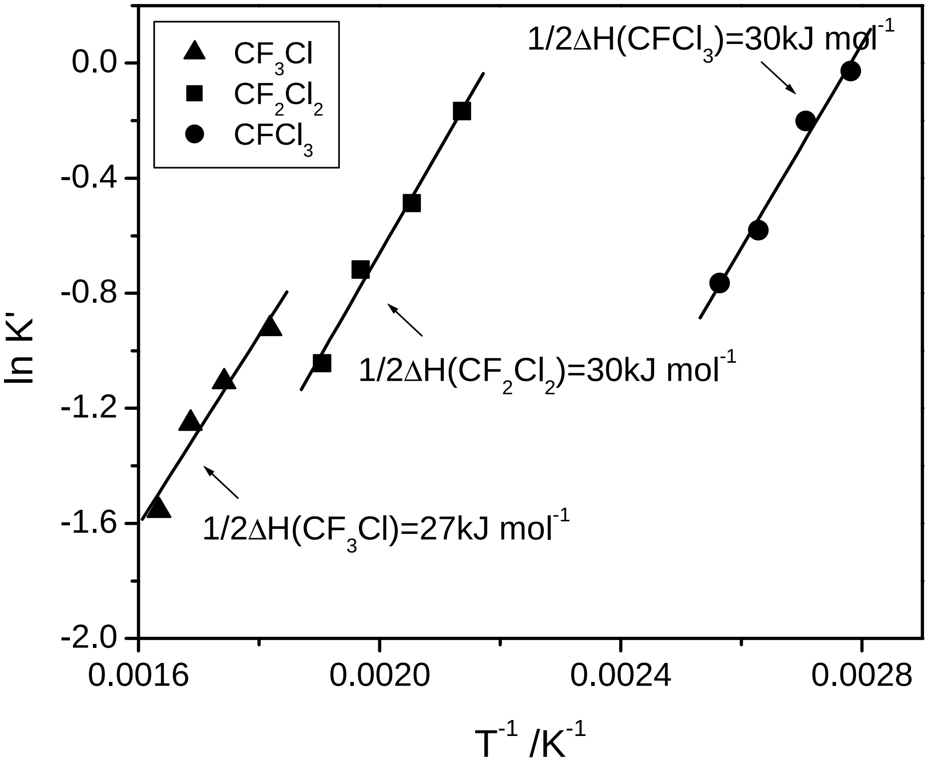

**Figure 3. ΔH for step 6: 2HCl + 2*=$H_2$ + 2Cl* in scheme 1 for $CF_{4-x}Cl_x$ (x=1-3) compounds**

### *3.4. Relationship between Intrinsic Activation Energy and C-Cl Bond energy of $CF_{4-x}Cl_x$ (x=1-3) Compounds*

In the last section, we have demonstrated that the intrinsic hydrodechlorination reaction activation energy of a CFC compound is related to its reactivity. Additionally, we found in a previous paper [26] that the reactivity of a group of CFC compounds could be correlated to the bond energy of first C-Cl bond to break in hydrodechlorination reaction. In this part, we want to examine the relationship between intrinsic activation energy and C-Cl bond strength in a quantitative way.

The bond energy of the first C-Cl bond to break during reaction for each of these compounds was calculated. In our study, we used a quantum chemistry calculation software package Gaussian 98 [42] to calculate the C-Cl bond energy of CFC compounds. The model used was B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(2d,p), essentially a DFT (Density Functional Theory) method. The bond energy was calculated by taking the energy difference of the molecule as a whole and its fragments, using the equation E(A-B)=E(A)+E(B)-E(AB).

Intrinsic activation energy values were plotted as a function of CFC C-Cl bond strength values for $CF4_{-x}Cl_x$ (x=1-3), producing a linear relationship between the two parameters (figure 4). In fact, this is a Polanyi type of relationship, which states for that for a family of reactants, the reaction activation energy is a linear function of reaction enthalpy [43].

The rate of hydrodechlorination for $CCl_4$ was also measured as it fits the series $CF_{4-x}Cl_x$ with x=4. Unlike $CF_3Cl$, $CF_2Cl_2$ and $CFCl_3$, severe catalyst deactivation was noticed during $CCl_4$ hydrodechlorination reaction, possibly due to coke formation [44]. Additionally, the deactivation pattern was dependent on temperature. The deactivation made the experimentally determined values of the reaction energetics discussed in 3.3 unreliable. The measured intrinsic activation was 48 kJ mol$^{-1}$, which does not fit the line in figure 4

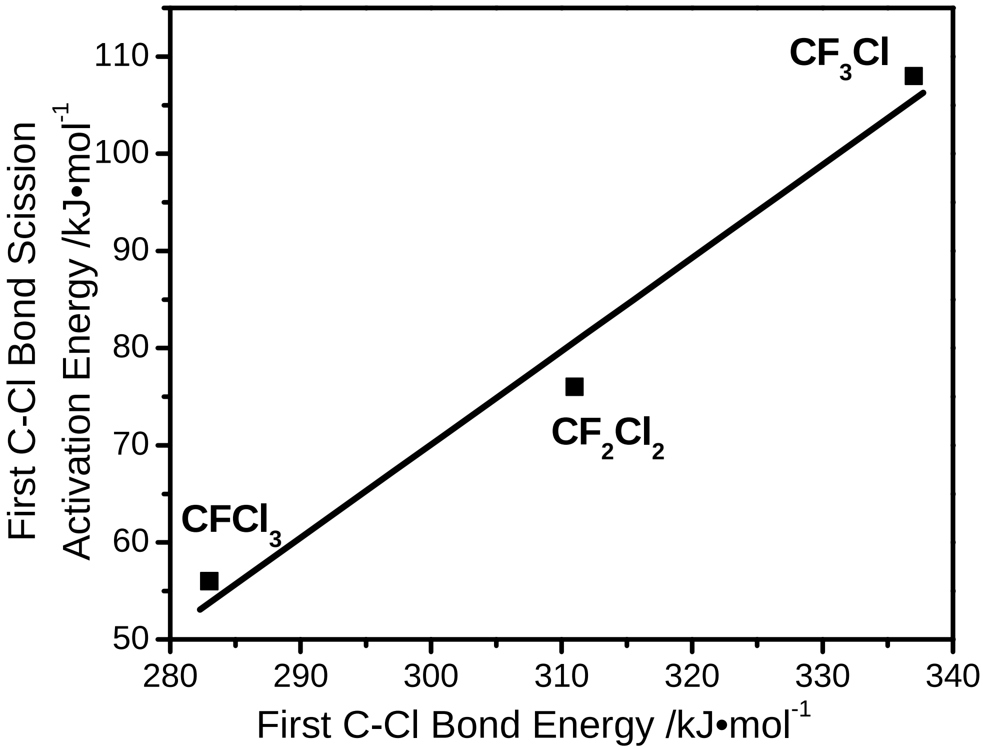

**Figure 4. Relationship between strength of the first C-Cl bond to break during hydrodechlorination reaction and intrinsic activation energy of rate limiting of $CF_{4-x}Cl_x$ (x=1-3) compounds**

### *3.5. Predicting Relative Hydrodechlorination Rate from C-Cl Bond Energy Value*

In a previous publication, we devised a method to estimate relative hydrodechlorination turnover rates using C-Cl bond energy values [26]. This method is mainly based on a Polanyi [43] relationship, which states that for a family of reactions, the difference in activation energy is linearly related to the difference in reaction enthalpy.

$$\Delta Ea = \alpha\Delta|\Delta H| \tag{11}$$

By using Arrhenius equation combined with the assumption that pre-exponential constant is identical for the rate expression of all the reactions in this group, the relative rates can be calculated for each member in the family using the following equation:

$$\frac{k_1}{k_2} = e^{-\Delta Ea/RT} = e^{-\alpha\Delta|\Delta H|/RT} \tag{12}$$

It should be noted that for calculating hydrodechlorination reaction rate, the $\Delta(\Delta H)$ term in equation 12 is for the heat of reaction of C-Cl bond scission on Pd surface, and not the gas phase dissociation energy C-Cl bond ($\Delta H_{\text{R-Cl}}$). However, we have demonstrated that by using a linear free energy formalism, similar to the one in the Hammett relation used in physical-organic chemistry, $\Delta|\Delta H|$ in equation 12 can be shown to be in a linear relationship with $\Delta H_{\text{R-Cl}}$: $\Delta\ |\Delta H| = (1-\beta)\Delta\ |\Delta H_{\text{R-Cl}}|$. Substituting the value for $\Delta\ |\Delta H|$ in equation 12 yield equation 13,

$$\frac{k_1}{k_2} = e^{-\Delta Ea/RT} = e^{-\alpha(1-\beta)\Delta|\Delta H|/RT} \tag{13}$$

This new equation allows one to calculate the relative turnover rate of any member in the series as a function of the rate constant of a reference member if the difference in enthalpy of the dissociation reaction in the gas phase $\Delta H_{\text{R-Cl}}$ is known. The experimental value that gives the best fit is one that corresponds to $\alpha(1-\beta) = 1$. The results obtained by using this method are also listed in Table 2. The calculated relative turnover rates match well with the experimentally measured rates.

| **Reactant** | **TOR ($s^{-1}$)$^a$** | **Relative TOR** | **C-Cl Bond Strength ($kJ\ mol^{-1}$)$^b$** | **Predicted Relative TOR** |
|---|---|---|---|---|
| $CF_3Cl$ | $2.49\times10^{-7}$ | 1 | 337 | 1 |
| $CF_2Cl_2$ | $8.1\times10^{-4}$ | $3.53\times10^3$ | 311 | $1.62\times10^3$ |
| $CFCl_3$ | $4.24\times10^{-2}$ | $1.02\times10^6$ | 283 | $4.46\times10^6$ |

[a] Rates corrected for 150 Torr $CF_2Cl_2$, 200 Torr $H_2$, 20Torr HCl, and 150°C

[b] Bond energy calculated using Gaussian, with the B3PW91/6-311+G(2d,p)//B3PW91/6-311+G(2d,p) model

**Table 2. Bond energy of $CF_{4-x}Cl_x$ (x=1-3) compounds and comparison of measured turnover rates with predicted turnover rates using Polanyi relationship**

### *3.6. Comparison the $CF_2Cl_2$ hydrodechlorination reaction kinetics with literature values*

We have tried to compare our $CF_{4-x}Cl_x$ (x=1-3) hydrodechlorination kinetic measurements, such as rate and reaction selectivity with literature reports. It is found that few reports contain kinetic information about $CF_3Cl$ and $CFCl_3$, but there are more reports about the reaction kinetics of $CF_2Cl_2$ because of the possible applications of its hydrodechlorination product as already discussed in the introduction [9, 12, 13, 24-27, 31]. However, even with these extensive results, we found it was difficult to make a direct comparison of $CF_2Cl_2$ hydrodechlorination reaction kinetics due to the diverse Pd catalyst systems used by different groups. One of the major obstacles here is the role of different catalyst supports. Some supports may alter hydrodechlorination reaction kinetics and thus make it hard to separate the intrinsic hydrodechlorination reaction kinetics from the results already altered by the support effects. The effect of catalyst support will be discussed in more detail later in this article.

To avoid possible artifacts from catalyst supports, we decided to compare our selectivity results with those measured on Pd model catalysts, such as the one published by Ramos *et al.* [27] for $CF_2Cl_2$ hydrodechlorination reaction on Pd foil, Pd(111) and Pd(110). This comparison, including selectivity, reaction rate, and apparent activation energy is summarized in table 3.

| **Catalyst** | **Products** | **TOR$^a$ (min$^{-1}$) (Selectivity$^b$)** | **$E_a$ (kJ mol$^{-1}$)** | **Reaction Order Dependence** | | |
|---|---|---|---|---|---|---|
| | | | | **CFC** | **$H_2$** | **HCl** |
| Pd/C (this work) | $CF_2H_2$ | 0.35 (87) | 94 | 0.77 | 0.39 | -0.85 |
| | $CH_4$ | 0.053 (13) | 96 | 0.71 | 0.32 | -0.82 |
| Pd foil$^c$ | $CF_2H_2$ | 2.037 (89) | 56 | 1.1 | 0.1 | -1$^d$ |
| | $CH_4$ | 0.262 (11) | 113 | 1.3 | 0.2 | -1$^d$ |
| Pd (111)$^c$ | $CF_2H_2$ | 0.528 (86) | 92 | 1.3 | 0.2 | -1$^d$ |
| | $CH_4$ | 0.087 (14) | 111 | 1.1 | -0.2 | -1$^d$ |
| Pd (110)$^c$ | $CF_2H_2$ | 0.519 (92) | 45 | 0.9 | 0.3 | -1$^d$ |
| | $CH_4$ | 0.046 (8) | 104 | 0.8 | 0.1 | -1$^d$ |

[a] Rates corrected for 8 Torr $CF_2Cl_2$, 80 Torr $H_2$, 0.02Torr HCl, and 200°C (the conditions used by Ramos *et al* [27].).
[b] The selectivity is independent of conversion.
[c] Results reported by Ramos *et al.* [27].
[d] Assumed HCl order.

**Table 3. Comparison of kinetic parameters for the hydrodechlorination reaction of $CF_2Cl_2$ reactant on Pd/C and Pd model catalysts**

### *3.7. Comparison of hydrodechlorination reaction kinetics of $CF_3CFCl_2$, $CF_2Cl_2$ and $CH_2Cl_2$*

The two most studied CFC compounds in the literature due to their wide practical applications are $CF_3CFCl_2$ and $CF_2Cl_2$. One common feature of these two compounds is that they have the $–CCl_2$ group in their molecules. By comparing hydrodechlorination reaction kinetics of CFCs with similar structure, we can learn more about the hydrodechlorination reaction steps. In table 4, we tabulated the relevant reaction kinetic parameters (including TOR, selectivity, apparent activation energy, apparent reaction orders and C-Cl bond strength value) of these three compounds. The procedure and reaction conditions for collecting $CF_3CFCl_2$ kinetics has been presented before [26]. The hydrodechlorination reaction of $CH_2Cl_2$ was conducted at 201°C, with 22 Torr of $CH_2Cl_2$ 196 Torr of $H_2$, and 38 Torr of HCl. The temperature range for measuring its apparent activation energy was 187-229 °C.

| **Reactant** | **Products** | **C-Cl Bond Strength (kJ mol$^{-1}$)[c]** | **TOR[a] (s$^{-1}$) (Selectivity[b])** | **$E_a$ (kJ mol$^{-1}$)** | **Reaction Order Dependence** | | |
|---|---|---|---|---|---|---|---|
| | | | | | **CFC** | **$H_2$** | **HCl** |
| $CF_3CFCl_2$ | $CF_3CH_3$ | 294 | $1.2 \times 10^{-2}$ (4) | 100 | 0.75 | 0.30 | -0.90 |
| | $CF_3CFH_2$ | | $2.7 \times 10^{-1}$ (84) | 100 | 0.75 | 0.35 | -0.85 |
| | $CF_3CFHCl$ | | $4.0 \times 10^{-2}$ (14) | 75 | 0.75 | 0.55 | -0.80 |
| $CF_2Cl_2$ | $CF_2H_2$ | 311 | $7.7 \times 10^{-4}$ (88) | 94 | 0.77 | 0.39 | -0.85 |
| | $CH_4$ | | $1.1 \times 10^{-4}$ (12) | 96 | 0.71 | 0.32 | -0.82 |
| $CH_2Cl_2$ | $CH_3Cl$ | 319 | $8.38 \times 10^{-3}$ (38) | 80 | 1.04 | 0.68 | -0.6 |
| | $CH_4$ | | $1.34 \times 10^{-2}$ (62) | 93 | 1.08 | 0.44 | -0.6 |

[a] Rates corrected for 150 Torr $CF_2Cl_2$, 200 Torr $H_2$, 20Torr HCl, and 150°C

[b] The selectivity is independent of conversion.

[c] Bond energy calculated using Gaussian, with the B3PW91/6-311+G(2d,p)//B3PW91/6-311+G(2d,p) model

**Table 4. Comparison of kinetic parameters for the hydrodechlorination of $CF_2Cl_2$, $CF_3CFCl_2$ and $CH_2Cl_2$ on Pd/C**

## 4. Discussion

### *4.1. Determination of the Rate Determining Step of Hydrodechlorination Reaction*

The results in figure 4 and table 2 provide insight into finding the rate determining step. We believe the rate determining step of hydrodechlorination reaction involves the first C-Cl scission in a chlorinated compound. This argument is supported by results in Table 4. The agreement between experimental data and predicted values in is acceptable if one considers the vast span of the reactivity of these compounds. The turnover rate of most reactive CFCl3 is almost 105 times higher than the least reactive CF3Cl. While using the bond energy of the first C-Cl bond to break during reaction as the only parameter for prediction of relative turnover rate of each CFC compound, the maximum error we made is only a factor of 3. It is thus concluded that the correlation between turnover rate and the first C-Cl bond strength observed CF3CF3-xClx (x-1-3) compounds is also present for CF4-xClx (x-1-3) compounds, and C-Cl bond scission is involved in hydrodechlorination rate determining step.

Additional support for this conclusion is figure 4, which shows that for these compounds a linear correlation between the intrinsic activation energy and gas phase bond strength of the first C-Cl to break during reaction. We have already pointed out in section 3.3 that the intrinsic activation energy in equation 3 is a linear summation of two terms: (1) heat of reaction of step 1, CFC adsorption on surface; and (2) activation energy of step 2, the proposed rate determining step. If C-Cl bond scission is indeed the rate limiting step, then the activation energy of this step should be in a linear relationship with gas phase C-Cl bond strength (we have demonstrated that the enthalpy of surface C-Cl bond scission is linearly related to gas phase bond dissociation energy of C-Cl bond in a chlorinated compound using a linear free energy relationship 31, 43), and then intrinsic activation energy should also be linearly dependence on C-Cl bond strength. In fact, this is what figure 5 shows.

This finding of C-Cl bond scission being hydrodechlorination reaction rate determining step also has practical implication since it shows that for most CFC compounds, the prediction for rate of hydrodechlorination for a family of compounds can be achieved with satisfactory accuracy using their bond energy data, which are available by theoretical calculation method

The new kinetic results of $CF_{4-x}Cl_x$ (x-1-3) compounds, including their reaction rates and intrinsic activation energy, provide more support for the view that the first C-Cl bond scission on catalyst surface in the hydrodechlorination reaction [26, 31, 38, 45]. We have shown before using isotopic tracing experiments that the equilibrium 6: HCl + 2*= 2Cl* + $H_2$ does exist during hydrodechlorination reaction. Combining all these facts, it can be seen that the main elementary steps of these $CF_{4-x}Cl_x$ (x-1-3) are similar to those shown in scheme 1, which were derived from the kinetic study of $CF_3CF_{3-x}Cl_x$ (x-1-3) compounds. We thus conclude that the proposed hydrodechlorination reaction steps valid and can be applied to describe hydrodechlorination reaction of other chlorinated compounds.

### *4.2. Apparent Activation Energy of $CF_{4-x}Cl_x$ (x=1-3) Compounds*

The kinetic results shown in table 2 show a trend in apparent activation energy of these compounds, that is, apparent activation energy is significantly lowered with the increase of chlorine numbers in a reactant. In other words, it is easier to remove the halogens from the CFCs with higher chlorine content than those with less chlorine atoms. A similar trend has also been reported before in the hydrodechlorination reaction of $CF_3CF_{3-x}Cl_x$ (x=1-3) compounds [25, 26]. With the identification of the rate limiting step in $CF_{4-x}Cl_x$ (x=1-3) hydrodechlorination reaction, it is easy to understand the trend in apparent activation energy of different compounds. From equation 9, it can be noticed that apparent activation energy has the contribution of intrinsic activation energy of k', and thus apparent activation energy values to reflect some of the properties of intrinsic activation energy. We have already shown in figure 4 that intrinsic activation energy of these compounds increases with the increase in their first C-Cl bond energy due to the fact that C-Cl bond scission is the rate determining step in hydrodechlorination. In this way, apparent activation energy of these CFC compounds is also related to the bond strength of first C-Cl to break in reaction. Since C-Cl bond energy in turn is influenced by the number of chlorine atoms present in a chlorinated compound, we can observe the previously described relationship between apparent activation energy and molecular structure of chlorinated compounds bond energy.

Another trend that exists for $CF_2Cl_2$ and $CFCl_3$ is that for each hydrodechlorination product, the apparent activation energy for their different hydrodechlorination reaction products increases as more halogens are removed (shown in table 1). Though the current set of proposed reaction steps can explain the apparent activation energy trend from one compound to another in a series of chlorinated compounds with similar structures by considering hydrodechlorination rate limiting step, as just demonstrated, it lacks the ability to predict kinetic parameters of reaction steps that happen after first C-Cl bond scission step. However, we think that this trend can still be understood by considering the bond energy difference between C-F bond and C-Cl bond. It is found C-F bonds are approximately 100 kJ $mol^{-1}$ stronger than C-Cl bonds in a CFC molecule. Thus, in order to break the C-F bond, more energy is required and this will lead to higher apparent activation energy for products formed through C-F bond scission.

### *4.3. Reaction Orders of Hydrodechlorination Reaction of $CF_{4-x}Cl_x(X=1-3)$ compounds*

In section 3.2, we have compared the kinetic results, such as reaction orders of $CF_{4-x}Cl_x$ (x=1-3) compounds with each other and also compared them with the kinetic data of $CF_3CF_{3-x}Cl_x$ (x=1-3) compounds. Some differences are noticed, for example, compared with other CFC compounds, the HCl order of $CF_3Cl$ is less negative; the CFC order of $CF_3Cl$ is smaller than 1 compared with other CFC compounds. We find that these differences can also be explained within the scope of the proposed reaction steps.

*4.3.1. Deviation of HCl Order in the Hydrodechlorination Reaction of $CF_3Cl$.* The problem for apparent HCl order of $CF_3Cl$ can be examined by considering the way apparent reaction orders are measured and defined. When measuring apparent reaction orders, rate expression 9 is considered to be of the form of a power law rate expression

$$r=[R\text{-}Cl]^a[HCl]^b[H_2]^c \qquad (14)$$

where a, b, and c are the apparent reaction orders. In equation 9, it can be noticed that if the term $K'[HCl]/[H_2]^{0.5}$ is much greater than 1, a simplification to the shape of equation 14 is possible and the value of a, b, c would be 1, -1 and 0.5, respectively. However, if this assumption is not valid, a power law approximation of the original rate expression 9 would certainly bring in error and thus the value b would be less negative than 1. This deviation will depend on the magnitude $K'[HCl]/[H_2]^{0.5}$, that is, a smaller $K[HCl]/[H_2]^{0.5}$ (K or K'?) value can lead to a larger deviation from -1. At this point, it can be calculated from the data shown in Figure 3 that for $CF_3Cl$ compound, the term $K'[HCl]/[H_2]^{0.5}$ would not be larger enough than 1 with its K' values listed in table 3, thus this "1+" term can not be ignored and equation 9 can not be further simplified into a power law rate expression as shown in equation 14. Under this circumstance, the apparent HCl reaction order measured by still using a power law rate expression would show a deviation from –1. We have also compared the magnitude of K' value of $CF_3Cl$ with that of $CF_3CFHCl$. From the results reported before, K' value from $CF_3CFHCl$ apparent reaction order measurement is 2.37, which is larger than the K' values of $CF_3Cl$. Thus, the apparent HCl reaction order (measured as -0.80) of $CF_3CFHCl$ shows a smaller deviation from -1 than apparent HCl orders of $CF_3Cl$. This difference in the magnitude of K' values also explains the HCl apparent reaction order difference between $CF_3Cl$ and the other two CFC compounds studied here.

We also showed apparent HCl orders were dependent on reaction temperature: when the reaction temperature went up, the apparent HCl reaction order would show more deviation from -1. One example was given for $CF_3Cl$. This is not difficult to understand with the help of the proposed reaction steps. We have just explained the deviation of apparent HCl order is linked to the value of reaction constant K'. Since K' is physically related to the equilibrium constant between the surface H, Cl and gas phase $H_2$, HCl (shown in scheme 1), thus it is also temperature related. We have shown that the heat of reaction of this equilibrium is negative (figure 4), thus K' values decreases with the increase in temperature (as can been seen in table 3), and this will lead to an even larger deviation of apparent reaction order of a CFC compound.

*4.3.2. Deviation of CFC Order in the Hydrodechlorination Reaction of $CFCl_3$.* The results in table 2 indicate the apparent CFC order of $CFCl_3$ is smaller than that of either $CF_3Cl$ or $CF_2Cl_2$, which is close to 1. However, both rate expression 9 and equation 13 predict the apparent CFC order of any chlorinated compounds should be 1. Here we want to examine this deviation to see whether it has any effect on the validity of the proposed reaction steps.

Deviation of apparent CFC reaction order from 1 has been noticed previously in the hydrodechlorination reaction of some other chlorinated compounds, such as $CF_3CFCl_2$,

$CF_3CCl_3$ [26]. One possible reason for this deviation is that the CFC reactant may condense in the pores of the carbon catalyst support. During the hydrodechlorination kinetic study of $CF_3CFCl_2$ [26], it was discovered that the CFC order of this compound was also lower than 1 on Pd catalyst with high surface area carbon (1640 $m^2$ $g^{-1}$), but once the support was changed to a low surface area carbon (29 $m^2$ $g^{-1}$), the CFC order increased from 0.5 to 0.8. Additionally, the adsorption isotherms of $CF_3CFCl_2$ on the high surface area carbon indicated that a substantial amount of the carbon support pores might be filled with condensed $CF_3CFCl_2$ (b.p. 3.6°C) even at 100°C. If a reactant is in liquid phase, it will not respond to changes of its gas phase concentration and the reaction order will be zero. Under these circumstances, when a portion of hydrodechlorination is in gas phase and a portion in liquid phase, the apparent CFC order will be somewhere between 0 and 1. In the case of $CFCl_3$ hydrodechlorination reaction on the Pd/C used here, even though the carbon support has less pores than the one used for $CF_3CFCl_2$ (107$m^2$ $g^{-1}$), the closeness between the reaction temperature (95°C) and $CFCl_3$ boiling point (23.7°C) still makes the $CFCl_3$ condensation in the support pores to be unavoidable and thus lower the apparent CFC reaction order. Note that in the hydrodechlorination reaction kinetics measurement of $CFCl_3$, we had to keep the reaction temperature low to avoid heat and mass transfer limitations.

From this analysis, it can be concluded that the deviation of apparent CFC order of $CFCl_3$ is just an artifact brought by Pd/C catalyst system, but this artifact does not affect any elementary step in the proposed reaction steps. The same reaction steps are still present for $CFCl_3$ compounds, for example, C-Cl bond scission is the rate limiting step, as shown in figure 4; HCl is the reaction inhibitor through step 6, as can be noticed by its apparent reaction order. This analysis also provides further support for our conclusion that the set of hydrodechlorination reaction steps can be also applied to $CFCl_3$ hydrodechlorination reaction.

### 4.4. Product Selectivity in the Hydrodechlorination Reaction of $CF_{3-x}Cl_x$ (x-1-3) Compounds

Another important kinetic parameter shown in table 2 is the reaction selectivity of the hydrodechlorination products of $CF_{3-x}Cl_x$ (x-1-3) compounds. By studying the selectivity, information about the surface intermediates during the hydrodechlorination reaction and the possible reaction steps leading towards these products can be gathered. In this section, the collected selectivity results will be discussed and, when possible, compared to literature values in the context of their relationship with reaction steps.

*4.4.1. The Independence of Hydrodechlorination Reaction Selectivity on Conversion and Its Mechanistic Implication.* One interesting feature of the reaction selectivity for $CF_2Cl_2$ and $CFCl_3$ is that the reaction selectivity is not dependent on the hydrodechlorination reaction conversion in the range we have studied *(data provided in section 3).* This behavior has been noticed before in the hydrodechlorination reaction of chlorinated compounds by several research groups [8, 25-27, 31]. It implies that once a hydrodechlorination reaction product is formed on the Pd surface, it desorbs and it does not react further. This result can be understood by considering the reactivity difference between the reactant and its products. Once a C-Cl bond is broken and a H atom added, the product becomes more inert than the original reactant. For example, $CF_3CFHCl$ is one of the hydrodechlorination reaction products of $CF_3CFCl_2$ (like $CF_2Cl_2$, it also has a $–CCl_2$ structure), but it is almost 2000 times less reactive than $CF_3CFCl_2$ [26, 27, 31]. Currently, this model of a parallel reaction network leading to different hydrodechlorination products has been generally accepted and used to explain the kinetic results of many hydrodechlorination reactions [26, 27, 31].

*4.4.2. Products distribution pattern in the Hydrodechlorination Reaction of $CF_2Cl_2$ and $CFCl_3$*. One question in the study of $CF_2Cl_2$ and $CFCl_3$ is why the under-hydrogenated products, such as $CF_2HCl$ (in $CF_2Cl_2$ reaction) and $CFHCl_2$ and $CFH_2Cl$ (in $CFCl_3$ reaction) were not detected. In our previously studied chlorinated compounds, such as $CF_3CF_2Cl$ [26, 27, 31], nearly 10% of the product was $CF_3$-CHFCl; while for $CF_2Cl_2$, which also has two C-Cl bonds, no $CF_2HCl$ was detected during reaction. However, in the literature reports, some authors did observe the formation of $CF_2HCl$ on Pd/$AlO_3$, but its selectivity was less than 1% [13]. One exception is a study by Wiersma *et al.* [30], in which they found $CHClF_2$ could be produced with 20% selectivity from the hydrodechlorination of $CF_2Cl_2$. However, later on they concluded that an impurity in the catalyst support was responsible for this abnormal high selectivity towards $CHF_2Cl$ [20].

To explain the absence of under-hydrogenated products in hydrodechlorination, it is worthwhile to consider some hypothesis concerning the hydrodechlorination selectivity of $CF_2Cl_2$ in the literature. Wiersma *et al.* [20] suggested that the amount of chlorine adsorbed on the Pd surface would determine the selectivity towards $CF_2HCl$ and $CF_2H_2$. A low surface Cl concentration will make the formation of surface precursor of $CF_2HCl$, $CF_2Cl^*$, more difficult and thus lead to a low selectivity of $CF_2HCl$. Ramos *et al.* [27] also adopted this model in explaining the absence of $CHF_2Cl$ in their $CF_2H_2$ hydrodechlorination kinetic results on Pd model catalysts. They further suggested that since it is proposed that surface H, Cl are in equilibrium with the gas phase $H_2$ and HCl [31], this lower surface Cl coverage was caused by the high $H_2$ pressure used in their experiments. However, their argument based on $H_2$ pressure cannot explain our observed results for $CF_3CFCl_2$. We also used a high concentration of $H_2$ for its hydrodechlorination kinetic measurements (170Torr CFC, 340 Torr $H_2$ and 50 Torr HCl), similar to the situation for $CF_2Cl_2$ shown in experimental section, but under-hydrogenation product $CF_3CFHCl$ was found. We suggest this problem should be addressed by comparing the difference in reaction temperatures used for the kinetic measurements of these two compounds. The reaction temperature used in $CF_3CFCl_2$ experiments was 130 °C, while for $CF_2Cl_2$ the temperature chosen was 193 °C. We have already shown section 4.1.2 that surface Cl concentration can be affected by reaction temperature. This Cl coverage can be calculated using equation 8 once the value once $K_0^{0.5}$ value is known.. In fact, $K_0^{0.5}$ is the K’ in rate expression 9, which can be extracted from kinetic data as shown in section 3.3. Using K’ of $CF_2Cl_2$ shown in figure 3 and K’ of $CF_3CFCl_2$ calculated from previous results, this calculation shows that the Cl surface coverage under typical $CF_2Cl_2$ hydrodechlorination reaction condition in is 74%; while for $CF_3CFCl_2$, this value increase to 97%. With this analysis, we can conclude that it is actually the temperature difference of $CF_3CFCl_2$ and $CF_2Cl_2$ reactions that results in the

Cl coverage difference. According to Wiesmar *et al*. [20], this low Cl coverage may turn lead to a low selectivity of $CF_2HCl$, which may beyond our detection limit. -However, This 74% percent of Cl coverage is not very different from the 97% coverage we found in $CF_3CFCl_2$, and can not fully explain the absence of under-hydrogenated products in CF2Cl2 hydrodechlorination reaction. Another possibility is that $CF_2Cl$-* intermediate formed by losing one Cl from $CF_2Cl_2$ may not be stable on Pd surface and it will keep on losing another Cl than get hydrogenated. This hypothesis is still needed to be examined using first principle surface calculation method.

It is also noticeable that in the hydrodechlorination reaction of $CF_2Cl_2$, and $CFCl_3$, $CH_4$ is formed through C-F bond scission. At a first sight, this is surprising since in the gas phase, the C-F bond is almost 100 kJ $mol^{-1}$ stronger than the C-Cl bond. Thus, by just considering the bond strength argument, the C-F bond should not break under the hydrodechlorination reaction conditions. However, it has already been found that C-F bond scission step exists during the hydrodechlorination reaction of many CFC compounds, such as the $CF_3CF_{3-x}Cl_x$ (x=1-3) series compounds [25, 26, 31]. To explain this issue, it is necessary to consider the remaining carbon-halogen bond strength after the initial C-Cl bond scission. Kumaran *et al.* [46] showed that for $CF_2Cl_2$, after the first C-Cl bond scission, the remaining bond strength of the gas phase radical became significantly lowered. Thus, it is possible that in the hydrodechlorination reaction of $CF_2Cl_2$, the C-F bond strength in the CFC fragments can be decreased to a certain point that it is possible to remove the fluorides after the C-Cl scission and thus over-hydrogenated products, such as $CH_4$ here, can be generated.

### *4.5. Comparison of $CF_2Cl_2$ Hydrodechlorination Kinetics on Pd/C and Pd Model Catalysts*

First we would like to compare the selectivity data to make sure that carbon support did not affect our kinetic measurement. The support can participate into the hydrodechlorination reaction. Coq *et al.* [8] reported the formation of $CF_3Cl$ on Pd/$AlF_3$ catalyst in $CF_2Cl_2$ hydrodechlorination reaction, which were also observed by Ocal *et al.* [18], the two authors attributed $CF_3Cl$ formation to be fluorine/chlorine exchange between the reactant and the F in catalyst support. Another frequently used catalyst support, $Al_2O_3$, can also interfere with the hydrodechlorination reaction and alter the reaction selectivity by catalyzing disproportionation reaction of CFC compounds. Juszcyk *et al.* [13] found that $Al_2O_3$ can transform $CF_2Cl_2$ into $CClF_3$, $CH_2F_2$, ethane and ethylene. However, our $CF_2Cl_2$ hydrodechlorination selectivity matches that reported by Ramos *et al*. [27] (table 3) on Pd model catalysts. This comparison indicates that our results are not contaminated by the possible metal-support interaction and are genuine kinetics parameters of the hydrodechlorination reaction of $CF_2Cl_2$. Our pervious results also shows the carbon used in our experiments does not play any role in the hydrodechlorination reaction [25, 26].

With the knowledge that our kinetic data is free of artifacts due to support, we can proceed to compare turnover rates obtained on these different systems. It can be noticed that when our TOR on Pd/C catalyst is compared with TORs on Pd model catalysts, the difference is at most a factor of 2. The agreement is still acceptable when one considers the possible errors due to the large difference in the catalyst surface area of these catalysts. This closeness of TORs on different Pd catalysts has also been noticed for our previously studied a series of $CF_3CF_{3-x}Cl_x$ (x=1-3). Their TORs were very close on supported Pd, Pd black, Pd foil and Pd single crystals [25]. This TOR comparison results again indicate that the carbon support used in our study does not play any significant role in hydrodechlorination reaction.

The last item for comparison is the activation energy values. From the results in table 3, it can be seen that our data agrees well with the $CF_2Cl_2$ activation energy measured on Pd(111) single crystal by Ramos *et al.* [27]. This agreement indicates that the structure of most the of the active sites in the Pd/C catalyst is close to that of Pd(111). However, it is surprising to see that the activation energy measured on Pd (110) single crystal is smaller than on the Pd(111). Ramos explained this difference to be the greater difficulty in breaking the C-Cl bond on the Pd(111) surface due to a weaker Pd-Cl interaction than on Pd(110) surface [27], which is supported by the chlorine adsorption experiments on Pd (110) and Pd (111) [47, 48]. It should be stressed again that in measuring apparent activation energy of hydrodechlorination reaction, the inhibition effect of HCl must be taken into account. Apparent activation energy is usually calculated by increasing the temperature and then measuring the corresponding TOR. When HCl is a reaction inhibitor but not added into reaction system, as the temperature is increased the rate will not increase as fast as expected because more HCl is also being formed to inhibit hydrodechlorination process. In this situation, it can be derived that the measured "apparent activation energy" will be one-half of the actual value. In fact, some of $CF_2Cl_2$ activation energy results in literature are unreliable to be compared with due to the HCl inhibition effect. For example, in measuring the $CF_2Cl_2$ activation energy on $Pd/Al_2O_3$, HCl was not added into the reaction system and its inhibition effect was not taken into consideration by Juszczyk *et al.* [13]. The apparent activation energy results reported by them [13] for $CF_2Cl_2$ are thus approximately a factor of 2 lower than those calculated in this study and the results reported for Pd(111) [27], as just discussed. It should be noted that HCl inhibition effect was recognized in the reports of Ramos *et al.* [27] and HCl reaction order of -1 was used in their calculation of $CF_2Cl_2$ hydrodechlorination reaction kinetics.

### *4.6. Comparison of Hydrodechlorination reaction of $CF_3CFCl_2$, $CF_2Cl_2$ and $CH_2Cl_2$*

When these three compounds, which all have a $–CCl_2$ structure, are compared, several differences can be noticed. The most noticeable difference in table 6 for the three compounds is their turnover rates. $CF_2Cl_2$ is the least reactive of all three reactants, with its hydrodechlorination turnover rate more than 2 orders of magnitude lower that the one for either $CF_3CFCl_2$ or $CH_2Cl_2$. In their paper, Ramos *et al.* [27] tried to explain the difference between the hydrodechlorination reaction rate of $CF_3CFCl_2$ and $CF_2Cl_2$. They have suggested that since bond strength of the C-Cl bond in $CF_2Cl_2$ is higher that of the $CF_3CFCl_2$, the C-Cl in $CF_2Cl_2$ is more difficult to break than the C-Cl bond in $CF_3CFCl_2$ and thus resulting in a lower hydrodechlorination rate [27]. Our bond energy results in table 4 also indicate the C-Cl bond of $CF_2Cl_2$ is 17 kJ $mol^{-1}$ higher than the C-Cl of bond in $CF_3CFCl_2$. Using this bond energy difference and the procedure shown in section 3.4, we can predict their turnover rate difference. It is calculated that the hydrodechlorination rate $CF_3CFCl$ should be at least 125 times faster than the rate of $CF_2Cl_2$. However, the bond energy comparison argument cannot explain the reactivity difference between $CH_2Cl_2$ and $CF_2Cl_2$. For $CH_2Cl_2$, the C-Cl bond strength is 319 kJ mol$^{-1}$ and is higher than the value for $CF_2Cl_2$, but $CH_2Cl_2$ has a higher hydrodechlorination reaction rate, as shown in table 6. A similar situation was noticed for $CH_3Cl$ and $CF_3Cl$. The bond energy of $CH_3Cl$ is 346 kJ mol$^{-1}$, while the bond energy of $CF_3Cl$ is 337 kJ mol$^{-1}$, but $CH_3Cl$ (TOR $1.5\times10^{-4}$ s$^{-1}$) is 2 orders more reactive than $CF_3Cl$. It is thus concluded that although comparing the bond strength can offer explanation for the reactivity difference inside one series of chlorinated compound with similar structure, it has to be used with great caution when one wants to compare the turnover rate of chlorinated compounds that belong to different series, such as $CH_2Cl_2$ and $CF_2Cl_2$ discussed here. However, a trend can be observed by comparing turnover rates the $CH_3Cl$, and $CH_2Cl_2$, with those of $CF_3Cl$ and $CF_2Cl_2$. It can be noticed that by increasing the fluorine number in a molecule, there is a corresponding decrease in the reaction rate. Gellman *et al.* [49, 50] found the same trend in the dechlorination study on Pd single crystal of a family of four chlorinated compounds with different fluorine content ($CH_3CHCl_2$, $CH_3CFCl_2$, $CH_2FCFCl_2$ and $CF_3CFCl_2$). To compare the rate of chlorinated compounds in different families, all the substitution groups on the C-Cl bond must be considered. Another problem with $CF_2Cl_2$ is that under-hydrogenated product $CF_2HCl$ is not found in its hydrodechlorination reaction, while $CF_3CFHCl$ and $CH_3Cl$ are present as the hydrodechlorination product of $CF_3CFCl_2$ and $CF_2Cl_2$, respectively. In previous sections, a hypothesis was proposed to explain this difference, that is, the lower Cl coverage during the $CF_2Cl_2$ hydrodechlorination.

## 5. Conclusions

The hydrodechlorination reaction kinetics of a series of $CF_{3-x}Cl_x$ (x=1-3) compounds has been studied on Pd/C catalyst to investigate their hydrodechlorination reaction steps. It is found that the intrinsic activation energy of the rate determining step of these CFC compounds is in a linear Polanyi relationship with the strength of the first C-Cl bond to break. Additionally, it has been shown in our report that by using known kinetic correlations and C-Cl bond energy, it is possible to predict the relative hydrodechlorination reaction rates of different chlorinated compounds in a family with acceptable accuracy. The kinetic results obtained from these experiments support a previously proposed Langmuir-Hinshelwood type of hydrodechlorination reaction mechanism. That is, (1) gas phase $H_2$ and HCl are in equilibrium with surface H and Cl; (2) adsorbed Cl is the most abundant surface intermediate and (3) the irreversible scission of the first C-Cl bond in chlorinated compounds is the rate-determining step. From this set of reaction steps, the overall rate of hydrodechlorination reaction can be derived as $r=k'[CFC]/(1+K'[HCl]/[H_2]^{0.5})$.

The kinetic results of $CF_{3-x}Cl_x$ (x=1-3) compounds has been compared with those of $CF_3$-$CF_{3-x}Cl_x$ (x=1-3) and $CH_{4-x}Cl_x$ (x=1-4) compounds. Many similar features, such as the relationship between rate and C-Cl bond strengths and negative reaction orders of HCl, can be noticed. This suggests that the proposed steps can be applied to describe the hydrodechlorination reaction kinetics of a large number of chlorinated compounds. However, under-hydrogenated products are not found in the hydrodechlorination reaction of $CF_{3-x}Cl_x$ (x=1-3). It is also noticed that the more fluorine atoms a chlorinated compound has, the lower would be its hydrodechlorination reaction rate, for example, the hydrodechlorination reaction rate of $CF_2Cl_2$ is lower than that of $CH_2Cl_2$. We have also compared the hydrodechlorination kinetics results of $CF_2Cl_2$ obtained on Pd/C catalyst with those obtained on Pd model catalysts and the agreement is good. This suggests that hydrodechlorination reaction might be structure insensitive and the carbon support used in our reactions does not bring artifacts into the kinetics measurements.

Although the proposed reaction steps can predict hydrodechlorination reaction rates, orders and activation energy trend of $CF_{3-x}Cl_x$ (x=1-3) compounds, it still lacks the ability to explain their hydrodechlorination selectivity. To achieve this goal, the current reaction steps model must be expanded to include more elementary steps beyond the rate limiting step, C-Cl bond scission.

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# Paper 7

## Kinetic Study of the Hydrodechlorination Reaction of 1,1-, 1,2-, 1,3- and 2,2-Dichloropropane on Pd/C Catalyst

## Abstract

The hydrodechlorination reaction kinetics of 1,1-, 1,2-, 1,3- and 2,2-dichloropropane were studied on Pd/C catalyst to investigate the reaction steps of doubly chlorinated hydrocarbons. We found that for these dichloropropanes, the hydrodechlorination reaction turnover rates correlated with the strength of the first C-Cl bond to break during reaction. It was noticed that a Polanyi type relationship existed between intrinsic activation energy and the bond energy of the first C-Cl bond to break during reaction. These facts indicate that the scission is the rate limiting step of hydrodechlorination reaction is the scission of first C-Cl bond. Hydrodechlorination product HCl was found to be an inhibitor in hydrodechlorination reactions of dichloropropanes, suggesting that adsorbed chlorine covers active Pd sites in hydrodechlorination reaction. Hydrogen and HCl were proposed to be in equilibrium with the surface H and Cl specie. The hydrodechlorination reaction overall rates of dichloropropanes can be derived as $r=k'[CFC]/(1+K'[HCl]/[H_2]^{0.5})$. Isotopic tracing experiments with deuterium revealed that besides C-Cl bond scission, C-H bond scission step was also present in the hydrodechlorination reaction of these dichloropropanes, and hydrodechlorination reaction product with multiple deuterium atoms were found.

**Keywords:** hydrodechlorination, reaction kinetics, dichloropropane, deuterium, isotope tracing

## 1. Introduction

In hydrodechlorination reaction, C-Cl bond(s) in an organic molecule is reduced into C-H bond(s) by $H_2$. This reaction is widely used in many chemical processes. For example, chlorine is used as “place holder” in the manufacture of $CF_3CFH_2$ (a widely used refrigerant), and in the last step of its synthesis, hydrodechlorination reaction is used to convert $CF_3CFCl_2$ into the desired product [1]. Hydrodechlorination reaction also can be used to transform unwanted products into useful ones. One example like this is conversion of $CCl_4$, a by-product generated by undesired side reactions in many chlorination processes, into solvent $CHCl_3$ or $CH_2Cl_2$ [2, 3] using hydrodechlorination reaction. With the increasing environmental consciousness of our modern society, hydrodechlorination reaction has gradually found applications as a way to address current environmental issues. It can be used to remove chlorine(s) on a compound that need to be disposed of. This kind of removal is sometimes mandatory before the compounds can be released due to its adverse effect on the environment. For instance, hydrodechlorination reaction can be applied in the area of waste water treatment [4, 5]. It can also be used to reduce the chlorinated aromatic compounds in petroleum refinery exhaust [6, 7], and this method is proposed to have advantages over traditional incineration method which produces other harmful multi-ring aromatic compounds. Another important possible application of catalytic hydrodechlorination reaction is to convert existing chlorofluorocarbons (CFCs) [1, 8], which are connected to the depletion of the earth’s ozone layer [1], into hydrofluorocarbons (HFCs). These HFCs are much less harmful to the environment, at the same time, they retain many of the useful properties of CFCs, and thus can serve as replacements for CFCs [9]. All these practical applications require the knowledge of catalytic hydrodechlorination reaction.

Most of previously published reports about hydrodechlorination reaction focused on CFC compounds such as $CF_2Cl_2$ (a previously widely used refrigerant), and single metal catalysts such as supported Pd catalysts [10-23]. However, a variation of hydrodechlorination reaction named hydrogen assisted dechlorination reaction on bimetallic catalyst systems, has recently received increasing attention. In this type of reaction, Cl is removed from a organic molecule, similar as regular hydrodechlorination reaction. However, the molecule is not further hydrogenated into saturated compound, instead, a double bond is remained. One of its possible applications is by-product reclamation. For example, 1,2-dichloropropane compound is formed as a by-product with substantial quantity in the commercial production of propylene oxide via propylene-chlorohydrin method. Since 1,2-dichloropropane can not found many uses as reactant or intermediate in other reactions, it has to be disposed of. However, the disposal process is both difficult and expensive. But, it is found that 1,2-dichloropropane can be converted back to propylene and recycled by hydrogen assisted dechlorination reaction using a Pt-Cu bimetallic catalyst [24]. Many research groups have since then studied hydrogen assisted dechlorination reaction of 1,2-dichloropropane and its structure analogue 1,2-dichloroethane with different bimetallic catalyst systems to optimize the reaction, to study the reaction mechanism and roles of different metals in the reaction [25-30]. There are also suggestions of using this reaction to transform $CF_2Cl_2$ into $CF_2{=}CF_2$ as monomer for Teflon production [25, 27, 28]. This reaction is also of interest to us and in this publication, we will expand our hydrodechlorination reaction study to a group of dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-). We will first conduct reaction kinetics study of these dichloropropanes on single metal catalyst Pd/C. It is hoped that the information obtained for this research on single metal can later on be applied to help us understand the hydrogen assisted dechlorination reactions of these dichloropropanes on bimetallic catalysts, which will be investigated later in our group.

More importantly, the kinetic results of this group of dichloropropanes will be used to probe the reaction steps of hydrodechlorination reaction on Pd catalyst. Base on our previous experience, we have discovered that studying families of chlorinated compounds with similar structure is an ideal way of generalize reaction step. A few papers have already addressed the possible reaction steps of this reaction [19-22, 31-37]. Based on these reports and our own reaction kinetics and isotopic tracing study of hydrodechlorination reaction kinetics of a series CFCs [19, 22, 35], we have proposed that the rate-determining step to be the irreversible scission of C-Cl bond in an chlorinated compound. The other gas phase species in the reaction system, $H_2$ and HCl, are proposed to be in equilibrium with surface adsorbed H and Cl. In this proposed reaction mechanism, surface adsorbed Cl was assumed to the most abundant surface intermediate. This set of reaction steps and the rate expression equation derived from them is summarized in scheme 1.

$\text{R-Cl} + * = \text{R-Cl}*$, with an equilibrium constant $K_{CFC}$ (1)

$\text{R-Cl}* \rightarrow \cdots$, rate-determining step with a rate constant $k_0$ (2)

$r = k_0K_{CFC}[R\text{-}Cl][*]$, rate expression (3)

$H_2 + 2* = 2H*$, equilibrated (4)

$H* + Cl* = HCl + 2*$, equilibrated (5)

$2HCl + 2* = H_2 + 2\,Cl*$, (4) + (5), with equilibrium constant $K_0$ (6)

$[*] + [Cl*] = [L]$, site balance (7)

$$[*] = \frac{[L]}{1 + \frac{[HCl]}{[H_2]^{0.5}}},$$ free site concentration (8)

**Scheme 1. Possible hydrodechlorination reaction steps**

Form this set of reaction steps, the overall hydrodechlorination rate can be calculated as:

$r = k'[R\text{-}Cl]/\{1 + K'[HCl]/[H_2]^{0.5}\}$, with $k' = k_0K_{CFC}[L]$ and $K' = K_0^{1/2}$ (9)

In this paper, our tasks will be generalizing the possible reaction steps of dichloropropanes and comparing them with this previously proposed reaction steps shown in scheme 1.

Some efforts will also be directed to exploring dichloropropane hydrodechlorination reaction steps beyond rate limiting step. In literature, isotopic tracing technique has been proved to a valuable tool for this purpose. Campbell and Kemball [38] found through reaction of $CH_3$-$CH_2Cl$ with $D_2$ on Pd films that C-H bond could also break during chloromethane hydrodechlorination reaction beside C-Cl bond scission. However, we reported before that in the reaction of $CF_3$-CFHCl with deuterium on Pd/C, only C-Cl bond broke and the most abundant product (98%) was the mono-deuterated product $CF_3$-CFHD [19]. In this paper, $D_2$ exchanged hydrodechlorination reactions will be performed on these dichloropropanes and their deuterated product distributions will be examined to find out whether C-H scission is present in their hydrodechlorination reaction steps.

## 2. Experimental Methods

### *2.1. Catalysts*

The catalyst used in this study was a 5% (weight percent) Pd catalyst supported on activated carbon obtained from Degussa with a serial number E 9011 XR/W 5%. It had a BET area of 107 $m^2$ $g^{-1}$ and a total pore volume of 1.15 $cm^3$ $g^{-1}$. The pore size distribution and pore volume of the Degussa catalyst were measured with a Quantachrom Autosorb-1 volumetric sorption analyzer. The original catalyst sample was ground with a mortar and pestle and the fraction between 40 and 60 mesh size was retained for use in hydrodechlorination reactions.

### *2.2. Reactants*

All the dichloropropane compounds were purchased from Sigma Chemical Company. The mixture of 21% HCl in He (used as HCl input during reactions) was from Matheson and was made with technical grade HCl and Matheson purity He. A mixture of $H_2$ and methane, certified as ultrahigh purity, was also obtained from Matheson. This mixture contained 1033 ppm methane, used as an internal standard. The hydrogen-methane mixture was passed through a filter containing 5% Pd/C catalyst to remove any oxygen in the line into water and trap it on the carbon support. The $H_2$ used for catalyst reduction (from BOC Gases) was also passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was obtained from BOC gases. For the helium used as GC-MS carrier gas, it was passed through a mass spectrometer gas trap (HP model 5182-3467) to be purified before feeding into the system. The deuterium used in this study was obtained from Cambridge Isotope Laboratories. It contained 99.6% $D_2$ and 0.4% HD, and before use it was passed through the same Pd membrane purifier used for the purification of $H_2$.

### *2.3. Reactor Configuration*

The gas manifold was constructed of 1/8" diameter stainless steel tubing. Gas flows were controlled with mass flow controllers (Porter Instrument Co.). The volumetric gas flow rates from the mass flow controllers had been carefully calibrated with a bubble flow meter except for the He/HCl mixture. In this case, its flow rate was determined by varying the composition of a mixture of the He/HCl gas and another $H_2/CH_4$ gas stream, then observing and analyzing the change in signal intensity of the methane peak by gas chromatography.

The reaction portion of the flow system was made of Pyrex glass and the reactor was made out of quartz with the catalyst held on a fritted disk. Most of the kinetic reactions were carried out in the well-mixed reaction system in continuous stirred tank reactor

(CSTR) mode. Heating of the reactor was provided a VWR 21100 tube furnace controlled by a Eurothem model 808 temperature controller. The reaction temperature inside the reactor was measured through a thermocouple well extending onto the catalyst bed. When running at CSTR mode, the inlet and outlet flow rates of the reactor were around 100 $cm^3$ $min^{-1}$. The mixing in the CSTR was provided by a bellows pump (Senior Flexonics, MB-21) with a circulation rate of 1400 $cm^3$ $min^{-1}$, allowing differential operation for the reactor and minimizing heat and transport effects during reaction. The presence of heat and mass transfer limitations that might exist in the reaction system had been tested using the Madon-Boudart test [39]. From the results presented in a previous work [22], heat and mass transfer limitations were not found even with the a Pd/C catalyst supported on high surface area carbon, where transport limitations would be most severe. We thus concluded that our results from the experiments were not affected by heat and mass transfer limitations artifacts.

The gas mixture coming out of the reactor was injected into a modified GC-MS (GC-HP 5880A and MS-HP5970A). The column used in the GC was a 5% Krytox 143AC, 60/80 Carbopack B HT 20' x 1/8"column from Supelco. The effluent from the GC column was simultaneously analyzed by a flame ionization detector (for quantitative analysis) on the GC and by the MS (for qualitative analysis). The gas was sampled into the mass selective detector through a fused silica polyimide capillary column (I.D. 51μm, O.D. 363μm) of 0.75m length. GC response factors for all dichloropropane reactants and their hydrodechlorination products had been calibrated against methane using the hydrogen-methane mixture gas. After exiting the reaction system, the gas effluent was flowed through a NaOH solution to neutralize the HCl present in the stream before releasing.

### *2.4. Data Collection Procedure*

Two to five hundred milligrams of fresh Pd/C catalyst was initially loaded into the reactor and reduced for 3 hrs at 300°C with 50 $cm^3$ $min^{-1}$ $H_2$. For repeated reactions, the catalyst was treated with 50 $cm^3$ $min^{-1}$ $H_2$ for 0.5 to 1 h at 150°C before the following hydrodechlorination experiments.

When conducting kinetic measurements in the CSTR reactor, the inlet gas concentrations were regulated by the mass flow controllers and the reaction temperature was adjusted by the temperature controller. For a particular set of conditions, the reaction would be let run for 30-60 minutes to get stabilized before a data point was taken. The gas mixture was sampled into the GC-MS system using an automatic valve on the GC. During the course of the experiments, the changes in concentration or temperature were chosen in random order so that any variation would not introduce a systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated and another data point taken. By ensuring that this last point agreed with the first point, it could be shown that there was no significant deactivation of the catalyst during the reactions.

The reaction conditions used for hydrodechlorination reaction kinetics of dichloropropanes are listed below. It can be noticed the reaction temperatures for the four compounds vary a lot. This is due to their different hydrodechlorination reaction activities, which will be shown later, and we would like to keep reaction conversion low (<5%) to maintain the concentration of reaction gases constant so as to simplify the mathematical treatment. In most reactions, excessive HCl was added into the reaction system, since we found HCl formed during hydrodechlorination process is an inhibitor of this reaction. By adding HCl, we could further reduce the variables in reaction system. Apparent activation energy was determined by measuring the reaction rate at different temperatures while keeping the reactant concentrations constant, and then using an Arrhenius plot. Reaction orders were determined by varying the amount of reactant to be studied while keeping all the other variables constant.

For 1,2-dichloropropane, the conditions for the determination of apparent activation energies were 181-219 °C, 35 Torr of dichloropropane, 341 Torr of $H_2$, and 62 Torr of HCl. For the chlorinated compound order determination, the conditions were 205 °C, 19-48 Torr of dichloropropane, 221 Torr of $H_2$, and 38 Torr of HCl. For the $H_2$ order, the conditions were 207 °C, 27 Torr of dichloropropane, 86-266 Torr of $H_2$, and 38 Torr of HCl. For the HCl order, the conditions were 206 °C, 28 Torr of dichloropropane, 220 Torr of $H_2$, 18-60 Torr of HCl. Additionally, HCl reaction order experiments were repeated at three other temperatures: 187,220 and 242 °C.

For 1,3-dichloropropane, the conditions for the determination of apparent activation energies were 173-214 °C, 21 Torr of dichloropropane, 350 Torr of $H_2$, and 60 Torr of HCl. For the chlorinated compound order determination, the conditions were 193 °C, 8-23 Torr of dichloropropane, 225 Torr of $H_2$, and 40 Torr of HCl. For the $H_2$ order, the conditions were 194 °C, 12 Torr of dichloropropane, 89-225 Torr of $H_2$, and 37 Torr of HCl. For the HCl order, the conditions were 193 °C, 12 Torr of dichloropropane, 244 Torr of $H_2$, 21-60 Torr of HCl. HCl reaction order experiments were repeated at: 175, 204 and 218 °C.

For 1,1-dichloropropane, the conditions for the determination of apparent activation energies were 125-170 °C, 50 Torr of dichloropropane, 330 Torr of $H_2$, and 60 Torr of HCl. For the chlorinated compound order determination, the conditions were 147 °C, 27-77 Torr of dichloropropane, 210 Torr of $H_2$, and 35 Torr of HCl. For the $H_2$ order, the conditions were 146 °C, 38 Torr of dichloropropane, 85-261 Torr of $H_2$, and 37 Torr of HCl. For the HCl order, the conditions were 148°C, 40 Torr of dichloropropane, 224 Torr of $H_2$, 20-76 Torr of HCl. HCl reaction order experiments were repeated at: 160,173 and 182 °C.

For 2,2-dichloropropane, the conditions for the determination of apparent activation energies were 117-147 °C, 41 Torr of dichloropropane, 300 Torr of $H_2$, and 91 Torr of HCl. For the chlorinated compound order determination, the conditions were 120 °C, 38-76 Torr of dichloropropane, 200 Torr of $H_2$, and 45 Torr of HCl. For the $H_2$ order, the conditions were 118 °C, 52 Torr of dichloropropane, 80-251 Torr of $H_2$, and 40 Torr of

HCl. For the HCl order, the conditions were 117 °C, 50 Torr of dichloropropane, 214 Torr of $H_2$, 23-78 Torr of HCl. HCl reaction order experiments were repeated at: 126, 136 and 147 °C.

We also performed deuterium exchanged hydrodechlorination reactions of these compounds. The reaction conditions for 1,2-dichloropropane were 30 Torr of dichloropropane, 224 Torr of $D_2$ and 202 °C; for 1,3-dichloropropane, the reaction conditions were 26 Torr of dichloropropane, 532 Torr of $D_2$ and 187 °C; for 1,1-dichloropropane, the reaction conditions were 50 Torr of dichloropropane, 459 Torr of $D_2$ and 158 °C; for 2,2-dichloropropane, the reaction conditions were 48 Torr of dichloropropane, 432 Torr of $D_2$ and 120 °C.

### *2.5. Surface Area Measurements*

The total surface area was measured using the BET method with $N_2$. The Pd metal surface area was measured by the hydrogen-oxygen titration method according to Benson *et al.* [40]. The experimental setup consisted of a volumetric system constructed in Pyrex and pumped by a liquid nitrogen trapped diffusion pump. The amount of gas adsorbed was determined by measuring pressure change in a pre-calibrated volume on the system with a pressure transducer (MKS model 127).

The samples were reduced in flowing $H_2$ (50 $cm^3$ $min^{-1}$) for 3 h at 300°C before the Pd surface area measurements. After the initial reduction, subsequent hydrogen-oxygen titration was conducted at 100°C. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression is valid under the assumption of spherical particles and a Pd atom density of $1.27\times10^{19}$ atoms $m^{-2}$ [41].

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced and then passivated catalysts was also conducted. Samples for XRD analysis were reduced in same manner as described above, and then passivated with 60 Torr of $O_2$. Particle size was determined from the width of the diffraction peak using X-ray line broadening technique. Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

### *2.6. Error Analysis*

We compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in reaction orders were at a maximum 10% or maximum 0.1 in 1.0 and errors in the apparent activation energy were at most 10 kJ $mol^{-1}$. Turnover rate reproducibility was better than 90%.

## 3. Results

### *3.1. Catalyst Properties*

The BET surface of the carbon support of the Pd/C catalyst 107 $m^2$ $g^{-1}$ and it was non-microporous in nature. Non-microporous carbon supported Pd was used in this study because in our previous research we found some CFC reactants, like CFC114a and CFC113a, could condense in the pores of microporous carbon support during reaction. This condensation effect caused a decrease of the reaction order for CFC in the hydrodechlorination reaction [22]. To prevent the condensation effect from causing artifacts in the measurement of the reaction orders, Pd supported on low specific surface area carbon was chosen as the catalyst. It has also been shown before that carbon support itself plays no role in the hydrodechlorination reaction [19, 22]. The PME value measured by $H_2$-$O_2$ titration method was 8.3% and based on this information the Pd particle size was calculated to be 13.3 nm. However, the Pd particle size measured by XRD line broadening for this Pd/C sample was only 5nm and was about three times smaller than that determined by chemisorption.

These parameters are representative of catalysts before the hydrodechlorination reaction. Except for 1,2-dichloropropane hydrodechlorination reaction, no significant deactivation was observed during the reaction of other reactants used in this research, thus we do not expect any significant change in the properties of the catalyst after reaction.

### *3.2. Hydrodechlorination Reaction Kinetics of Dichloropropanes*

The kinetic parameters for the hydrodechlorination of dichloropropanes on Pd/C, including apparent activation energy, reaction orders, selectivity and reaction rate, are summarized in table 1. Note that the reaction rates reported in table 1 are corrected to a standard condition so as to make the comparison of the reactivity of different compounds possible. The standard condition is 150 Torr of the chlorinated compound, 200 Torr $H_2$, 20 Torr HCl, 390 Torr balance He and 150 °C.

Three products were formed in the hydrodechlorination reaction of 1,2-dichloropropane, corresponding to Cl removal from different positions, with propane as the dominant product. It is also interesting that in the conversion range explored (2%-14%), when the first C-Cl bond breaks, the Cl attached to the secondary carbon was removed preferentially to the Cl on primary carbon. The selectivity of 1-chloro-propane was about 8 times higher than that of 2-chloro-propane. Compared with the reaction orders of previously reported CFC compounds [22], whose HCl orders were very close to -1, the observed HCl order of 1,2-dichloropropane were less negative. This kind of HCl order deviation has been noticed before in some chlorinated hydrocarbon compounds such as chloromethane compounds. There was a trend for the activation energies of the two products, that is, as the number of Cl removed increased, the apparent activation energy also increased.

Two products were formed in the hydrodechlorination reaction of 1,3-dichloropropane. However, in the conversion range we studied (0.7%-4%), propane was not the dominant product as in hydrodechlorination reaction of 1,2-dichloropropane, instead, 1-chloropropane was now the major product. Again, it was found that the observed HCl order of 1,3-dichloropropane was less negative than -1, and the apparent activation energy of different products increased corresponding to the increase in the number of Cl removed, similarly to the situation in 1,2-dichloropropane. This trend was also observed for the other two dichloropropane compounds studied here. The corrected reaction rate of 1,3-dichloropropane was slightly lower than that of 1,2-dichloropropane.

The kinetic results on 1,1-dichloropropane had to be conducted under comparatively lower temperature due to its higher reactivity than either 1,2- or 1,3-dichloropropane, which can be seen from its corrected turnover rate listed in table 1. Two products, propane and 1-chloro-propane were present during the reaction. In a conversion range of 0.6% to 6%, the selectivity was constant at a level of about 73% and 27%, respectively. Interestingly, this product distribution is very similar to what we observed in $CH_2Cl_2$ hydrodechlorination, in which $CH_3Cl$ and $CH_4$ were also produced with around 70% and 30% selectivity. The apparent HCl reaction orders of this compound still showed deviation from the expected value of -1.

For 2,2-dichloropropane, there are two chlorines attached to the same carbon, similarly to 1,1-dichloropropane, but its hydrodechlorination reaction turnover rate was almost 9 times higher than that of 1,1-dichloropropane. However, their product distributions were comparable, with about 70% under-hydrogenated product and 30% fully-hydrogenated product, similarly to $CH_2Cl_2$ and the previously discussed 1,1-

dichloropropane. Selectivity was independent of reaction conversion in the range from 4% to 27%.

| Reactant | Coversion range | Products | Reaction Orders | | | Ea (kJ·mol$^{-1}$) | Selectivity | TOR[a] (s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | | HCl | $H_2$ | DCPA | | | |
| 1,2-dichloropropane | 2-14% | Propane | -0.46 | 0.21 | 1.14 | 108 | 74% | $1.71\times10^{-3}$ |
| | | 1-chloro-Porpane | -0.49 | 0.63 | 1.21 | 78 | 23% | $5.68\times10^{-4}$ |
| | | 2-chloro-propane | -0.45 | 0.44 | 0.77 | 88 | 3% | $5.47\times10^{-5}$ |
| 1,3-dichloropropane | 0.7-4% | Propane | -0.47 | 0.06 | 0.91 | 85 | 32% | $4.93\times10^{-4}$ |
| | | 1-chloro-propane | -0.75 | 0.51 | 0.98 | 73 | 68% | $1.05\times10^{-3}$ |
| 1,1-dichloropropane | 0.6-6% | Propane | -0.55 | 0.27 | 0.90 | 96 | 73% | $1.71\times10^{-2}$ |
| | | 1-chloro-propane | -0.44 | 0.54 | 0.93 | 81 | 27% | $6.73\times10^{-3}$ |
| 2,2-dichloropropane | 4-27% | Propane | -0.55 | 0.22 | 0.78 | 102 | 68% | $1.53\times10^{-1}$ |
| | | 2-chloro-propane | -0.45 | 0.41 | 0.68 | 71 | 32% | $1.04\times10^{-1}$ |

[a]Rates corrected for 150 Torr chlorinated compounds, 200 Torr $H_2$, 20 Torr HCl, and 150°C.

**Table 1. Kinetic results for dichloropropane compounds**

### *3.3. Extracting k’ and K’ in Rate Expression 9 and Calculating Reaction Energetics*

There are two constants k’ and K’ in the reaction expression $r=k'[R\text{-}Cl]/\{1+K'[HCl]/[H_2]^{1/2}\}$ and they contain information about the reaction energetics. The rate constant k’ in equation 3 is the product of the equilibrium constant of CFC adsorption on the Pd surface (step 1) and the rate constant for the rate-determining step (step 2). Thus, the measured activation energy extracted from k’ is the sum of the heat of reaction of and activation energy. This sum will be called “intrinsic activation energy” of hydrodechlorination reaction, to distinguish it from the overall apparent activation energy listed in table 1; K' is defined in scheme 1 as the square root of the equilibrium constant of step 6, and the energy term associated with K' is one half of the heat of reaction of step 6. We found it was possible to measure k' and K' and thus the reaction energetics for dichloropropanes.

*3.3.1. Procedure for Extracting k', K' from Kinetic Measurements*. One procedure to extract k', K' from kinetic measurement is to linearize the rate expression to the following form:

$$1/r=1/\{k'[R\text{-}Cl]\}+\{K'[HCl]/[H_2]^{1/2}\}/k[R\text{-}Cl]\} \qquad (10)$$

in this equation, if we keep the [R-Cl] concentration constant and use the term $[HCl]/[H_2]^{1/2}$ as the independent variable, then a plot of variable 1/r against $[HCl]/[H_2]^{1/2}$ will yield a straight line. The intercept and slope of this straight line the kinetics can be used to calculate the rate constant k' and equilibrium constant K'. One way to change $[HCl]/[H_2]^{1/2}$ value is to alter the HCl partial pressure during reaction while keeping the $H_2$ partial pressure constant. In fact, this experimental procedure is the same as the one used for HCl reaction order measurement, in which only HCl partial pressure is varied under a constant temperature. From this analysis, it is found that the turnover rate results from hydrodechlorination apparent HCl reaction order measurement can be processed with equation 10 to obtain k' and K'. One example for calculating k' and K' for 1,3-dichloropropane is shown in figure 1.

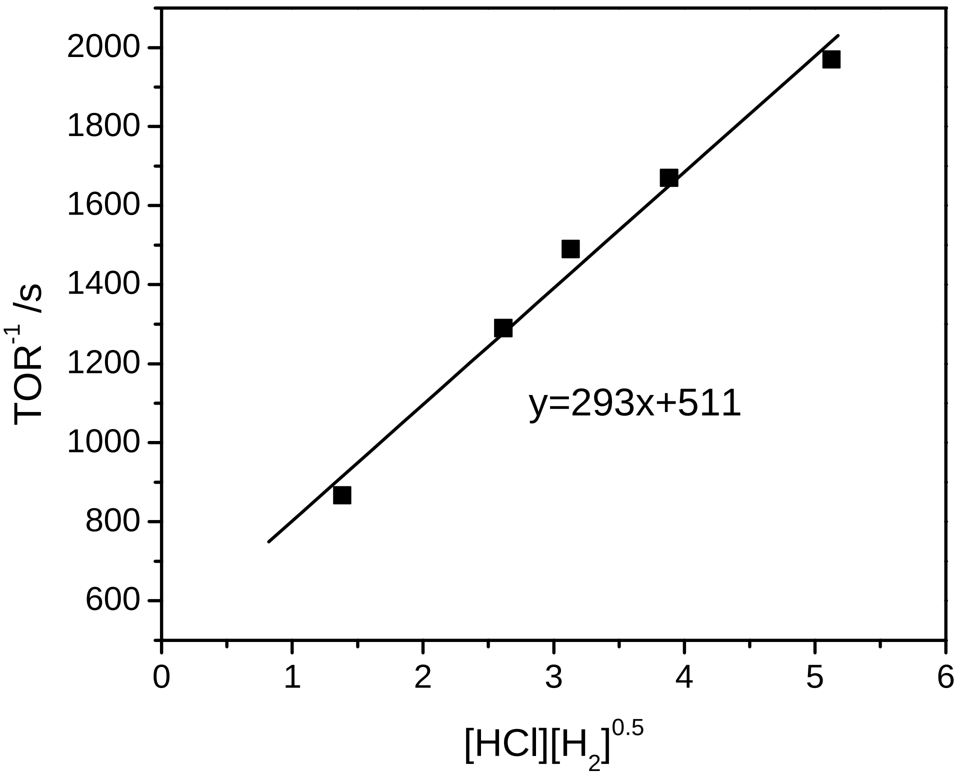

**Figure 1. Calculating reaction constant k' and K' for 1,3-dichloropropane. Reaction was performed with the 17 Torr of CFC, 241 Torr of $H_2$, 21-60 Torr of HCl, and reaction temperature 191°C.**

With the values of k' and K' extracted, one can then use equation 9 to predict the hydrodechlorination reaction rates at a certain temperature. This procedure is illustrated for 1,3-dichloropropane in figure 2. It can be seen that equation 9 can predict the rates with an error of at most 10%.

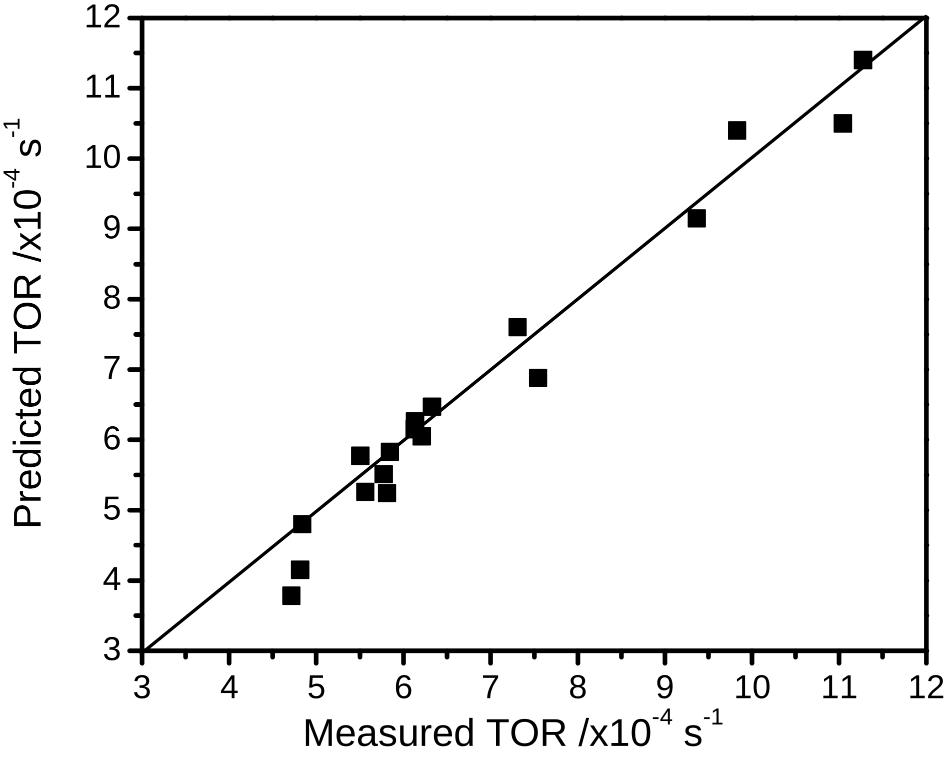

**Figure 2.** **Comparison between measured hydrodechlorination reaction rate and predicted rate using equation 9 of 1,3-dichloropropane**

### *3.3.2. Calculating Reaction Energetics*

The rate (k') and equilibrium (K') constants are extracted at different temperatures to calculate the intrinsic activation energy of equation 3 and heat of reaction of step 6. It required the measurement of rates as a function of HCl concentration for each dichloropropane compound at four different temperatures. As an example, table 2 shows the extracted k' and K' values of 1,3-dichloropropane at different temperatures using equation 10. Apparent HCl orders obtained from the experiments are also listed in table

2. This parameter was found to be temperature dependent and became less negative as the reaction temperature increased. The natural logarithm of k' and K' of all dichloropropanes are plotted against $T^{-1}$ in two graphs, one for the calculation of intrinsic Ea of equation 3 (figure 3); the other for the calculation of ΔH (figure 4). The ΔH of step 6 was around 60 kJ $mol^{-1}$ for three compounds (1,3-, 1,1-, 2,2- dichloropropanes). However the enthalpy value measured for 1,2-dichloropropane was about 40 kJ $mol^{-1}$ higher than the value of the other compounds.

| **Reactant** | **Kinetics constants** | | | | |
|---|---|---|---|---|---|
| 1,3-dichloropropane | Temperature(°C) | 175 | 190 | 204 | 218 |
| | K' | 0.61 | 0.54 | 0.41 | 0.35 |
| | k' | $6.91\times10^{-5}$ | $1.21\times10^{-4}$ | $1.79\times10^{-4}$ | $3.26\times10^{-4}$ |
| | HCl order | 0.69 | 0.62 | 0.53 | 0.46 |

**Table 2. Rate constant k' and equilibrium constant K' in equation 9 and apparent HCl orders of 1,3-dichloropropane**

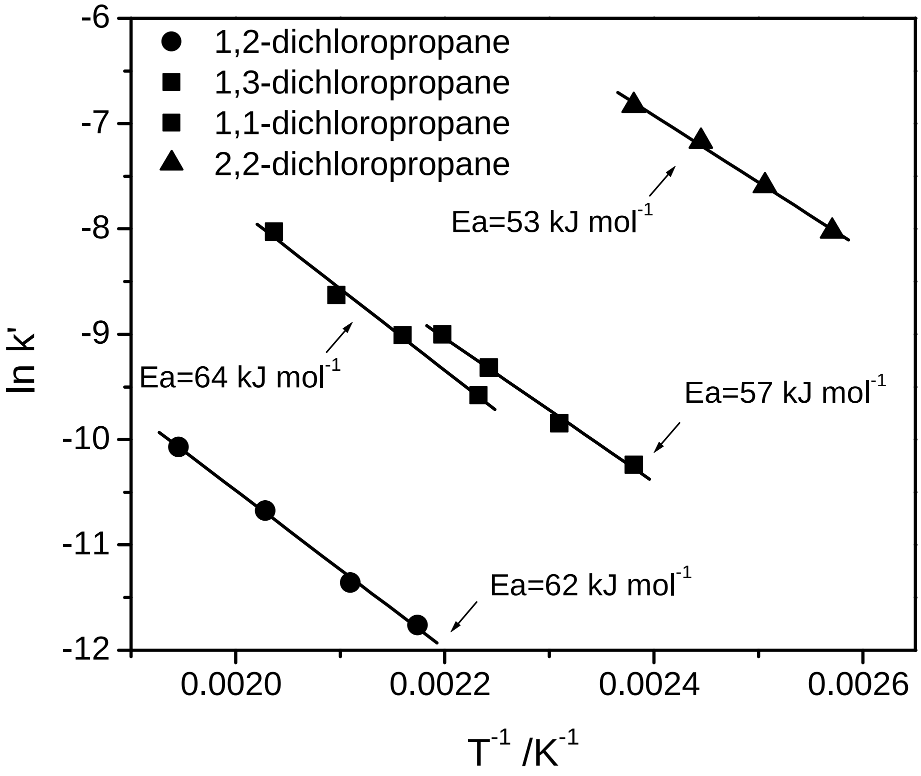

**Figure 3. Intrinsic activation energy of the rate limiting step in scheme 1 for dichloropropane compounds**

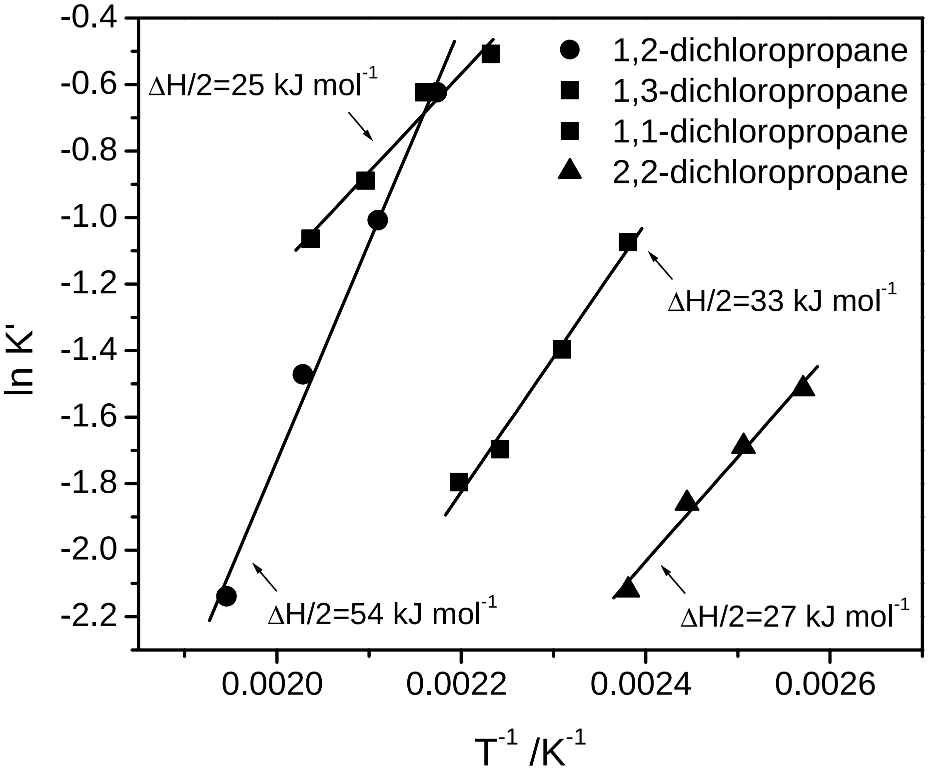

**Figure 4. Determination of ΔH of equilibrated step 6: 2HCl + 2*=$H_2$ + 2Cl* in scheme 1 for dichloropropane compounds**

### *3.4. C-Cl Bond Energy of Dichloropropanes and Prediction of Hydrodechlorination Reaction Rates*

The bond strength of the first C-Cl bond to break during hydrodechlorination reaction of a chlorinated compound is of special interest to us, since we have found for a family of chlorinated compounds with similar structures, such as $CF_3CF_{3-x}Cl_x$ (x=1-3) compounds studied before, that there is a correlation between a chlorinated compound's hydrodechlorination reaction rate and the bond strength of the first C-Cl to break from the molecule[22]. To further study the relationship between bond strength and hydrodechlorination reaction kinetics, we calculated gas phase C-Cl bond energy for all the dichloropropanes studied here. In our study, we used a quantum chemistry calculation software package Gaussian 98 [42] to achieve this purpose. DFT (Density Functional Theory) calculation method was used and the model used was B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(2d,p). Bond energy was calculated by taking the energy difference of the molecule as a whole and its fragments, that is, E(A-B)=E(A)+E(B)-E(AB). These calculated bond energy values are shown in table 3.

| **Reactant** | **TOR ($s^{-1}$)$^a$** | **Relative TOR** | **C-Cl Bond Strength ($kJ \cdot mol^{-1}$)$^b$** | **Predicted Relative TOR** |
|---|---|---|---|---|
| 1,3-dichloropropane | $1.54\times10^{-3}$ | 1 | 334 | 1 |
| 1,2-dichloropropane | $2.35\times10^{-3}$ | 1.5 | 329 (at 1 position)<br>319 (at 2 position) | 8.4 |
| 1,1-dichloropropane | $2.38\times10^{-2}$ | 15 | 312 | 22 |
| 2,2-dichloropropane | $3.27\times10^{-1}$ | 145 | 301 | 110 |

[a] Rates corrected for 150 Torr dichloropropane, 200 Torr $H_2$, 20Torr HCl, and 150°C

[b] Bond energy calculated using Gaussian, with the B3PW91/6-311+G(2d,p)//B3PW91/6-311+G(2d,p) model

**Table 3. Bond energy of dichloropropane compounds and comparison of measured turnover rates with predicted turnover rates using Polanyi relationship**.

We have shown a procedure for predicting relative hydrodechlorination reaction rate from gas phase C-Cl bond strength in a previous paper [22]. This method starts with a Polanyi-type relationship [43], which suggests that for a family of similar reactions the difference in activation energy is linearly related to the difference in reaction enthalpy,

$\Delta Ea = \alpha\Delta|\Delta H|$. Combined with rate expression $k = k_0 e^{-Ea/RT}$ and with the assumption that $k_0$ is the same for a group of reactants with similar structure, it is possible to express the relative rate (under the same reaction conditions) as a function of heat of reaction difference of surface C-Cl scission process.

$$\frac{r_1}{r_2} = \frac{k_1}{k_2} = e^{-\Delta Ea/RT} = e^{-\alpha\Delta|\Delta H|/RT} \qquad (11)$$

It should be noted that for calculating the hydrodechlorination reaction rate, the $\Delta H$ term in equation 11 is for the heat of reaction of C-Cl bond scission on Pd surface, and not the gas phase dissociation energy C-Cl bond ($\Delta H_{R\text{-}Cl}$). The heat of reaction $\Delta H$ of surface C-Cl bond scission is difficult to measure with our experimental techniques. However, we have demonstrated that by applying a linear free energy formalism [44], similar to the one in the Hammett relation used in physical-organic chemistry, $\Delta|\Delta H|$ in equation 11 can be shown to vary linearly with the difference in gas phase C-Cl bond energy $\Delta H_{\text{R-Cl}}$ of a family of chlorinated compounds, that is: $\Delta|\Delta H| = (1-\beta)\Delta|\Delta H_{\text{R-Cl}}|$. Substituting the value for $\Delta|\Delta H|$ in equation 11 yields equation 12:

$$\frac{k_1}{k_2} = e^{-\Delta Ea/RT} = e^{-\alpha(1-\beta)\Delta\left|\Delta H_{R-Cl}\right|/RT} \qquad (12)$$

This new equation allows one to calculate the relative turnover rate of any member in the series as a function of the rate constant of a reference member if the difference in enthalpy of the dissociation reaction in the gas phase $\Delta H_{\text{R-Cl}}$ is known. The experimental value that gives the best fit is one that corresponds to $\alpha(1-\beta) = 0.5$. The predicted relative rate results using this method and experimentally measured relative TORs are also shown in Table 3. It can be noticed that the calculated relative turnover rates match well the experimentally measured rates.

### *3.5. The Relationship between the Strength of the First C-Cl Bond to Break During Reaction and Intrinsic Activation Energy of Equation 3 for Dichloropropanes*

In section 3.3, when predicting relative hydrodechlorination reaction rates of these dichloropropanes, we made the assumption that there is linear relationship between the activation energy of rate limiting step and first C-Cl bond strength (please change this expression throughout). To verify if this assumption is valid or not, we plotted the intrinsic activation energy of these compounds against the bond strength of the first C-Cl bond to break during reaction. Though we can not measure the activation energy of rate limiting step directly, we have pointed out that the intrinsic activation energy is a linear summation of heat of reaction of adsorption of a chlorinated compound and the activation energy value of its rate limiting step, thus intrinsic activation energy can be used as a proper indicator of activation energy of rate limiting step. This plot is shown in figure 5 and it reveals a linear relationship between the two parameters. In fact, it is similar to the Polanyi relationship we just discussed in section 3.4, which states that reaction activation energy is a linear function of reaction enthalpy for a family of reactions.

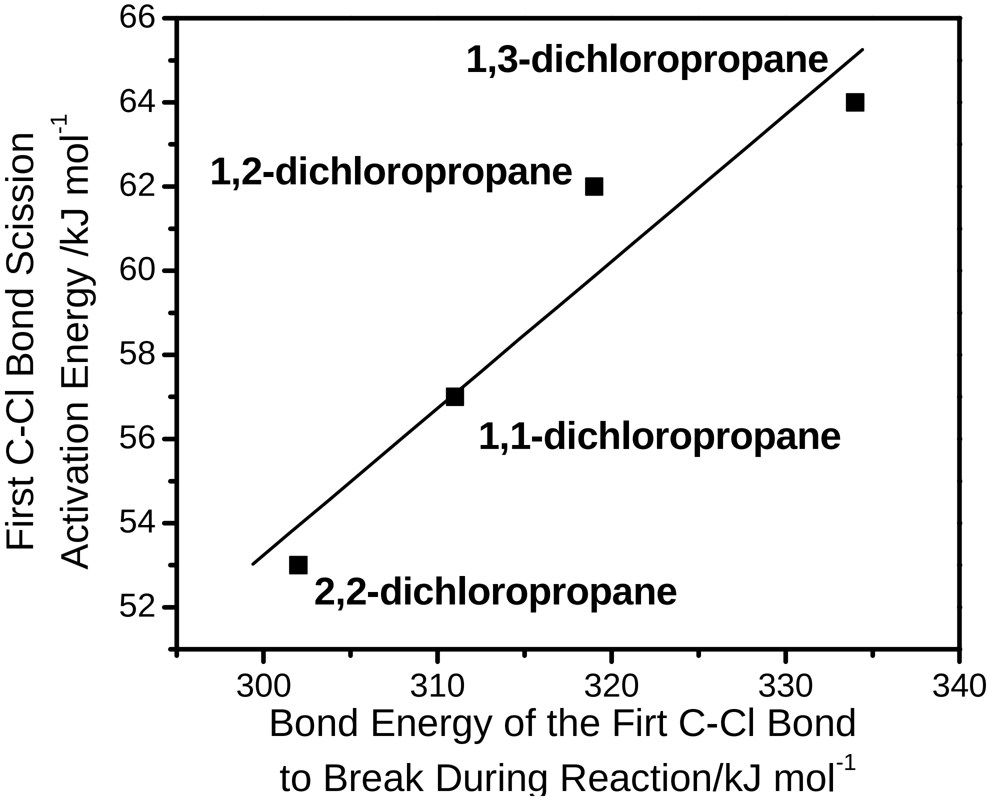

**Figure 5. Relationship between the first C-Cl bond strength and intrinsic activation energy of rate limiting step of dichloropropane compounds**

### *3.6. Product Distribution of Deuterium Exchanged Hydrodechlorination Reaction of Dichloropropanes.*

Deuterium exchanged hydrodechlorination experiments of dichloropropanes were conducted to study whether C-H bond scission occurs during hydrodechlorination. For each of the dichloropropane compounds, the reaction mixture was analyzed by GC-MS, and the distribution of deuterated products was calculated. These results are summarized in table 4. It can be seen from the results that for all dichloropropanes, C-H bond scission was present in their hydrodechlorination reaction, similar to the case of ethane chloride 38. There was also a trend in the product distribution, that is, the level of deuterium exchange increased with the degree of dechlorination. In the case of 1,3-dichloropropane, when the first Cl is removed, although some C-H bond could be exchanged into C-D, chloropropane with only one deuterium was still the main product; however, when the second C-Cl bond was broken to form propane, the most abundant product was fully deuterated propane, indicating nearly all C-H bonds in the reactant were exchanged to a C-D bond.

| **Reactant** | **Conversion** | **Product** | **Percentage of deuterated Species (%)**[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | ***d1*** | ***d2*** | ***d3*** | ***d4*** | ***d5*** | ***d6*** | ***d7*** | ***d8*** |
| 1,3-dichloropropane | 4% | Propane | | 1 | 1 | 7 | 15 | 8 | 19 | 49 |
| | | 1-chloro-propane | 71 | 19 | 3 | 1 | 2 | 2 | 3 | |
| 1,2-dichloropropane | 8% | Propane | 1 | 12 | 1 | 5 | 10 | 8 | 25 | 38 |
| | | 1-chloro-propane | 48 | 12 | 11 | 7 | 6 | 11 | 6 | |
| | | 2-chloro-propane | 38 | 8 | 10 | 11 | 10 | 13 | 10 | |
| 1,1-dichloropropane | 5% | Propane | | 6 | 14 | 3 | 4 | 7 | 15 | 55 |
| | | 1-chloro-propane | 63 | | 28 | | 8 | | | |
| 2,2-dichloropropane | 7% | Propane | | | 4 | 4 | 3 | 9 | 29 | 62 |
| | | 2-chloro-propane | 14 | 21 | 14 | 9 | 11 | 16 | 14 | |

[a] the number that follows “d” indicates the number of deuterium atoms in a product.

**Table 4. Product distribution of deuterium exchanged hydrodechlorination reaction of dichloropropanes**

## 4. Discussion

### *4.1. Possible Reaction Steps of Hydrodechlorination Reaction of Dichloropropanes*

One purpose of this research is to learn whether the reaction steps of dichloropropanes are comparable to the reaction steps listed in scheme 1, which were derived from CFC hydrodechlorination reaction [19, 20, 22]. We would like to investigate if the hydrodechlorination reactions of dichloropropanes are the same as in scheme 1.

First, we will find out the rate limiting step of hydrodechlorination. From our kinetic data, we believe the hydrodechlorination rate limiting step of these dichloropropane compounds is still the removal of the first Cl atom from a molecule. This conclusion is also supported by the results in table 3. It shows C-Cl bond energy is closely related to hydrodechlorination reaction rate. The agreement between experimental data and predicted values in table 3 is acceptable if one considers the vast span of reactivity for these compounds. The turnover rate of most reactive 2,2-dichloropropane is more than $10^2$ times higher than the least reactive 1,3-dichloropropane. While using the bond energy of the first C-Cl bond to break during reaction as the only parameter for prediction of relative turnover rate of each compound, the maximum error we made is at most a factor of 3. This good agreement suggests that the removal of the first Cl from a chlorinated compound is indeed involved in hydrodechlorination rate determining step. The result presented in figure 5 is another support for our rate determining step assumption. We have already shown that the intrinsic activation energy of equation 3 is a linear summation of the heat adsorption (step 1) and activation energy of the rate-determining step (step 2). Additionally, using a linear free energy relationship [20, 43], we have also demonstrated the enthalpy of surface C-Cl bond scission is linearly related to gas phase bond dissociation energy of first C-Cl bond in a chlorinated compound. If C-Cl bond scission is indeed the rate limiting step, then activation energy of step 2 should be in a Polanyi relationship with the strength of gas phase C-Cl bond energy and the activation energy of step 3 would also in turn be linearly dependent on C-Cl bond strength. In fact, figure 5 does show such dependence. Thus, we can conclude that the removal of the first Cl atom on Pd surface is the rate determining step of hydrodechlorination reactions of dichloropropanes.

Secondly, we also need to investigate the role of HCl and $H_2$ in the hydrodechlorination reaction system. In table 2, we have shown that the apparent HCl reaction order of these dichloropropanes are negative, indicating it is an inhibitor and Cl* is occupying active Pd sites in their hydrodechlorination reactions, as proposed by scheme 1. We have shown in another publication [35] with isotope tracing technique that $D_2$ and HCl are in equilibrium with surface adsorded D and Cl species, and the forward and reverse rates of this equilibrium are nearly 400 times faster than the hydrodechlorination reaction rate of $CF_3CFCl_2$ at 150 °C. It is noticed that the reactivity of these dichloropropanes is lower or comparable to that of $CF_3CFCl_2$ (corrected turnover rate at standard conditions $3\times10^{-1}$ $s^{-1}$), thus it is believed that the hydrodechlorination rates of these dichloropropanes are also smaller than the forward or reverse rate of the equilibrium between HCl and $H_2$. For example, for the most reactive 2,2-dichloropropane, its hydrodechlorination reaction rate is $2.63\times10^{-1}$ $s^{-1}$ at standard condition, while the forward and reverse rate of equilibrium 6 is would be $1.2\times10^{-1}$ $s^{-1}$. This comparison further strengthens the view that C-Cl bond scission in the rate limiting step of hydrodechlorination reactions of dichloropropane compounds.

In summary, the newly obtained kinetic results of hydrodechlorination reactions of dichloropropane compounds, shows that they also follow the same hydrodechlorination reaction steps as shown in scheme 1, that is (1) C-Cl bond is the rate limiting step; (2) $H_2$ and HCl are in equilibrium with surface H* and Cl* and (3) Cl* is the most abundant surface intermediate. In fact, the results in figure 2 showing it is possible to predict hydrodechlorination reaction rate using derived overall rate expression 9 and calculated k', K', provides further support for the validity of this set of reaction steps. It is thus concluded scheme 1 is a general set of reaction steps of most chlorinated compounds.

### *4.2. Reaction Rates of Dichloropropanes*

As can be seen from the data reported in table 1, the hydrodechlorination reaction rates of the dichloropropanes seem to be related to their structure. The corrected turnover rates can be sorted in the following order: 1,3-dichloropropane<1,2-dichloropropane<1,1-dichloropropane<2,2-dichloropropane. Generally, the hydrodechlorination reaction rate increases with the addition of more Cl atoms in the same carbon. A similar trend has also be noticed in the turnover rates of other families of chlorinated compounds: $CF_3CF_2Cl$ $<CF_3CFCl_2<CF_3CCl_3$ [20], $CF_3Cl<CF_2Cl_2<CF_3Cl$, $CH_3Cl<CH_2Cl_2<CHCl_3<CCl_4$. With our knowledge of hydrodechlorination reaction steps of these dichloropropanes, it is possible to explain this trend by considering their C-Cl bond energies.

We have suggested in section 4.1 that the first C-Cl bond scission is the rate limiting step in the hydrodechlorination reaction. As a result, for a family of chlorinated compounds, the hydrodechlorination reaction rate will correlate with the C-Cl bond strength. Furthermore, as shown in table 3, as additional chlorines are introduced into one carbon, the C-Cl bond strength will drop substantially. With this analysis, it is understood why the rates on 1,1- and 2,2- dichloropropanes are more than 2 orders of magnitude higher than either 1,2-dichloropropane or 1,3-dichloropropane. The bond energy comparison can also help to explain why the 2,2-dichloropropane hydrodechlorination rate is higher than that of 1,1-dichloropropane; although they have two chlorines attached to one carbon, due to the difference of the chemical environment around the C-Cl bond, the first C-Cl bond strength of 2,2- dichloropropane is about 10 kJ mol$^{-1}$ lower than that of 1,1-dichloropropane, resulting in a higher rate at the same reaction condition. In fact, the prediction based solely on calculated C-Cl bond strength in table 3 does show that 2,2-dichloropropane should be 5 times more reactive than 1,1-dichloropropane, which is close to experimental observation.

### *4.3. Reaction Orders of Dichloropropanes*

The proposed reaction steps can also be used to explain the apparent reaction orders of dichloropropanes. In our previous studies [19, 20, 22] and literature reports [15], we found for CFC compounds, their reaction orders were approximately first order in CFC, half order in $H_2$ and negative first order in HCl, and this prompted us to propose the Langmuir-

Hinshelwood type of reaction steps shown in scheme 1. However, there is a noticeable discrepancy between the apparent HCl order of dichloropropanes parameters and those of CFC compounds. For dichloropropanes, the HCl orders were all less negative, as shown in table 1. We believe this difference is caused by the way the apparent HCl reaction order is defined. In measuring the HCl apparent order, rate expression equation 9 is further simplified into a power law rate expression: $r=k''[R\text{-}Cl]^a[H_2]^b[HCl]^c$. When the term "$K'[HCl]/[H_2]$" in equation 9 is much larger than 1 in the denominator of the original rate expression, a should be 1, b should be close to 0.5 and c should be close to -1, which is the result we have seen for CFC compounds. However, for dichloropropanes, with the K' values of all the dichloropropanes shown in table 2 and figure 4, the magnitude of $K'[HCl]/[H_2]$ is not much larger than 1, and a power law simplification will produce an apparent HCl order between 0 and –1 and $H_2$ reaction order between 0 and 0.5.

Table 3 shows that the apparent HCl order of 1,3-dichloropropane becomes less negative when the reaction temperature goes up. This is also related to the magnitude of K' values. Since K' is the equilibrium constant between surface H, Cl and gas phase $H_2$, HCl (shown in scheme 1), it is a temperature dependent term. We have shown that the heat of reaction of this equilibrium is negative (figure 4), thus the K' value decreases with increasing temperature (as can been seen in table 3), and this will lead to a larger deviation of apparent reaction order for a CFC compound.

Studying reaction orders can also help us in learning more details about the proposed reaction steps. From the results in table 1, it can be noticed that for all dichloropropanes, the reaction orders of chlorinated compounds are very close to 1, as we have found for most of the CFC compounds. The first order of chlorinated organic compounds suggests that for the rate-determining step, C-Cl bond scission, the active site may consist of one Pd atom. In a previous paper [22], we have proposed that the rate-determining step (RDS) for a generic R-Cl reactant is the oxidative addition, forming the surface intermediate R-Pd-Cl, with Pd making a σ-bond with the carbon atom in the R fragment. This type of addition can be found in the organotransition metal chemistry literature. The oxidative addition of an alkyl halide R-X on a Pd(0) species to produce a σ-alkyl metal halide complex has been reported [45], although examples are more common when R is aryl or vinyl [46]. At this point, we have no direct evidence for this proposed step, and the hypothesis is largely based on the analogy with organometallic chemistry. But the oxidative addition model can best explain the experimental observations, such as the order of chlorinated species.

### *4.4. Reaction Selectivity*

All the dichloropropane species studied here have multiple reaction products, corresponding to different degree of hydrogenation. In the selectivity results shown in table 1, for most of the compounds, fully hydrogenated product, propane, is the most abundant hydrodechlorination product, and this preferential production of fully hydrogenated product has been noticed for the hydrodechlorination reactions of many chlorinated compounds on Pd catalysts [15, 19, 23, 47]. But for 1,3-dichloropropane, 1-chloro-propane is the main product. The higher selectivity of 1,3-dichloropropane towards under-hydrogenated product can be explained by considering the structure of this compound. In 1,3-dichloropropane, there are two chemically identical C-Cl chlorine bonds, and removal of either of them will lead to the formation of 1-chloro-propane. Thus, statistically more under-hydrogenated product can be formed in the hydrodechlorination reaction of 1,3-dichloropropane;.

Comparing C-Cl bond energy in a chlorinated molecule can also explain the selectivity of 1,2-dichloropropane. For this compound, it has two C-Cl bonds at different carbon positions. Thus, during its hydrodechlorination reaction, when removing the first C-Cl bond, two products, 1-chloropropane and 2-chloropropane can be produced. But as can be seen from the data in table 1, much more 1-chloropropane is formed than 2-chloropropane, indicating it is easier to remove the Cl on center carbon that the Cl on side carbon. When the bond strengths of these two C-Cl bonds are compared using the values listed in table 4, it can be noticed that the C-Cl bond at primary carbon position is stronger than the C-Cl bond at the secondary carbon position. Because of this difference, the removal of the C-Cl bond at 1 position is more difficult than removing the chlorine on the centre carbon. The measured apparent activation energy of this compound also support this idea, to remove the chlorine atom at 1 position, the energy barrier is 88kJ mol$^{-1}$; to remove the chlorine at 2 position, the energy barrier is only 78kJ mol$^{-1}$. Consequently, 1-chloropropane is formed preferentially with higher selectivity than 2-chloropropane.

We also noticed that 1,1-dichloropropane and 2,2-dichloropropane have similar selectivity, with about 70% towards fully hydrogenated product and 30% towards under hydrogenated product, even though 2,2-dichloropropane is 14 times more reactive than 1,1-dichloropropane. Similar selectivity was also found for dichloromethane. These observations indicate that as long as there is a $–CCl_2$ structure in chlorinated hydrocarbons, the hydrodechlorination reaction selectivity on Pd catalyst would be constant. These findings suggest that hydrodechlorination selectivity is also affected by the structure of chlorinated compounds.

In our previous study, we found the hydrodechlorination reaction selectivity of many chlorinated compounds is independent of reaction conversion [20, 22]. This is due to the fact that the reaction products are much less reactive than the reactant. Once a product is formed, it does not undergo further hydrodechlorination under the reaction conditions used for the original reactant and thus all the reaction products are formed in parallel pathways. For the dichloropropanes, the parallel reaction pathway hypothesis is still valid for 1,1 and 2,2-dichloropropane. We have calculated the C-Cl bond strength in 1-chloropropane and 2-chloropropane, which are 343 kJ $mol^{-1}$ and 335 kJ $mol^{-1}$, respectively, and much stronger than the first C-Cl bond in 1,1 and 2,2-dichloropropanes. These two compounds are thus less reactive than either 1,1- or 2,2- dichloropropane. Though we did not measure the hydrodechlorination reaction rate of 1-chloropropane, we do have the result of hydrodechlorination reaction rate of its structural analogue chloromethane, it was $2\times10^{-4}$ $s^{-1}$ on Pd/C catalyst under the standard conditions used in this paper. In this way, 1-chloropropane or 2-chloropropane would not undergo hydrodechlorination reaction under the hydrodechlorination reaction conditions we used for kinetics measurements of 1,1- or 2,2-dichloropropane. However, the parallel reaction pathway model is not valid for 1,3- and 1,2-dichloropropane. For these two compounds, the C-Cl bond energy in the reactant is comparable to the values of the one on the products 1- and 2-chloropropane. In fact, a selectivity test for 1,3-dichloropropane under constant temperature shows that when the reaction conversion is increased, more propane is formed. The selectivity for 1,2- and 1,3-dichloroproapnes are thus extrapolated to zero conversion.

### *4.5. Investigation of reaction steps beyond the rate determining step and possible surface intermediates.*

The product distribution data shown in table 4 of deuterium exchanged hydrodechlorination reactions of the dichloropropanes shows that besides C-Cl bond scission, C-H bond scission was also present in hydrodechlorination reactions of dichloropropanes and a significant amount of reaction products with multiple deuterium atoms could be formed. This finding is similar to what have been reported for $CH_3CH_2Cl$ by Campbell and Kemball. [38] , who found doubly deuterated ethane was the main product of hydrodechlorination reaction of chloroethane with $D_2$. We have also repeated deuterium exchanged hydrodechlorination reaction of $CH_3CH_2Cl$, and confirmed that C-H bond can be broken during the reaction, and 58% of product ethane had more than one deuterium in the molecule. These results imply that for some hydrogen containing chlorinated compounds, C-H bond scission is also an important elementary step in their hydrodechlorination reaction mechanism. However, it should be stressed that not all hydrogen containing chlorinated compounds have significant C-H bond scission. For example, for $CF_3CFHCl$, which also has both C-H and C-Cl bond, it was found that less than 1% of its hydrodechlorination product contains deuterium during its $D_2$ exchanged reaction. Another example is $D_2$ exchanged hydrodechlorination reaction of $CH_3Cl$ and $CH_2Cl_2$, which are also chlorinated hydrocarbons like the dichloropropanes studied here. For $CH_3Cl$'s reaction with $D_2$, only 2% of methane products were with deuterium in a conversion range from 3% to 14%; while for $CH_2Cl_2$, only 3% of chloromethane (formed through first C-Cl bond scission) contained deuterium. By comparing these $D_2$ exchange experiment results, we found C-H bond scission only happens to chlorinated hydrocarbons with longer carbon chains, for example, chloroethane and dichloropropanes. It is thus concluded from the comparison of all of these experiments that the $CH_3$- or $CH_2$- groups adjacent to the C-Cl bond could undergo C-H bond scission and lead to products with higher deuterium content.

Another conclusion we can make here is that when a chlorinated compound has more than one chlorine, the deuteration level increases with the degree of dechlorination. For example, as shown in table 4, for 1,3-dichloropropane, after the first C-Cl scission, only 29% of product 1-chloro-propane had more than one deuterium in the molecule; however, when the second C-Cl bond breaks, nearly all the product propane had more than two deuterium atoms, and almost 50% of the propane was fully deuterated. A similar situation has been noticed for other chlorinated compounds with multiple chlorines, such as $CH_2Cl_2$. For its first C-H bond, only 3% product $CH_3Cl$ has more than one deuterium; for its fully dechlorinated product $CH_4$, the percentage of isotopic analogue with exchanged deuterium increases to 21%. This trend might be due to the fact that when chlorine is removed from a chlorinated compound, the bond energy of the remaining bonds in the molecule decreases substantially [48].

## 5. Conclusions

The hydrodechlorination reactions of a family of four dichloropropane compounds (1,1-, 1,2-, 1,3- and 2,2-) were studied on Pd/C catalyst by means of kinetic measurements and isotopic tracing. we found that by using the calculated C-Cl bond energy, it was possible to predict the relative hydrodechlorination reaction rates of the dichloropropanes with acceptable accuracy. Furthermore, it was found that the activation energy of the rate determining step of these dichloropropane compounds was in a linear Polanyi relationship with their the bond strength of the first C-Cl bond to break during hydrodechlorination reaction. These results indicate that the removal of the first chlorine atom from a chlorinated compound is the rate limiting step of hydrodechlorination reaction. Hydrodechlorination product HCl was found to be an inhibitor for the dichloropropanes' hydrodechlorination reactions. This fact suggests that adsorbed chlorine occupies active Pd sites during hydrodechlorination reaction. The kinetic measurements can be best explained by a previously proposed Langmuir-Hinshelwood type of hydrodechlorination reaction mechanism. That is, (1) gas phase $H_2$ and HCl are in equilibration with the surface H and Cl; (2) adsorbed Cl is assumed to be the most abundant surface intermediate and (3) irreversible removal of the first Cl atom in chlorinated compounds to be the rate-determining step. From this set of reaction steps, the overall rate of hydrodechlorination reaction can be derived as $r=k'[CFC]/(1+K'[HCl]/[H_2]^{0.5})$. The kinetic~~s~~ results of dichloropropanes also suggest that this set of reaction steps can be used to describe hydrodechlorination reaction of a large number of chlorinated compounds.

Isotopic tracing experiments revealed that C-H bond scission step was also an important elementary step for dichloropropanes hydrodechlorination reactions. Hydrodechlorination products with multiple deuterium atoms were formed during the $D_2$ exchanged reactions. This behavior is similar to $CH_3CH_2Cl$ hydrodechlorination reaction with $D_2$ reported in literature [38]. However, no significant C-H bond scission was noticed for another group of chlorinated hydrocarbons $CH_{4-x}Cl_x$ (x=1-3) studied before. It seems the $CH_3$-, $CH_2$- groups adjacent to C-Cl bond can undergo C-H bond scission during hydrodechlorination reaction. It is also found for chlorinated hydrocarbons with multiple chlorines, that as the degree of dechlorination is increased more C-H bond can be broken and exchanged to C-D bond.

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# Chapter 5

# Future Works

The results presented in chapter 4 represent the progress we have made in the study of hydrodechlorination reaction. Based on obtained kinetic results of four groups of chlorinated compounds, a set of possible hydrodechlorination reaction steps has been proposed by analyzing their reaction kinetics. These reaction steps have been examined using isotopic tracing techniques and using reaction energetics extracted from kinetic results, it is found that the set of proposed reaction steps is valid for the description of the CFC hydrodechlorination reactions. At the same time, $D_2$ exchanged hydrodechlorination reactions have been used to reveal more elementary steps beyond the rate determining step and the possible surface reaction intermediates. When these obtained results are judged against the proposed research objectives outlined in the introductory part of this presentation, it is apparent that we have already achieved most of the goals. But with hydrodechlorination reaction being such a broad research topic, more efforts are still needed to advance the knowledge of the hydrodechlorination reaction. Some of the most important areas are, in my opinion, measurement of the hydrodechlorination reaction of more chlorinated compounds to provide raw data; further corroboration of the validity of the proposed reaction steps; probing the reaction steps beyond the rate determining steps and the reaction surface intermediates; calculation of the reaction energetics of elementary steps; a simple and effective strategy for the prediction of reaction rate and selectivity of hydrodechlorination reaction; and study of hydrodechlorination on catalysts other than Pd. The in-depth investigations of these problems would greatly advance the knowledge of hydrodechlorination reaction.

At the end of this dissertation, I would like to make some general suggestions on how to further study the reaction kinetics and reaction steps of hydrodechlorination reaction within our research capacity. The relevance of these works will be analyzed to show how they can help us make progress from the current position of our research. Some preliminary results will also be presented.

1. *Studying hydrodechlorination reaction kinetics of more chlorinated compounds.*

   In this study, we have found that compared with studying the hydrodechlorination reaction of only a few typical CFC compounds such as $CF_3CFCl_2$ or $CF_2Cl_2$, the study of series chlorinated compounds has the advantage of yielding more detailed information of the possible reaction steps such as what are kinetically important steps in the hydrodechlorination reaction. It can also be applied to investigate relationships between kinetics and structure such as the question of what is the rate determining step. The comparison among the series can also be used to verify whether they are following the same reaction steps and thus make the generalization of a widely applicable hydrodechlorination reaction mechanism more feasible. It is thus concluded that this research methodology of studying series chlorinated compounds should be continued. In this work, we have studied one chlorinated ethane species, that is, $C_2H_5Cl$. In future research, we would like to include the hydrodechlorination reactions of 1,1-dichloroethane, 1,2-dichloroethane and trichloroethanes. In this way, we can make a new chloroethane series. In fact, people are already showing some interest on the hydrodechlorination of chloroethanes in literature. By studying this new series, not only can we supply their kinetic results to the researchers or industries who might be interested in these compounds, we can also use them as raw data for our hydrodechlorination reaction steps study.

Other chlorinated compounds, even though they might not fit to the series we have studied, would be studied due to industrial interest. For example, 2,3- and 1,3-dichloropropylene compound are industrial by-products and their reclamation can generate economical values. In these two compounds, beside the C-Cl bond, they is a C=C double bond. It will be interesting to find out whether the Cl atom can be removed without hydrogenation of the double bond. This type of study not only can supplement our existing in-depth research of the hydrodechlorination reaction, it also has practical applications. We are going to cooperate with the Dow Chemical Company in studying these dichloropropane compounds.

Some specific questions of hydrodechlorination reaction kinetic studies will also be visited. For example, the structure sensitivity of hydrodechlorination is still under debate. While this work and other research groups believe that this reaction is structure insensitive, some other authors have reached the opposite conclusion based on their results and have found hydrodechlorination reaction rate increases with Pd particle size. However, after analyzing their reports, we think that their data are probably contaminated by the followings artifacts, these are, metal-support interaction, formation of carbon species and thus carbiding of Pd surface during reaction, omitting Cl poisoning effect on hydrodechlorination reaction and formation of Pd hydride. In future study, we would like to prepare a series of Pd catalysts with varying particle sizes supported on comparatively inert carbon support and study hydrodechlorination reaction with proper reaction conditions, such as using excessive HCl feed and avoiding bulk hydride formation. By conducting this study, we hope we can produce conclusive results to resolve the controversies about structure sensitivity now existing in hydrodechlorination literature.

2. *Further corroboration of the validity of the proposed reaction steps*.

The proposed hydrodechlorination reaction steps obtained from CFC studies has been found to be also applicable for the four series we have already studied. This reaction steps will again to be examined using the kinetics data for from the proposed new series compounds. Bond energy of the first C-Cl bond to break during hydrodechlorination of these compounds will be calculated using theoretical quantum chemistry calculation software such as Gaussian to find out whether there is a relationship between bond energy and hydrodechlorination reaction rate. If we can again observe this kind of relationship, it will strengthen our hypothesis the first C-Cl bond scission step is the rate-determining step of hydrodechlorination and thus further prove the universality of the proposed hydrodechlorination reaction steps. The HCl orders for the new series compounds will also be studied to investigate the role of Cl* on hydrodechlorination reaction.

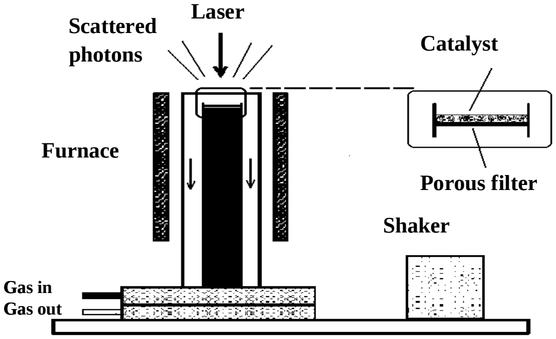
We expect to see the same inhibition effect of this surface species. The suggested equilibrated step HCl + 2* = $H_2$ + Cl* will also continue to be investigated. Based on our already presented results, we found that the HCl orders in the chlorinated hydrocarbon series were less negative than those in the CFC compounds even at the same reaction conditions, which was attributed to the difference in equilibration constants for these two series. At the same time, we found that in the chlorinated methane compounds, the heat of reaction of this step varies from one compound to the other. These two observations are hard to explain, and it is hoped that the study the HCl orders and kinetic results of the hydrodechlorination reactions of more chlorinated compounds can offer some clues for understanding the details of the equilibration step HCl + 2* = $H_2$ + Cl*.

3. *Probing the reaction steps beyond the rate determining steps and the reaction surface intermediates.*

The study of more reaction steps and reaction intermediates of hydrodechlorination reaction is very important, because the information obtained can be useful in assembling a more comprehensive hydrodechlorination reaction mechanism which can be used to predict both reaction rate and reaction selectivity. We have demonstrated that $D_2$ exchanged hydrodechlorination reaction can be used to studying the surface intermediates and possible reaction steps beyond the rate determining steps in the hydrodechlorination reaction. In fact, with the help of this method, we have revealed the existence of C-H bond scission in $C_2H_5Cl$ and dichloropropane compounds. Isotopic tracing experiments with $D_2$ will also be applied in the study of proposed chloroethane series compounds to investigate the surface intermediates during the hydrodechlorination reaction, and to study any possible C-H scission step that may accompany the breakage of C-Cl bond. Additionally, more chlorinated propane compounds, such as singly chlorinated propanes will be studied use this method. By analyzing these isotope experiments, we want to study whether for all chlorinated hydrocarbon compounds, there is C-H bond scission in their hydrodechlorination reaction. We hope to offer more insight into the hydrodechlorination reaction and the results may be used in assembling a more comprehensive hydrodechlorination reaction mechanism which can be used to predict the reaction selectivity.

However, even with the help of isotopic tracing technique, we have only observed and identified a small number of possible reaction intermediates and many of the proposed reaction steps beyond the rate determining step are still hypothetical and without experimental supports. New technologies must be applied to study hydrodechlorination steps. The best situation will be the in situ detection or capture of reaction intermediates during the hydrodechlorination process. In this way, all the experimental observations are obtained under reaction conditions and can be used directly for mechanism study. In fact, isotopic tracing technique is an in situ method [1], but it can only reveal a limited fraction of reaction intermediates. Some reports in literature show that two other techniques, Laser-Raman spectrometry[2-5] and ATR (attenuated total reflection)-FTIR [6, 7] spectrometry can be used for surface intermediate study. We have explored their application in hydrodechlorination reaction. A reaction cell for Raman spectrometry have be constructed and shown in scheme 1. A laser beam is shot onto the catalyst surface during reaction. Most of this light is reflected off unchanged. However a small proportion interacts with the surface or surface adsorbed species and is scattered. The scattered portion of light, known as the Raman effect, is collected by a detector to produce a spectrum. Each species has a unique spectrum associated with it and therefore could be used as to identify them. Figure 1 one shows an experiment of $CCl_4$ hydrodechlorination. Surface Cl and H are clearly visible and we are now trying to identify more surface species and quantify these qualitative results so as to correlate them to hydrodechlorination kinetic results. Another method, called ATR (attenuated total reflection)-FTIR spectrometry has also been tested (scheme 2). Attenuated total reflectance infrared (ATR/IR) spectrometry can provide valuable information related to the catalyst surface during reaction. Mid-infrared spectra are obtained by pressing small particles of catalyst against an internal reflection element (IRE), e.g., zinc selenide (ZnSe) or germanium (Ge). IR radiation is focused onto the end of the IRE. Light enters the IRE and reflects down the length of the crystal. At each internal reflection, the IR radiation actually penetrates a short distance (~1 μm) from the surface of the IRE into the catalyst layer. It is this unique physical phenomenon that enables one to obtain infrared spectra of samples placed in contact with the IRE and thus identify these species. Figure 2 shows our preliminary result on $CCl_4$ adsorption on $Pd/ZrO_2$

catalyst, and it can be seen that surface $CCl_4$ signal was detected and its intensity change with respect to He flush time could be monitored in real time. These two techniques are very promising in revealing hydrodechlorination reaction intermediates and helping to generate a more complete set of hydrodechlorination. We are now working on identifying more surface species and developing /modifying these systems to produce more and better quantitative information.



**Scheme 1. Laser Raman spectrometry reaction cell**

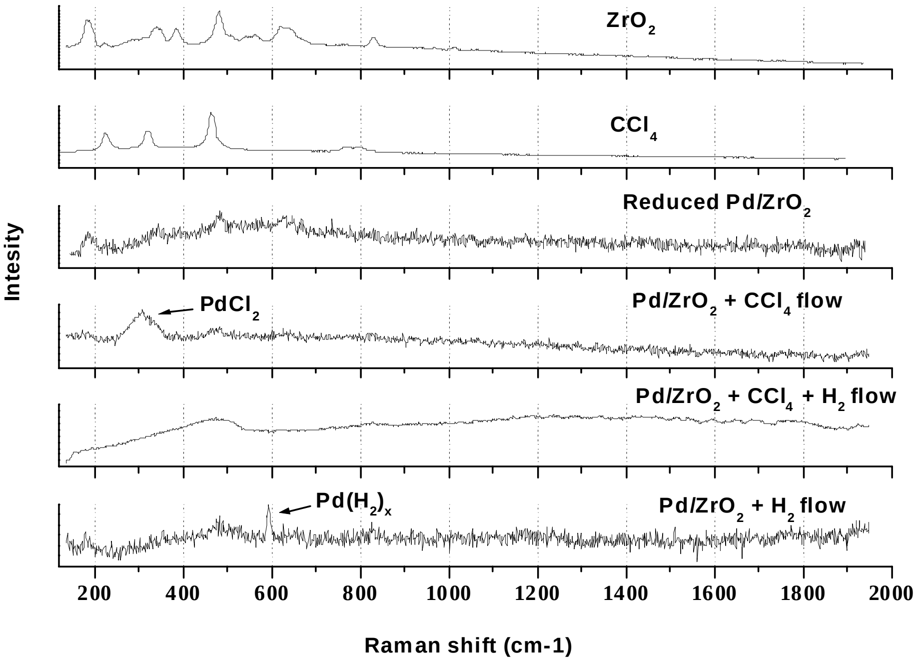
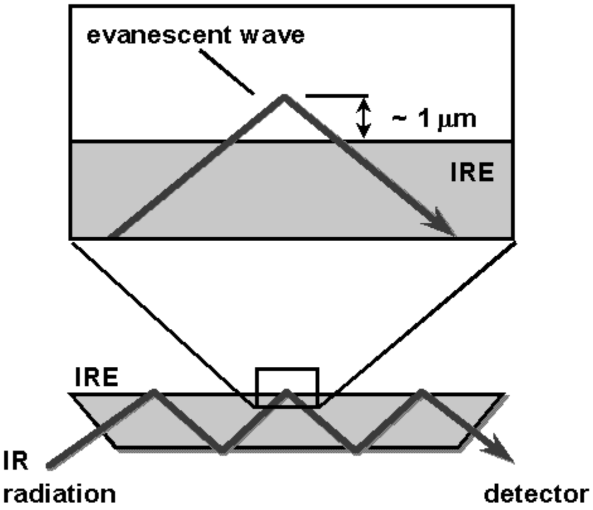


**Figure 1.** **Raman spectrum in $CCl_4$ hydrodechlorination reaction on $Pd/ZrO_2$ catalyst**



**Scheme 2. ATR-IR principle**

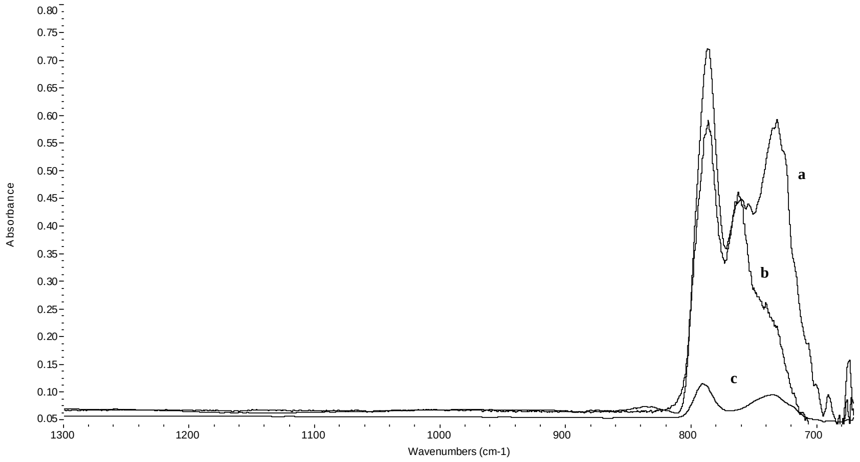


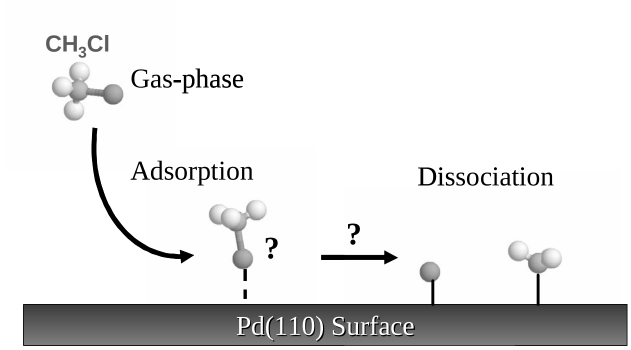
**Figure 2. Absorbance ATR-IR spectrum after reaction of dechlorination of $CCl_4$ on $Pd/ZrO_2$ catalyst: a) after reaction, b) 2 min of He flushing, c) 15 min of He flushing**

4. *Measuring the reaction energetics of hydrodechlorination elementary steps.*

In the study of the four families of chlorinated compounds discussed here, we formulated a procedure to extract the rate constant for the C-Cl scission step and equilibration constant. These reaction constants measured at different temperatures can be used to calculate the reaction energetics of the kinetically important steps, such as the heat of reaction of the equilibration step HCl + 2* = $H_2$ + Cl* and the intrinsic activation energy of the C-Cl scission step. By analyzing the relationship between C-Cl bond scission activation energy and C-Cl bond strength for each of the compounds in the two new series chlorinated compounds, we can study the rate-determining step in the hydrodechlorination reaction. For the proposed new chloroethane series, we plane to continue to use this procedure to study some of their reaction energetics and we hope a linear Polanyi relationship between intrinsic Ea and C-Cl bond strength in can be found for these compounds. These energetics values can also be used for the purposed of predicting the hydrodechlorination reaction rates. There are other experimental studies of hydrodechlorination reaction energetics, such as adsorption energy and C-Cl bond dissociation energy, on model catalyst.

However, the experimental measurement of reaction energetics can be very time consuming and might be subject to experiment errors. At the same, the previous procedure can only be used to find out reaction energetics related to hydrodechlorination reaction rate. To be able to predict hydrodechlorination reaction rate and selectivity, we also need reaction energetics of other species and reaction steps beyond rate limiting steps. One way to study reaction energetics is to use first principle theoretical surface calculation (scheme 3). Some reports on hydrodechlorination reaction have been published on this subject using calculation packages such as VASP (Vienna Ab Initio Simulation Package) [8-10].

In future study, we will take advantage of this method and perform a series of calculation for the chlorinated compounds studied here to provide surface energetics data for prediction of hydrodechlorination rate and selectivity. We have already started this part of work on $CH_{4-x}Cl_x$ (x=1-4) compounds. Their adsorption energy and C-Cl dissociation energy were calculated and shown in figure 3 and 4. We can notice that heat of adsorption and C-Cl bond dissociation energy on surface show linear dependence on gas phase C-Cl bond energy, as what have proposed before. Apparently, these preliminary results will be checked with experimental result to refine our calculation method. Then we can use it to do more detailed investigation on other reaction energetics of interest, such as activation energy of C-Cl bond scission on Pd surface, exploring possible reaction intermediates and so on.



**Scheme 3. Reaction energetic of $CH_3Cl$ hydrodechlorination**

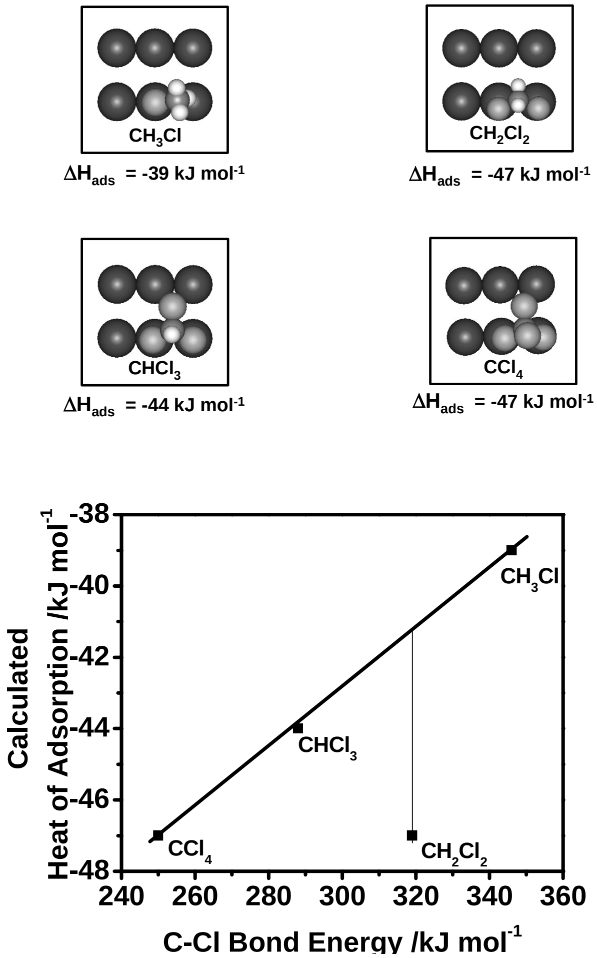


**Figure 3. Relationship between calculated heat of adsorption of $CH_{4-x}Cl_x$ (x=1-4) compounds and their gas phase C-Cl bond strength**

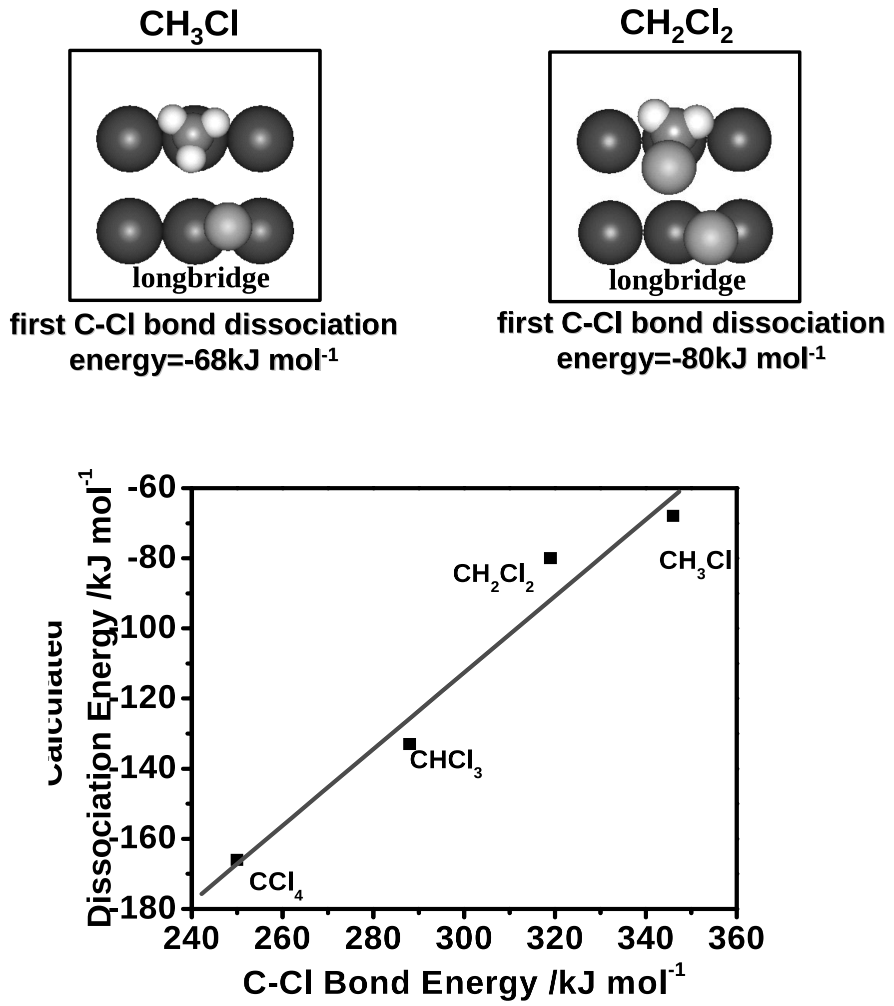
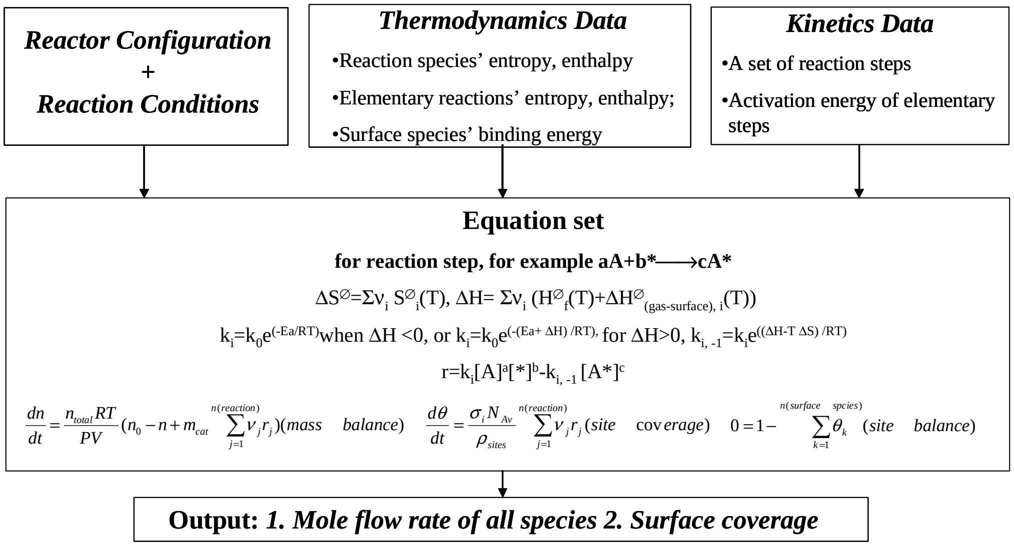


**Figure 4. Relationship between C-Cl bond dissociation energy on Pd surface of $CH_{4-x}Cl_x$ (x=1-4) compounds and their gas phase C-Cl bond strength**

5. *New strategy for the prediction of reaction rate and selectivity of hydrodechlorination reaction.*

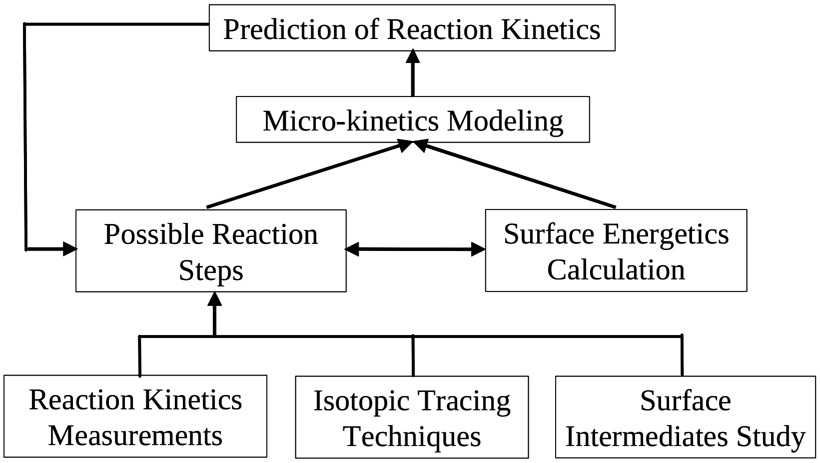
In the process of this study, by analyzing and generalizing the results we obtained from the study of CFC compound and chlorinated methane compounds, we have proposed a method for predicting the hydrodechlorination reaction rate. Using the reaction steps we proposed, a rate expression can be derived. Since we found that for a family or chlorinated compounds the hydrodechlorination rate is related to the bond strength of the first C-Cl to break during hydrodechlorination reaction and this relationship can be quantitatively describe by Polanyi relationship, once we know a reference compound's hydrodechlorination reaction rate and the other compounds' C-Cl bond strength in this family, their rate can be calculated quite accurately. This method is comparatively simple, but it also has some defects. Firstly, this method for predicting the rate needs to measure the hydrodechlorination reaction rate of one compound in a family as a reference rate, and this may bring experimental errors. Secondly, this method still requires defining and classifying the large number of chlorinated compounds into "families" in order to predict the hydrodechlorination reaction rate more precisely. For example, we found that the slopes of Polanyi relationship for the CFC compounds and chlorinated hydrocarbons are quite different. This classification may limit the application of this method. Finally, this method is derived from the kinetics data, so it can not predict the reaction selectivity, what we can do now is just estimate how many types products we can get from the hydrodechlorination reaction of a certain chlorinated compounds. In order to overcome these shortcomings of the current methods, a new strategy that can predict the both the hydrodechlorination reaction rate and selectivity accurately and conveniently has to be found.

We are going to conduct some preliminary microkinetics study of the hydrodechlorination reaction. In constructing a microkinetics model for hydrodechlorination reaction, the calculated reaction energetics of the elementary steps from either experimental measurement or using theoretical first principle calculation method, such as the adsorption energy of the surface species, heat of reaction and reaction activation energy, would be used to provide raw data for the model [11-13]. Then with a complete and correct hydrodechlorination reaction steps assembled and validated from the kinetics and mechanistic studies, this model can be used for the prediction of the hydrodechlorination rate and selectivity by calculating surface coverage, reaction rate, selectivity, apparent activation energy and reaction orders in any reactor systems (scheme 3). This type of microkinetics modeling work is underway for $CH_3Cl$ compound. In the future, this work should be expanded to other more complex chlorinated compounds to explore the problem of how to predict the hydrodechlorination reaction selectivity by incorporating elementary steps beyond the rate-determining step into the microkinetics model. We hope that by conducing microkinetics modeling studies, a more convenient and effective way for predicting the hydrodechlorination reaction rate and selectivity can be established.



**Scheme 4. microkinetics modeling of hydrodechlorination reaction**

These suggestions for our future hydrodechlorination reaction kinetic study are summarized in scheme 4, as a systematic approach that would be adopted later. It can be seen that future research will be greatly expanded to include new ideas, up-to-date research tools and technologies. By conducting these studies, we hope we can supply fundamental understanding of hydrodechlorination reaction kinetics for academic industrial researchers and who might be interested in this type of reaction.



**Scheme 5. Future research strategy of hydrodechlorination reaction**

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# Chapter 6

# Conclusions

In this research work, we studied the hydrodechlorination reactions of four families of chlorinated compounds; $CF_3CF_{3-x}Cl_x$(x=1-3), $CH_{4-x}Cl_x$ (x=1-4), $CF_{4-x}Cl_x$ (x=1-4) and dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-) on supported palladium catalysts using kinetic measurements and isotopic tracing experiment in order to find a way to predict hydrodechlorination rate of chlorinated compounds and to explore the reaction mechanism of hydrodechlorination reaction.

It was found that for each of these four families of compounds, the rate of hydrodechlorination reaction could be related to the strength of the first C-Cl bond to be hydrogenated in chlorinated organic compounds, thus indicating that the C-Cl bond scission was involved in the rate limiting step. Hydrodechlorination product HCl was found to be an inhibitor of hydrodechlorination reaction and its reaction order was negative for all the chlorinated compounds studied here, indicating adsorbed Cl was competing with chlorinated reactant for Pd active site. For a specific chlorinated organic compound, its hydrodechlorination reaction rate was found to be comparable on different types of Pd catalysts (Pd on different supports, Pd with different particle size and different Pd model catalysts, including Pd black, Pd (111), Pd (110) Pd foil), suggesting hydrodechlorination reaction might be structure insensitive and that the C-Cl bond scission might required only one Pd atom. Additionally, hydrodechlorination reaction selectivity was found to be independent of reaction conversion, suggesting that the different hydrodechlorination products were formed in parallel routes and these products were less reactive than the reactant itself.

A possible set of elementary reaction steps of hydrodechlorination reaction was proposed from based on these kinetic results:

| | | |
|---|---|---|
| $R\text{-}Cl + * = R\text{-}Cl^*$, | with an equilibrium constant $K_{CFC}$ | (1) |
| $R\text{-}Cl^* \rightarrow \cdots$, | rate-determining step with a rate constant $k_0$ | (2) |
| $r = k_0 K_{CFC}[R\text{-}Cl][*]$, | rate expression | (3) |
| $H_2 + 2* = 2H^*$, | equilibrated step | (4) |
| $H^* + Cl^* = HCl + 2*$, | equilibrated step | (5) |
| $2HCl + 2* = H_2 + 2\,Cl^*$, | (4) + (5), with equilibrium constant $K_0$ | (6) |
| $[*] + [Cl^*] = [L]$, | site balance | (7) |
| $[*] = \dfrac{[L]}{1 + \dfrac{[HCl]}{[H_2]^{0.5}}}$, | free site concentration | (8) |
| $R^* + H^* = RH + 2*$ | formation of hydrogenation product | (9) |

In this set of reaction steps the irreversible scission of the first C-Cl bond in a chlorinated compound was proposed to be the rate-determining step (step 2); gas phase $H_2$ and HCl were suggested to be in equilibrium with surface H and Cl species (step 6); adsorbed Cl was assumed to be the most abundant surface intermediate; hydrodechlorination products were formed by the combination of surface H and chlorinated organic compound fragments after losing Cl atoms (step 9). The overall rate of hydrodechlorination reaction could be derived from these reaction steps as $r = k'[R\text{-}Cl]/(1+K'[HCl]/[H_2]^{0.5})$. In this rate equation, k' is the product of the adsorption equilibrium constant of the chlorinated compound on the catalyst surface (step 1) times the rate constant for the scission of the first C-Cl bond scission step (step 2), and K' is one half of the equilibrium constant for the equilibrium between $H_2$, HCl and their corresponding surface species: 2HCl + 2* ↔ $H_2$ + 2Cl*.

The isotope experiments were performed to provide more supports for this set of reaction steps. The hydrodechlorination reaction of $CF_3CFCl_2$ was performed with $H^{37}Cl$ to study the reversibility of C-Cl bond scission (step 2). Because HCl adsorbs and dissociates preferentially on the surface, the use of $HCl^{37}$ allowed the Pd surface to be saturated with $^{37}Cl$; if C-Cl bond scission is reversible then the reactant would be enriched in $^{37}Cl$. It was found that the ratio of $CF_3CFCl^{35}Cl/CF_3CFCl^{37}Cl$ in the reactant was close to 3.10, the natural $^{35}Cl/^{37}Cl$ ratio, which supported the proposed assumption that the first C-Cl bond scission step was an irreversible step. Hydrodechlorination experiments of $CF_3CFCl_2$ with $D_2$ and HCl mixture revealed that $D_2$ and HCl were in equilibrium with surface adsorbed hydrogen and chlorine during reaction. The forward rate and reverse rate of this equilibrium were at least 400 times higher than the overall hydrodechlorination rate. This result supported the assumption of equilibrium for step 6. Deuterium isotope effect in hydrodechlorination was also studied. It was found that the hydrodechlorination reaction rate with $H_2$ and with $D_2$ were similar, indicating that H or D was not involved in the rate-determining step. An experiment of $CF_3CFHCl$ with $H_2$-$D_2$ co-feed stream showed that $CF_3CFH_2$ was formed preferentially to $CF_3CFHD$ and this observation could be predicted using a combination of existing isotope effect theory and the proposed reaction steps.

The set of proposed reaction steps were also verified by studying the hydrodechlorination reaction energetics of these compounds. By definition, the activation energy of step 3 is the sum of two terms, one being the heat of adsorption of chlorinated compounds on the catalyst surface (step 1) and the other the activation energy of hydrodechlorination for the rate limiting step (step 2). We have found that the heat of adsorption on Pd surface of a chlorinated compound (step 1) is linearly related to its C-Cl bond strength using *ab initio* surface calculation technique. If the hydrodechlorination reaction rate-limiting step is indeed the removal of the first Cl from a chlorinated compound, then a Polanyi relationship should exist between the activation energy of step 2 and the C-Cl bond strength of the first C-Cl bond to break during reaction. In this way, activation energy of rate expression 3 would also show a linear dependence on C-Cl bond energy. Activation energy of rate expression 3 was calculated from hydrodechlorination reaction kinetics results of $CH_{4-x}Cl_x$ (x=1-4), $CF_{4-x}Cl_x$ (x=1-4) and dichloropropanes (1,1-, 1,2-, 1,3-, 2,2-) compounds. It was found that for each of the three series compounds, a linear relationship did exist between C-Cl bond scission activation energy of step 3 and C-Cl bond strength. This observation indicates that our assumption that the first C-Cl bond scission step is the rate-determining step in hydrodechlorination reaction might be valid.

All the kinetic and isotope experimental results obtained from this study support the proposed reaction steps shown above (equations 1-7) for the chlorinated compounds tested. Additionally, this set of reaction steps can be used to predict hydrodechlorination reaction rate of a chlorinated compound, once its C-Cl bond energy is known and the turnover rate of a reference chlorinated compound with similar structure is known.

Future research works of hydrodechlorination reaction kinetics is proposed and should focus on studying hydrodechlorination reaction steps and reaction intermediates beyond the rate-limiting step. Some work has been done in this area during our study. Isotope tracing experiments with $D_2$ were used to examine the possible existence of C-H bond scission in H-containing chlorinated organic compounds. It was found that C-H bond scission was present in chlorinated hydrocarbons with a carbon chain greater than two carbon atoms. It was thus concluded that $CH_3$-, $CH_2$- groups adjacent to C-Cl bond could undergo C-H bond scission. The study of surface mechanism using *ab initio* methods, including calculation of rate constants, is also under way. Preliminary calculations for the $CH_{4-x}Cl_x$ (x=1-4) family showed that the heat of adsorption and C-Cl bond dissociation energy on Pd surface of these compound were linearly related to their gas phase C-Cl bond strength. Other investigations to be carried out in our group include: in situ investigation of reaction intermediates using Raman and FTIR technique, and micro-kinetic modeling of the hydrodechlorination reaction.

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