

DEGRADATION OF ENVIRONMENTAL POLLUTANTS USING RHODIUM
HYDRIDES

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CHAPTER ONE

INTRODUCTION

1.1 MOTIVATION

Hundreds of millions of persistent chlorocarbons are produced annually, many of which are toxic and bioaccumulative.¹⁻³ These chlorocarbons end up in our ground water and are a vast environmental problem. In particular, chlorinated ethylenes are highly toxic and on the Environmental Protection Agency's (EPA's) list of high priority groundwater pollutants. In addition to problematic chlorocarbons, fluorocarbons are emerging pollutants, due to their recently increasing use in pharmaceuticals and materials. They are also of serious environmental concern due to their persistent nature. In general, dehalogenation effectively removes the toxic effects of these pollutants. However, partial dehalogenation is not enough. Natural bio-attenuation of chlorinated ethylenes leads to build-up of more toxic lower chlorinated ethylenes.⁴⁻⁷ This has prompted the study of new, engineered remediation methods, such as pump-and-treat technology.^{8,9} In one type of implementation of this strategy, the contaminated groundwater is passed through noble metal catalyst in the presence of a reducing agent, often hydrogen, yielding non-toxic products, such as ethylene and ethane.¹⁰⁻¹⁴ Although shown to be effective, little is known about the mechanism by which reductive dehalogenation occurs in these systems. However, metal hydrides are thought to be important reactive intermediates in these noble metal catalytic systems. The involvement of these intermediates in reductive dehalogenation may be integral to their effectiveness as catalysts. Understanding the fundamental chemistry of metal hydrides in catalytic dehalogenation processes could lead to improved engineered systems capable of decontaminating groundwater.

1.2 ENVIRONMENTAL POLLUTANTS: CHLORINATED ETHYLENES

Chlorinated ethylenes are a class of persistent, mobile and toxic chlorocarbons, and contain the molecules perchloroethylene (PCE), trichloroethylene (TCE), *cis*-1,2-dichloroethylene (*cis*-DCE), *trans*-1,2-dichloroethylene (*trans*-DCE), 1,1-dichloroethylene (1,1-DCE), and vinyl chloride (Figure 1.1).^{11,15,16} All of the chlorinated ethylenes are potential carcinogens, and have been shown to cause liver and kidney tumors in animal studies.¹⁷⁻²⁸ The toxic effects associated with these molecules are related to the chlorine substituents. Accordingly, removal of the chlorine atoms leads to detoxification.²⁹ A good example of this is vinyl chloride, a carcinogen, which yields non-toxic ethylene upon dechlorination.¹⁸

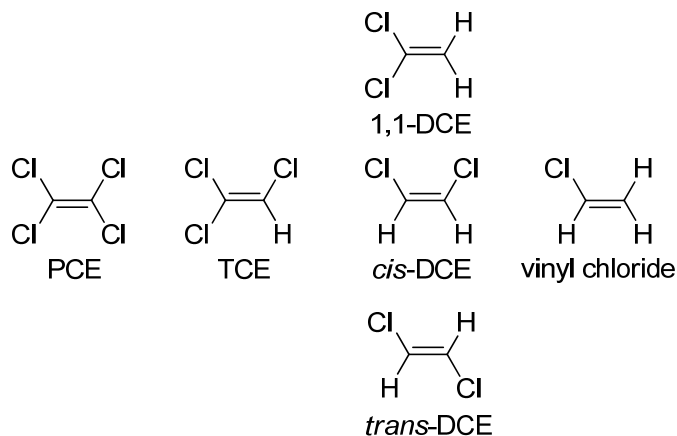


Figure 1.1. Structures of chlorinated ethylenes.

Chlorinated ethylenes are widespread pollutants. Specifically, PCE and TCE are found in both soil and water systems.^{1-3,15,17,30-34} These chlorinated ethylenes are primarily used as dry cleaning solvents, metal cleaners, and industrial degreasers.^{2,17} At the height of manufacturing of PCE (in 1980) and TCE (in 1970) the rate of production was 800 and 700 million pounds per year, respectively.^{1,2} Currently, the manufacturing rate of each of these is approximately 200 and 100 million pounds each year,

respectively.^{1,2} Both PCE and TCE are on the EPA's high priority pollutant list.^{2,15,16} The maximum contaminant levels for PCE and TCE in drinking water was set to 5 µg/L under the provisions of the Safe Water Drinking Act in 1985, and these chemicals are rarely observed above this level.^{12,13,24,34}

1.3 REMEDIATION STRATEGIES

Microbial remediation strategies

Remediation strategies for PCE and TCE by dechlorination has involved the use of zero-valent metals,^{14,34-52} electrochemical processes,^{44,53-57} and microbial degradation.^{6,30,31,46,58-62} Studies of biologically-mediated dehalogenation reactions have been a major focus because microbial communities can dehalogenate pollutants *in situ*. In biological systems, both PCE and TCE are reduced to less chlorinated congeners, including *cis*-DCE, vinyl chloride, ethylene, and ethane.^{6,31} These reactions are mediated by enzymes containing tetrapyrrole cofactors, containing cobalt, nickel, and iron. Cobalamin (cobalt-containing tetrapyrrole, Figure 1.2) is the dominant catalyst.^{17,31,32,59,60,63-68}

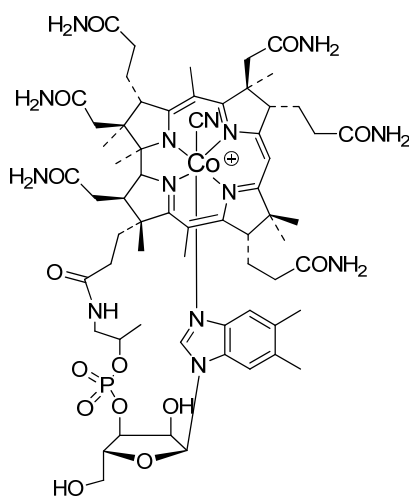


Figure 1.2. Structure of cobalamin.

The mechanism for dechlorination of PCE and TCE by cobalamin and its model complexes has been extensively studied.⁶³⁻⁷⁷ In the presence of a bulk reductant, titanium(III) citrate, cobalamin has been shown to be the active catalyst in the reductive dechlorination of chlorinated ethylenes. Cobalamin quickly degrades PCE to TCE and the major product of TCE degradation is *cis*-DCE. Under these reaction conditions *cis*-DCE is poorly degraded.³² In the major degradation pathway, sequential replacement of chlorine by hydrogen occurs until ethylene is formed. The rate constant of each degradation step was determined and the relative constants, normalized to *cis*-DCE degradation (the slowest substrate), are listed in Figure 1.3.^{31,32,63}

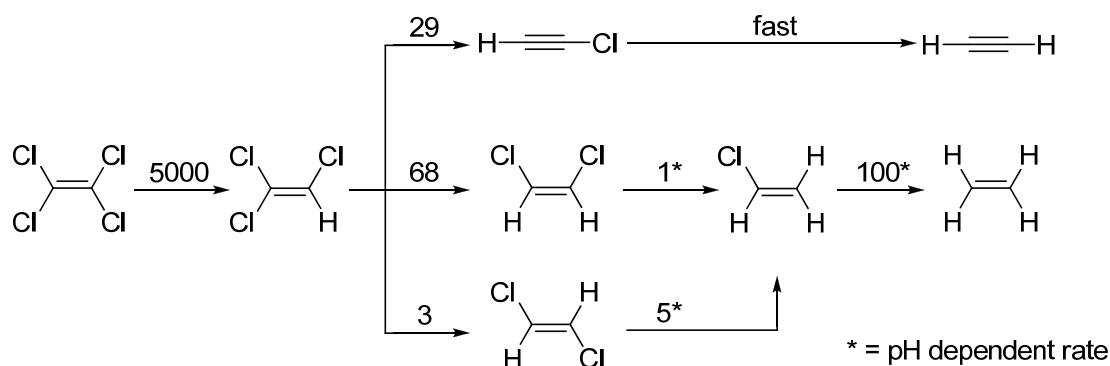


Figure 1.3. Degradation products and relative rates of degradation of chlorinated ethylenes using cobalamin as the catalyst and titanium(III) citrate as the bulk reductant. All rate constants are relative to *cis*-DCE degradation, and the pH dependent rates are marked with *.^{31,32,63} (Adapted from reference 66)

With cobalamin as the degradation catalyst, the lesser chlorinated congeners accumulate due to their lower reaction rates. Field sites that were originally contaminated with PCE and TCE are now contaminated with toxic *cis*-DCE.^{1,2,4-7,15,52} Therefore, we have been exploring the use of alternate catalysts that are capable of rapidly dechlorinating the lower chlorinated congeners.

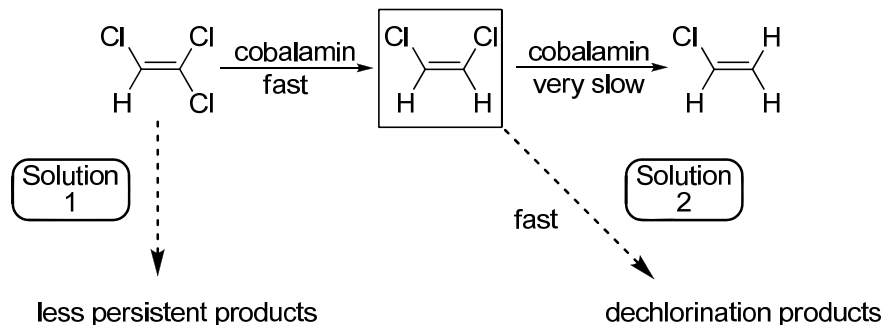


Figure 1.4. Overall goal of this dissertation work was to alleviate the problem of *cis*-DCE accumulation by formation of less persistent products than *cis*-DCE from TCE degradation, or development of a system with faster *cis*-DCE degradation than observed by natural attenuation with cobalamin as the catalyst.

The overall goal of the research presented in this dissertation was to alleviate the problem of *cis*-DCE accumulation from natural attenuation in one of two ways: by (1) alteration of the product ratio so that *cis*-DCE was no longer the major product of TCE degradation, or (2) development of a remediation strategy that degraded *cis*-DCE faster (Figure 1.4).

Pump-and-treat

One remediation method that was hypothesized to accomplish this goal is an engineered remediation strategy: pump-and-treat, which is an economical and fairly successful alternative to natural attenuation. Pump-and-treat is just that, pumping the contaminated groundwater out, treating it, and then pumping it back into the groundwater system.^{8,9,78} Using noble metal catalysts as part of the treatment process is attractive from a chemical perspective because they are highly efficient, and active sites are not consumed during the reaction.^{79,80} Noble metals have been implemented in pump-and-treat systems with hydrogen gas as the reducing agent.⁸⁰⁻⁸² The high costs of the noble metal are offset by high activity and the maximization of surface area with low metal loading on supports. An added benefit of noble metal catalysts is their

heterogeneous nature in water systems allowing ease of catalyst recovery. Several heterogeneous metal catalysts have been shown to degrade chlorinated ethylenes and other chlorocarbons.^{47,48,54,55,79-89} Platinum,^{79,83} gold,⁸³ nickel,^{48,84,85} copper,⁴⁸ ruthenium,⁸³ rhodium,^{79,90} and palladium,^{47,48,54,55,79-83,86,87} have been studied as catalysts, with supports of carbon, silica (SiO₂) and alumina (Al₂O₃).

In order for these systems to operate, they require not only the noble metal catalyst, which is responsible for transferring electrons to the substrate molecule, but also a source of electrons. Two main strategies for reducing agents have been implemented, using H₂ as the reductant,^{54,55,79,80,82,86,88-90} or using bimetallic blends,^{47,48,83-85} such as Pd/Fe; in this case iron is the source of electrons to palladium. These systems have exceptional promise due to their high activity and low levels of toxic, halogenated byproducts.^{79,80} They have also been shown to be resistant to corrosion, and important property in a system involving oxygenated water.^{55,82}

Reinhard *et al.* studied the catalytic degradation of chlorinated ethylenes using palladium on alumina support (Pd/Al₂O₃) as the catalyst and H₂ as the reducing agent.^{54,55,80-82,86,87} This system is especially exciting as it degrades all of the chlorinated ethylenes with similar rates, and the lower chlorinated ethylenes are degraded slightly faster (Table 1.1).⁸⁶ The final degradation product was ethane for all of the chlorinated ethylenes studied.

Table 1.1. Observed rate constants for the degradation of chlorinated ethylenes using Pd/Al₂O₃ and H₂. The pseudo-first order rate constants are normalized to the amount of catalyst (k_{rxn}).⁸⁶ The k_{rel} are determined compared to the slowest substrate, PCE (0.53).

Substrate	k_{rxn} (L g _{cat} ⁻¹ min ⁻¹)	k_{rel}
PCE	0.53	1.0
TCE	0.64	1.2
1,1-DCE	0.70	1.3
<i>trans</i> -DCE	0.78	1.5
<i>cis</i> -DCE	0.83	1.6

The possible pathways for hydrodechlorination of PCE to ethane are depicted in Figure 1.5, with sequential chlorine removal and replacement with hydrogen (k_1 - k_8) followed by hydrogenation of ethylene to ethane (k_9), or the possibility of direct pathway to ethane (k_{10}) from TCE. During the dechlorination of chlorinated ethylenes, specifically TCE, with Pd/Al₂O₃ in H₂ saturated water, no lower chlorinated ethylenes are detected, only ethane.⁸⁶ This led to the proposal that once bound to Pd/Al₂O₃, TCE was degraded completely to ethane before becoming unbound, following k_{10} (Figure 1.5).⁸⁶ It was also found that at lower concentrations of H₂ some lower chlorinated ethylenes were detected during the hydrodechlorination of TCE, however, again sequential hydrodechlorination was not proposed.⁵⁵ This hypothesis was explored in this dissertation work and is discussed in chapter 4.

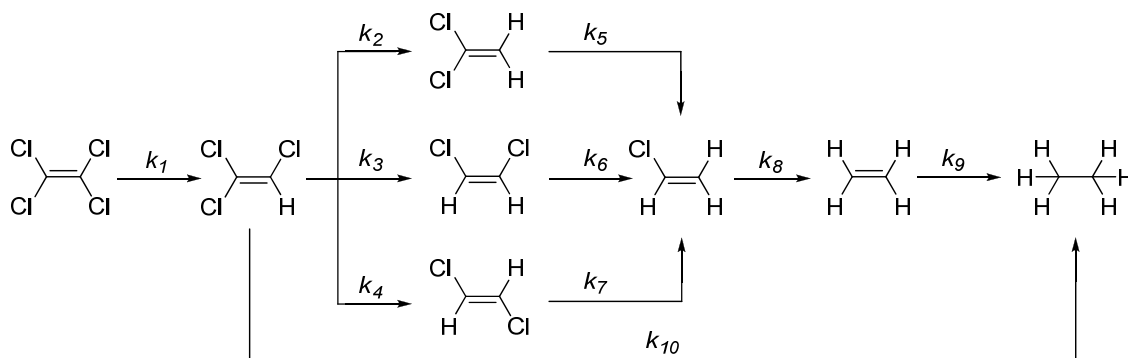


Figure 1.5. Possible degradation pathways of chlorinated ethylenes to ethane. With either sequential hydrodechlorination (k_1 - k_8), followed by hydrogenation (k_9), or direct degradation of TCE to ethane (k_{10}) (adapted from reference 86).

Palladium⁹¹⁻¹⁰⁴ and rhodium^{95-99,102,105-108} have also been studied as heterogeneous hydrodechlorination catalysts in the degradation of aryl chlorides including polychlorinated biphenyls.^{91-94,100-107} Heterogeneous rhodium catalysts have also been shown to degrade chloromethanes, again with hydrogen as the reducing agent.

109-112

A recent study compared palladium, platinum, and rhodium on alumina catalyst in the hydrodechlorination of 4-chlorophenol under mild conditions (20-40 °C and H₂).¹⁰⁶ In this system palladium and rhodium out-performed platinum, and rhodium displayed the highest activity (Table 1.2).¹⁰⁶

Table 1.2. Apparent activation energies (E_a) for the hydrodechlorination of 4-chlorophenol using Pt/Al₂O₃, Pd/Al₂O₃, Rh/Al₂O₃ as the catalyst and H₂ as the reducing agent.¹⁰⁶

Catalyst	E_a (kJ/mol)
Pt/Al ₂ O ₃	21.0 ± 0.1
Pd/Al ₂ O ₃	26.2 ± 5.6
Rh/Al ₂ O ₃	15.3 ± 0.7

Heterogeneous rhodium catalysts have been used previously to dechlorinate alkenes and alkanes. Bozzelli *et al.* reported that at 91-280 °C and 0.1 MPa of H₂, Rh/Al₂O₃ dechlorinated TCE more readily than 1,2-dichloroethane.⁹⁰ However, no mechanistic information was presented. Dichloropropane,¹¹³ dichlorobutenes,¹¹⁴ PCE,¹¹⁵ TCE⁹⁰ and 1,2-dichloroethane^{90,116,117} have all been dechlorinated using Rh/Al₂O₃, Rh/SiO₂ or RhCl₃ catalysts in the presence of H₂.

Little is known mechanistically about these systems due to their heterogeneous nature. By studying well-defined model homogeneous catalytic systems and applying that knowledge to the noble metal heterogeneous systems, a better understanding of the dechlorination processes can be attained. The fundamental understanding of the model systems can assist in improved design and implementation of optimal catalyst in real-world applications.

It is hypothesized that metal hydrides play a role in the degradation of chlorinated ethylenes in heterogeneous noble metal catalytic system that use H₂ as the reducing agent. We propose that insertion of the sp²-hybridized C-Cl bond into the metal hydride bond is a step in the degradation process, followed by β-Cl elimination (Figure 1.6). This was tested with homogenous metal hydride model systems, and then Rh/Al₂O₃ and H₂ (1atm) at 25 °C.

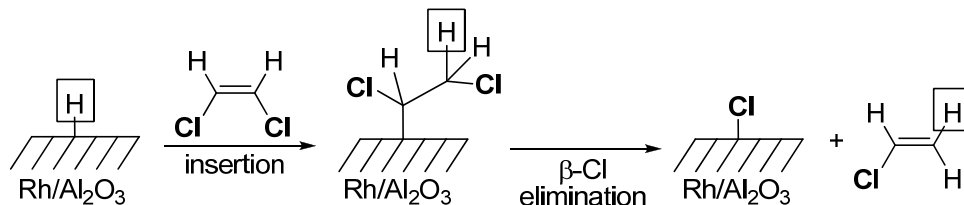


Figure 1.6. Metal hydrides are hypothesized to play a vital role in the mechanism of degradation of chlorinated ethylenes in heterogeneous noble metal systems. We propose that an insertion/ β -Cl-elimination mechanism may be important in the activation of sp^2 -hybridized C-Cl bonds. *Cis-DCE* is the substrate depicted as being dechlorinated in this scheme.

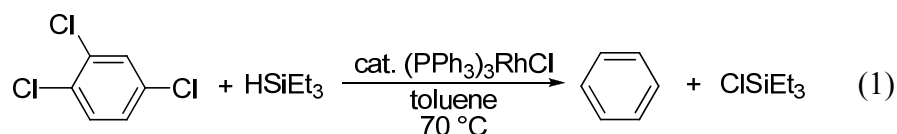
1.4 HOMOGENEOUS DECHLORINATION USING METAL HYDRIDES

Metal-mediated hydrodechlorination has been studied with a variety of metals and reaction conditions.^{29,118,119} The major area of focus for homogenous catalytic dechlorination using metal hydrides has been the degradation of aryl chlorides. Homogenous catalysts have been used for hydrodehalogenation of aryl chlorides with a variety of reducing agents. These methods involve the use of molecular hydrogen,¹²⁰⁻¹²³ alkaline-alcohols,^{98,124-127} cyclic amines,¹²⁸ triethylsilane,¹²⁹⁻¹³¹ magnesium dihydride,^{132,133} sodium hydride,¹³⁴ sodium formate,^{124,135} and alkyl Grignard reagents¹³⁶ as the hydrogen source.

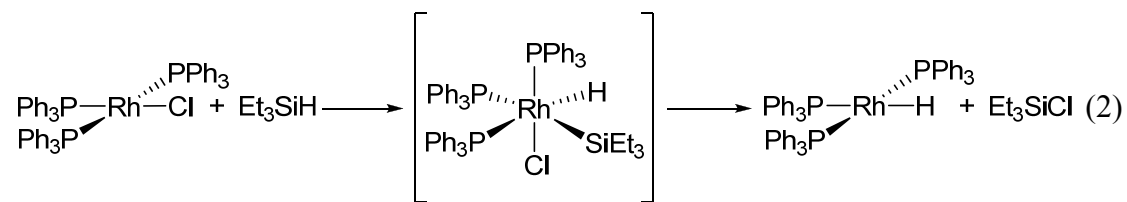
One early study that stands out was undertaken by Green and Knowles in 1973, in which they used $(C_5Me_5)_2WH_2$ to activate a wide variety of carbon-halogen bonds.¹³⁷ In this study chlorinated ethylenes were sequentially hydrodechlorinated, i.e. PCE to TCE, TCE to *cis*-DCE, etc.¹³⁷ The rate of hydrodechlorination decreased with loss of chlorine, PCE was degraded the fastest; and vinyl chloride degraded the slowest.¹³⁷ The major hydrodechlorination product of TCE was *cis*-DCE (91%), but all three isomers of DCE were observed.¹³⁷ All of the DCE isomers degrade directly to ethylene, as no

vinyl chloride was detected.¹³⁷ Incidentally, the Mo analogue (Cp_2MoH_2) does not react with TCE.¹³⁸

Homogenous hydrodechlorination catalysts have been studied by others, most notably, using phosphinorhodium and hydrogen to degrade chlorofluoromethanes¹³⁹ and chloroalkanes,^{117,140} and the system that Esteruelas *et al.* has studied using chlorotris(triphenylphosphino)rhodium, $(\text{PPh}_3)_3\text{RhCl}$, as a homogeneous catalyst in the presence of triethylsilane (Et_3SiH) to dehalogenate chlorinated cyclic¹³⁰ and aryl^{129,131} compounds (i.e., γ -hexachlorocyclohexane, chlorobenzene and polychlorinated benzenes) (eq 1).



The first step of the reaction was proposed to be oxidative addition of Et_3SiH to $(\text{PPh}_3)_3\text{RhCl}$ followed by reductive elimination of Et_3SiCl , yielding $(\text{PPh}_3)_3\text{RhH}$ as the active catalyst (eq. 2).¹³⁰



The major dechlorination product of hexachlorocyclohexane was benzene.¹³⁰ From, the formation of benzene, as well as spectroscopic evidence of different phosphinorhodium complexes during the reaction, an oxidative addition/ β -chloride elimination mechanism was proposed (Figure 1.7).¹³⁰ The authors propose that after oxidative addition of hexachlorocyclohexane to the $(\text{PPh}_3)_3\text{RhH}$, the chlorocyclohexane remains bound to the

rhodium until all chlorines are removed by β -chloride elimination. (Figure 1.7).¹³⁰ This process is facilitated by loss of H_2 from a dihydride-alkyl intermediate formed from reaction of another equivalent of Et_3SiH and loss of Et_3SiCl . Short-lived π -olefin rhodium and π -diolefin rhodium intermediates were proposed.¹³⁰

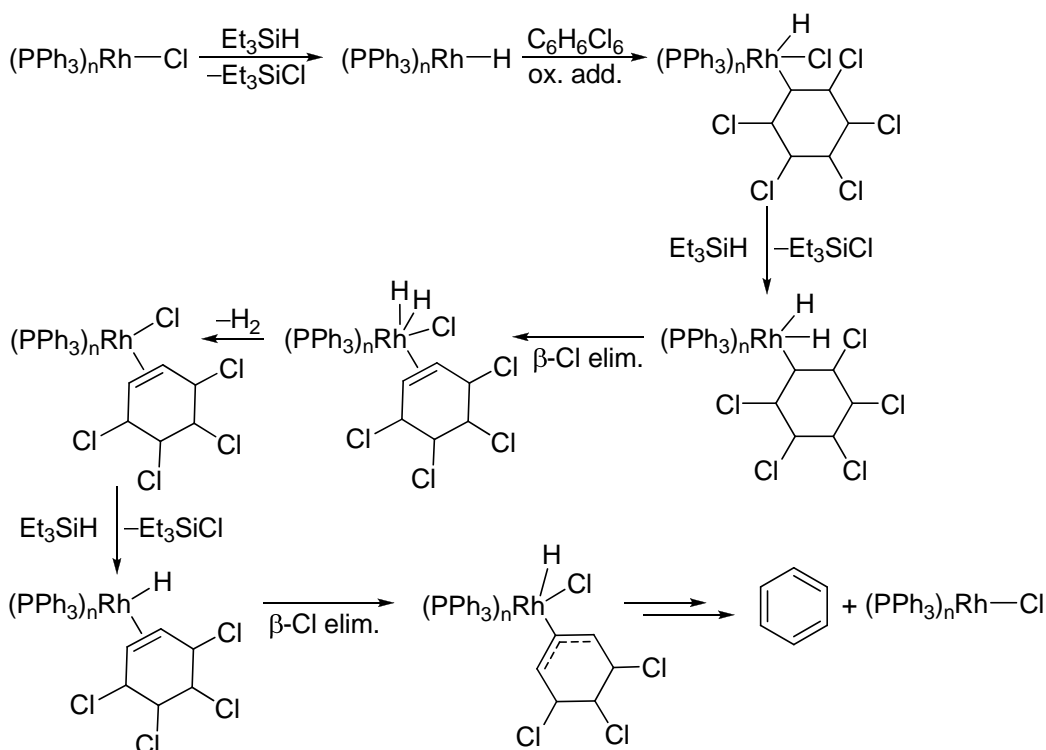


Figure 1.7. The proposed mechanism for the degradation of hexachlorocyclohexane to benzene from $(PPh_3)_3RhCl$ and Et_3SiH .¹³⁰ (Figure adapted from reference 130.)

In this dissertation work a similar catalytic system, $(PPh_3)_3RhCl$ and Et_3SiH , was explored for the dehalogenation of chlorinated and fluorinated ethylenes. Direct evidence for sequential dehalogenation is presented as well as a mechanism for the degradation of halogenated ethylenes. In our system, we propose a similar first step of the reaction, with $(PPh_3)_3RhH$ being the active catalytic species, and an insertion/ β -halo-elimination mechanism in which both *syn* and *anti* elimination can occur (Chapters 2 and 3).

1.5 CATALYTIC DEFLUORINATION

C-F bond containing pollutants

Fluorocarbons are a class of emerging environmental pollutants. This is related to the C-F bond being the strongest single bond carbon can form (120–129 kcal/mol for aliphatic and olefinic C–F bonds, and up to 154 kcal/mol in C₆F₆).¹⁴¹ Fluorine also has high electronegativity, low polarizability, and a small covalent radius.¹⁴¹ These characteristics result in fluorocarbons being thermally stable, water repellent, and resistant to chemical degradation, making them ideal for product such as: refrigerants, pharmaceuticals, pesticides, and non-adhesive polymers. Unfortunately, these same properties cause fluorocarbons to be environmentally persistent compounds. As of 2005, at least one C-F bond is found in 30-40% of agrochemicals and 20-30% of pharmaceuticals.¹⁴² Removing the C-F bonds eliminates the potential hazards associated with these compounds, however C-F activation is hard to achieve, even with transition metals, as fluorocarbons are poor ligands (Lewis bases) and poor substrates for nucleophilic substitution or oxidative addition to metals.

Catalytic C-F bond activation

Interest in transition metal promoted C-F bond activation has been increasing in recent decades, mirroring the growth of fluorocarbons in new materials, pharmaceuticals, and other applications.¹⁴²⁻¹⁵⁵ However, catalytic homogeneous hydrodefluorination was not reported until the last decade, with the first report by Aizenberg and Milstein in 1994.¹⁵⁶ Since then, there have been other reports of catalytic C-F bond activation systems.¹⁵⁶⁻¹⁸⁴

The catalytic phosphinorhodium systems have the highest activity toward sp^2 -hybridized C-F bonds and are active toward fluorinated arenes^{156-160,182} and alkenes.^{161,169,180,181} In these studies, H_2 and various silanes have been employed as reducing agents, and alkyl and aryl phosphines have been used as ancillary ligands. Most notably, hexafluorobenzene was defluorinated to pentafluorobenzene using $(PMe_3)_3RhC_6F_5$ and H_2 (80 psi),^{156,157} fluoronaphthalene was taken to naphthalene using $(PCy_3)_2Rh(H)Cl_2$ and H_2 (80 psi),¹⁶⁰ and hexafluoropropene to 1,1,1-trifluoropropane using $(PEt_3)_3RhH$ and H_2 and a variety of silane complexes^{161,169,181} (Figure 1.8).

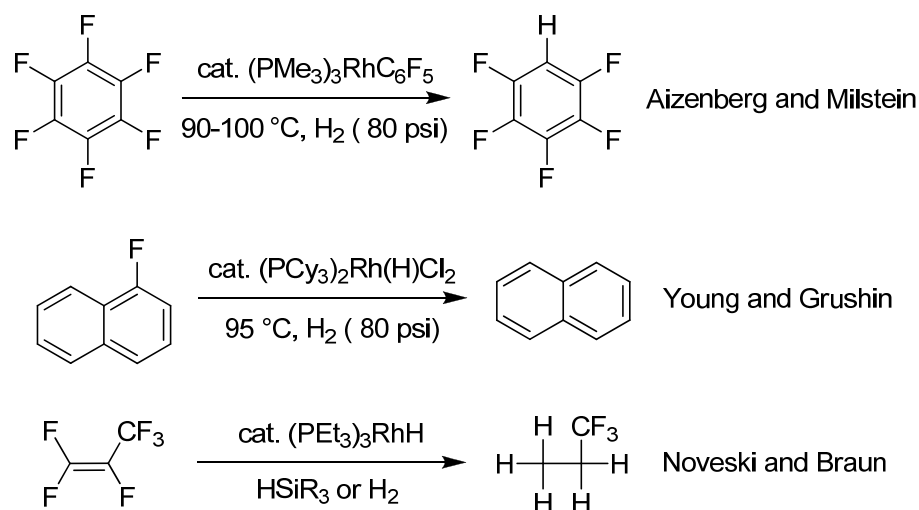


Figure 1.8. Notable catalytic defluorination systems for the degradation of sp^2 -hybridized C-F bonds, all using phosphinorhodium catalyst and H_2 and various silanes as reducing agents.

In 1995, Aizenberg and Milstein proposed a mechanism for the catalytic C-F bond activation of hexafluorobenzene with $(PMe_3)_4RhH$ and H_2 in the presence of NEt_3 (Figure 1.9).¹⁵⁷ They isolated $(PMe_3)_3Rh(C_6F_5)$, which reacts with H_2 to form, $(PMe_3)_3RhH_2(C_6F_5)$, which undergoes reductive elimination of C_6F_5H (Figure 1.9).¹⁵⁷

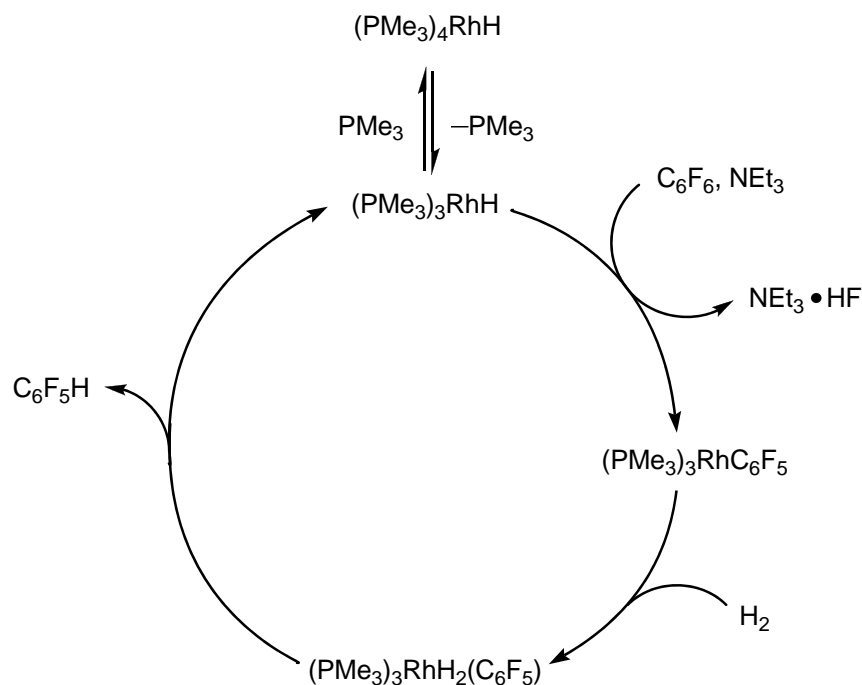


Figure 1.9. Proposed catalytic cycle for the defluorination of C₆F₆ by (PMe₃)_nRh-H complexes.¹⁵⁷ (Adapted from reference 157.)

We became interested in phosphinorhodium catalysts with H₂ or silane as the reducing agent due to their apparent preference for sp²-hybridized C-F bonds, and our interest in haloalkene dehalogenation.^{75,76,185} The homogeneous model systems we studied used (PPh₃)₃RhCl as the pre-catalyst and both Et₃SiH, and H₂ were explored as the reducing agent. In both systems rhodium-hydrides were active intermediates, and were active toward both C-Cl and C-F bonds. These systems also fulfill the requirements of a homogenous model system for use in understanding the heterogeneous catalyst mechanisms of noble metal catalysts with hydrogen reducing agent used in pump-and-treat remediation of contaminated water. The mechanistic information obtained from this system was then applied to the heterogeneous system of Rh/Al₂O₃ using H₂ as the reducing agent.

The overall goal of mechanistically studying a homogeneous metal hydride system and then applying the knowledge gained to a heterogeneous model was attained. The goal of finding a solution to the major problem of *cis*-DCE accumulation was accomplished (Figure 1.4). The rhodium hydride systems studied showed a preference for lower halogenated substrates over higher halogenated substrates; monohaloethylenes were degraded the fastest, and PCE was degraded the slowest.

1.6 SCOPE OF DISSERTATION

The objective of this work was to study the dehalogenation of environmental pollutants mediated by rhodium hydrides. The product distribution and mechanism of dehalogenation was explored and the information obtained can possibly be applied to improve future remediation strategies. In Chapter 2, the dehalogenation of chlorinated and fluorinated ethylenes was explored using $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH , and counter-intuitively, vinyl fluoride was dehalogenated *6 times faster* than vinyl chloride. This study established substrate scope and preferences for the Et_3SiH and $(\text{PPh}_3)_3\text{RhCl}$ catalytic system. In Chapter 3, the mechanism for dehalogenation of chlorinated and fluorinated ethylenes was elucidated using H_2 as the reducing agent with the pre-catalyst $(\text{PR}_3)_3\text{RhCl}$. These results were compared to those from using Et_3SiH as the reducing agent. Dehalogenation using $(\text{PPh}_3)_3\text{RhCl}$ and either H_2 or Et_3SiH support an insertion/ β -chloride elimination mechanism; however the two systems display distinct differences. Based on these differences, the dominant pathway for Et_3SiH is proposed to involve rhodium(I), while the H_2 system is proposed to primarily involve rhodium(III). In Chapter 4, a heterogeneous catalytic system using $\text{Rh}/\text{Al}_2\text{O}_3$ as the catalyst and H_2 as the reducing agent was investigated. Consistent with the homogenous system of $(\text{PPh}_3)_3\text{RhCl}$ and H_2 , the data from this system also supports an insertion/ β -Cl-elimination mechanism as the dominant degradation pathway. Ultimately, the goal of this work was to facilitate the preparation of engineered pump-and-treat strategies that will function to effectively degrade environmental pollutants to benign products with no halogen substituents.

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CHAPTER TWO

CATALYTIC DEHALOGENATION OF sp^2 C-F AND C-Cl BONDS IN FLUORO- AND CHLOROALKENES

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Catalytic dehalogenation of fluorinated and chlorinated ethylenes by $(\text{PPh}_3)_3\text{RhCl}$ in the presence of Et_3SiH at 35°C is described, and product identity and kinetic parameters were determined. This system has an *intramolecular* preference for Cl over F removal, an *intermolecular* preference for F- over Cl-containing alkenes, and a strong preference for sp^2 - over sp^3 -hybridized carbon-halogen bonds. Both the substitution pattern and the substituent identity are important in determining the rate of the dehalogenation.

2.1 INTRODUCTION

Interest in transition metal promoted C-F bond activation has been increasing in recent decades, mirroring the growth of fluorocarbons in new materials, including: pharmaceuticals, refrigerants, pesticides, and non-adhesive polymers.¹⁻¹¹ The C-F bond is the strongest bond carbon can form (120–129 kcal/mol for aliphatic and olefinic C–F bonds, and up to 154 kcal/mol in C₆F₆).¹² Fluorine also has high electronegativity, low polarizability, and a small covalent radius.¹² These characteristics make fluorocarbons thermally stable, water repellent, and resistant to chemical degradation, which is great for material applications, but also makes them environmentally persistent. As of 2005, at least one C-F bond is found in 30-40% of agrochemicals and 20-30% of pharmaceuticals.³ Removing the C-F bonds eliminates the potential hazards associated with these compounds.

While there have been substantial advances in C-F activation reactions, catalytic systems remain rare.¹³⁻³¹ Since the initial report, in 1994, of catalytic C-F activation by Aizenberg and Milstein,¹³ phosphinorhodium complexes have emerged as promising homogenous defluorination catalysts, as they activate fluorinated arenes¹³⁻¹⁷ and alkenes.^{18,26} In these studies, H₂ and various silanes have been employed as reducing agents, and alkyl and aryl phosphines have been used as ancillary ligands. We became interested in these systems due to their apparent preference for sp²-hybridized C-F bonds, and our interest in haloalkene dehalogenation.³²⁻³⁴

To this end we initiated a study of phosphinorhodium catalyzed dehalogenation of simple mono- and disubstituted fluoro- and chloroalkenes. These substrates are important to study, not only for their environmental relevance, but also because they

represent elementary sp^2 -hybridized structures that may yield valuable mechanistic information. Herein we report on catalytic dehalogenation of halogenated ethylenes catalyzed by $(PP_3)_3RhCl$ in the presence of Et_3SiH as the reducing agent. Kinetic parameters are presented, as well as substrate scope and reaction preferences.

2.2 EXPERIMENTAL PROCEDURES

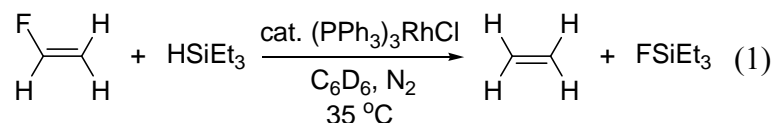
General Considerations. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox (M. Braun Unilab) kept at or below 1 ppm oxygen. All solvents and reagents were purchased from commercial suppliers unless otherwise stated; solvents were dried prior to use. Benzene- d_6 and *p*-xylene were distilled from a sodium/benzophenone ketyl under nitrogen and stored in a sealed flask. *Cis*-dichloroethylene, 1,1-dichloroethylene, dichloromethane, and trichloroethane were dried over CaCl_2 and vacuum transferred into a sealed flask and stored in the dark over 4 Å molecular sieves. Fluorobenzene was dried over P_2O_5 and vacuum transferred to a sealed flask. All fluorine containing gases, purchased from SynQuest Labs, Inc, and vinyl chloride were used as received. $(\text{PPh}_3)_3\text{RhCl}$ and $(\text{PPh}_3)_3\text{RhF}$ were prepared and characterized according to literature procedure.^{35,36} Dechlorination reactions were performed in sealed NMR tubes to prevent volatilization of reactants or products. NMR spectra were acquired on Varian UNITY Inova NMR spectrometers (300 MHz, 500 MHz, and 600 MHz) and referenced to the residual protiated solvent. ^{19}F NMR and ^{31}P NMR spectra were acquired at 282.12 and 121.4 MHz respectively with ^{31}P referenced to 85% phosphoric acid and ^{19}F referenced to trichlorofluoromethane, both as external standards.

Reaction Kinetics. A stock solution containing $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), HSiEt_3 (125 mM) and *p*-xylenes (3.3 mM; used as an internal standard), was prepared in C_6D_6 . An aliquot (700 μL) of this stock solution was added by syringe into a sealable NMR tube. The substrate was then added either via syringe in the glovebox or transferred as a gas on a Schlenk line using a known volume bulb. The reaction mixture was kept

frozen until immediately prior to placement in the NMR probe; NMR probe temperature was set to 35 °C. The data was collected in an arrayed experiment set to scan every two to five minutes. The rates of dehalogenation were determined by quantifying the disappearance of the substrate resonances. This data was plotted as concentration versus time and fit to a first-order exponential decay function. Products of the dehalogenation reactions were determined by comparing the NMR resonances, chemical shifts, and coupling constants to authentic standards.

2.3 RESULTS AND DISCUSSION

Treatment of vinyl fluoride (20 mM in C₆D₆) with Et₃SiH (125 mM) and a catalytic amount of (PPh₃)₃RhCl (2.4 mM) at 35 °C leads to complete defluorination in 50 minutes (eq. 1). The initial products are Et₃SiF, Et₃SiCl and ethylene. The yield of this process is nearly quantitative as 90% of the C₂ mass is accounted for as ethylene as determined by ¹H NMR integration versus an internal standard, *p*-xylene. With extended reaction times, ethylene is consumed yielding Et₃SiCHCH₂, ethane, and butenes. If fluoride is transferred to the rhodium during the course of the reaction, (PPh₃)₃RhF may be an intermediate. While not proof of its intermediacy, it is noteworthy that the defluorination reaction can be performed starting with (PPh₃)₃RhF, which was prepared independently.³⁶ No reaction is observed when vinyl fluoride is treated with either Et₃SiH or (PPh₃)₃RhCl alone.



Under identical reaction conditions, vinyl chloride undergoes dechlorination to yield ethylene. Ethylene is also consumed at long reaction times in this system, but the downstream products are butenes presumably arising from dimerization and isomerization.³⁷⁻⁴¹

Mixed fluorochloroethylenes also undergo dehalogenation. Reaction of 1,1-chlorofluoroethylene proceeds rapidly giving complete dehalogenation in 120 minutes at 35 °C. The dechlorination product, vinyl fluoride, is observed by ¹H NMR as an intermediate during the reaction. No vinyl chloride was observed indicating that *intramolecular* competition favors chloride over fluoride elimination. Dehalogenation

of a mixture of 1,2-chlorofluoroethylenes shows similar selectivity. As with 1,1-chlorofluoroethylene, only vinyl fluoride is observed during the dehalogenation of the 1,2-chlorofluoroethylene mixture, reinforcing the conclusion that intramolecular competition favors chloride loss in this system.

To further characterize this fundamental C-F bond activation process, a study of the reaction kinetics was undertaken. The kinetic experiments were conducted in a temperature-controlled NMR probe under the same conditions described above. Concentrations of the reactants and products were determined by integration of the ^1H NMR resonances relative to those of the internal standard (*p*-xylene). All substrates exhibited pseudo first-order kinetics, and the relative rate constants of substrate loss are summarized in Figure 2.1. The observed rate constants for all substrates are listed in Table 2.1. A representative linearized degradation of each substrate versus time is displayed in Figure 2.2. A representative set of kinetic data for vinyl fluoride degradation is shown in Figure 2.3.

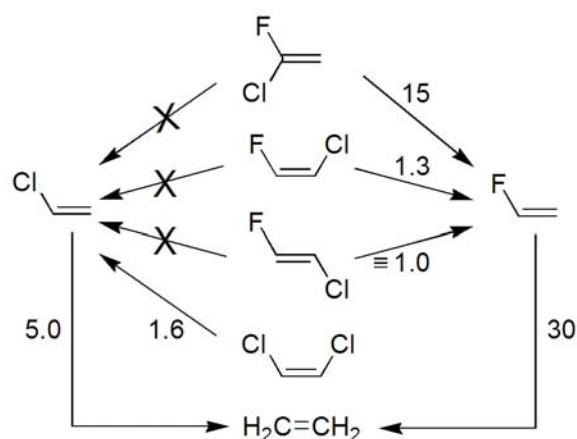


Figure 2.1. Relative rate constants of dehalogenation for chlorinated and fluorinated ethylenes and their subsequent reaction products. Values were determined from loss of substrate over time using ^1H NMR at 35 °C and are relative to the rate of dehalogenation for *trans*-1,2-chlorofluoroethylene ($k_{\text{obs}} = 1.7 \times 10^{-5} \text{ s}^{-1}$). Each sealable NMR tube contained substrate (20-30 mM), catalyst $((\text{PPh}_3)_3\text{RhCl}$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6 .

Table 2.1. Average observed rate constant of substrate degradation (k_{obs}) from replicate kinetic runs, error is the standard deviation of the replicate experiments. Values were determined from loss of substrate versus time using ^1H NMR at 35 °C. Each sealable NMR tube contained substrate (20-30 mM), catalyst $((\text{PPh}_3)_3\text{RhCl}$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6 .

Substrate	k_{obs} (s^{-1})
vinyl fluoride	$(5.0 \pm 0.5) \times 10^{-4}$
1,1-chlorofluoroethylene	$(2.4 \pm 0.8) \times 10^{-4}$
vinyl chloride	$(8 \pm 1) \times 10^{-5}$
1,1-dichloroethylene	$(4 \pm 2) \times 10^{-5}$
<i>cis</i> -1,2-dichloroethylene	$(2.7 \pm 0.8) \times 10^{-5}$
<i>cis</i> -1,2-chlorofluoroethylene	$(2.2 \pm 0.3) \times 10^{-5}$
<i>trans</i> 1,2-chlorofluoroethylene	$(1.7 \pm 0.4) \times 10^{-5}$

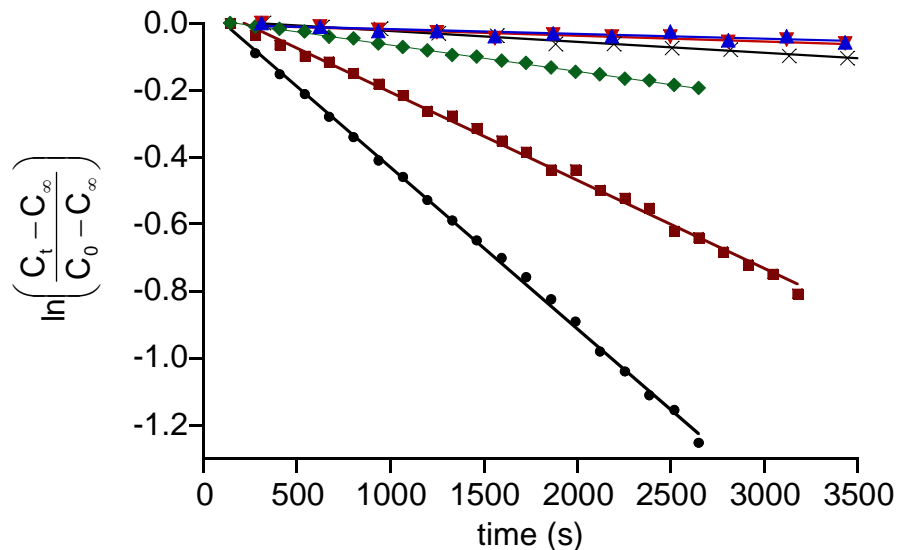


Figure 2.2. Representative linearized degradation of each substrate versus time. Values were determined from loss of substrate using ^1H NMR at 35 °C. Each sealable NMR tube contained substrate (20-30 mM), catalyst $((\text{PPh}_3)_3\text{RhCl}$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6 . Lines are linear fits to the experimental data. Vinyl fluoride (●); 1,1-fluorochloroethylene(■); vinyl chloride(◆); 1,2-*cis*-dichloroethylene(×); 1,2-*cis*-fluorochloroethylene(▲); 1,2-*trans*-fluorochloroethylene(▼).

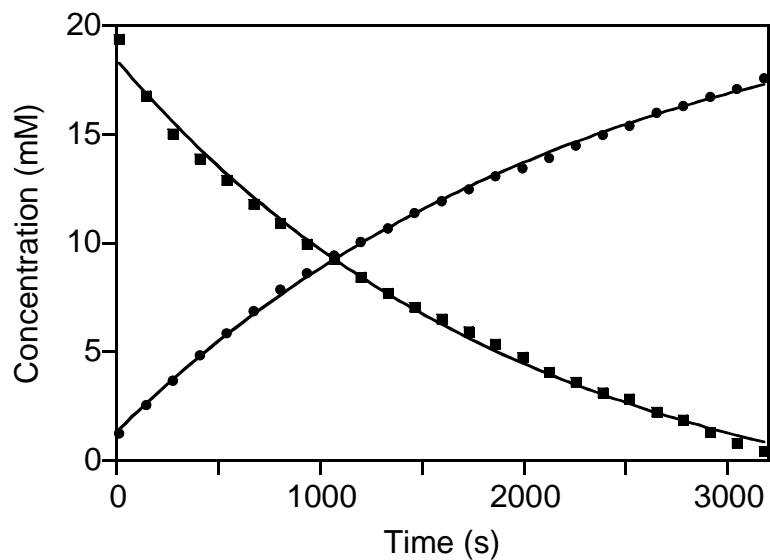


Figure 2.3. Vinyl fluoride degradation by $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM) and Et_3SiH (125 mM) at 35 °C and the subsequent appearance of ethylene as a reaction product. Curves represent nonlinear first-order decay and growth fits to the data for vinyl fluoride and ethylene respectively.

The reaction was performed with a catalyst loading as low as 0.5%. The measured dehalogenation rate varies linearly with catalyst concentration from 0.1 mM to 2.4 mM (Figure 2.4).

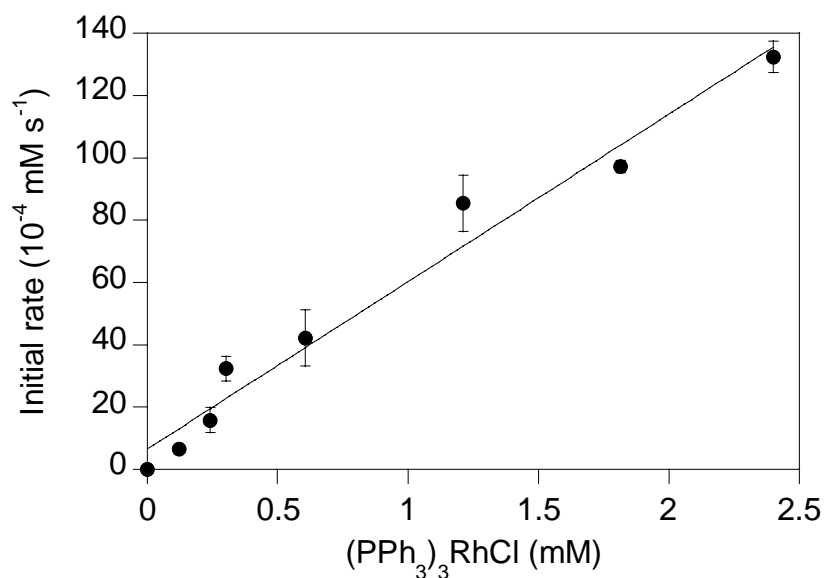


Figure 2.4. Observed degradation rate of *cis*-1,2-dichloroethylene in the presence of 125 mM Et₃SiH and increasing concentration of catalyst (0.1 mM to 2.4 mM) in C₆D₆. Values were determined using initial rates for loss of substrate using ¹H NMR at 55 °C. The fit is linear to the initial rate data, R² = 0.9721. Error bars were determined from the standard error in the linear fit in the initial rate plots.

Given the generally lower reactivity of C-F bonds compared to C-Cl bonds, it was surprising to find vinyl fluoride to be the fastest substrate with a dehalogenation rate six times that of vinyl chloride. This *intermolecular* kinetic preference for the fluorinated substrate stands in contrast to the preferential C-Cl cleavage seen in chlorofluoroalkenes, the result of *intramolecular* competition. Another striking kinetic result was the much faster dehalogenation of 1,1-chlorofluoroethylene compared to 1,2-chlorofluoroethylenes, with the latter substrates taking hours instead of minutes to complete.

The inherently lower reactivity of 1,2-dihaloalkenes compared to 1,1-dihaloalkenes in this system is also seen with *cis*-1,2-dichloroethylene and 1,1-dichloroethylene. Both substrates were found to yield vinyl chloride as an intermediate. No isomerization of the *cis*-1,2-dichloroethylene to *trans*-1,2-dichloroethylene was observed during the dechlorination. Similar to the fluorochloroethylenes, 1,1-dichloroethylene was dechlorinated faster than *cis*-1,2-dichloroethylene at 35 °C. Taken together, the results indicate that the substitution pattern is potentially as important as the substituent identity in determining the dehalogenation rate.

This system shows a marked preference for sp^2 -hybridized C-X bonds versus sp^3 -hybridized bonds. For example, many of the kinetic runs were conducted with a small amount of CH_2Cl_2 present due to co-crystallization with $(PPh_3)_3RhCl$. No decay of the CH_2Cl_2 peak area was observed during the dehalogenation of sp^2 -hybridized C-X bond containing substrates. The same lack of reactivity was found when CH_2Cl_2 was employed alone as a substrate, in the absence of any potential competitors. Similarly, 1,1,2-trichloroethane and 1-fluorooctane show no dehalogenation under the reaction

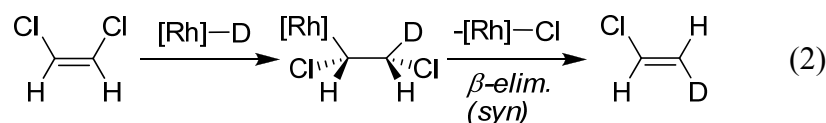
conditions. The lack of reactivity with sp^3 C-F bonds is notable as it indicates that the reactive species is not Et_3Si^+ , which has been shown to catalytically and selectively defluorinate sp^3 C-F bonds.³¹

Not all sp^2 -hybridized C-F bonds are reactive; fluorobenzene shows no defluorination under these conditions. Other groups working with closely related systems have also noted the recalcitrant nature of fluorobenzene.¹³⁻¹⁷ Young and Grushin were able to activate the C-F bond of 1-fluoronaphthalene using $(PCy_3)_2Rh(H)Cl_2$ under more forcing conditions (95 °C and 80 psi H_2) than employed in this study.¹⁷

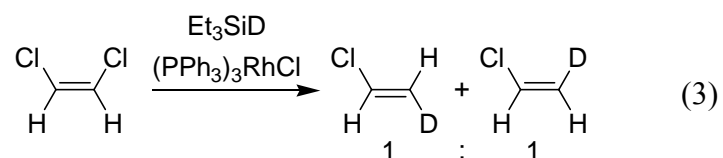
The catalytic defluorination system using $(PPh_3)_3RhCl$ as a pre-catalyst in the presence of Et_3SiH is defined by three notable features: fluoroalkenes react faster than fluoroarenes and fluoroalkanes; vinyl fluoride reacts faster than vinyl chloride; and, (in an apparent contradiction) when both fluoro and chloro substituents are present, such as in 1,1-chlorofluoroethylene, the chloro substituent is removed preferentially. These facts suggest a mechanism that has (at least) two steps, rate-determining insertion of the alkene into a metal-hydride or metal-silyl bond followed by cleavage of the C-X bond. Such a general scheme would account for the enhanced reactivity of the vinyl fluoride owing to the small steric profile and good π -donating ability of the fluoro substituent. It also allows for an intramolecular preference of C-Cl cleavage over C-F cleavage, if chloride is a better leaving group than fluoride in this system, so long as it occurs after the rate-determining step.

While the reaction mechanism has not been established, we have been able to exclude two leading candidates: insertion/*syn*- β -halide elimination and hydrosilation forming haloalkylsilane intermediates.

A two-step process that involves insertion of a haloalkene into the Rh-H bond to yield a *syn*- β -haloalkyl rhodium species followed by *syn*- β -halogen elimination predicts stereospecific placement of the incoming hydride. The example of Rh-D and 1,2-*cis*-dichloroethylene is shown in eq. 2.



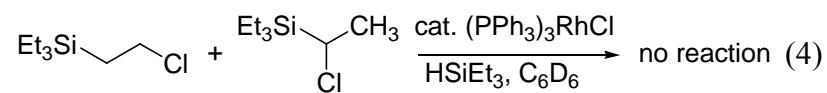
When 1,2-*cis*-dichloroethylene is treated with Et₃SiD and (PPh₃)₃RhCl, a 1:1 mixture of *E*- and *Z*-1-chloro-2-deuteroethylene is produced, even at early reaction times (eq. 3).



This is strong evidence against the simple insertion/*syn*- β -elimination mechanism (eq. 2).

A second mechanism involves catalytic hydrosilation of the vinyl halides to give haloalkylsilanes. These haloalkylsilanes would then eliminate Et₃SiX and the dehalogenated alkene. Independent preparation of α - and β -chloroalkylsilane, the hydrosilation product of vinyl chloride, was accomplished by chlorinating Et₄Si using Cl₂ with PCl₅ catalyst under ultraviolet light.^{42,43} Subjecting this mixture to the catalytic dehalogenation conditions ((PPh₃)₃RhCl, Et₃SiH, C₆D₆) resulted in no reaction up to 72

hours (eq. 4). The stability of these haloalkylsilanes to the reaction conditions rules out their intermediacy.



These preliminary mechanistic studies exclude mechanisms for specific substrates, *cis*-1,2-dichloroethylene and vinyl chloride, respectively, but it should be noted that it is possible that these mechanisms are operative for other substrates. Further mechanistic studies are discussed in Chapter 3.

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CHAPTER THREE

PHOSPHINORHODIUM-CATALYZED DEHALOGENATION OF CHLORINATED AND FLUORINATED ETHYLENES: DISTINCT MECHANISMS WITH TRIETHYLSILANE AND DIHYDROGEN

I would like to acknowledge Kristen A. Thoreson for synthesis of some of the $(\text{PR}_3)_3\text{RhCl}$ complexes, as well as help on the phosphine:rhodium ratio studies.

Catalytic dehalogenation of chlorinated and fluorinated ethylenes by $(PR_3)_3RhCl$ complexes is described. The C-Cl and C-F bonds are activated by the catalyst in the presence of triethylsilane (Et_3SiH) or dihydrogen (H_2). Spectroscopic studies in addition to substrate preference indicate that rhodium hydride species are important intermediates. Kinetic parameters and product distribution for dehalogenation reactions were determined using NMR spectroscopy. Evidence for sequential chlorine removal was obtained, and the rates of dehalogenation were found to increase with decreasing halogen content. It was also shown that this catalytic system has a preference for sp^2 -over sp^3 -hybridized carbon halogen bonds. Dechlorination using $(PPh_3)_3RhCl$ and either H_2 or Et_3SiH support an insertion/ β -chloride elimination mechanism; however the two systems display distinct differences. Based on these differences, the dominant pathway for Et_3SiH is proposed to involve rhodium(I), while the H_2 system is proposed to primarily involve rhodium(III). This is supported with isotopic labeling studies using D_2 , Et_3SiD , and $(PPh_3)_3RhD$ which yield different stereochemistry of dechlorinated products. With D_2 , only products consistent with *syn*- β -chloride elimination were observed, while with Et_3SiD and $(PPh_3)_3RhD$ both *syn*- and *anti*- β -chloride elimination products were observed. In addition, NMR spectroscopic evidence of different hydride intermediates in the H_2 and Et_3SiH systems were obtained. Different pathways for dehalogenation with Et_3SiH and H_2 is further supported by the observation of 1,2-addition (hydrogenation) products using H_2 and lack of 1,2-addition (hydrosilation) products using Et_3SiH .

3.1 INTRODUCTION

Thousands of tons of persistent chlorocarbons are produced annually, many of which are toxic and bioaccumulative.¹⁻³ Chlorinated ethylenes, specifically perchloroethylene (PCE) and trichloroethylene (TCE), are potential carcinogens that are found in both soil and water systems.¹⁻⁸ The toxic effects associated with these complexes is related to the chlorine substituents. Accordingly, removal of the chlorine atoms leads to detoxification.⁹ A good example of this is vinyl chloride, a carcinogen, which yields non-toxic ethylene upon dechlorination.¹⁰

Remediation of these pollutants by dechlorination has involved the use of zero-valent metals,¹¹⁻¹⁹ electrochemical processes,²⁰⁻²⁵ and microbial degradation.^{5,7,26-28} Several heterogeneous noble metals have also been shown to degrade chlorinated ethylenes and other chlorocarbons using H₂ as the reductant.^{22,23,29-35} In these systems the noble metal is the catalyst and H₂ is the reducing agent. We propose that metal hydrides play an active role in these systems as H₂ is needed for degradation to occur. In order to probe this mechanistic hypothesis, we have explored the use of homogenous rhodium hydrides as catalysts for the degradation of chlorinated ethylenes.

Heterogeneous rhodium-based catalysts have been used to dechlorinate chlorinated alkenes and alkanes. For example, Rh/alumina, Rh/SiO₂ or RhCl₃ catalysts in the presence of H₂ fully dechlorinate dichloropropane,³⁶ dichlorobutenes,³⁷ perchloroethylene,³⁸ trichloroethylene²⁹ and 1,2-dichloroethane.^{29,39,40} However due to difficulties associated with studying reaction mechanisms in heterogeneous systems, little is known about the mechanism of these reactions.

There are also a few examples of homogenous catalytic systems that use a phosphinorhodium catalyst and hydrogen to degrade chlorofluoromethanes⁴¹ and chloroalkanes.^{40,42} Furthermore, Esteruelas *et al.* employed chlorotris(triphenylphosphino)rhodium, (PPh₃)₃RhCl, as a homogeneous catalyst in the presence of triethylsilane (Et₃SiH) to dehalogenate chlorinated cyclic⁴³ and aryl^{44,45} compounds (i.e., γ -hexachlorocyclohexane, chlorobenzene and polychlorinated benzenes). The proposed first step of this reaction is the production of Et₃SiCl and (PPh₃)₃RhH as the active catalytic intermediate, and for hexachlorocyclohexanes, an oxidative addition/ β -chloride elimination mechanism was proposed.⁴³

Phosphinorhodium complexes also catalytically activate sp²-hybridized C-F bonds, including fluorinated arenes⁴⁶⁻⁵¹ and alkenes.⁵²⁻⁵⁶ In these systems, H₂ and various silanes have been employed as reducing agents, and alkyl and aryl phosphines have been used as ancillary ligands.⁴⁶⁻⁵⁶

Previously we reported that dehalogenation of vinyl fluoride, vinyl chloride, and chlorofluoroethylenes occurs in the presence of (PPh₃)₃RhCl and Et₃SiH.⁵² This reaction was found to have an *intermolecular* preference for C-F bond activation versus C-Cl bond activation, with vinyl fluoride degrading the fastest of the substrates tested with a pseudo-first-order k_{obs} of $5.0 \pm 0.5 \times 10^{-4} \text{ s}^{-1}$ at 35 °C in C₆D₆. The data also supports an *intramolecular* preference for C-Cl bond activation versus C-F bond activation. Specifically, dehalogenation of chlorofluoroethylenes resulted in the observation of only vinyl fluoride and not vinyl chloride. The rate of dehalogenation increased with sequential halogen removal, such that dihaloalkenes were degraded slower than monohaloalkenes. The substitution pattern also affected the rates; 1,1-

dihaloalkenes were degraded faster than the 1,2-dihaloalkenes. No isomerization of the 1,2-dichloroethylenes was observed during the dehalogenation. This system showed marked preference for sp^2 -hybridized C-X bonds versus sp^3 -hybridized bonds. Halogenated ethylenes were readily degraded under the conditions, but 1-fluorooctane, 1,1,2-trichloroethane, dichloromethane, and 1,2-dichloroethane were not. While this earlier study established substrate scope and preferences, a firm mechanistic understanding was not attained.

Herein we report on the catalytic dehalogenation of halogenated ethylenes catalyzed by $(PR_3)_3RhCl$. We expand on our preliminary communication of the dehalogenation reactions catalyzed by $(PPh_3)_3RhCl$ in the presence of Et_3SiH , and investigate the dehalogenation using H_2 as the reducing agent. These two systems were found to exhibit significant differences. We propose mechanisms for the reduction with Et_3SiH , which favors a Rh(I) pathway, and reduction with H_2 , which favors a Rh(III) pathway.

3.2 EXPERIMENTAL PROCEDURES

General Considerations. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox (M. Braun Unilab). All solvents and reagents were purchased from commercial suppliers unless otherwise stated; solvents were dried prior to use. Benzene- d_6 and *p*-xylene were distilled from a sodium/benzophenone ketyl under nitrogen and stored in a sealed flask. *Cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene (TCI America), trichloroethylene, perchloroethylene, 1,1-dichloroethylene, dichloromethane (Sigma-Aldrich), 1,2-dichloroethane and trichloroethane (Acros) were dried over CaCl_2 and vacuum transferred into a sealed flask and stored in the dark over 4 Å molecular sieves. Tetrahydrofuran- d_8 , was dried over 4 Å molecular sieves. Vinyl chloride and d_1 -triethylsilane (Et_3SiD) purchased from Sigma-Aldrich, all fluorine containing gases purchased from SynQuest Labs, Inc, H_2 purchased from Airgas, and deuterium purchased from Matheson Gas Products, Inc were used as received. $(\text{PPh}_3)_3\text{RhCl}$,⁵⁷ $(\text{PPh}_3)_4\text{RhH}$,⁵⁸ $(\text{PPh}_3)_3\text{RhH}$,⁴³ $(\text{PPh}_3)_3\text{RhF}$,⁵⁹ $(\text{PMe}_3)_3\text{RhCl}$,⁶⁰ and $(\text{PEt}_3)_3\text{RhCl}$ ⁶⁰ were prepared according to literature procedure and characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Dechlorination reactions were performed in sealed NMR tubes to prevent volatilization of reactants or products. NMR spectra were acquired on Varian UNITY Inova NMR spectrometers (300 MHz, 500 MHz, and 600 MHz) and referenced to the residual protiated solvent ($\text{C}_6\text{D}_5\text{H}$, 7.16 ppm). ^{19}F NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired at 282.12 and 121.4 MHz respectively with ^{31}P referenced to 85% phosphoric acid and ^{19}F referenced to trichlorofluoromethane, both as external standards.

[P(*p*-FC₆H₄)₃RhCl, [P(*p*-MeOC₆H₄)₃RhCl. The syntheses were modified from the procedure described by Montelatici *et al.*⁶¹ 1,5-Cyclooctadienerhodium(I) chloride dimer ([COD)RhCl]₂) was dissolved in toluene and three molar equivalents of the desired phosphine were added. The solution was left to stir for 14 hours at ambient temperature. Complexes were purified by crystallization from toluene. Crystals were isolated by filtration and dried *in vacuo*. The complexes were characterized by ¹H and ³¹P{¹H} NMR and compared to the literature.⁶¹

Reaction Kinetics with Et₃SiH. Kinetic experiments were performed in sealed NMR tubes monitoring the reaction by ¹H NMR spectroscopy. The reaction mixture was kept frozen until immediately prior to placement in the NMR probe; NMR probe temperature was set to 35 °C or 55 °C. The kinetic data was collected in an arrayed experiment set to scan every two to five minutes. The rates of dehalogenation were determined by quantifying the disappearance of the substrate resonances, integrating versus internal standard *p*-xylene. This data was plotted as concentration versus time and fit to a first-order exponential decay function.

Relative reaction rates with H₂. Substrate disappearance after 60 minutes was determined using sealed NMR tubes and monitoring the reaction by ¹H NMR spectroscopy. The reaction mixture was kept frozen until immediately prior to placement in the NMR probe; NMR probe temperature was set to 22 °C. A quantitative NMR spectrum was taken to determine the initial concentration of the substrate. The NMR tube was then immediately frozen in liquid nitrogen until ready to mix by inversion. The tube was thawed to room temperature and mixed by repeated inversion, at a rate of 15 inversions per minute, for 60 minutes and then frozen in liquid nitrogen.

The final NMR spectrum was taken with the same parameters as the first NMR spectrum. The percentages of substrate dehalogenation were determined by quantifying the disappearance of the substrate resonances, integrating versus internal standard *p*-xylene, and determining the amount reacted by comparing the initial NMR and final NMR integration.

Dechlorination using Et₃SiH. A stock solution containing (PPh₃)₃RhCl (2.4 mM), Et₃SiH (125 mM), and *p*-xylene (3.3 mM; used as an internal standard), was prepared in C₆D₆. An aliquot (700 μL) of this stock solution was added by syringe to a sealable NMR tube. The substrate was then added either via syringe in the glovebox or transferred as a gas on a Schlenk line using a known volume bulb. Kinetic data collection was performed as described above. Products of the dehalogenation reactions were determined by comparing the NMR resonances, chemical shifts, and coupling constants to authentic standards.

Dechlorination using H₂ (or D₂) gas. A stock solution containing (PPh₃)₃RhCl (2.4 mM), NEt₃ (150 mM), and *p*-xylene (3.3 mM; used as an internal standard), was prepared in C₆D₆. An aliquot (700 μL) of this stock solution was added by syringe into a sealable NMR tube. The substrate was then added either via syringe in the glovebox or transferred as a gas on a Schlenk line using a known volume bulb. The headspace was evacuated from the tube by freezing the solution and placing it under vacuum. The mixture was warmed to room temperature and the headspace was filled with approximately 1 atm H₂ (or D₂). The tube was inverted 3 times to mix H₂ into the C₆D₆ and then immediately froze in liquid N₂. Products of the dehalogenation reactions were

determined by comparing the NMR resonances, chemical shifts, and coupling constants to authentic standards.

Dechlorination using $(\text{PPh}_3)_4\text{RhH}$. A stock solution containing $(\text{PPh}_3)_4\text{RhH}$ (2.4 mM) and *p*-xylene (3.3 mM; used as an internal standard) was prepared in C_6D_6 . An aliquot (700 μL) of this stock solution was added by syringe into a sealable NMR tube. Substrate (20-30 mM) was added to this solution by syringe. The tube was mixed by inversion. Products and reaction progress was monitored using NMR spectroscopy at room temperature.

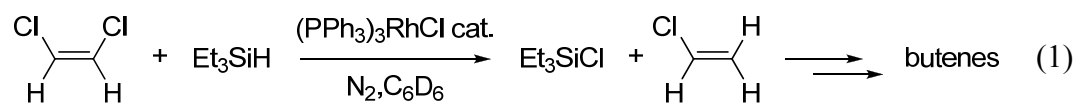
Dechlorination using $(\text{PPh}_3)_3\text{RhH}$ (or $(\text{PPh}_3)_3\text{RhD}$). A procedure similar to the literature was adapted.⁴³ A solution containing $(\text{PPh}_3)_3\text{RhCl}$ (10 mM) and $\text{Et}_3\text{SiH(D)}$ (30 mM) was prepared in C_6D_6 in a sealable NMR tube. The solvent and volatile materials were removed under vacuum on a Schlenk line. The solid was then redissolved in 700 μL of C_6D_6 in the sealable NMR tube, and an NMR taken to confirm only $(\text{PPh}_3)_3\text{RhH(D)}$ was present. Substrate (20 mM) was then added to this solution by syringe. The tube was mixed by inversion. Products and reaction progress were monitored using NMR spectroscopy at room temperature.

$(\text{PPh}_3)_n\text{RhCl}$ for use in phosphine ratio experiments. The catalyst was prepared *in situ* as described above using $[(\text{COD})\text{RhCl}]_2$ and PPh_3 . Appropriate equivalents of triphenylphosphine were added to a 2.4 mM Rh solution with 1.7 mM *p*-xylene in C_6D_6 . The solutions were left overnight to react. The Et_3SiH (125 mM) and *cis*-DCE (30 mM) were added by syringe. The sealable NMR tubes were frozen immediately and stored in liquid nitrogen until inserted in the NMR probe. Kinetic data collection was performed as stated above.

3.3 RESULTS

Dechlorination using Et₃SiH

Treatment of *cis*-1,2-dichloroethylene (*cis*-DCE, 30 mM in C₆D₆) with Et₃SiH (125 mM) and a catalytic amount of (PPh₃)₃RhCl (2.4 mM) at 55 °C leads to complete dechlorination in 80 minutes (*t*_{1/2} of 23 minutes) (eq. 1). The reaction was monitored by ¹H NMR spectroscopy. The initial products observed were vinyl chloride and Et₃SiCl (eq.1). Vinyl chloride was quickly dechlorinated to ethylene. Over the course of the reaction, 1-butene, and eventually *cis*- and *trans*-2-butene were also produced. After *cis*-DCE was fully degraded, a small amount of ethane was also observed. These results suggest that dechlorination to ethylene is followed by dimerization to 1-butene and ultimately isomerization to 2-butenes. These dimerization,^{62,63} and isomerization⁶⁴⁻⁶⁶ reactions are known. The yield of observed products was essentially quantitative, as vinyl chloride, ethylene, and butenes comprise over 95% of the C₂ mass. The product yields were determined by ¹H NMR integration versus an internal standard, *p*-xylene.



To further characterize this C-Cl bond activation process, a study of the reaction kinetics was undertaken. Kinetic experiments were conducted in a temperature-controlled NMR probe and concentrations of the reactants and products were determined by integration of the ¹H NMR resonances relative to those of the internal standard (*p*-xylene). Pseudo-first-order reaction kinetics were observed for the loss of *cis*-DCE under these reaction conditions. A sample kinetic plot depicting the

exponential degradation of *cis*-DCE with concomitant growth of products is shown in Figure 3.1. The C₂ mass balance is also depicted.

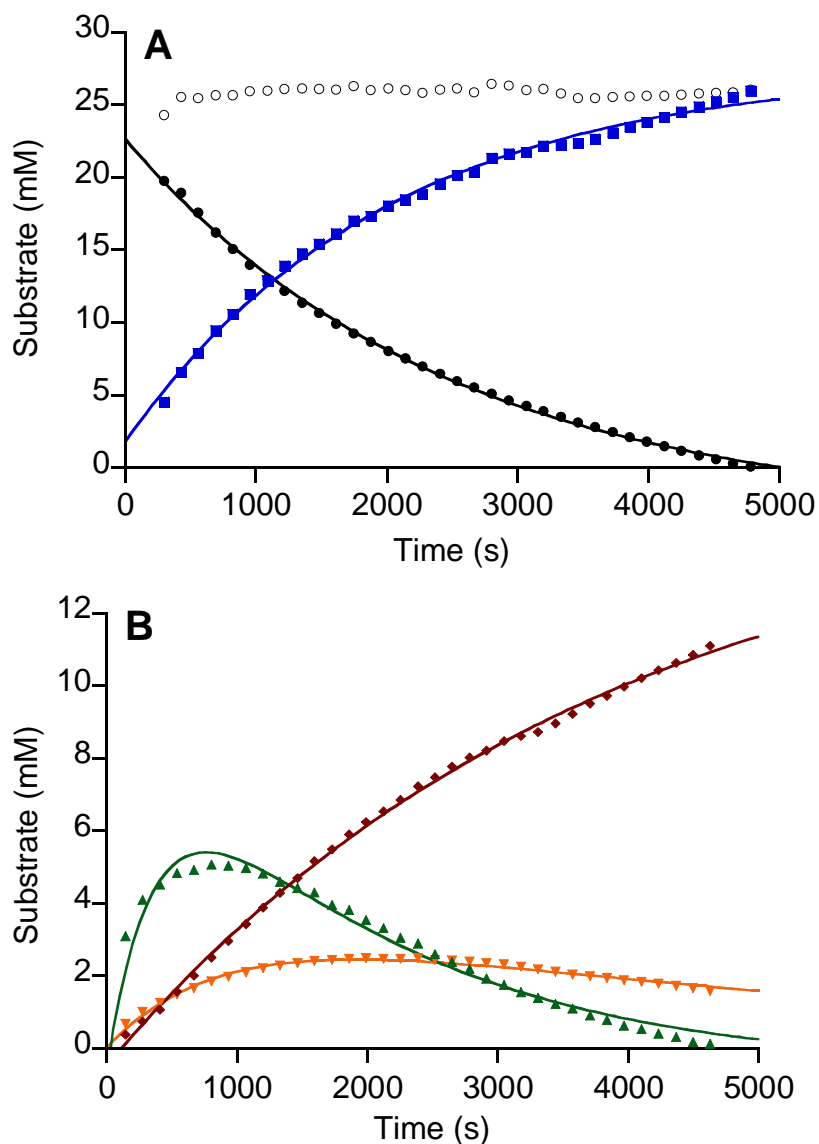


Figure 3.1. (A) *cis*-DCE degradation (●) by (PPh₃)₃RhCl (2.4 mM) and Et₃SiH (125 mM) at 55 °C and the subsequent appearance of reaction products (■ = sum of reaction products C₂ mass), as well as C₂ mass balance(○). (B) Growth of specific reaction products during the course of *cis*-DCE degradation: vinyl chloride (▲); ethylene (▼); butenes(◆). Data is fitted with first-order decay (*cis*-DCE) first-order exponential growth and decay (vinyl chloride and ethylene) and first-order exponential growth (butenes).

All products were observed after 10 minutes of reaction time at 55 °C. This is consistent with fast degradation of the vinyl chloride intermediate.⁵² The dimerization and isomerization reactions occurred while chlorinated substrates were still present in the reaction mixture.

Recently we reported that dehalogenation of vinyl fluoride, vinyl chloride, and chlorofluoroethylenes occurs in the presence of $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH .⁵² Pseudo-first-order observed rate constants for those previously reported as well as for *trans*-1,2-dichloroethylene (*trans*-DCE), TCE, and PCE are compiled in Table 3.1, and representative linearized plots are depicted in Figure 3.2. Reinforcing the previous conclusions about the reaction, the rate of dehalogenation was found to increase with sequential chlorine removal, such that PCE is degraded slowest, followed by TCE and the dihaloalkenes. The most facilely degraded substrates were the monohaloalkenes. When comparing the dichloroethylenes, the relative rates of degradation are very similar, with 1,1-dichloroethylene (1,1-DCE) reacting the fastest of the three.

Table 3.1. Average observed rate constant of substrate degradation (k_{obs}) from replicate kinetic runs, error is the standard deviation of the replicate experiments. Values were determined from loss of substrate versus time using ^1H NMR at 35 °C. Each sealable NMR tube contained substrate (20-30 mM), catalyst ($(\text{PPh}_3)_3\text{RhCl}$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6 . Relative rate constants (k_{rel}) are relative to the rate of dehalogenation of TCE ($0.7 \times 10^{-5} \text{ s}^{-1}$).

Substrate	$\text{Et}_3\text{SiH } k_{\text{obs}} (10^{-5} \text{ s}^{-1})$	k_{rel}
vinyl fluoride	$50 \pm 5^{\text{a}}$	71.4
1,1-chlorofluoroethylene	$24 \pm 8^{\text{a}}$	34.3
vinyl chloride	$8 \pm 1^{\text{a}}$	11.4
1,1-DCE	$4 \pm 2^{\text{a}}$	5.7
<i>cis</i> -DCE	$2.7 \pm 0.8^{\text{a}}$	3.9
<i>trans</i> -DCE	2.5 ± 0.9	3.6
<i>cis</i> -1,2-chlorofluoroethylene	$2.2 \pm 0.3^{\text{a}}$	3.1
<i>trans</i> -1,2-chlorofluoroethylene	$1.7 \pm 0.4^{\text{a}}$	2.4
TCE	0.7 ± 0.3	1.0
PCE	< 0.1	< 0.1

^aRef 52

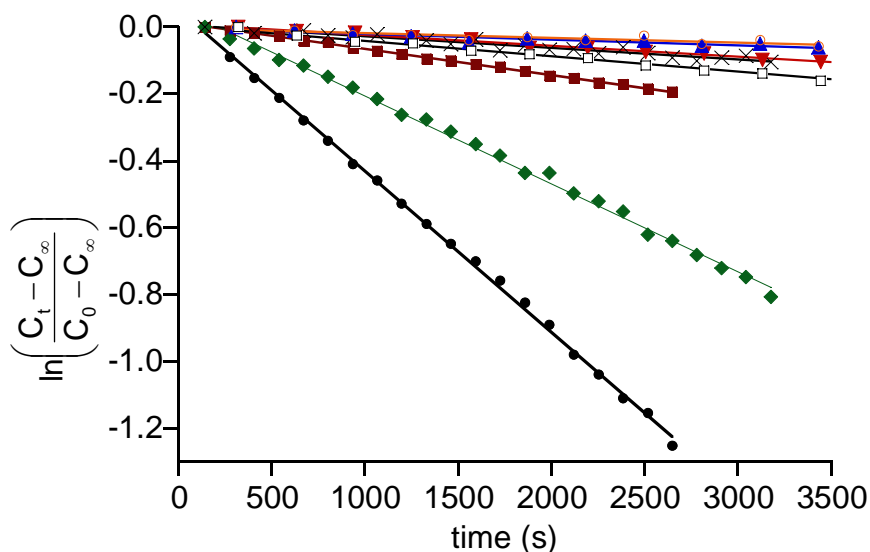


Figure 3.2. Representative linearized degradation of halogenated ethylene substrates versus time. Values were determined from loss of substrate using ^1H NMR at 35 °C. Each sealable NMR tube contained substrate (20-30 mM), catalyst ($(\text{PPh}_3)_3\text{RhCl}$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6 . Lines are linear fits to the experimental data. Vinyl fluoride (●); 1,1-fluorochloroethylene (◆); vinyl chloride (■); 1,1-dichloroethylene (□); 1,2-*cis*-dichloroethylene (▼); 1,2-*trans*-dichloroethylene (×); 1,2-*cis*-fluorochloroethylene (○); 1,2-*trans*-fluorochloroethylene (▲).

Et₃SiCl was the major silane product observed during the dehalogenation reactions; however it was not the only silane product observed as hexaethyldisilane (Et₃Si-SiEt₃) and vinyltriethylsilane (Et₃SiCHCH₂) were also observed. During the dechlorination of 1,1-DCE, TCE, and vinyl chloride a small amount of Et₃SiCHCH₂ was observed by ¹H NMR spectroscopy. With all substrates, Et₃SiCHCH₂ was observed after the halogenated substrates were completely consumed in the catalytic reaction. This suggests that the Et₃SiCHCH₂ is produced from the ethylene, and some substrates inhibit its formation. This was tested by reacting ethylene under the dehalogenation reaction conditions. When ethylene was reacted with (PPh₃)₃RhCl and Et₃SiH under identical reaction conditions, Et₃SiCHCH₂, ethane and Et₃SiCl (small amount from loss of Cl from (PPh₃)₃RhCl) were observed.

Experiments were performed to determine the reaction order in catalyst, using (PPh₃)₃RhCl, and Et₃SiH. Dechlorination was found to be first-order in catalyst, (PPh₃)₃RhCl, at concentrations ranging from 0.1 mM to 2.4 mM (Figure 3.3). This was determined by measuring the initial rates of *cis*-DCE degradation under pseudo-first-order reaction conditions at 55 °C in the presence of a constant amount of Et₃SiH, 125 mM and varying amounts of catalyst. The reaction was found to be zero-order in Et₃SiH by measuring the pseudo-first-order *k*_{obs} for *cis*-DCE degradation at 55 °C and monitoring the reaction by ¹H NMR spectroscopy. The studies were conducted from 20 mM to 300 mM Et₃SiH using 2.4 mM (PPh₃)₃RhCl (Figure 3.4). The rate of rhodium-mediated dechlorination does not depend of Et₃SiH concentrations, when concentrations above 20 mM are used.

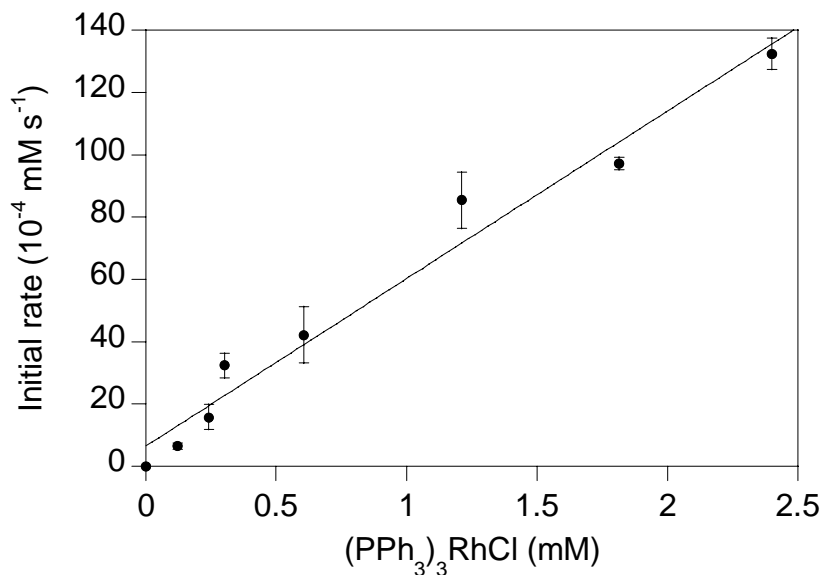


Figure 3.3. Observed degradation rate of *cis*-DCE in the presence of 125 mM Et₃SiH and increasing concentration of catalyst (0.1 mM to 2.4 mM) in C₆D₆. Values were determined using initial rates for loss of substrate as monitored by ¹H NMR at 55 °C. The fit is linear to the initial rate data, R² = 0.9721. Error bars were determined from the standard error in the linear fit in the initial rate plots.

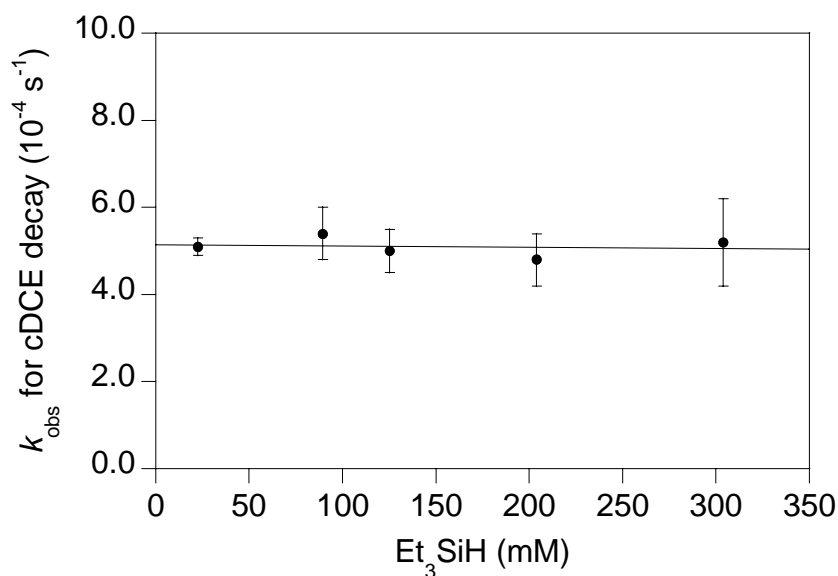
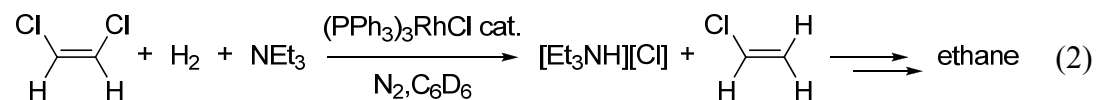


Figure 3.4. Observed *cis*-DCE degradation (k_{obs}) in the presence of 2.4 mM (PPh₃)₃RhCl and increasing concentrations of Et₃SiH (from 22-300 mM) in C₆D₆. Error bars were determined from the standard error in the exponential fit to the substrate decay kinetic plots, except 125 mM in which the error is the standard deviation of 11 experiments.

Dehalogenation using Dihydrogen

Dihydrogen, H₂, was also used as the reducing agent for catalytic dehalogenation. Treatment of *cis*-DCE (30 mM in C₆D₆) with (PPh₃)₃RhCl (2.4 mM) and H₂ (1 atm) at room temperature, resulted in complete dechlorination after 80 minutes (eq. 2). In this case, NEt₃ (150 mM) was added to scavenge the resulting HCl. In the absence of NEt₃, catalyst degradation and formation of [HPPH₃][Cl] was observed. The reaction was mixed by inverting continuously until analyzed. The suite of products observed from dehalogenation using H₂ was similar to that observed using Et₃SiH. Initially, vinyl chloride and ethylene were produced. However, unlike the Et₃SiH, no butenes were observed. Hydrogenation was observed during the dechlorination reaction, resulting in ethane and a small amount of 1,2-dichloroethane and 1-chloroethane. In all cases, 93% of the C₂ mass was accounted for. The 1,2-dichloroethane and 1-chloroethane products account for 2% of the C₂ mass balance.



The relative reactivity of (PPh₃)₃RhCl with halogenated substrates was further examined using H₂ as the reducing agent. Kinetic studies in the NMR probe were not performed due to the low solubility of H₂ in C₆D₆ and slow mass transfer kinetics, which made it difficult to maintain pseudo first-order conditions. The substrates were compared by quantifying substrate lost after 60 minutes of reaction at 22 ± 1 °C. Each reaction mixture consisted of substrate (20-30 mM), (PPh₃)₃RhCl (2.4 mM), NEt₃ (150 mM), and the headspace in the NMR tube was filled with H₂ at 1 atm. The percent reacted after 60 minutes was calculated for the chlorinated ethylenes and is compiled in

Table 3.2. The general reactivity trends were the same as when Et₃SiH was employed. The rate of dechlorination increases with loss of chlorine, as vinyl chloride degraded the fastest and TCE the slowest. However, unlike the Et₃SiH system, *cis*-DCE is degraded at a similar rate as vinyl chloride while 1,1-DCE and *trans*-DCE degraded at a slower rate. All of the dichloroethylenes produce vinyl chloride as a reactive intermediate, which was then dechlorinated to ethylene and further hydrogenated to ethane. When ethylene was reacted as the substrate in this system (with H₂, NEt₃, and (PPh₃)₃RhCl) hydrogenation occurs, and ethane is observed.

Table 3.2. Average percent of substrate degradation with H₂ as the reductant. Values were determined from loss of substrate after 60 minutes of constant inversion using quantitative ¹H NMR spectroscopy at room temperature, 22 ± 1 °C. Each sealable NMR tube contained substrate (20-30 mM), catalyst ((PPh₃)₃RhCl, 2.4 mM), H₂ (1 atm), NEt₃ (150 mM), and internal standard (*p*-xylene, 3.3 mM) in C₆D₆. The estimated error is the standard deviation of three trials. Relative rate constants were determine relative to the rate of TCE degradation after 60 minutes.

Substrate	Percent reacted (%)	<i>k</i> _{rel} ^a
vinyl chloride	75 ± 1	10.2
<i>cis</i> -DCE	75 ± 3	10.1
<i>trans</i> -DCE	44 ± 4	4.2
1,1-DCE	31 ± 6	2.7
TCE	13 ± 8	1.0

^aassuming a first-order degradation model

The reaction was found to be first order in catalyst, (PPh₃)₃RhCl, when H₂ was used as the hydride source. The fraction of *cis*-DCE degraded in 60 minutes versus catalyst concentration (0 to 2.4 mM) is depicted in Figure 3.4. The data are plotted on a logarithmic scale, which should linearize the data set if the reaction is pseudo-first-order and first-order in catalyst. Indeed, a linear relationship is observed (Figure 3.5). There is no effect on the percent *cis*-DCE degraded in 60 minutes when varying the

concentration of NEt_3 from 50 to 200 mM while the amount of $(\text{PPh}_3)_3\text{RhCl}$ was kept constant (2.4 mM) (Figure 3.6).

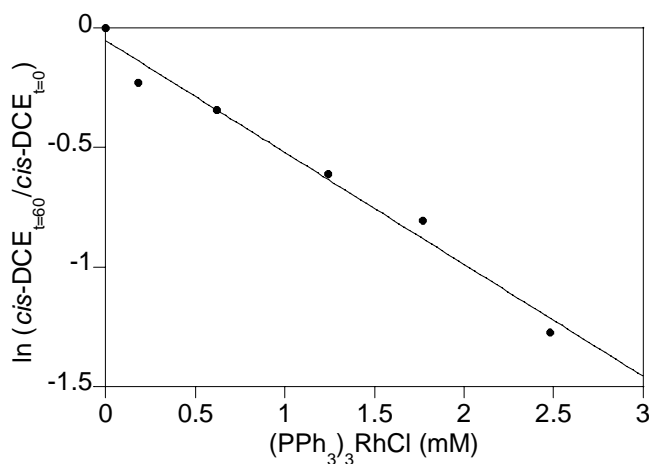


Figure 3.5. Natural log of the fraction of *cis*-DCE degraded in 60 minutes versus catalyst concentration. Reaction conditions: 22 ± 1 °C, 1 atm H_2 , 150 mM NEt_3 and increasing the concentration of catalyst (0 mM to 2.4 mM) in C_6D_6 . The fit is linear to the data, $R^2 = 0.9799$.

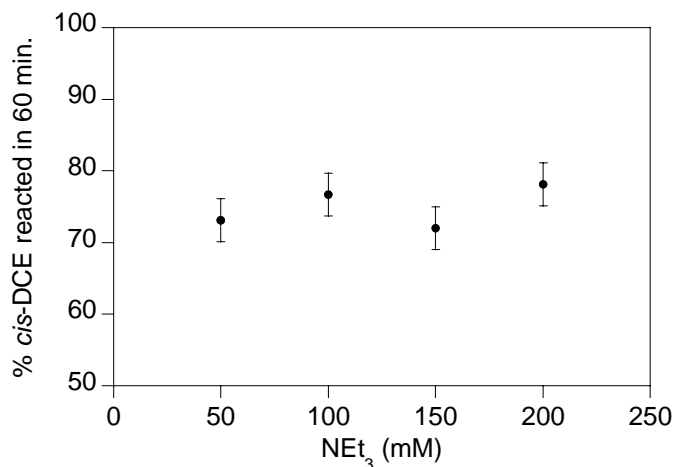


Figure 3.6. Percent *cis*-DCE degraded in 60 minutes at room temperature in the presence of H_2 (1 atm), $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), and varying concentrations of NEt_3 (50 mM to 200 mM) in C_6D_6 . Values were determined by calculating loss of substrate using ^1H NMR at 22 °C. Error bars are set to three percent, which is based on the standard deviation of triplicate *cis*-DCE degradation.

When vinyl fluoride (25 mM) is reacted with $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM) and H_2 (1 atm) in the presence of NEt_3 (150 mM), the major reaction pathway is hydrogenation, as the major product is fluoroethane and the minor product is ethylene. Because defluorination was not the major degradation pathway, the percent reacted in 60 minutes is not included in Table 3.2.

Fluoroethane and ethylene were observed from the reaction of vinyl fluoride with independently prepared $(\text{PPh}_3)_3\text{RhF}$ ⁵⁹ and H_2 . This observation is consistent with $(\text{PPh}_3)_3\text{RhF}$ being a potential intermediate in the catalytic cycle.

Chlorofluoroethylenes were reacted with $(\text{PPh}_3)_3\text{RhCl}$, H_2 , and NEt_3 and the first product observed was vinyl fluoride and no vinyl chloride was detected during the dehalogenation, which was similar to the Et_3SiH system. Some hydrogenation product, chlorofluoroethane, was also observed. The major final product was fluoroethane, the hydrogenation product of the vinyl fluoride.

Sp³-hybridized carbon-halogen bonds

Similar to Et_3SiH , when H_2 is used as the reducing agent under identical reaction conditions there is no reaction with 1,2-chloroethane or dichloromethane after two days at room temperature.

NMR observation of intermediates

When Et_3SiH and $(\text{PPh}_3)_3\text{RhCl}$ were combined in a 1:1 or 2:1 ratio, a new ^1H NMR resonance consistent with a Rh-H species was observed at -7.9 ppm. Esteruelas *et al.* observed the same result and assigned the resonance to $(\text{PPh}_3)_3\text{RhH}$.^{43,67} In our system, when excess Et_3SiH (>10 equivalents) is allowed to react with $(\text{PPh}_3)_3\text{RhCl}$ the only rhodium hydride complex observed initially is

(PPh₃)₂RhH(Cl)SiEt₃, identified by the upfield hydride resonance (δ -14.7, $J_{\text{Rh-H}} = 22$ Hz) in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum and its $^{31}\text{P}\{^1\text{H}\}$ resonance (δ 39.7, d, $J_{\text{Rh-P}} = 128$ Hz).⁶⁸ With time the (PPh₃)₂RhH(Cl)SiEt₃ ^1H resonance at -14.7 ppm disappears and the (PPh₃)₃RhH resonance, -7.9 ppm, appears.⁶⁷ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows the same behavior, with the (PPh₃)₂RhH(Cl)SiEt₃ doublet at 39.7 ppm giving way to the (PPh₃)₃RhH doublet at 42 ppm (158 Hz). We propose that the solution of Et₃SiH and (PPh₃)₃RhCl is in equilibrium, such that L_nRh(I)-H and L_nRh(III)-H complexes are present during the catalytic cycle. This is supported by the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances observed during dechlorination reactions, both (PPh₃)₂RhH(Cl)SiEt₃ (δ 39.2, d, $J_{\text{Rh-P}} = 130$ Hz) and (PPh₃)₃RhH (δ 42, d, $J_{\text{Rh-P}} = 156$ Hz) are observed. This differs from what Esteruelas *et al.* observed during the dechlorination of hexachlorocyclohexane. They observed a doublet at 39.4 (115 Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and two hydride peaks in the ^1H NMR spectra (-9.38 ppm and -16.73 ppm) that they assigned to (PPh₃)₃RhH₂Cl.^{43,63,69}

(PPh₃)₃RhH can be isolated by reacting (PPh₃)₃RhCl with excess Et₃SiH and removing Et₃SiCl and unreacted Et₃SiH under vacuum. (PPh₃)₃RhH isolated in this way was found to react immediately with *cis*-DCE to yield vinyl chloride and ethylene as well as (PPh₃)₃RhCl. Furthermore, independently synthesized and isolated (PPh₃)₄RhH (2.4 mM) reacted readily with *cis*-DCE (20 mM) in C₆D₆ upon mixing at room temperature. (PPh₃)₃RhCl and free PPh₃ were formed in these reaction as indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The dechlorination products produced were ethylene and vinyl chloride, and 90% of the C₂ mass was accounted for by these products and unreacted *cis*-DCE.

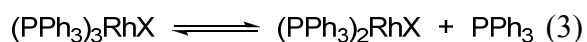
When H₂ (1 atm) was reacted with (PPh₃)₃RhCl, only (PPh₃)₃RhH₂Cl^{43,63,69} was produced. This was indicated by ¹H NMR resonances observed at -9.4 ppm and -16.7 ppm. The ³¹P{¹H} NMR spectrum contained a doublet at 39.4 ppm (116 Hz) and a broad peak at 20 ppm. During the dehalogenation reactions with H₂ and (PPh₃)₃RhCl the major species observed by ³¹P{¹H} NMR spectroscopy was (PPh₃)₃RhH₂Cl. A small amount of (PPh₃)₃RhCl and (PPh₃)₂RhCl(alkene) (36.6 ppm, 129 Hz)⁷⁰ were also observed in the ³¹P{¹H} NMR spectrum. No resonances attributable to (PPh₃)₃RhH were observed in either ¹H or ³¹P{¹H} NMR spectra.

Effect of phosphine:rhodium ratio on rate

The phosphine dependence of the dechlorination of *cis*-DCE was explored in order to gain insight into the active catalytic species and to determine the optimum rhodium to phosphine ratio for *in situ* catalyst generation. Reactions were performed with *cis*-DCE (30 mM) and Et₃SiH (125 mM). The catalyst was formed *in situ* by mixing PPh₃ with [(COD)RhCl]₂ at various ratios from 1:0 to 1:5 Rh:PPh₃. The total Rh and Et₃SiH concentrations were kept constant in all experiments and the amount of PPh₃ was varied accordingly. The effect of phosphine concentration on the rate was determined by measuring the pseudo-first-order *k*_{obs} for *cis*-DCE degradation at 55 °C using ¹H NMR spectroscopy.

The optimal rate was achieved with three equivalents of phosphine and the reaction rate decreased with additional phosphine (Figure 3.7), and no dehalogenation was observed in the absence of phosphine. This result differs from previous reports on hydrogenation and dechlorination reactions where an initial ligand dissociation step is

thought to produce $(\text{PPh}_3)_2\text{RhCl}$, with a 2:1 $\text{PPh}_3:\text{Rh}$ ratio, yielding the optimal rate of reaction (eq. 3).^{43,61,63,71}



The inhibitory effect of greater than three equivalents of phosphine was further verified in an independent experiment where one equivalent of PPh_3 was added to a reaction mixture containing Et_3SiH , *cis*-DCE and $(\text{PPh}_3)_3\text{RhCl}$. Under these conditions, a three-fold decrease in the observed rate constant was observed compared to the same experiment without added phosphine. A similar result was also observed by Esteruelas *et. al.* for chlorinated benzene dechlorination.^{43,44}

The *cis*-DCE degradation rate constant, k_{obs} , for *in situ* generated $(\text{PPh}_3)_3\text{RhCl}$ ($\text{PPh}_3:\text{Rh}$ ratio of 3:1) was an order of magnitude lower than when the reaction was performed with isolated and purified $(\text{PPh}_3)_3\text{RhCl}$ (Figure 3.8). The source of this discrepancy was found to be 1,5-cyclooctadiene, which acted as an inhibitor for *cis*-DCE dechlorination by $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH (Figure 3.9).

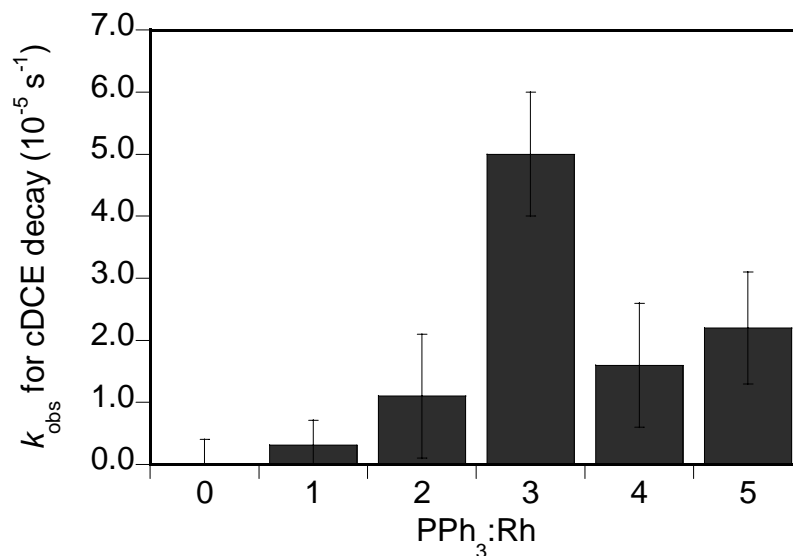


Figure 3.7. Observed rate constants (k_{obs}) for *cis*-DCE degradation are compared to the phosphine:rhodium ratio for the reaction of *cis*-DCE with Et₃SiH and the catalyst at 55°C in C₆D₆. In these studies the catalyst was made from the *in situ* reaction of [(COD)RhCl]₂ with PPh₃. Error bars are the error in the exponential fit of the ¹H NMR data.

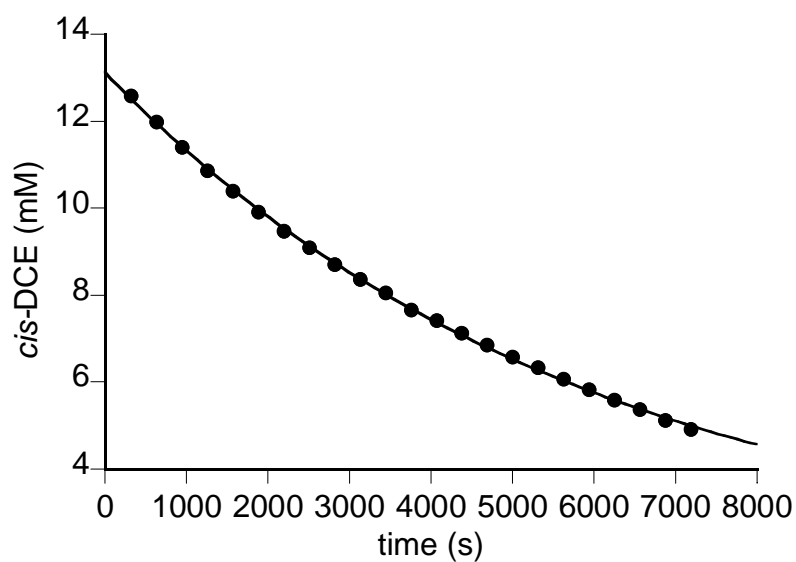


Figure 3.8. *cis*-DCE degradation by (PPh₃)₃RhCl (2.4 mM) and Et₃SiH (125 mM) at 55 °C in the presence of 2.4 mM PPh₃. Concentrations of *cis*-DCE determined versus internal standard, *p*-xylene (3.3 mM). Fit is a nonlinear exponential first-order decay, $k_{\text{obs}} = 1.7 \times 10^{-4} \text{ s}^{-1}$.

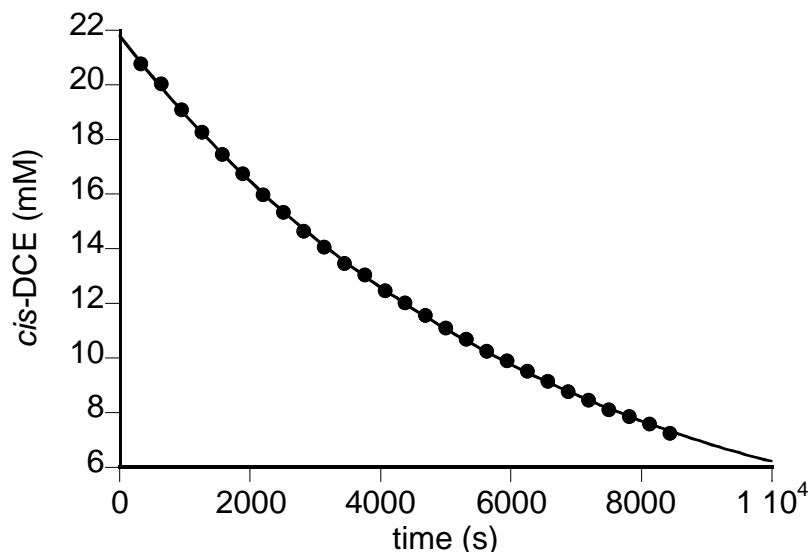


Figure 3.9. *cis*-DCE degradation by $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM) and Et_3SiH (125 mM) at 55 °C in the presence of 2.4 mM COD. Concentrations of *cis*-DCE determined versus internal standard, *p*-xylene (3.3 mM). Fit is a nonlinear exponential first-order decay, $k_{\text{obs}} = 1.6 \times 10^{-4} \text{ s}^{-1}$.

In the H_2 system, the percentage of *cis*-DCE dechlorinated in 60 minutes in the presence of $(\text{PPh}_3)_3\text{RhCl}$ (2.4 mM), NEt_3 (150 mM), 1 equivalent of PPh_3 (2.4 mM) and H_2 (1 atm) was found to be $42 \pm 6 \%$. This was a relative decrease of 2.5 to the reaction without the extra equivalent of PPh_3 , signifying that the addition of PPh_3 inhibited dechlorination of *cis*-DCE when H_2 was used.

Effect of phosphine structure on rate

We also examined the effect of the electronic nature of the phosphine used in $(\text{PR}_3)_3\text{RhCl}$ on the reaction kinetics with *cis*-DCE and Et_3SiH by preparing $(\text{PPh}_3)_3\text{RhCl}$ analogs with trimethylphosphine, triethylphosphine, tris(*p*-methoxyphenyl)phosphine and tris(*p*-fluorophenyl)phosphine. The observed rate of reaction with *cis*-DCE decreased monotonically with the basicity of the phosphine, with $[\text{P}(p\text{-FC}_6\text{H}_4)_3]_3\text{RhCl}$ being the most active (Table 3.3) while $(\text{PMe}_3)_3\text{RhCl}$ and $(\text{PEt}_3)_3\text{RhCl}$ complexes were

found to be inactive. This trend was also observed by Montelatici *et al.* for the activation of hydrogen by, $(\text{PPh}_3)_2\text{RhX}(\text{C}_6\text{H}_6)$.⁶¹ It was proposed that this was due to both steric and electronic reasons.⁶¹

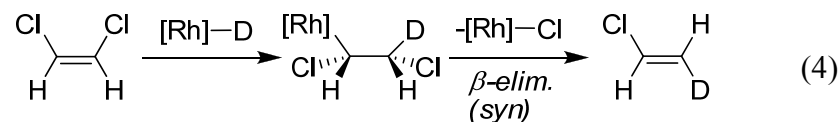
Table 3.3. Rate constants obtained for various $(\text{PR}_3)_3\text{RhCl}$ complexes with *cis*-DCE and Et_3SiH and the corresponding phosphine properties.⁷²

Isolated catalyst	k_{obs} (10^{-4} s^{-1}) 35°C	k_{obs} (10^{-4} s^{-1}) 55°C	pKa (PR_3H^+)	Cone angle θ
$[\text{P}(p\text{-FC}_6\text{H}_4)_3]_3\text{RhCl}$	1.9 ± 0.7	n.d. ^a	1.97	145
$(\text{PPh}_3)_3\text{RhCl}$	0.27 ± 0.08	5.0 ± 0.5	2.73	145
$[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]_3\text{RhCl}$	n.d. ^a	0.40 ± 0.02	4.59	145
$(\text{PEt}_3)_3\text{RhCl}$	< 0.01	< 0.01	8.69	132
$(\text{PMe}_3)_3\text{RhCl}$	< 0.01	< 0.01	8.65	118

^an.d. = not determined

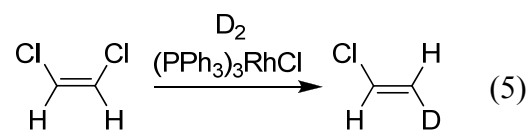
Isotope Labeling

Our leading hypothesis for the dehalogenation process is an insertion/ β -chloride elimination mechanism. The first step of this mechanism involves insertion of the alkene into the Rh-H bond, yielding a β -chloroalkyl complex, which then undergoes *syn*- β -chloride elimination. This process gives rise to stereospecific incorporation of the hydride-derived hydrogen. This mechanism is illustrated in eq. 4.



To test this mechanistic hypothesis, an experiment was performed using D_2 as the hydride source with $(\text{PPh}_3)_3\text{RhCl}$ and *cis*-DCE. The *syn*- β -chloride elimination product, *E*-1-chloro-2-deuteroethylene ($J_{\text{H-H}}$ 15 Hz), was observed in the ^1H NMR spectrum (eq. 5), as hypothesized. No other chlorodeuteroethylenes were observed. These results, along with the reaction preferences previously discussed, support an

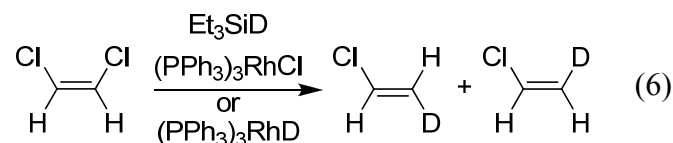
insertion/*syn*- β -chloride elimination mechanism when hydrogen is used as the hydride source. This is also the only product observed when either Et_3SiCl or Et_3N was added to the reaction mixture of *cis*-DCE, D_2 , and $(\text{PPh}_3)_3\text{RhCl}$, indicating that these species play no role in the β -Cl elimination product formed.



A similar result was obtained in the reaction of *trans*-DCE with $(\text{PPh}_3)_3\text{RhCl}$ and D_2 in C_6D_6 . Only resonances for the *syn*- β -chloride elimination product were observed, *Z*-1-chloro-2-deuteroethylene ($J_{\text{H-H}}$ 7 Hz).

However, in a similar experiment using Et_3SiD with $(\text{PPh}_3)_3\text{RhCl}$ and *cis*-DCE, a 1:1 mixture of *E*- and *Z*-1-chloro-2-deuteroethylene was observed in the ^1H NMR spectrum, as previously reported (eq. 6).⁵² When isolated $(\text{PPh}_3)_3\text{RhD}$ was reacted with *cis*-DCE the same 1:1 mixture of products was observed (eq. 6). Switching solvents to tetrahydrofuran- d_8 , for the reaction of Et_3SiD with $(\text{PPh}_3)_3\text{RhCl}$ and *cis*-DCE, changed the product ratio to a 1:7 mixture of *E*- and *Z*-1-chloro-2-deuteroethylene.

Fully protonated (undeuterated) vinyl chloride is also observed with time in the Et_3SiD reaction and when the $(\text{PPh}_3)_3\text{RhD}$ is reacted with *cis*-DCE. The independent reaction of vinyl chloride with Et_3SiD and $(\text{PPh}_3)_3\text{RhCl}$ resulted in no deuterium incorporation into the residual vinyl chloride. This indicates that vinyl chloride is not isomerized under these conditions.



When the $(\text{PPh}_3)_3\text{RhCl}/\text{Et}_3\text{SiD}$ system was treated with *trans*-DCE, a 1:1.5 ratio of *E*- to *Z*-1-chloro-2-deuteroethylene was observed. The same product ratio (1:1.5, *E:Z*) was also observed when $(\text{PPh}_3)_3\text{RhD}$ was reacted with *trans*-DCE.

3.4 DISCUSSION

Proposed Mechanism

The data for dehalogenation of halogenated ethylenes using $(\text{PPh}_3)_3\text{RhCl}$ with Et_3SiH and H_2 supports similar, yet distinct, mechanisms for the two reducing agents. The Et_3SiH and H_2 systems are characterized by four major differences:

1. Hydride complexes observed during reaction
2. Stereochemistry of elimination
3. Occurrence of hydrogenation/hydrosilation products
4. Vinyl fluoride products

We propose two mechanisms that account for these differences, with the key distinction between them being that reduction with Et_3SiH occurs through a Rh(I)-type pathway (Figure 3.10), while the H_2 reduction occurs through a Rh(III)-type pathway (Figure 3.11). The mechanisms are presented first followed by a discussion of how they account for each of the observations in the Et_3SiH and H_2 systems.

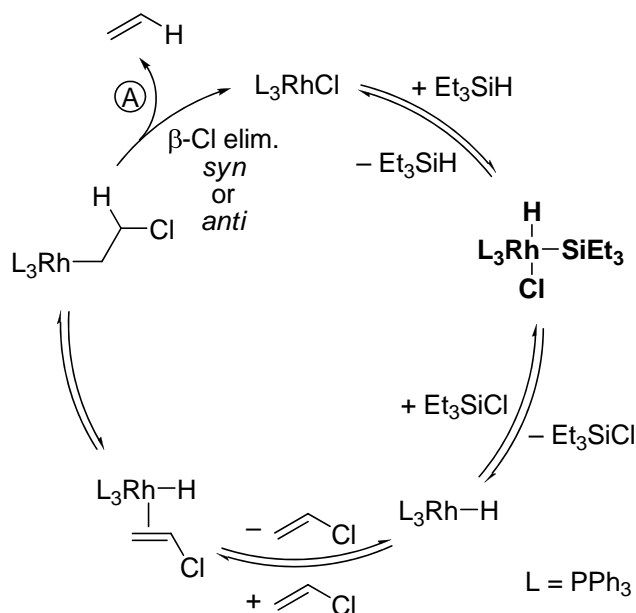
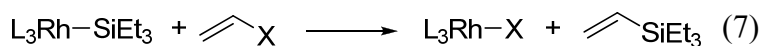


Figure 3.10. The proposed mechanism for the catalytic dehalogenation of chlorinated and fluorinated ethylenes using $(\text{PPh}_3)_3\text{RhCl}$ and Et_3SiH , illustrated using vinyl chloride. The product elimination step is labeled A. It is proposed that reduction with Et_3SiH occurs primarily through the Rh(I) and pathway, the Rh(III) complex is illustrated in **bold**.

In the proposed mechanism, illustrated using vinyl chloride, when Et_3SiH is employed, the first step is oxidative addition of Et_3SiH to $(\text{PPh}_3)_3\text{RhCl}$ forming $(\text{PPh}_3)_3\text{RhH}(\text{Cl})\text{SiEt}_3$, which undergoes reductive elimination of Et_3SiCl , giving $(\text{PPh}_3)_3\text{RhH}$. Alkene association with $(\text{PPh}_3)_3\text{RhH}$, followed by insertion into the Rh-H bond leads to a Rh-alkyl complex. The alkyl complex may then undergo β -X elimination (step A), yielding the dehalogenated alkene as well as the return of the catalyst $(\text{PPh}_3)_3\text{RhX}$ (Figure 3.10). This Rh-alkyl complex can undergo either *syn*- or *anti*- β -X elimination, consistent with the D-labeling data, as described in the stereochemistry of elimination section below. We have depicted the Rh-alkyl complex as a tris(triphenylphosphine) complex; however, there is no direct evidence for this. Elimination could occur from, for example, bis or tris phosphine complexes. The

observation of $\text{Et}_3\text{SiCHCH}_2$ suggests the possibility that a similar minor pathway involving $(\text{PPh}_3)_3\text{Rh-SiEt}_3$ may exist (eq 7).



The observation of $\text{Et}_3\text{Si-SiEt}_3$ lends credence to the presence of Rh-silyl species, as these are known intermediates in dehydrocoupling of silanes.⁷³⁻⁷⁷

With fluorinated alkenes, the same mechanism is proposed. However, following β -F-elimination $(\text{PPh}_3)_3\text{RhF}$ is generated. This species has been shown to be a competent catalyst.⁵²

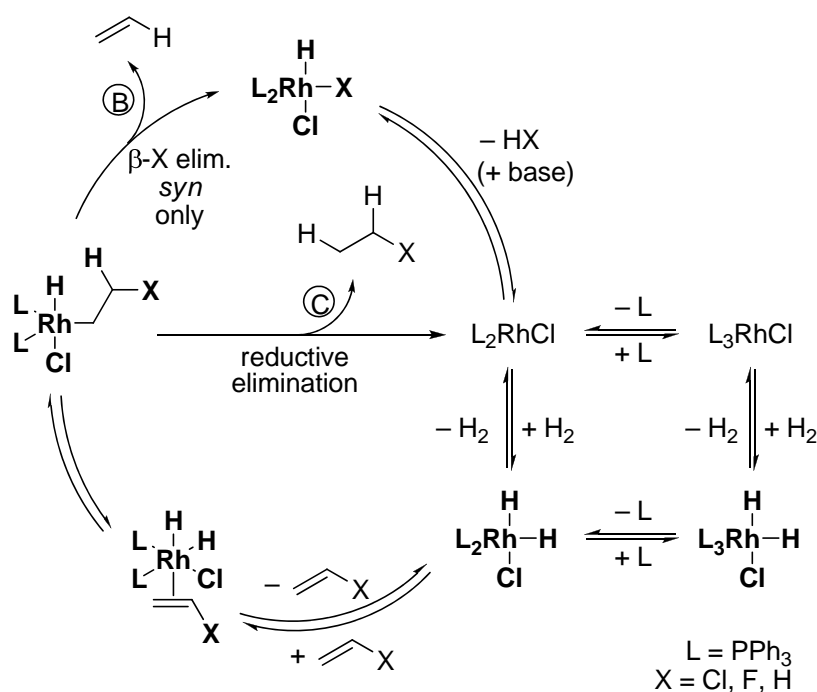
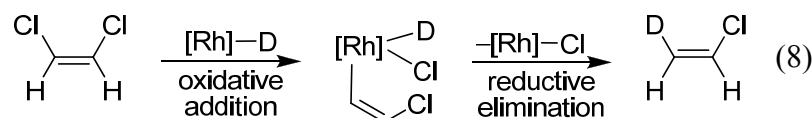


Figure 3.11. The proposed mechanism for the catalytic dehalogenation of chlorinated and fluorinated ethylenes using $(\text{PPh}_3)_3\text{RhCl}$ and H_2 . It is proposed that reduction with H_2 occurs primarily through a Rh(III) pathway with two possible product forming reactions: *syn*- β -X-elimination (B) and reductive elimination (C). All Rh(III) complexes are depicted in **bold**.

When H₂ is used, the dominant pathway is proposed to be the Rh(III)-H pathway. Here, the initial step in the reaction is oxidative addition of H₂ to (PPh₃)₃RhCl (either before or after phosphine dissociation). Alkene association at the open coordination site of (PPh₃)₂RhH₂Cl followed by insertion into one of the Rh(III)-H bonds leads to a Rh-alkyl complex (Figure 3.11). From here, reductive elimination (step C, Figure 3.11), yields hydrogenation products, and *syn*-β-X elimination (step B, Figure 3.11), yields dehalogenation products. As shown, the chloro ligand remains bound to the Rh throughout. Not shown explicitly is the hydrodehalogenation process that leaves the haloalkene halogen bound to the rhodium. In the case of fluoro substituents, this produces (PPh₃)₂RhF. We have verified that (PPh₃)₃RhF is also a competent catalyst using H₂ as the reducing agent.

C-X oxidative addition mechanism

Before considering in detail how the proposed mechanism accounts for the experimental observations, it is worth pointing out how the data do not support an alternative mechanistic hypothesis involving C-X oxidative addition (eq. 8).



In an oxidative addition/reductive elimination mechanism, isotopic labeling studies would show retention of stereochemistry (eq. 8). In fact, the isotopic labeling studies show inversion (with D₂) and scrambling (with Et₃SiD). Oxidative addition is expected to show a preference for weaker sp³-hybridized C-X bonds over sp²-hybridized C-X bonds, as well as similar reactivity toward vinyl C-X and aryl C-X bonds. Neither was observed. Vinyl fluoride was degraded faster than vinyl chloride,

which is also contrary to the expectations of an oxidative addition mechanism, as insertion into C-F bonds is more difficult than C-Cl insertion. Finally, the observation of hydrogenation products when H₂ is used as the reducing agent also supports insertion of the alkene into a Rh-H bond.

Hydride complexes observed during reaction

Numerous lines of evidence support the intermediacy of rhodium hydride species in both the Et₃SiH and H₂ dehalogenation processes. First, conditions that produce Rh-H species were needed for dehalogenation. In the Et₃SiH system, no reaction was observed when *cis*-DCE was treated with either Et₃SiH or (PPh₃)₃RhCl alone. Similarly in the H₂ catalytic system, no reaction occurs when *cis*-DCE was reacted with either (PPh₃)₃RhCl or H₂ alone. Both (PPh₃)₃RhCl and either Et₃SiH or H₂ need to be present for reaction to occur. Second, the isolated Rh-H complex, (PPh₃)₄RhH, reacts directly with the halogenated ethylenes to give dehalogenation products. Finally, Rh-H complexes were observed during the dehalogenation reactions by ¹H NMR spectroscopy.

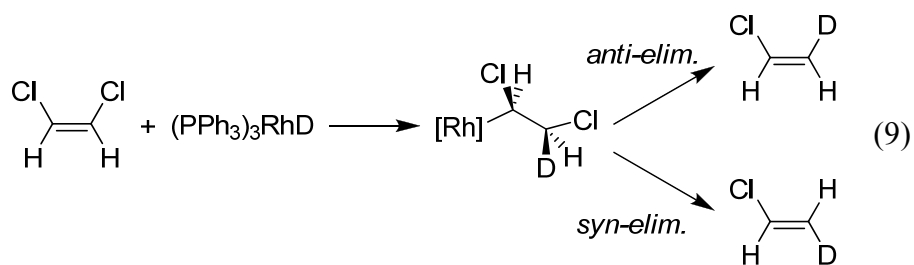
However, the spectroscopic data suggest that H₂ and Et₃SiH favor different pathways. During the course of the dehalogenation reactions with Et₃SiH, the Rh(I) hydride, (PPh₃)₃RhH, is the primary hydride species observed. Under H₂, both ¹H and ³¹P{¹H} NMR spectra show that the Rh(III) complex, (PPh₃)₃RhH₂Cl, is present. Presumably the difference in the two systems is the strong driving force for reductive elimination of Et₃SiCl (or Et₃SiF in defluorination reactions), which pushes the silane system toward (PPh₃)₃RhH.

Stereochemistry of elimination

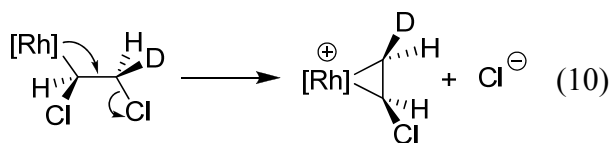
When D_2 is reacted with $(PPh_3)_3RhCl$ and *cis*-DCE or *trans*-DCE, the stereochemistry of the 1-chloro-2-deuteroethylene products (*E*-1-chloro-2-deuteroethylene or *Z*-1-chloro-2-deuteroethylene, respectively) are consistent with exclusive *syn*- β -Cl-elimination (step B, Figure 3.11).

When Et_3SiD is reacted with $(PPh_3)_3RhCl$ and *cis*-DCE in C_6D_6 a 1:1 mixture of *E*- to *Z*-1-chloro-2-deuteroethylene is observed, and when *trans*-DCE is reacted a slightly different product ratio of 1:1.5 (*E*:*Z*) is observed. The same product ratios are observed when $(PPh_3)_3RhD$ is used as the Rh-D source, supporting Et_3SiD/H following a Rh(I)-H pathway (step A, Figure 3.10).

The mixture of *syn*- and *anti*-elimination products with Et_3SiH rules out the possibility that it reacts by the same pathway as H_2 . Furthermore, spectroscopic evidence shows a mixture of Rh(III)-H and Rh(I)-H species with Et_3SiH and only Rh(III)-H with H_2 . Taken together the data suggests that β -haloalkyl complexes of Rh(III) give exclusively *syn*-elimination products, while β -haloalkyl complexes of Rh(I) can give both *syn*- and *anti*-elimination products (eq. 9). This is based on experiments with $(PPh_3)_3RhD$ and *cis*-DCE that show 1:1 mixture of *E*-1-chloro-2-deuteroethylene and *Z*-1-chloro-2-deuteroethylene. In this system, it seems unlikely that Rh(III) species are involved and that both products come from the same dichloroethylrhodium(I) intermediate.



We speculate that the nucleophilicity of the metal center enhances the favorability of the *anti*-elimination pathway with Rh(I) over Rh(III). Pseudo-backside displacement of the leaving group by rhodium would lead directly to an alkene complex (eq 10).



A noteworthy difference between the proposed *syn*- and *anti*-elimination pathways is that significant charge build-up is expected in the *anti*-elimination pathway en route to the product ion pair. No such charge separation is expected in the *syn*- β -Cl-elimination pathway. Support for this model was obtained by switching to a more polar solvent. Reacting *cis*-DCE with Et₃SiD and (PPh₃)₃RhCl in tetrahydrofuran-*d*₈ resulted in a product ratio of 1:7 *E*- to *Z*-1-chloro-2-deuteroethylene, contrasting the 1:1 ratio observed in C₆D₆. We propose that the shift to increased amounts of the *anti*-elimination product (*Z*-1-chloro-2-deuteroethylene) is due to better stabilization of the *anti*-elimination transition state with the more polar solvent.

The difference in the *E*:*Z* ratio of the 1-chloro-2-deuteroethylene products starting from either the *cis*-DCE or *trans*-DCE is puzzling and informative. From a Newman projection analysis, the same three rotameric conformers are available starting

from insertion of *cis*- or *trans*-DCE into a Rh-D bond (Figure 3.12). If bond rotation interconverting these rotomers were fast compared to elimination, this analysis suggests that *cis*- and *trans*-DCE should give the same ratio of products. We conclude that the converse must be true, that elimination is competitive with C-C bond rotation. The kinetic product mixture is observed as the rotomers do not have time to fully equilibrate. Another possibility is that conformer interconversion is fast, but that the position of the conformer equilibrium is perturbed by the site of deuteration.

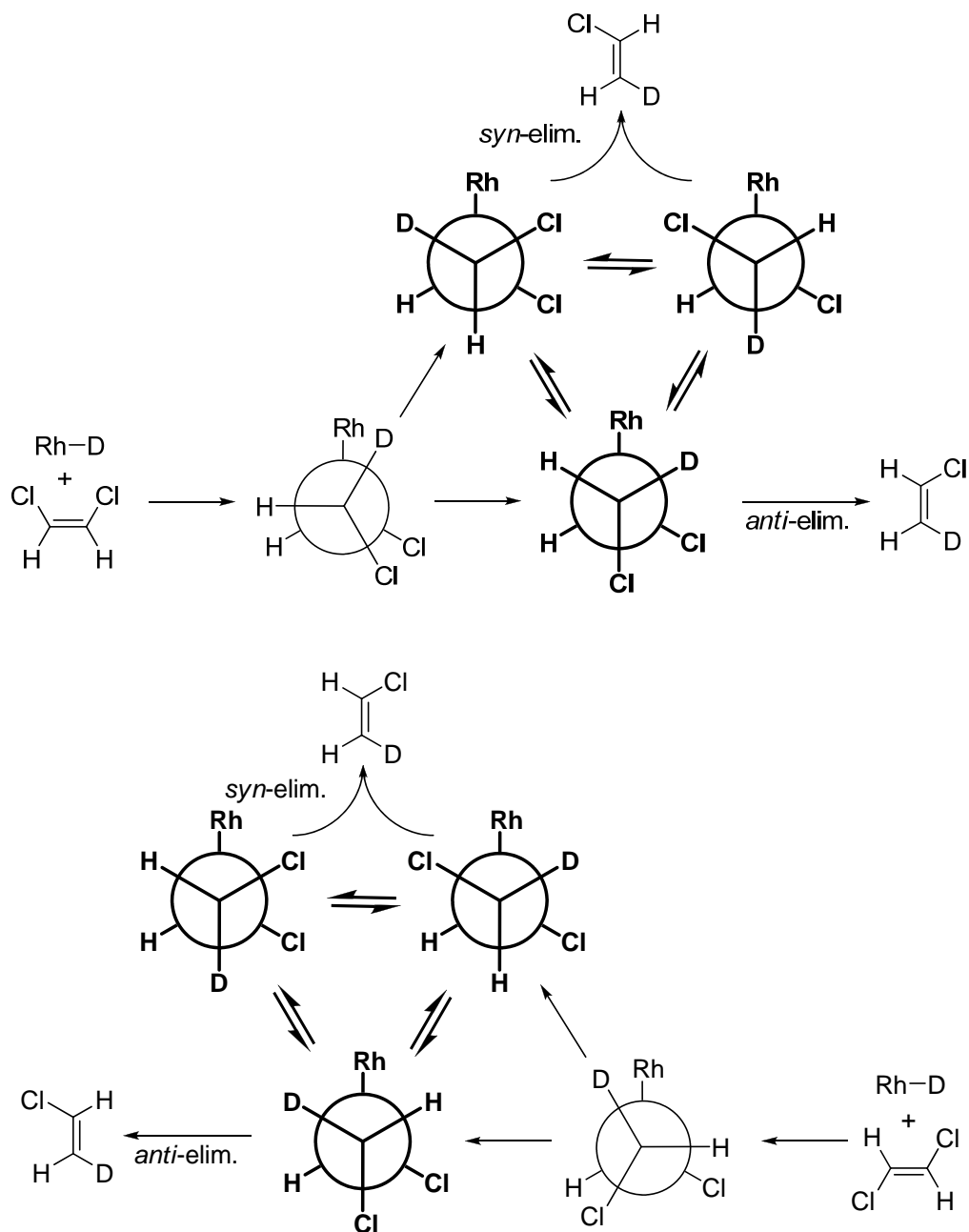


Figure 3.12. Newman Projections depicting the three rotamers that result from insertion of *cis*-DCE (top) or *trans*-DCE (bottom) into a Rh-D to form a dichloroalkylrhodium. The three rotamers are the same for both DCEs (**bold**), and are depicted in the same relative positions in the figures to illustrate this. The stereospecific products that would result from both *syn*- and *anti*- β -chloride elimination are also shown.

Occurrence of hydrogenation/hydrosilation products

Hydrogenation (1,2-addition) products are only observed in the H₂ catalytic system, providing further support for the involvement of a Rh(III)-H pathway with H₂. Hydrogenation products (dichloroethane, chloroethane, fluoroethane, chlorofluoroethane and ethane) were observed during the degradation of various halogenated ethylenes with H₂ and (PPh₃)₃RhCl supporting the involvement of a Rh(III)-alkyl complex in this catalytic system, as reductive elimination is not favorable from a Rh(I) center. Therefore observation of hydrogenation products supports the assertion that hydrogenation occurs from a Rh(III) complex.

No 1,2-addition (hydrosilation) products were observed during the degradation of halogenated ethylene when Et₃SiH was used as the reducing agent. Hydrosilation products would arise from insertion of the alkene into the Rh-SiEt₃ bond followed by reductive elimination to form Et₄Si. By contrast, Braun *et al.* recently reported hydrosilation products in the degradation of hexafluoropropene catalyzed by a triethylphosphine rhodium complex.⁵⁶

Vinyl fluoride products

Differences in the products observed when (PPh₃)₃RhCl reacts with vinyl fluoride in the presence of Et₃SiH and H₂ provides further support for different degradation pathways with the two reducing agents. When Et₃SiH, (PPh₃)₃RhCl and vinyl fluoride were reacted, the major degradation product is ethylene. However, when vinyl fluoride is reacted with H₂ and (PPh₃)₃RhCl the major degradation product was fluoroethane and the minor degradation product was ethylene. With Et₃SiH, the active Rh(I)-H would favor β-F-elimination, giving ethylene as the product (step A, Figure

3.10). While with H₂, the active Rh(III)-H allows for either β-F-elimination (producing ethylene, step B, Figure 3.11) or reductive elimination (producing fluoroethane, step C, Figure 3.11) after the insertion of the vinyl fluoride into the Rh-H bond.

Other mechanistic observations

In the Et₃SiH system all of the dichloroethylenes are degraded at a similar rate (Table 3.1), while in the H₂ system *cis*-DCE is degraded more readily than *trans*-DCE and 1,1-DCE (Table 3.2). A proposed hypothesis for this difference in reactivity, is that in the H₂ system, the active catalyst is a Rh(III)-H and is more sterically crowded and more selective in terms of alkene association.

Conclusions

Catalytic dechlorination of chlorinated ethylenes by (PR₃)₃RhCl occurs with Et₃SiH and H₂ as reducing agents. These complexes are therefore effective catalysts for the degradation of an important class of environmental contaminants. Rhodium hydride complexes are the active intermediates for the degradation of the halogenated ethylenes studied. The use of both Et₃SiH and H₂ is consistent with an insertion/β-chloride elimination mechanism, but due to distinct differences in the two systems it is proposed that a Rh(I) pathway is favored for Et₃SiH and a Rh(III) pathway is favored for H₂. From the Rh(I) pathway both *syn*- and *anti*-β-halo-elimination can occur, and from the Rh(III) pathway, only *syn*-β-halo-elimination occurs. The difference in reactivity between Et₃SiH and H₂ leads to different stereochemistry of elimination products and different propensities for giving 1,2-addition products. Therefore, direct comparisons between H₂ and Et₃SiH in this system need to be considered carefully.

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CHAPTER FOUR

AQUEOUS-PHASE, CATALYTIC HYDRODECHLORINATION OF CHLORINATED ETHYLENES USING RHODIUM ON ALUMINA AND HYDROGEN GAS

Catalytic hydrodechlorination of chlorinated ethylenes by 5 wt % rhodium on alumina catalyst in the presence of dihydrogen as the reducing agent is described. Kinetic parameters and product distribution for hydrodechlorination reactions were determined using gas chromatography-mass spectrometry head space analysis. The catalyst was found to perform at 100 % efficiency, defined by TCE degradation, over greater than 744 turnovers. Evidence for sequential chlorine removal was obtained, and the rates of hydrodechlorination were found to increase with decreasing chlorine content. Only trace lower chlorinated ethylenes were observed during the degradation reactions. It was also shown that this catalytic system has a preference for sp^2 - over sp^3 -hybridized carbon chlorine bonds. This catalytic system is compared to 1 wt % palladium on alumina, and both systems were found to degrade trichloroethylene at similar rates. Through comparisons to a previously studied model homogenous system, an insertion/*syn*- β -chloride-elimination mechanism is proposed.

4.1 INTRODUCTION

Remediation of contaminated groundwater is a major environmental challenge. Chlorocarbons, specifically chlorinated ethylenes such as perchloroethylene (PCE) and trichloroethylene (TCE) represent a major class of groundwater pollutants. These persistent, mobile and toxic chlorocarbons are potential carcinogens that are found in both soil and water systems.¹⁻⁵ The toxic effects associated with these molecules are related to the chlorine substituents. Accordingly, removal of the chlorine atoms leads to detoxification.⁶

Various strategies, including the use of zero-valent metals,⁷⁻¹⁵ electrochemical processes,¹⁶⁻²¹ and microbial agents²²⁻²⁶ have been used to degrade chlorocarbons. Microbially based dehalogenation reactions, which are often mediated by cobalamin (cobalt-containing tetrapyrrole) have been studied in detail and PCE and TCE are reduced to less chlorinated congeners, including *cis*-1,2-dichloroethylene (*cis*-DCE), vinyl chloride, ethylene, and ethane in these systems.^{22,23} Although the substrates can be fully dechlorinated, the major product of cobalamin-mediated dechlorination of PCE and TCE is *cis*-DCE,²⁷ and under standard reaction conditions *cis*-DCE is poorly degraded.²⁸ Field sites that were originally contaminated with PCE and TCE are now contaminated with toxic *cis*-DCE.^{1,2,4} Therefore we have been exploring the use of alternate catalysts that are capable of rapidly dechlorinating the lower chlorinated congeners.

One attractive alternative to biologically-mediated systems are pump-and-treat systems with catalytic degradation using noble metals for the catalysts and dihydrogen (H₂) as the reducing agent. Noble metals in the presence of H₂ as the reducing agent

have been shown to be active hydrodechlorination catalysts,^{18,19,29-35} and the most active dechlorination catalysts contain, platinum, palladium, and rhodium.³⁶ A notable example, studied by Reinhard and coworkers, for the catalytic degradation of chlorinated ethylenes uses palladium on alumina support (Pd/Al₂O₃) as the catalyst and H₂ as the reducing agent.^{18,19,30-32,37,38} This system is especially exciting as it degrades all of the chlorinated ethylenes with similar rates, and the lower chlorinated ethylenes are degraded slightly faster.³¹ The final degradation product was ethane for all of the chlorinated ethylenes studied.

A recent study compared palladium, platinum, and rhodium on alumina catalyst in the hydrodechlorination of 4-chlorophenol under mild conditions (20-40 °C and H₂).³⁶ In this system palladium and rhodium out-performed platinum, and rhodium displayed the highest activity.³⁶ Heterogeneous rhodium catalysts have been used previously to dechlorinate alkenes and alkanes, but no mechanistic information was presented. Dichloropropane,³⁹ dichlorobutenes,⁴⁰ PCE,⁴¹ TCE,³⁵ and 1,2-dichloroethane^{5,35,42} have been dechlorinated using Rh/Al₂O₃, Rh/SiO₂ or RhCl₃ catalysts in the presence of H₂. Furthermore, Bozzelli *et al.* reported that TCE was more readily degraded than 1,2-dichloroethane at 91-280 °C and 1 atm of H₂, using rhodium on alumina support (Rh/Al₂O₃).³⁵

We have previously shown that homogenous rhodium complexes are extremely active dechlorination catalysts.^{43,44} In the homogenous systems, rhodium hydrides were active intermediates and an insertion/ β -Cl-elimination mechanism was supported.

Herein we explore a heterogeneous analogue using Rh/Al₂O₃ as the catalyst and H₂ as the reducing agent, and compare the results to the homogenous model system.

The results support a similar mechanism for the two systems, an insertion/ β -Cl elimination mechanism.

4.2 EXPERIMENTAL PROCEDURES

General Considerations. All reagents were purchased from commercial suppliers. PCE, TCE, *trans*-1,2-dichloroethylene (*trans*-DCE), 1,2-dichloroethane, and vinyl chloride were purchased from Sigma-Aldrich. 1,1,2-Trichloroethane and *cis*-1,2-dichloroethylene (*cis*-DCE) supplied by Acros and 1,1-dichloroethylene (1,1-DCE) supplied by Alpha Aeser. Ethane, ethylene and deuterium purchased from Matheson Gas Products, Inc and H₂ from Airgas. Vinyl fluoride was purchased from SynQuest Labs, Inc. All compounds were used as received without further purification. NMR spectra were acquired on Varian UNITY Inova NMR spectrometers (500 MHz and 600 MHz) and referenced to the residual protiated solvent (HOD).

Catalysts. The 5 wt % Rh/Al₂O₃ powder and 1 wt % Pd/Al₂O₃ powder were used as received from Aldrich; no special precautions were taken to avoid catalyst exposure to air prior to kinetic experiments. The 5 wt % rhodium and 1 wt% palladium content specified by the manufacturer was assumed to be accurate. Brunauer-Emmett-Teller (BET) surface area was determined from 77 K nitrogen adsorption-desorption isotherms (Quantachrome, model OS-7).

Kinetic Experiments. The hydrodehalogenation experiments were performed in a 1 L Schenk flask fitted with a septum on the top, kept in a constant temperature oil bath at 25.0 ± 0.3 °C. The flask was filled with 750 mL of pH 7 high ionic strength phosphate buffer (9.67 g potassium monophosphate basic and 19.34 g sodium phosphate dibasic in 1 L DI water), sodium chloride (350 mM), and catalyst (0.0149 g Rh/Al₂O₃ or 9.93 × 10⁻⁴ g Rh/L). The solution was purged with H₂ for 20 minutes to remove dissolved gases and saturate with H₂. The flask was kept under constant H₂ pressure during the

course of the reaction (1 atm), using a bubbler system. Halogenated substrate (150-400 μM) was added through the septum on top of the flask. The substrates needed about 25 minutes to equilibrate between the aqueous phase and the headspace. All reaction mixtures were mixed using an IKAMAG® RCT Basic Magnetic Hot Plate Stirrer. The stir motor setting was 8. No stir rate-associated change in reaction rate was observed as long as the solution was mixed at a rate fast enough so that no catalyst settled out of solution.

Caution: The catalyst must be added before purging with H_2 as the reaction of $\text{Rh}/\text{Al}_2\text{O}_3$ powder and H_2 is exothermic.

Headspace reaction aliquots (200 μL) were extracted from the septum in the top of the flask using a valve-lock gas-tight 500 μL syringe, and a tight-fitting polypropylene cap was placed in the septum in between time points. The headspace aliquots were analyzed by gas chromatography coupled to a mass spectrometer (GC-MS) using an Agilent GC 6890 (Restek Rtx®-1 Crossbond® 100% dimethyl polysiloxane, 30 m \times 0.32 mm \times 5 μm film thickness) coupled to an Agilent MS 5973 Mass Selective Detector operated in scan mode. The oven temperature profile was: 40 $^\circ\text{C}$ for 7 min., ramp 40 $^\circ\text{C}$ / min. to 140 $^\circ\text{C}$ and hold at 140 $^\circ\text{C}$ for 7 min. This method allowed for resolution of all parent compounds and products in a single run. The concentrations of halogenated ethylene were determined from standard calibration curves based on the total amount added to the flask; calibration curves were made without H_2 , under N_2 , with no other modifications to the reaction matrix.

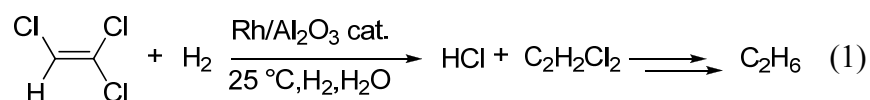
The reactions were performed under pseudo-first-order reaction conditions. The concentration of H_2 was assumed to be constant and not taken into account. The rates

of dechlorination were determined by quantifying the disappearance of the substrate over time. The observed pseudo-first-order reaction rate constants (k_{obs}) were determined by plotting the data as concentration versus time and fit to a first-order exponential decay function, or from linear regressions of $\ln(C_t/C_0)$ versus time plots. Products of the dehalogenation reactions were determined by comparing the retention time and mass spectra to authentic standards.

Mass transfer limitations (liquid-solid, gas-liquid, and intraparticle mass transfer limitations) were considered to be negligible due to the similarity in this reaction system to the Pd/Al₂O₃ and H₂ dechlorination system studied by Lowry and Reinhard.³¹

4.3 RESULTS AND DISCUSSION

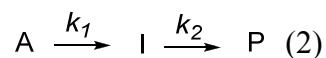
Treatment of TCE (300 μ M) with a catalytic amount of Rh/Al₂O₃ (9.93×10^{-4} g Rh/L) in H₂ saturated water under H₂ (1 atm) at 25 °C leads to complete dechlorination in 210 minutes ($t_{1/2}$ of 44 minutes) (eq. 1). The major product observed was ethane with trace amounts of 1,1-dichloroethylene (1,1-DCE), *cis*-DCE, vinyl chloride and ethyl chloride observed (eq.1). Both Rh/Al₂O₃ and H₂ need to be present for reaction to occur; no reaction occurs when TCE is reacted with either Rh/Al₂O₃ or H₂ alone.



Interestingly the lower chlorinated ethylenes appear in the first time points as the reaction is monitored, account for less than 1% of the C₂ mass when present, and degrade to a level below the detection limit prior to TCE being completely degraded. Over the course of the reaction, saturated and unsaturated C₄ and C₆ hydrocarbons were also observed. After TCE was fully degraded, more hydrocarbons were observed. These results suggest that dechlorination to ethane is followed by dimerization to butenes and hydrogenation to butanes as well as oligomerization to hexenes and hydrogenation to hexane. The yield of observed products was essentially quantitative, as ethane alone comprises over 91% of the C₂ mass. HCl is also a product of this reaction; when the reaction is run unbuffered the pH decreases during the reaction.

It is also noteworthy that this system appears to have a strong kinetic preference for sp²-hybridized C-Cl bonds over sp³-hybridized C-Cl bonds, as no reaction occurs during the reaction with 1,1,2-trichloroethane or 1,2-dichloroethane under these conditions.

To further characterize this C-Cl bond activation process, a study of the reaction kinetics was undertaken. Kinetic experiments were conducted in a temperature-controlled reaction flask and concentrations of the reactants and products were determined by authentic standard calibration curves. Pseudo-first-order reaction kinetics were observed for the loss of TCE under these reaction conditions. A sample kinetic plot depicting the exponential degradation of TCE with concomitant growth of ethane is shown in Figure 4.1. The growth of ethane was fit as the product of consecutive first order reactions (eq 3 and 4).⁴⁵ The fit accounts for the induction period in which some intermediate, I, is formed, indicating ethane is not formed directly from TCE, but instead forms from a(n) active intermediate(s) in the reaction mixture. We propose that the active reaction intermediates are dichloroethylenes and vinyl chloride.



$$[P]_t = [A]_0 \left(1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right) \quad (3)$$

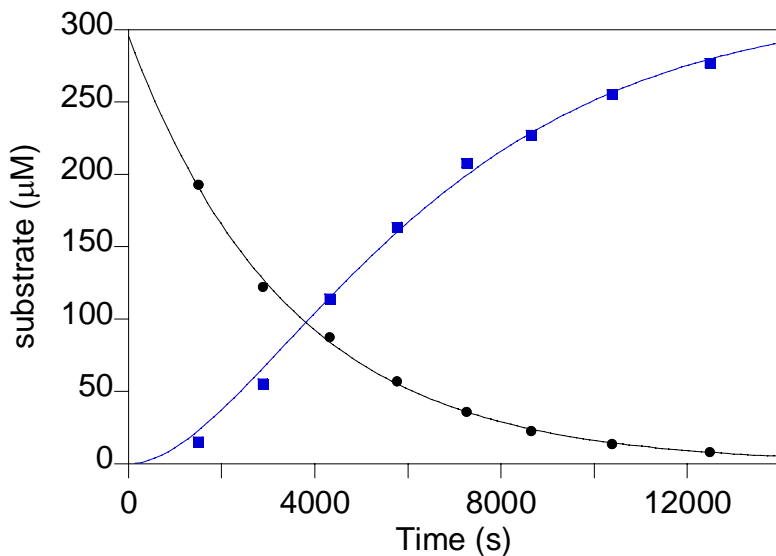


Figure 4.1. TCE degradation by Rh/Al₂O₃ (9.93×10^{-4} g Rh/L) and H₂ (1 atm) at 25 °C, and the subsequent appearance of ethane as a reaction product in pH 7 phosphate buffered H₂O with 350 mM NaCl. Curves are fits to the data: TCE was fit to nonlinear first-order decay and ethane was fit as the product of consecutive first order reactions (eq 2 and 3).

This is in contrast to the Pd/Al₂O₃ system studied by Lowry and Reinhard in which they observe only ethane in the hydrodechlorination of TCE, and propose a direct pathway from TCE to ethane without intermediates.³¹

In order to control for the formation of HCl during the course of the reaction, the system was buffered, and sodium chloride (NaCl) was added to control the ionic strength. The reactions were performed with 350 mM NaCl in pH 7 phosphate buffer. Without phosphate buffer the pH of the reaction decreased during the course of the reaction. For example, starting with an initial pH value of 6.8, a final value of 2.6 was observed. With the phosphate buffer, the pH of the system remained constant at 6.8 over the course of several reactions. The rate of TCE degradation did not change with use of phosphate buffer or the addition of NaCl under identical reaction conditions.

The reaction was found to be first-order in catalyst, Rh/Al₂O₃. This was established by the linear relationship between the k_{obs} of TCE degradation with varied catalyst amounts from 0 to 1.65 mg Rh/L (Figure 4.2).

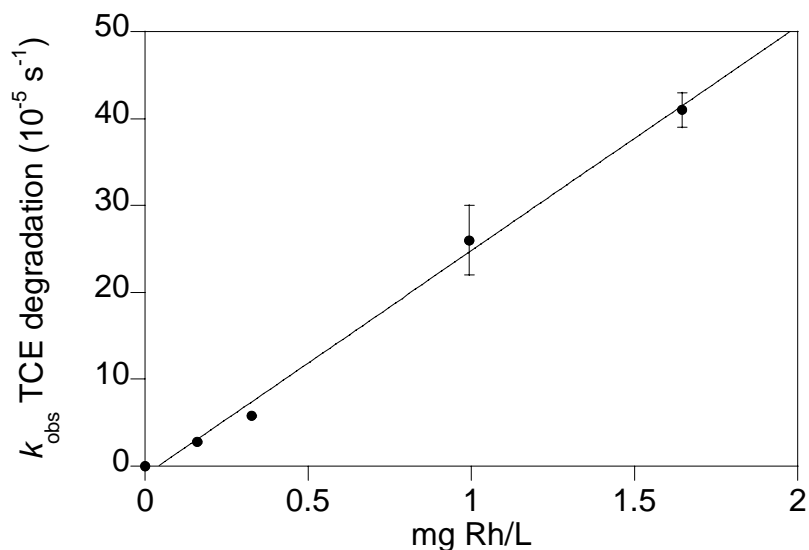


Figure 4.2. Observed degradation rate constants (k_{obs}) of TCE under 1 atm H₂ and increasing amounts of catalyst (0 to 1.65 mg Rh/L) in pH 7 phosphate buffered H₂O with 350 mM NaCl. Values were determined for loss of substrate with time at 25 °C. The fit is linear to the data $R^2 = 0.9953$. Error bars were determined from the standard error in the fit of the TCE degradation versus time plots.

The catalyst was still performing at 100 % efficiency after 744 turnovers. The turnover number (TON) was calculated as moles of C-Cl bonds broken per mole of rhodium (eq 4).

$$\text{TON} = \frac{\text{moles of C - Cl bonds broken}}{\text{moles of Rh}} \quad (4)$$

Comparison to Pd/Al₂O₃

In order to directly compare the 5 wt % Rh/Al₂O₃ results to the 1 wt % Pd/Al₂O₃ system, TCE was hydrodechlorinated using Pd/Al₂O₃. The reactions were performed under identical conditions as the Rh/Al₂O₃ experiments, with the amount of noble metal kept constant. TCE (300 μM) was reacted with a catalytic amount of Pd/Al₂O₃ (9.93×10^{-4} g Pd/L), H₂ (1 atm), and 350 mM NaCl, in pH 7 phosphate buffered water at 25 °C (Figure 4.3). During the course of the reaction, all three dichloroethylenes were observed as well as vinyl chloride, and trace ethyl chloride. Saturated and unsaturated C₄ and C₆ hydrocarbons were also observed. The major product was ethane as it accounted for over 85 % of the C₂ mass.

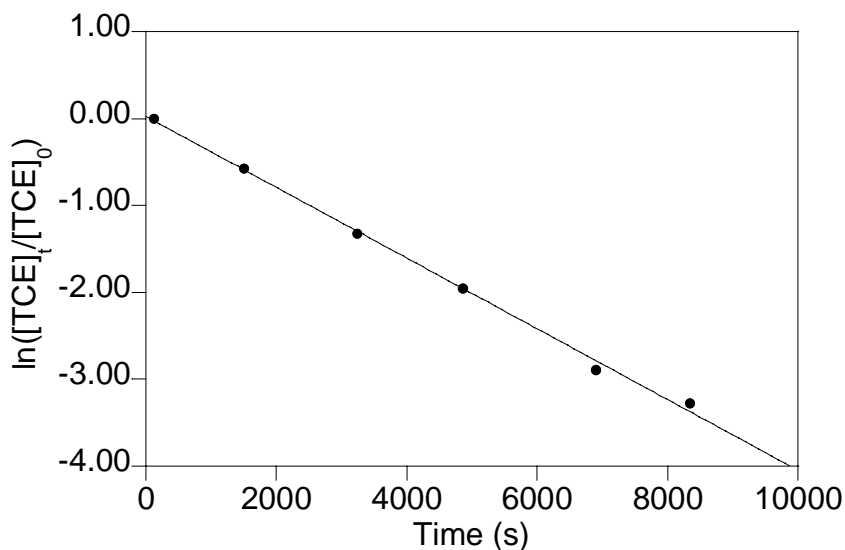


Figure 4.3. Linearized TCE degradation by Pd/Al₂O₃ (9.93×10^{-4} g Pd/L) and H₂ (1 atm) at 25 °C with 350 mM NaCl in 750 mL pH 7 phosphate buffered water. The fit is a linear regression to the data with $R^2 = 0.9972$.

Table 4.1. The degradation of TCE for the comparison of Rh/Al₂O₃ and Pd/Al₂O₃ as the catalyst and H₂ (1 atm) as the reducing agent with 350 mM NaCl in 750 mL pH 7 phosphate buffered water at 25 °C.

	Rh/Al₂O₃	Pd/Al₂O₃
Wt % metal	5	1
BET surface area (m²/g)	126	95
Amount (mg)	14.9	74.5
mg metal/L	0.993	0.993
<i>k</i>_{obs} (10⁻⁴ s⁻¹)	2.6 ± 0.4	4.0 ± 0.1
Rate normalized to SA (m⁻²s⁻¹)	1.4 × 10 ⁻⁴	0.57 × 10 ⁻⁴
Lower chlorinated products	< 1%	> 2%
Conversion to ethane (%)	91	85

The Rh/Al₂O₃ and Pd/Al₂O₃ catalysts reacted very similarly under the reaction conditions used in this study. The same product suite was observed with both catalysts; with the Pd/Al₂O₃ hydrodechlorinating TCE slightly faster than Rh/Al₂O₃ for the same catalyst loading of g metal/L, but also producing slightly higher percentage of lower chlorinated products. When the rates are normalized to the surface area of the catalyst the Rh/Al₂O₃ degraded TCE 2.5 times faster.

Substrate scope and relative reactivity

In order to characterize the relative rates of substrate degradation using Rh/Al₂O₃ and H₂, each of the various chlorinated ethylenes were subjected to identical conditions to those described above for TCE. Concentrations of the reactants and products were determined by GC-MS. All substrates exhibited pseudo-first-order kinetics, and the relative rate constants of substrate loss are summarized in Table 4.2. A representative linearized degradation of each substrate versus time is displayed in Figure 4.4.

Table 4.2. Average observed rate constant of chlorinated ethylene degradation (k_{obs}) from replicate kinetic runs, error is the standard deviation of the replicate experiments. Values were determined from loss of substrate versus time at 25 °C using GC-MS. Each kinetic run contained substrate (150-400 μM), catalyst ((Rh/Al₂O₃, 9.93×10^{-4} g Rh/L), NaCl (350 mM), and where in 750 mL of pH 7 phosphate buffer. Relative rate constants (k_{rel}) are normalized to the rate of dehalogenation of PCE ($0.41 \times 10^{-4} \text{ s}^{-1}$).

Substrate	k_{obs} (10^{-4} s^{-1})	k_{rel}	Ethane yield (%)
<i>cis</i> -DCE	6.3 ± 0.5	15.2	91
<i>trans</i> -DCE	3.2 ± 0.2	7.7	91
1,1-DCE	2.7 ± 0.1	6.5	99
TCE	2.6 ± 0.4	6.4	91
PCE	0.41 ± 0.04	1	83

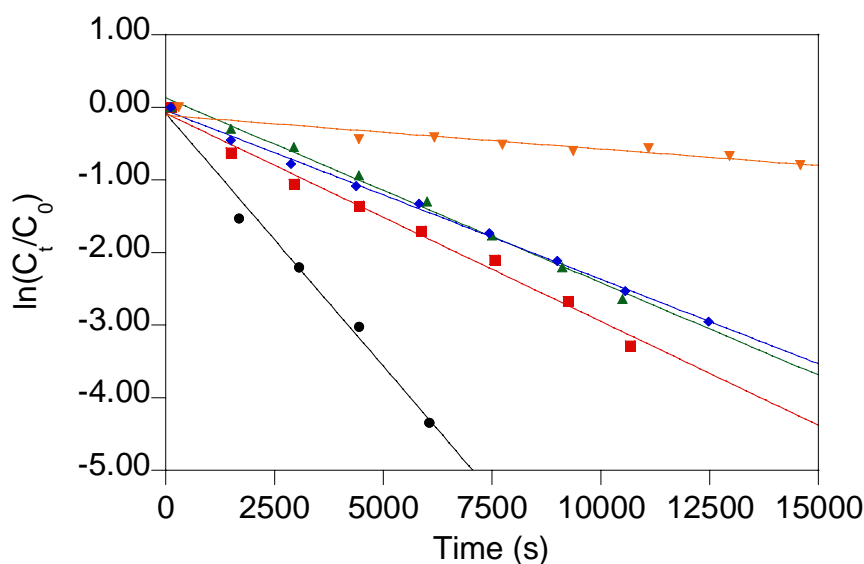


Figure 4.4. Representative linearized degradation of each substrate versus time. Values were determined from loss of substrate using GC-MS at 25 °C. Each kinetic run contained substrate (150-400 μM), catalyst ((Rh/Al₂O₃, 9.93×10^{-4} g Rh/L), H₂ (1 atm), and 350 mM NaCl in pH 7 phosphate buffer in H₂O. Lines are linear fits to the experimental data. *cis*-DCE (●); *trans*-DCE (■); 1,1-DCE (▲); TCE (◆); PCE (▼).

Under these reaction conditions PCE is degraded the slowest. *Cis*-DCE was the fastest substrate, and was degraded 15 times faster than PCE. The major hydrodechlorination product of all chlorinated ethylenes was ethane, as it accounted for over 90 % of the C₂ mass for all substrates except PCE. Trace vinyl chloride was observed during the degradation of all substrates, dichloroethylenes were observed during the degradation of TCE, and TCE was observed during the degradation of PCE. This strongly suggests that the chlorinated ethylenes are sequentially hydrodechlorinated, with the rate increasing with loss of chlorine. It is proposed that ethylene is formed from the degradation of vinyl chloride, but is hydrogenated quickly to ethane under these reaction conditions; however, since ethylene co-elutes with nitrogen using this method of head-space GC-MS analysis, data directly supporting this hypothesis were not obtained.

A noteworthy observation is that trace lower chlorinated ethylenes account for less than 1% of the C₂ mass balance, and they degraded before the higher chlorinated substrate was fully degraded. This is consistent with the catalyst having a stronger affinity for the lower chlorinated ethylenes. The lower chlorinated ethylenes appear to competitively inhibit TCE degradation when they are present in the reaction mixture. The catalytic system having a stronger preference for the lower chlorinated ethylene was supported by reaction of the chlorinated ethylenes together with similar starting concentrations. The dichloroethylenes were observed to degrade first, followed by TCE, then the PCE.

We propose that the degradation of TCE to ethane, under the reaction conditions studied, occurs step-wise as depicted in Figure 4.5 (k_1 - k_9), and not through a direct pathway (k_{10}). Evidence for sequential chlorine removal was obtained by the observation of lower chlorinated substrates during the hydrodechlorination reactions, as well as the initial incubation period before ethane grows in, indicating the presence of reactive intermediates. The rates increasing with loss of chlorine also supports the lack of build-up of lower chlorinated ethylenes during the degradation process.

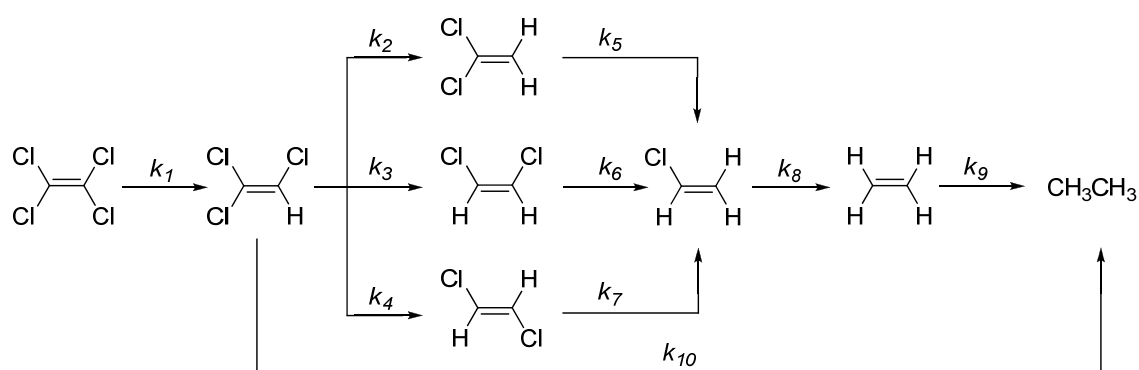


Figure 4.5. Degradation of PCE sequentially to form ethane as the final product. With Rh/Al₂O₃ as the catalyst and H₂ the reducing agent it is proposed that degradation is sequential and k_{10} is not an active degradation pathway (Figure adapted from Ref 31).

Mechanistic comparisons

Even though direct comparisons cannot be made between the homogenous model system we previously studied using (PPh₃)₃RhCl as the catalyst and Et₃SiH and H₂ as the reducing agents, since Rh/Al₂O₃ is a surface mediated processes, some mechanistic information can be obtained by comparing the systems.^{43,44} The homogenous model system of (PPh₃)₃RhCl and H₂ and the heterogeneous system of Rh/Al₂O₃ and H₂ have several similar characteristics including: a marked preference for sp²- over sp³- hybridized C-Cl bonds, similar relative reactivity with chlorinated

ethylenes, and some hydrogenation of products observed. Another similarity between the two systems is that when vinyl fluoride was reacted the major product was fluoroethane, the hydrogenation product.

Due to these characteristics a similar mechanism is proposed for the Rh/Al₂O₃ system as was proposed for the (PPh₃)₃RhCl and H₂ system. We propose the involvement of an insertion/ β -Cl-elimination mechanism and that Rh surface-bound hydrides play a role in the hydrodechlorination mechanism. Further, these hydrides display reactivity more like homogeneous Rh(III) than Rh(I) complexes.

The lack of reactivity in the absence of either Rh/Al₂O₃ or H₂ points toward rhodium hydrides as active intermediates in the catalytic cycle. The preference for sp²-hybridized C-Cl bonds further indicates that oxidative addition of the carbon-halogen bond is not important and is consistent with a β -H insertion/ β -Cl elimination mechanism.

The previously studied homogenous model system, (PPh₃)₃RhCl and hydrogen, and the heterogeneous system studied here both have the highest relative rate of reactivity for *cis*-DCE and the slowest relative rate with PCE. Neither system dechlorinates 1,2-dichloroethane. Trace hydrogenation products were observed in both systems, and the major product of vinyl fluoride degradation was fluoroethane. Based on these similarities, it is reasonable to propose a similar mechanism for the two systems. The proposed mechanism is depicted in Figure 4.6, using *cis*-DCE as the substrate. The first step in the mechanism is insertion of the sp²-hybridized C-Cl bond of *cis*-DCE into a Rh-H bond. This forms a Rh-dichloroalkyl complex, which can then

undergo *syn*- β -chloride-elimination to form vinyl chloride, with the hydrogen from the Rh-H *trans* to the chlorine.

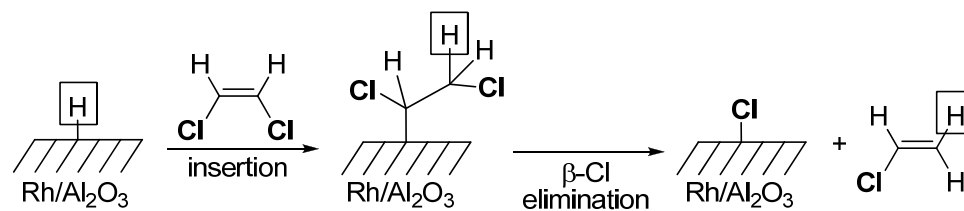
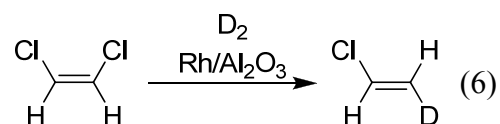


Figure 4.6. Proposed mechanism for the hydrodechlorination of chlorinated ethylenes with $\text{Rh}/\text{Al}_2\text{O}_3$ as the catalyst and H_2 as the reducing agent is an insertion/*syn*- β -Cl-elimination mechanism. *cis*-DCE is the substrate depicted as being hydrodechlorinated, and the H in the box is the hydrogen from the Rh-H.

This mechanistic proposal was further tested using D_2 as the reducing agent and *cis*-DCE as the substrate. The prediction based on the mechanism is that only one isomer of d_1 -vinyl chloride will be produced if the reaction involves *syn*-elimination. The only labeled vinyl chloride observed from the reaction of *cis*-DCE and D_2 with $\text{Rh}/\text{Al}_2\text{O}_3$ in D_2O , was *E*-1-chloro-2-deuteroethylene ($J_{\text{HH}} = 15$ Hz), which was determined by monitoring the reaction with both ^1H NMR spectroscopy and GC-MS (eq 6). This is the expected product from *syn*- β -Cl-elimination.



The isotope labeling studies coupled with all of the other mechanistic similarities suggest that a similar mechanism to the homogeneous model system of $(\text{PPh}_3)_3\text{RhCl}$ and H_2 , is occurring in the $\text{Rh}/\text{Al}_2\text{O}_3$ and H_2 system: an insertion/*syn*- β -Cl-elimination mechanism.

Environmental Significance

The Rh/Al₂O₃ catalyst system has been shown to have many favorable traits. The system exhibits rapid dechlorination rates for trichloroethylene and perchloroethylene with no accumulation of lower chlorinated congeners. Such accumulation plagues cobalamin-based systems. The catalyst system also is water compatible, remains active with repeated use, and has low sensitivity to oxygen. Even given these intriguing facts, numerous other factors must be considered before this type of system is ready for use in the field. Foremost among these is the sensitivity of the catalyst to water constituents, including organic matter and metal ions. Nevertheless, the Rh/Al₂O₃ catalyst system shows promise for the remediation of chloroethylene-contaminated water.

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