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**Investigation of Catalyzed Hydrodechlorination Reactions
of Organochlorines in Supercritical Carbon Dioxide**

by

Bio Aikawa, B. Sc.

Thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of
the requirement for the degree of

Doctor of Philosophy

Department of Chemistry

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Ottawa, Ontario
August, 2001
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**Investigation of Catalyzed Hydrodechlorination Reactions
of Organochlorines in Supercritical Carbon Dioxide**

Submitted by

Bio Aikawa, B.Sc. (Hons.)

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

ABSTRACT

The use of supercritical CO₂ as a solvent to perform catalyzed hydrodechlorination of different classes of organochlorines was investigated in this work. The molecules of interest included 1-chlorooctadecane, 9,10-dichlorostearic acid, and 12,14-dichlorodehydroabiatic acid, as well as some selected PCB congeners varying in the number of chlorines (mono- to penta-chlorobiphenyl).

Dechlorination method optimization was performed mainly with 1-chlorooctadecane. Complete dechlorination was achieved when all the experimental parameters (temperature, pressure, concentrations of reagents) were optimized and the role of each parameter was thoroughly examined.

Their structural differences as well as polarity and size of the reacting molecule were considered to be important factors controlling the reaction. Kinetic analysis of dechlorination determined the rate-limiting step was adsorption of the reactant molecule for 1-chlorooctadecane, 9,10-dichlorostearic acid, and 12,14-dichlorodehydroabiatic acid in supercritical CO₂. Dechlorination of 1-chlorooctadecane resulted in the same rate-limiting step and apparent activation energy in supercritical CO₂ and in liquid isopropanol, evidence of the reaction mechanism is the same in both cases. On the other hand for 4-monochlorobiphenyl, the rate-limiting step was the surface reaction.

The selectivity of dechlorination pathways of PCBs indicated that loss of more than one chlorine atom can take place prior to desorption and the effect becomes more significant for higher chlorinated congeners. This was considered due to the increase in the number of possible interaction sites as the number of chlorine increases which suggested that the point of interaction with the catalyst surface is not the aromatic ring. An attempt to use a theoretical approach (i.e., correlation to bond dissociation energy, rotational energy barrier and molecular orbital coefficients) was also taken to explain the observed effects although only a partial elucidation was possible.

An investigation on the use of supercritical CO₂ for selective extraction of components of pulp and paper pitch deposits was also performed.

ACKNOWLEDGEMENTS

Many people have helped me, supported me, and encouraged me through the last five years of my Ph.D. studies in many different ways. I would like to thank *all of you* for your involvement in my life which has lead to the completion of my studies at Carleton University.

This thesis would not be complete without acknowledging the following people for their contribution.

To my parents, for always being a great support, source of encouragement, and being someone I look up to.

To Bob Burk, for being a good supervisor since my undergraduate years. I have learnt great deal of science from him over the years and it has been my pleasure to be a student in his research group.

To Jim Logan, for providing much technical support for a variety of instrumental to computer problems, and to Ken Sadowski for construction and modification of the reaction cell. Special thanks to both Jim and Ken for being always patient enough to come back to help me, although there were occasions they had tried to hide from me unsuccessfully.

To Bruce Sitholé at Paprican, for being always very helpful throughout my Ph.D. work, the majority of which was conducted in collaboration with Paprican.

To Barb Gauthier and Cheryl MacPhee, for measurements of rate constants and activation energy measurement for monochlorobiphenyls in liquid isopropanol, and also for sharing good laughs in the lab.

To Erin Johnson for helping me with most of the theoretical calculations.

To Rocio Aranda and Meredith Curren for sharing a good part of our Ph.D. studies containing a variety of memories.

To John Murimbo for not only being always on call for many 'emergencies' but also for much insight he provided on my research. To Nouri Hassan, Gerald McManas, Victoria Nawaby, Jeff Guthrie, Rupa Mandel for being good companies and providing many support over the years.

To Fred Cassalman for his support through my teaching assistant times.

To Mary Orser and Lisa Ralph for being a great source of encouragement whenever I needed.

And finally but not lastly, to Ruth Lifeso, for being a wonderful and encouraging support though all my years at Carleton.

Thank you to everyone at the Department of Chemistry.

PUBLICATIONS AND PRESENTATIONS

Portions of this work have been published and presented as listed:

PUBLICATIONS

B. Aikawa, R. C. Burk, and B. B. Sitholé, Catalytic Dechlorination of 1-Chlorooctadecane in Supercritical Carbon Dioxide, *Applied Catalysis B: Environmental*, 2001, 848, 1-12.

B. Aikawa, R. C. Burk, Catalytic Hydrodechlorination of 1-Chlorooctadecane, 9,10-Dichlorostearic acid, and 12,14-Dichlorodehydroabietic acid in Supercritical Carbon Dioxide, manuscript in preparation.

B. Aikawa, R. C. Burk, Congener Specific Kinetic Analysis of Catalytic Hydrodechlorination of PCBs in Supercritical Carbon Dioxide, manuscript in preparation.

Bio Aikawa, Robert Burk, and Bruce Sitholé, Dechlorination of Chlorinated Model Wood Resin Compounds in Supercritical Carbon Dioxide: Implications for Improved Analysis of Chlorinated Pitch Deposits, *Miscellaneous Report MR 430*, Pulp and Paper Research Institute of Canada, November 2000.

B. Aikawa, R. C. Burk, Dechlorination of 1-Chlorooctadecane, 9,10-Dichlorostearic Acid, and 12,14-Dichlorodehydroabietic Acid in Supercritical Carbon Dioxide, in the conference proceedings of *EnviroAnalysis 2000*, R. Burk, R. E. Clement, Eds., Polyscience Publications Inc., 2000, 435-440.

B. Aikawa, R. C. Burk, Supercritical Fluid Extraction of Pitch Deposits from a Kraft Mill, in the conference proceedings of *EnviroAnalysis '98*, R. Burk, R. E. Clement, Eds., Polyscience Publications Inc., 1998, 177-182.

CONFERENCE PRESENTATIONS

Dioxin 2000, Monterey, California, USA, 2000 with R.C. Burk and B. B. Sitholé.

EnviroAnalysis 2000, Ottawa, Canada, 2000 with R.C. Burk and B. B. Sitholé.

10th ISWPC meeting, Yokohama, Japan, 1999, with R.C. Burk and B.B. Sitholé.

AIChE annual meeting, Miami Beach, USA, 1998, with R.C. Burk and B. B. Sitholé

EnviroAnalysis '98, Ottawa, Canada, May 1998, with R.C. Burk and B. B. Sitholé.

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GLOSSARY OF TERMS

ΔG^0	Gibb's free energy
ΔH^0	heat of enthalpy
ΔS^0	heat of entropy
$[9_a]$	concentration of PCB009 adsorbed on the catalyst
$[9_s]$	concentration of PCB009 in solution
A	acetone
$A^\bullet$	acetone radical
AS	adsorbed acetone
atm	atmosphere
BDE	Bond Dissociation Energy
BET	Brunauer-Emmett-Teller
C	1-chlorooctadecane, or $C_{18}\text{-Cl}$
$C_{18}\text{-Cl}$	1-chlorooctadecane
C_A	concentration of species A
C_{AS}	concentration of the adsorbed species A
$Cl^\bullet$	chlorine radical
CS	adsorbed 1-chlorooctadecane
C_t	concentration of the total active site on the catalyst
C_v	concentration of the vacant site on the catalyst surface
DHA- Cl_2	12,14-dichlorodehydroabiatic acid
E_a	apparent activation energy
ECD	electron capture detector
FID	Flame Ionization Detector
GC	Gas Chromatography
H	hydrochloric acid, HCl
$H^\bullet$	hydrogen radical ($H^\bullet$)
HS	adsorbed HCl
I	isopropanol
IS	adsorbed isopropanol
k_{9-1}	rate constant for dechlorination of PCB009 to PCB001
K_{eq}	equilibrium constant
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
MS	Mass Spectrometry
O	octadecane
$O^\bullet$	octadecane radical
OS	adsorbed octadecane
R	gas constant
SC	supercritical
SFE	supercritical fluid extraction
Stearic- Cl_2	9,10-dichlorostearic acid

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Chapter 1

Introduction

1.1 BACKGROUND

1.1.1 Organochlorines in the Environment

Most organochlorines are anthropogenic and their presence in the environment is of great concern as many of them are persistent, toxic, and they bioaccumulate. These compounds include chlorinated low molecular weight aliphatic molecules such as CCl_4 and CHCl_3 to high molecular weight polychlorinated biphenyls (PCBs). Many insecticides and pesticides are also heavily chlorinated and although the production of many have been banned for more than a few decades, their presence is still reported in the environment. The complete removal of those compounds from the environment will remain a challenge.

The pulp and paper industry has been a subject for contaminating the environment by effluent emission of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofureons (PCDFs) due to a heavy use of chlorine in the bleaching process. Although not as well known, this process also creates many other chlorinated compounds such as chlorinated wood resins, which are collected with the fibers and other inorganic materials and accumulate as solid deposits known as pitch. There is not a clear consequence to the environment due to the accumulation of these compounds, however, they are the main cause of problematic deposition in the mills, which has severe economic impacts in the industry.

Polychlorinated biphenyls or PCBs are a group of chlorinated compounds discovered in 1881 and commercially produced beginning in 1929 [1]. The production of PCBs was banned in the USA in 1979 as their toxicity and environmental impact were recognized. The total world production prior to 1980 was of the order of 10^9 kg, of which approximately half was produced by Monsanto (the major North American manufacturer) and although its production has been banned, a significant amount still exists in the environment. PCBs are chemically very stable to oxidation and heat, have low water solubility, low vapour pressure, and excellent dielectric properties. They have been used as transformer oil, flame retardants, heat transfer fluids, and in the manufacture of paints, plastics, adhesives, etc. Their chemical and physical stability were very useful in many industries, however, for this reason PCBs have become such a widespread environmental contaminant [2].

PCB contaminated wastes are disposed by storage or incineration with very restrictive regulations, specifying destruction at the 'six nines' level (i.e., 99.9999%) to be achieved. Not only the high energy consumption required for incineration, but the process needs to be completely oxygen free to avoid formation of more toxic PCDDs and PCDFs as byproducts.

There are 209 PCB congeners (possible chlorine substitution patterns on a biphenyl nucleus) with the formula $C_{12}H_{10-n}Cl_n$ where n ranges from 1 to 10.

Figure 1.1-1: General formula of Polychlorinated biphenyls ($x + y = n$, $1 \leq n \leq 10$)

Identification numbers are assigned to all 209 congeners according to the International Union of Pure and Applied Chemistry (IUPAC) system. PCBs are most often referred to in their abbreviated form by these identification numbers, as the proper chemical nomenclatures are excessively long. For example, 2,2',4,5,5'-pentachlorobiphenyl is referred to PCB101 or #101. A member of the PCB class of compounds is called a congener regardless of number or position of chlorines.

PCBs were commercially produced as complex mixtures by direct chlorination of biphenyl with chlorine gas. Monsanto produced a series of mixtures under the registered trade-mark of Aroclor®. Each Aroclor mixture has a four digit code, such as Aroclor 1254, where the first two digits indicating 12 carbon atoms in biphenyl and the last two digits indicating the weight percent of chlorine in the mixture (i.e., 54 %).

US EPA classified PCBs as probable human carcinogens. As the number and position of chlorine atoms in PCB could be any one of 209 possible combination, the toxicity of PCBs varies among the congeners. The most toxic congeners known are those with 'non-ortho' substitution or the one which referred to as co-planar PCBs are known to behave similarly to dioxins. They include PCB077 (3,3',4,4'-tetrachlorobiphenyl), PCB081 (3,4,4',5-tetrachlorobiphenyl), PCB126 (3,3',4,4',5-pentachlorobiphenyl) and PCB169 (3,3',4,4',5,5'-hexachlorobiphenyl) [3, 4].

In this study, chlorinated fatty and resin acids as well as some specific PCB congeners were selected to study dechlorination reactions in supercritical CO₂. The former compounds are the major component in wood resins which are known to cause problems in pulp and paper mills. The environmental impact of the PCBs are well known. Both groups of the selected compounds have either economic or environmental impact to the current society and their destruction was considered important to pursue.

1.1.2 Dechlorination of Organochlorines

An extensive review of catalytic hydrodehalogenation of organic compounds was published by Lunin and Lokteva in 1996 [5]. Although it covered a wide range of dechlorination systems, most aspects of catalytic hydrodehalogenation mechanisms were not clearly described. The mechanism depends on various conditions and catalysts. Basic differences in reaction conditions such as the source hydrogen (gaseous hydrogen or organic hydrogen-containing donor molecules) can change the mechanism for each and particular case.

Homogeneous Catalysis

Many homogeneous hydrodechlorination reactions of both alkyl and aryl chlorides have been done using palladium [6, 7, 8], nickel [9, 10], or rhodium complexes [11]. For example, a successful reductive dechlorination of chlorobenzenes was performed using a rhodium catalyst obtained from $[(\text{CH}_3)_5\text{C}_5\text{RhCl}_2]_2$ under a hydrogen atmosphere at 75°C [11]. The reaction was performed in isopropanol which was considered to act as a hydrogen donor in this reaction.

Heterogeneous Catalysis

Group VIII metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) are widely used for hydrodechlorination of both alkyl and aryl halides. Of those transition metals, nickel group metals (Ni, Pd, Pt) are used most frequently [5 -19]. Dechlorination is most commonly carried out under a hydrogen atmosphere at relatively high temperature (i.e., 200 - 700°C) and moderate pressure (i.e., 0.5 - 10 bar) [2-14].

Palladium has been used in many studies on hydrodechlorination of various organochlorines including CCl_4 , polychlorinated ethanes, Freons, PCBs, chlorobenzenes, chlorotoluenes, and chlorophenols [12, - 18] . Palladium is usually introduced into the system directly on a support, commonly activated carbon or Al_2O_3 .

Hydrodechlorination has also been performed under milder conditions. For example, a complete hydrodechlorination of chlorophenols using Pd/C at 35°C and 2.4 atm was achieved by Hoke, et al [18]. Hydrodechlorination of PCBs to biphenyl was also successfully performed in isopropanol with sodium hydroxide using Pd/C or Rh/C at 82°C [12]. This reaction was selected for the studies in the following chapters due to the simplicity of the reaction system and high dechlorination yield obtained. Isopropanol was considered to be the hydrogen donor in this reaction system and this was also investigated further both in isopropanol and supercritical CO₂.

Bimetallic systems are also used for dechlorination. Low molecular weight organochlorines (chlorinated ethylenes, CCl₄, CHCl₃, and CH₂Cl₂) at low concentrations in aqueous solutions (20 ppm) were successfully dechlorinated within a few minutes on the surface of palladized iron [20]. Nickel-chromium catalysts have also been used for partial dechlorination of chloro-alkanes. [5]

Zero-valent metal has also been used for reductive dechlorination of CCl₄ and CHCl₃ [21, 22], or halogenated ethylenes [23] under mild conditions. These studies showed that the dechlorination generally took longer than a few hours. Aroclor mixture has been dechlorinated in supercritical CO₂, however quantitative analysis was not performed [42].

Other Methods of Dechlorination

Dechlorination of various organochlorines has also been performed by phase-transfer catalysis [5, 24, 25], electrochemical [5], photochemical [5, 26], or radiolytic methods [27 - 30]

Phase-transfer catalyst is considered useful for removing the hydrochloric acid formed after the dechlorination from the catalyst surface [24,25]. The electrochemical dechlorination of chlorinated insecticides has been done successfully yet it generally takes a long time to complete. [5]. Partial dehalogenation of 1,1,2-trichlorotrifluoroethane

was performed by illumination of air-free suspensions of TiO_2 particles containing formate ions [26].

Radiolytic dechlorination using γ -ray as a energy source has been generally applied in alkaline isopropanol solutions [27, 28, 29,30]. Reactants undergo stepwise radiolytic dechlorination via a chain reaction involving the acetone radical anion. A chain reaction in a neutral system involves the α -hydroxyisopropyl radical and has been observed to be less efficient than in a alkaline system.

It is generally understood that the presence of base enhances the dechlorination rate in an isopropanol solution. Palladium is known to work well in such systems, as well as the conventional hydrogenation system under a hydrogen atmosphere. Time required to complete the dechlorination varies from a few minutes to hours and it takes longer under mild conditions.

There are many dechlorination methods available with high yield, however, there are not many systems that have been studied extensively with respect to the reaction mechanisms. For many industrial and practical purposes, attainment of high dechlorination yield with less amount of catalyst in a short period of time is the primary goal. Perhaps this is the main reason for the lack of information on the detailed mechanism on heterogeneous catalytic hydrodechlorinations. Another major problem with this system is the difficulty in obtaining information on surface species.

Determination of the reaction mechanism was of main interest in this thesis in addition to achieving complete dechlorination yield.

1.1.3 Kinetic Studies of Catalytic Reactions

A catalyst can be defined as a substance modifying the rate of chemical reaction without altering its equilibrium state, and its small amount is sufficient to increase the reaction rate [31]. In other words, it is a substance that lowers the free energy of activation [32]. The extent of reaction is defined by;

$$\xi \text{ (mole)} = \frac{n_i - n_i^0}{\nu_i} \quad (1.1.3-1)$$

where n_i^0 and n_i are the quantity of component in mole, at time zero or at any time respectively, and ν_i is the stoichiometric coefficient of component. Reaction rate is defined in the most general way by;

$$\text{rate} = \frac{d\xi}{dt} \text{ mols}^{-1} \quad (1.1.3-2)$$

or in practice is normalized by unit area of the catalyst as:

$$\frac{1}{A} \frac{d\xi}{dt} \text{ molcm}^{-2}\text{s}^{-1} \quad (1.1.3-3)$$

It is more precise to express it per the number of active sites on the catalyst surface.

For the reaction;

The reaction rate at time t will be given by the derivative of the concentration of any of the species involved with respect to time:

$$\text{Rate} = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} \quad (1.1.3-4)$$

However, the reaction rate is proportional to the concentrations of all the species taking part in the reaction. If it is the change in the concentration of one of the reaction products, P being measured, then,

$$\text{Rate} = \frac{d[P]}{dt} = k[A][B] \quad (1.1.3-5)$$

Where k is the rate constant and represents the reaction rate per unit concentration of reactants. The sum of the exponents of $[A]$ and $[B]$ in the above equation is known as the reaction order; thus, the reaction above is second order.

If one of the reactants (B) is present in a large excess, its concentration change becomes negligible. In such a case, the reaction is considered to be pseudo-first order in $[A]$ and the rate equation can be written as $\text{rate} = k'[A]$.

Practical treatment of kinetic data

Method of Initial Slope

Method of initial slope measures the slope of the initial raise of the curve to determine the rate (or rate constant) of the reaction. This method is based on the understanding that initial rates are linearly proportional to the initial catalyst concentration $[C]_0$ and relates to minimal complications from side reactions.

In the case of a first-order reaction, the change in the concentration of a reactant (A) is expressed as;

$$-\frac{d[A]}{dt} = k[A] \quad (1.1.3-6)$$

Integrating both sides of equation (1.1.3-6) from time 0 to t will result in

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (1.1.3-7)$$

where k is the rate constant, $[A]_t$ and $[A]_0$ are the concentrations of A at time t and zero.

Thus a plot of $\ln [A]_t / [A]_0$ versus time will have a slope of $-k$.

Slope measurements evaluate $d(\text{concentration})/dt$ at any given time during the reaction. This method is used often for the multi-point rate evaluations of the reaction profile as it is used later in Chapter 5 for determination of individual reaction constants for intermediate PCBs.

1.1.4 Supercritical Fluids

States of matter are conventionally divided into solid, liquid, and gas and these states are well described by a phase diagram (Figure 1.1-2). Lines of sublimation, melting, and vaporization define the equilibrium between two phases; solid and gas, solid and liquid, and liquid and gas, respectively. All three lines come together at a triple point, where all three phases coexist in equilibrium. When the temperature and pressure is increased along the line of vaporization, eventually a critical point is reached and beyond this point, the distinction between liquid and gas disappears. This region is defined as a supercritical fluid. A precise definition of a supercritical fluid is when the fluid's temperature exceeds the critical temperature. It is called the sub-critical state when temperature is below its critical value where the fluid can separate into two phases at the gas-liquid equilibrium line. Carbon dioxide is the most commonly used supercritical fluid, and has a critical pressure of 72.85 atm, and critical temperature of 31°C. The easily attainable levels of temperature and pressure is one of the major reasons for CO₂ to be a popular choice.

Figure 1.1-2: Phase Diagram of Carbon Dioxide

Thermodynamic Properties: Equations of State

An equation of state relates the pressure, volume, the number of moles, and temperature of any substance and any one of the variables can be specified as a function of the other three. For an ideal gas, an equation of state is

$$PV_m = RT \quad (1.1.4-1)$$

where P is the pressure, V_m is the molar volume, R is the gas constant and T is the absolute temperature.

An equation of state of a real gas deviates from that of the ideal gas because of molecular interaction; repulsive forces contribute to expansion and attractive forces contribute to compression. Thus the behavior of a real gas reflects the distance between the molecules, which can be expressed by plotting the compression factor Z against pressure where Z is defined as

$$Z = \frac{PV_m}{RT} \quad (1.1.4-2)$$

$Z = 1$ for an ideal gas and at very low pressures, real gases also have $Z = 1$ and behave ideally. When repulsive forces are dominant (i.e., at high pressures), $Z > 1$ and the compression of a real gas will be more difficult. When attractive forces are dominant at intermediate pressures $Z < 1$ and compression is favored.

The perfect gas law was modified by Van der Waals to include contribution of attractive and repulsive forces present between the molecules.

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1.1.4-3)$$

which can be expressed as a cubic function;

$$PV_m^3 - (Pb - RT)V_m^2 + aV_m - ab = 0 \quad (1.1.4-4)$$

where 'b' refers to the size of molecules and 'a' refers to intermolecular forces. Critical constants can be obtained by calculating the first and second derivatives of the equation.

The critical constants expressed in terms of Van der Waals coefficients are;

$$V_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb} \quad (1.1.4-5)$$

And using the critical constants, the critical compression factor, Z_c is expressed as;

$$Z_c = \frac{P_c V_c}{RT_c} = 0.375 \quad (1.1.4-6)$$

for all gases. This is not the case in reality, but it stays quite close or less in most of cases.

The principle of corresponding states proposed by Van der Waals states the fundamental importance of normalizing the properties of gases. For this purpose, reduced parameters are defined where each variable is divided by the corresponding critical constants.

$$T_r = \frac{T}{T_c} \quad (1.1.4-7)$$

and similarly for V_r , P_r , ρ_r , Z_r . Real gases at the same volume and temperature thus have the same reduced pressure. This approximation holds true only for spherical non-polar molecules.

Another variation of the cubic equation of state was introduced by Peng-Robinson in 1976.

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) - b(V - b)} \quad (1.1.4-8)$$

In this equation, a is a function of temperature and of the acentric factor which accounts for the non-sphericity of a molecule.

The ideal gas equation only holds true at very low pressures while Van der Waals equation starts to deviate significantly around 100 atmosphere. Peng-Robinson equation stays relatively close to the experimental values over a wide range of pressures.

Transport Properties

The physical and transport properties of supercritical fluids fall between those of a liquid and a gas as shown on Table 1.1-1 by the typical orders of magnitude obtained for density, viscosity, and diffusivity for each state. Viscosity of supercritical fluids is closer

to that of gases than that of liquids although increasing pressure increases viscosity quite rapidly near the critical point. The diffusivity of the supercritical fluid on the other hand is higher by about an order of magnitude than that of a liquid and lower by about three orders of magnitudes than that of a gas. Increasing pressure increases viscosity and hence decreases diffusivity.

Table 1.1-1: Orders of magnitude for typical physicochemical values for liquid, supercritical fluid, and gas

	Liquid	Supercritical fluid	Gas
Density (g/cm^3)	1	0.1 – 0.5	10^{-3}
Viscosity ($\text{g cm}^{-1}\text{s}^{-1}$)	10^{-3}	$10^{-4} - 10^{-5}$	10^{-5}
Diffusivity (cm^2/s)	10^{-5}	10^{-4}	10^{-1}

Mass transport in supercritical fluids is therefore higher than in a liquid, and many extractions and reactions can take advantage of this property by using it as an extraction or a reaction fluid which generally results in higher efficiency.

While increasing the pressure near the critical point increases density of the fluid quite dramatically, increase in temperature has an opposite effect. Figure 1.1-2 shows a plot of density versus pressure for supercritical CO_2 at three different temperatures. The plot illustrates the high density dependency on pressure near its critical point as well as a decrease in such dependency as temperature is increased. When the temperature is relatively low, a small change in pressure results in a significant change in density in the vicinity of a critical point. This is an important property where both extraction and reaction selectivity can be controlled extensively in this region as the solvating power of a fluid also changes accordingly.

Figure 1.1-3: Isotherms of density as a function of pressure for carbon dioxide

Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) of organic compounds from a solid matrix is most often done with carbon dioxide. In addition to the ease of attaining supercritical conditions, its non-toxicity, non-flammability, and cheapness are also the reasons for its frequent use.

High diffusivity and low viscosity of a supercritical fluid are the definite reason that it is a useful extraction fluid as both properties lead to faster and more efficient extraction. Equivalent or better recoveries are obtained, and most importantly, separation of multi-component mixture can be achieved. This is done by controlling the density of the fluid (and consequently its solvating power) which changes dramatically in the vicinity of its critical point. It enables it to extract wide range of compounds sequentially by increasing the pressure. This does not involve using more than one type of organic solvent as it is required in conventional liquid extractions.

One possible disadvantage that carbon dioxide has is that it is a non-polar molecule and even at high densities has a limited ability to solvate polar molecules. This can be overcome by the addition of a miscible polar fluid to CO₂, referred to as a modifier or co-solvent. Addition of this second component by a few mole percent can usually enhance the solvating power of supercritical CO₂ quite dramatically. Methanol, chloroform, or acetonitrile are commonly used [33].

Another advantage of supercritical fluids as an extraction solvent is that it does not have surface tension as other solvents. Extraction of organic compounds in solid matrices such as soil are difficult by liquid extraction as they are unreachable due to the surface tension of an extraction solvent. Supercritical fluids on the other hand can wet the matrix surface completely, resulting in higher recovery than the liquid extractions.

Reactions in Supercritical Fluids

In addition to their wide use in extractions, supercritical fluids have also been receiving attention as reaction media [34 - 39]. Due to the large difference in the density of supercritical fluids near its critical point, the selectivity of reactions in a supercritical fluid can be changed by controlling its density. Well studied Diels-Alder reactions are good examples of this where the product can be in a different conformation depending on the selected density. The rate of the reaction can be changed, and if there is a solubility difference in the reaction products, it is possible to isolate them at the same time. Many more organic reactions including photochemical reactions and polymerization reactions have been performed in supercritical carbon dioxide [40]. For a homogeneous catalytic reaction, the main challenge seems overcoming the possible insolubility of the catalyst in supercritical fluids [41].

Heterogeneous Catalysis in Supercritical Fluids

The difference in heterogeneous catalysis from homogeneous catalysis is that the reactants and catalyst are in different phases, so that the mass and heat transfer through boundaries becomes unavoidable. The process of heterogeneous catalytic reactions can be broken down into the following individual steps [39].

1. External diffusion: Diffusion of the reactants from the bulk fluid to the external surface of the catalyst pores.
2. Internal diffusion: Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
3. Adsorption of a reactant (A) onto the catalyst surface.
4. Reaction on the surface of the catalyst ($A \rightarrow B$)
5. Desorption of the products (B) from the surface.
6. Internal diffusion: Diffusion of the products from the interior of the pellet to its external surface.
7. External diffusion: Diffusion of the products from the external pellet surface to the bulk fluid.

Figure 1.1-4 illustrates a conceptual view of a molecule diffusing through liquid or supercritical fluid phase towards catalyst surface. The boundary thickness is significantly reduced in a supercritical fluid than in a liquid.

As the solute and the solvent molecules differ in size, shape, interaction strength, and polarity in most supercritical reaction mixtures, solvent molecules form a non-uniform spatial distribution about a solute molecule, often referred to as local density enhancement or clustering. Solute-solute and solute-solvent interactions are normally much stronger than those of solvent-solvent interaction, and as a consequence, the local environment around the solute can be very different in density and composition from the bulk fluid. This can affect the reaction rate and selectivity.

The same theory can be applied to supercritical fluid/solid boundaries as a consequence of different interaction strength of solute (reactant) and solvent with the solid surface. Unfortunately there has not been any fundamental research on this aspect of heterogeneous catalysis which is essential for understanding catalytic surface reactions in solute-solvent systems.

Higher diffusivity and the reduced thickness of boundaries in supercritical fluids would result in significantly enhanced mass transfer than in a liquid phase. Easier products separation and control of reaction system can be achieved by pressure change leading to rate and selectivity control. However, there is still a limited amount of information available to be able to connect the observed effects and the contribution from each parameter. Consequently, quantitative analysis of surface mechanisms is difficult and homogeneous catalytic reactions have been preferred for fundamental studies.

Figure 1.1-4: Concentration profile of liquid reactant (A) through liquid (a) or supercritical fluid phase (b) towards catalyst surface indicating the smaller boundary phase (B)

There are a few examples of heterogeneous catalysis in supercritical fluids which have indicated pronounced advantages over conventional gas or liquid phase reactions.

The cis/trans isomerization of 1-hexene [37] or stilbene [34] in supercritical CO₂ are good examples where the ratio of the reaction products can be easily controlled by changing the fluid density in supercritical fluids especially near the critical point [35,37]. The significant change in viscosity of a fluid near its critical point was considered to be the main reason.

Another example is the well studied Fischer-Tropsch synthesis [34, 36, 37]. The products of this reaction range from methane to waxes, and the waxes tend to be adsorbed on the catalyst surface leading to deactivation of the catalyst in the gas phase. Also, since the reaction is exothermic, efficient heat removal is crucial. These problems are reduced when the synthesis is performed in supercritical hexane. The reaction rate is only slightly lower than in the gas phase and faster than in the liquid phase due to higher diffusivity and improved mass transfer in supercritical fluids. [39]

Subramaniam and co-workers extensively studied the isomerization of 1-hexene catalyzed by Pt/Al₂O₃. A significant difference in catalyst deactivation in hexene/CO₂ mixtures was observed between subcritical and supercritical pressures at the same temperature; no catalyst deactivation was observed at supercritical pressures. Deposition of higher molecular weight oligomers on the catalyst pores was considered to be the reason for catalyst deactivation, which did not occur in supercritical fluids due to their high solvent power. Their work was a clear indication that the deposition of higher molecular weight compounds can be prevented in supercritical fluids. Further studies resulted in optimization of reaction conditions so as to maximize the isomerization rates while minimizing the catalyst deactivation rates near the critical region [39]. Yet another advantage of using supercritical fluids as reaction media for heterogeneous catalysis is that in-situ catalyst reactivation is possible at relatively mild conditions [34,37].

Catalytic Hydrodechlorination in supercritical fluids

Destruction and dechlorination of organochlorines is of interest to many researchers and there have been many studies on dechlorination of such compounds. However not many have attempted to perform such a reaction in supercritical fluids. Only two reports on dechlorination in supercritical CO₂ were published within the last year [42, 43] . These concerned the reductive dechlorination of chlorophenol and PCBs using zero-valent metal as catalysts and required high temperature for the reaction (200 – 400°C). Dechlorination of PCB mixtures was successful but was not quantitative [42].

1.2 FOCUS OF RESEARCH

The work reported in this thesis is focused on investigation of the use of supercritical CO₂ as an extraction and reaction fluid for elimination / destruction of chlorinated compounds from environmental sources. Many organochlorines are persistent in the environment and their destruction is important issue in the current society. Due to such need, there have been many reports of dechlorination of organochlorines of environmental significance by different methods. Most of the studies however focused on the development of a complete and efficient method of dechlorination.

Many reactions have also been performed in supercritical fluids. Supercritical fluids are used as reaction solvents for many practical reasons. However, there is very little reported on catalytic dechlorination of organochlorines in supercritical fluids, which only came out in a recent year. Therefore dechlorination in supercritical fluids, as the combined subject, has not yet been investigated to a great extent.

The significance of this work is therefore twofold - to study hydrodechlorination reactions and to advance our understanding of the mechanisms of heterogeneous catalysis in supercritical fluids.

Another important feature of supercritical fluids, which is their ability to fractionate a mixture of compounds by selective extraction, was also investigated. This part of work had its specific objective to simplify the characterization of wood resins in pitch deposits and is discussed in Chapter 2.

As the previous objective could also be achieved by elimination of chlorinated wood resins by applying dechlorination to reduce the number of chlorinated isomers during the extraction, this was carried out in supercritical CO₂. The subject of Chapter 3 is the optimization of a dechlorination method in supercritical CO₂ using standard compounds

commonly found in chlorinated wood resins. They are chlorinated fatty and resin acids; 9,10-dichlorostearic acid (Stearic-Cl₂) and 12,14-dichlorodehydroabietic acid (DHA-Cl₂) as well as 1-chlorooctadecane (C₁₈-Cl) as a model for a chlorinated fatty acids. Optimization of the experimental conditions as well as the system design to achieve complete dechlorination is the focus of this chapter.

The mechanism of catalytic hydrodechlorination of three standard compounds introduced in Chapter 3 (C₁₈-Cl, Stearic-Cl₂, and DHA-Cl₂) is thoroughly discussed in Chapter 4.

The kinetic analysis of the reaction with the knowledge gained from the previous chapter leads to a better understanding of the reaction in supercritical CO₂. Comparison to the liquid system was also being investigated.

Finally in Chapter 5, polychlorinated biphenyl (PCB) is used for further investigation of the selectivity of the hydrodechlorination reaction. Polychlorinated compounds such as PCBs would lead to many dechlorination intermediates which may or may not be more toxic than the starting compound. Understanding the selectivity of the reaction is thought to give more insight into the current knowledge of heterogeneous catalytic reactions in supercritical CO₂.

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Chapter 2

Selective Extraction of Wood Resins from Pitch Deposits Using Supercritical Carbon Dioxide

2.1 INTRODUCTION

2.1.1 Wood Resins in Pitch Deposits from Pulp and Paper Mills

Pitch deposits are an on-going problems in the pulp and paper industry. Deposits are comprised of wood resin and a variety of materials such as fibers, soaps, bark, and pulp and paper making additives such as defoamers, dyes, fillers, pigments, etc. The main components in wood resin fraction include fatty and resin acids, waxes, alcohols, terpenes, sterols, steryl esters, and glycerides [1, 2]. Figure 2.1-1 shows some representative extractive components [3]; abietic acid (resin acid), linoleic acid (fatty acid), triolein (triglyceride), and β -sitosterol (sterol). Those extractives are often categorized into two classes; saponifiables and unsaponifiables [4]. Compounds classed as saponifiables are the ones that form soaps under alkaline conditions. General classes of these compounds are fatty acids, resin acids, some steryl esters and glycerides. Unsaponifiables are the compounds which do not form soaps under alkaline conditions (i.e., waxes, sterols, etc.).

Dunlop-Jones found that the production of pitch deposits is proportional to the resin content in trees [5]. Chen calculated that the total extractives do not contribute much to the main cause of the pitch deposition, but rather the ether extractable components (non-polar compounds) are the main cause [6]. Further investigation by Allen and Sitholé showed that sterol esters/waxes play a significant role in pitch deposits. Pine and a few hardwood species are known to cause the most significant deposition [4].

Figure 2.1-1: Representative extractive components in pitch; Abietic acid (resin acid), linoleic acid (fatty acid), triolein (glyceride), and β -sitosterol (sterol)

Abietic acid

Linoleic acid

Triolein

β -sitosterol

The composition of pitch deposits varies among the types of tree being used and the process of pulping, however a general categorization can be made as follows; 9 – 16 % ash (silica, fibers, etc.), 10 – 47 % CaCO_3 , 0 - 30 % metal soaps, and 8 – 49 % wood resin [7, 8]. The lipophilic extractives of pitch deposits can then be categorized into different groups of compounds; 69 - 76 % fatty acids, 17 – 90 % resin acids, 4 % fatty alcohols, 1% hydrocarbons, 5% sterols, 15 % terpenes and triterpenoids [6, 9, 10, 11]

Pine has a significantly higher content of resin acids (90 %) as summarized in Table 2.1-1, and among all the resin acids, dehydroabietic acid the highest concentration.

Table 2.1-1: Total lipophilic acids in pine analyzed by Chen [6]

Relative %		Relative %	
<i>Fatty acids:</i>		<i>Resin acids:</i>	
Palmitic	1.1	Pimaric	6.1
Stearic	0.5	Sandaracopimaric	1.5
Oleic	2.4	Isopimaric	10.4
Linoleic	2.2	Palustric	25.5
Linolenic	0.6	Dehydroabietic	29.7
Arachidic	1.7	Abietic	12.6
Eicosenoic	1.2	Neoabietic	4.5

In bleached Kraft pulp mills that use chlorine and /or chlorine containing compounds in the bleaching process, the wood resin is chlorinated and becomes very tacky. These are also referred to as polymerized pitch which contains saturated carbon bonds with approximately 30 % chlorine by weight [12].

GC analysis of pitch deposits containing chlorinated wood resin is often not quantitative. This is because the analysis will detect only low molecular weight compounds (i.e., chlorinated resin and fatty acids) but not the high molecular weight chlorinated

compounds such as glycerides that are not volatile enough to be analyzed by GC. Typically at least 25% of the acetone extractives of a pitch deposit from a bleached Kraft mill may not elute through a GC column.

Even in the portion which can be analyzed by GC, the complex nature of pitch results in a large number of unresolved peaks on a chromatogram and consequently identification of each peak becomes very difficult. This is the main reason that the direct analysis of pitch deposits by GC is not feasible. In order to simplify the analysis, performing sequential extraction prior to GC analysis is proposed in the work reported in this chapter. Analysis of a smaller group of components should minimize the number of unresolved peaks and therefore lead to easier identification of each component.

2.1.2 Extraction of Wood Resins

Analyses of wood resins in pitch deposits are done by extraction followed by chromatography such as gas chromatography, ion-exchange chromatography or high-performance liquid chromatography [1, 4 - 6, 9]. Typical extraction methods include Soxhlet extraction, Soxtec extraction, solid phase extraction, and supercritical fluid extraction.

Solid phase extraction is generally used in combination with other extraction techniques for fractionation of the extracts. At the extraction step, the aim is to extract as much of everything as possible in the sample. The extractives are then fractionated to simplify the analysis. The first two steps are combined in the current work for further simplification.

For extraction of any organic compounds, the choice of solvent is required to be the primary parameter. Demirbas [13] reported that solvents such as acetone or ethanol-benzene extracted significant amounts of materials, while complete extraction was not attained with hydrocarbon solvents (i.e., hexane, benzene, or toluene). Acetone was found to show an excellent extraction yield for fats and fatty acids, however, there was no single solvent that can accomplish a complete removal of all wood extractives.

Soxhlet Extraction

Soxhlet extraction, established by Soxhlet in 1930s, is an extraction technique for various components from solid matrices. The sample of interest is placed in a thimble inside an extractor where a boiled solvent condenses on and extracts dissolved compounds. When the extractor becomes full, the solution is drained to a round-bottom flask and a fresh solvent starts to condense on to the extractor. The extracted components remains in the round-bottom flask as long as their boiling points are lower than that of the solvent. The technique is based on the establishment of a new equilibrium between the extraction solvent and the solid matrices which is established every time fresh solvent fills the extractor. This is the most commonly used technique for extraction of wood resins.

The standard method for analysis of wood extractives was established by Zinkel [14].

Soxhlet extraction is generally applied on a sample mass ranging 1 to 10 g with a typical solvent volume of 200 mL for 8 to 18 hours [15 - 20]. Acetone [15, 16, 19] or dichloromethane [18, 20] is used most often used as an extraction solvent.

Although widely used, Soxhlet extraction generally takes long time to complete. It also requires large extraction solvent volume which limit its applicability to only thermally stable compounds. A modified version of Soxhlet extraction, Soxtec extraction, can overcome these demerits to a certain extent by achieving a shorter extraction time (i.e., 30 minutes to a few hours) and less solvent volume (i.e. 70 mL). The sample is placed in the thimble and immersed in boiling solvent from the beginning of the extraction. Then the thimble is raised from the solvent, and the sample is rinsed repeatedly by condensed solvent dropping through the sample [4, 21].

Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) has been performed by many researchers and has shown many advantages over Soxhlet extraction, in terms of interference, selectivity, recovery, and extraction time [13, 22 - 28]. Some examples where SFE was applied on wood resins are introduced in this section. Carbon dioxide was used for most extractions.

Modey, et al [22] compared SFE and Soxhlet extraction of *Cedrela toona*. The optimum extraction yield with SFE was 83 % relative to Soxhlet extraction with hexane. While Soxhlet extraction took 5.5 hours, SFE was done in less than 1 hour at 43°C and 390 atm.

Klink, et al [23] extracted fatty acids and sterols from plant tissues and sediments by SFE and ultrasonic extraction using acetone and methylene chloride. The optimum yield for SFE was obtained at the highest pressure (400 atm), and was as high as for ultrasonic extraction. The temperature did not have as significant effect as the pressure.

Terauchi, et al [24] performed SFE and hot-water distillation of wood and obtained higher extraction yield by SFE for 30 min than by the distillation for 8 hours. The SFE extracted more high-molecular weight compounds (i.e., terpenes, resins, and pigments) than the distillations.

Demirbas [13] compared SFE on beech wood with Soxhlet extraction. The extraction yield obtained after 30 min at 240°C and 60 - 65 atm was approximately 4 times higher than Soxhlet extraction with acetone for 18 hours (9.55 % versus 2.54 %). The yield of fatty acids was 10 times higher with SFE, indicating that the solubility of fatty acids under these conditions was higher in CO₂ than in acetone at its boiling temperature.

Ohira and Yatagai [26] extracted *cis*-abienol using supercritical CO₂. It was extracted with the highest yield (13.60 %) from the bark by SFE at 98 atm and 40°C in 60 minutes while the highest yield obtained with solvent extraction was only 0.96% with diethyl ether.

McDonald, et al [28] extracted Western red cedar with supercritical acetone and methanol. Increasing temperature increased the extraction yield in both cases.

Generally speaking, SFE yields comparable or even higher extraction efficiencies with significantly shorter extraction time than Soxhlet extraction. While Soxhlet extraction is

the most commonly and widely used extraction method, it takes a long time (6 to 18 hours) and extraction temperature is limited to the boiling point of the solvent, which could be a limitation for thermally labile compounds. It also uses large volume of solvent, which is undesirable especially from an environmental perspective. Soxtec extraction overcomes this long extraction time and requires less solvent volume, but suffers from low recoveries compared to Soxhlet extraction. SFE shows its ability to perform extractions in a short time and at relatively lower temperatures.

All of the above studies focused on obtaining the maximum extraction yield and fractionation was done in subsequent steps. There are no reports of attempts to combine these two steps by performing selective extraction for wood resins. When the matrix is as complex as wood resins from pitch deposits, combining these two steps is expected to improve the method with shorter analysis time and cleaner extracts while maintaining the extraction yield.

The research objective in this chapter is therefore to demonstrate the ability of SFE to perform selective extraction of wood resins in pitch deposits. This was expected to simplify the method of identification of the components with a shorter analysis time required.

2.2 METHODS AND MATERIALS

2.2.1 Materials

Pitch deposit SL479 was collected from a Kraft mill at Thuso, Quebec (James McLaren Industries Inc.) in October, 1996. Fresh aspen was used in this mill. All the solvents (hexane, toluene, chloroform, acetone, methanol, and isopropanol) were at least HPLC grade or optima grade and purchased from Fisher Scientific.

2.2.2 Soxhlet Extraction

The pitch deposit (0.7892 ± 0.002 g) was sequentially extracted five times using a Soxhlet apparatus with 100 mL of hexane, toluene, chloroform, acetone then methanol. Each extraction was performed for 18 hours. The extracts were dried and methylated using diazomethane prior to GC/MS analysis. The remaining material was analyzed by a scanning electron microscope/energy dispersive spectrometry (SEM/EDS) to identify the composition of non-extractable materials.

2.2.3 Supercritical Fluid Extractions

An extraction cell was constructed with a 6.2 cm 1/4" stainless steel tube (1.1 ± 0.1 cm³ internal volume) with frit (2 μ m 1/4" o.d.) at each end placed in with 1/4" zero-volume nut and ferrule. The inlet and outlet of the cell were connected to a piston pump (Milton-Roy) and a restrictor, respectively using 1/16" stainless steel tubings. The restrictor was made with 20 cm silica tube (25 mm i.d.).

Supercritical fluid extraction (SFE) of the pitch deposits (0.4000 ± 0.002 g) was first performed with CO₂ at 22°C. Extraction was performed at different pressures starting at 102, then 136, 204, and 306 atm. Each extraction was 30 min and extraction at 306 atm was repeated 9 times until no more extractable was collected. Total extraction time was 6 hours.

Selective SFE of the pitch deposits (0.2335 ± 0.002 g) was performed with CO₂ at 40°C. Extractions were performed sequentially at CO₂ densities of 0.31, 0.49, 0.62, 0.70, and 0.92 g/mL by setting appropriate pressure obtained by SF-Solver program [29]. Each extraction was performed for 1 hour at a time and repeated until extraction at that pressure was complete before starting the next set. The extraction time for each set was 4, 6, 8, 9, and 8 hours at 0.31, 0.49, 0.62, 0.70, and 0.92 g/mL, respectively. Same procedure was repeated at 80°C with the total extraction time of 20 hours. SFE was then performed with addition of an organic modifier at 22°C with 6.3 % (molar) isopropanol and 80°C with 1.2 % (molar) isopropanol which was extracted for the total of 7 hours and 11 hours, respectively.

All extracts were collected in 7 mL of isopropanol, dried, then methylated with diazomethane prior to analysis by GC/MS.

2.2.4 Analytical Methods

A Varian 3400 with Saturn II system was used for the GC/MS analysis. The column used was a 30m DB-5 (J&W Scientific, 0.25mm i.d., 0.25µm film thickness). The column temperature was started at 120°C, held for 3 minutes, then ramped at 5°C/min to 310°C and held for 10 min, giving a total analysis time of 51 min. Injector temperature was at 280°C. Analysis was done in electron impact mode (70 eV) from 50 to 650 amu with a scan rate of 1 s⁻¹.

2.3 RESULTS AND DISCUSSION

2.3.1 Composition of Pitch Deposits

The Scanning Electron Microscope analysis of the non-extractable materials in pitch deposit SL479 is summarized in Table 2.3-1.

Table 2.3-1: Percent Composition of Detected Elements in Pitch Deposit Residue (Percent Composition Relative to Total Percentage) Determined by SEM/EDS

Element	Si	Ca	Mg	Fe	Cl	Total
Sample 1	12.7 (39.4)	8.8 (27.1)	7.8 (24.3)	1.2 (3.7)	1.8 (5.4)	32.3 (100.0)
Sample 2	14.1 (41.6)	8.6 (25.3)	8.3 (24.5)	1.1 (3.2)	1.9 (5.5)	34.0 (100.0)
Sample 3	5.9 (27.2)	6.0 (27.9)	7.4 (34.4)	1.4 (6.6)	0.9 (4.0)	21.6 (100.0)

Silicon, calcium, and magnesium occupied majority of the constituent in all three samples due to the presence of Talc in the pitch deposits. Calcium is most likely in the form of calcium carbonate as the presence of carbonate was confirmed by IR spectrum. In total, 20 to 35 % of the residues consisted of inorganic matter and the remaining was mostly fibers. Calculation of mass balance determined the composition of the pitch deposits to be; 40% organic matter, 30% inorganic matter and 30% fibers by mass.

2.3.2 Extraction Yield

Table 2.3-2 summarizes the extraction yield obtained by various extraction conditions. The highest yield with SFE (28.2 %) was obtained at the highest temperature in the presence of isopropanol. This was still lower than the yield obtained by Soxhlet extraction (38.6 %), but was a significant increase from the yield obtained without addition of the organic modifier (co-solvent) at 22°C (8.9 %). Such increase was as expected as the solvating power of the extraction fluid has significantly increased in the

presence of an organic modifier. Even though CO₂ can extract many organic compounds, the extraction yield decreases as the molecule being extracted becomes more polar. In such a case, addition of organic modifier can enhance the extraction yield as clearly shown in this case.

Comparison of all values in Table 2.3-2 also illustrates that increasing temperature increases the extraction yield. This is in agreement with the majority of results obtained for extraction of various compounds and matrices [13 - 28].

Table 2.3-2: Comparison of extraction yield obtained by SFE

Fluid Type	T (°C)	Total % Extracted (w/w)
CO ₂	22	8.9
CO ₂	40	15.6
CO ₂ + 6.3 % isopropanol	22	17.1
CO ₂	80	23.8
CO ₂ + 1.2 % isopropanol	80	28.2
Soxhlet with 5 solvents*	65 - 96	38.6

* hexane, toluene, chloroform, acetone and methanol in this order

2.3.3 Selectivity of Extraction

The main components found in pitch deposits which were identifiable were fatty acids (C14-C22). Two large peaks near the end of the chromatogram were not identified, however were named as 'P-1' and 'P-2' for simplification of further discussion. Soxhlet extraction was not capable of fractionation of extracts even by a sequential extraction as clearly shown by Figure 2.3-1. All components were extracted at the first extraction step (with hexane) and the subsequent extractions did not contain much components. Hexane

is the most non-polar solvent used, however, it was still capable of extracting quite polar components such as sterols at its boiling temperature with a high yield.

Figure 2.3-1: Significant components of pitch deposits extracted by Soxhlet Extraction; C14 – C22 are fatty acids with corresponding carbon numbers, y-axis indicates the extraction order (1-hexane, 2-toluene, 3-isopropanol, 4-acetone, and 5-methanol), z-axis indicates relative yield.

The difference between the supercritical fluid extraction (SFE) and the sequential Soxhlet extraction was quite apparent. Pronounced selectivity was found at either 40 or 80°C with SFE as shown in Figure 2.3-2, a) and b), respectively. The trend of selectivity was the same at both temperatures; fatty acids with lower carbon number were extracted more at lower density of CO₂ while fatty acids with higher carbon number, P-1 and P-2 were not extracted until the higher density of CO₂ was attained, indicating that the solvating power of CO₂ is related to its density. This is in agreement with the fact that polar compounds

are not extracted until the density is high enough, and is due to strong intermolecular force among solutes (or solutes and the solid surface) that can only be overcome by a large number of solvent-solute interactions which occur at high density.

The difference in selectivity for two extraction methods can be seen by comparing Figure 2.3-1 and Figure 2.3-2 (b), or by Figure 2.3-3 for better illustration of the difference. Two chromatograms shown in Figure 2.3-3 compare the extraction selectivity between Soxhlet extraction and SFE. For Soxhlet extraction shown in Figure 2.3-3 a), most of the extractable fatty acids including two sterols were extracted at the first extraction step with hexane (top) so that there were hardly any components left to be extracted with the second extraction step with toluene (bottom). On the contrary, Figure 2.3-3 b) shows a clear distinction between the first and second steps of extraction. Only the lower molecular weight fatty acids were extracted at the first extraction stage at lower density (top) while higher molecular weight fatty acids, P-1 and P-2 were not extracted until the second stage of extraction (bottom).

The temperature dependency of selectivity can be shown by comparing Figures 2.3-2 a) and b). Although the trend of selectivity is the same in both cases, hardly any components were extracted at the lowest density at 40°C while most of the fatty acids with lower carbon number were all extracted at the lowest density at 80°C. This indicates that increasing the temperature of the system enhances the desorption of analytes from the matrix surface into the extraction fluid. P-1 and P-2 were extracted when the density of CO₂ was at 0.45 g/mL at 80°C while not all P-1 nor P-2 were extracted at 0.49 g/mL at 40°C. Hence it is not only the density of a fluid which determines the solvating power but also temperature which plays a significant role. The separation of fatty acids with lower carbon number from higher carbon number and sterols was more significant at 80°C than at 40°C, showing that selectivity is more pronounced at higher temperature.

Figure 2.3-2: a) Significant components of pitch deposits extracted by SFE: CO₂ at 40°C (C22 was not at a detectable level)

b) Significant components of pitch deposits extracted by SFE: CO₂ at 80°C; z-axis: relative peak area

Figure 2.3-3: Comparison of chromatograms of the first and second steps of sequential extraction of extracted components from pitch deposits;

a) Soxhlet Extraction; hexane followed by toluene (corresponding to Figure 2.3-1)

b) Supercritical Fluid Extraction with CO₂ at 80°C; $\rho = 0.35$ g/mL followed by 0.45 g/mL (corresponding to Figure 2.3-3)

The selectivity of SFE was diminished by addition of an organic modifier (isopropanol) as illustrated by Figure 2.3-4. Addition of isopropanol would not be advantageous in performing selective extraction although it increases the extraction yield by a significant amount.

Pitch deposits from fresh aspen are known to contain significant amounts of sterols and glycerides which were hardly detected with the current work. These are polar, higher molecular weight compounds and may have not been extracted during extraction. Even in a case where they were extracted, they may not be detected by GC analysis due to their low volatilities. This is consistent with an observation that an accumulation of non-volatile extracts in a GC injector liner was always quite significant after a number of analyses were performed.

Figure 2.3-4: Significant components of pitch deposits extracted by SFE: CO₂ + 1.2% isopropanol at 80°C

2.4 SUMMARY AND CONCLUSIONS

The ability of SFE to perform selective extraction of compounds from pitch deposits was clearly illustrated in this chapter. Soxhlet extraction with five solvents in the order of increasing polarity resulted in the highest extraction yield, however did not exhibit any selectivity. On the other hand, a pronounced selectivity was observed with SFE by varying the density of carbon dioxide near its critical point. The selectivity of SFE was found to be temperature dependent; higher temperature resulted in more defined selectivity than at lower temperature. Addition of an organic modifier reduced the selectivity, although the extraction yield was increased significantly. This is consistent with the idea that the solvent strength is significantly increased by the addition of organic modifier which consequently results in higher extraction of all components.

SFE can perform simultaneous extraction and fractionation and showed its potential to simplify the analysis of complex sample. However, the limitation observed with CO₂ for polar compounds prevent its applicability to a full analysis of wood resins in pitch deposits containing a wide range of compounds of different polarity. As the problematic compounds in pitch deposits are mainly polar and high molecular weight, application of SFE to identify such compounds would not be feasible. Some polar compounds however are extractable, and therefore the method should mainly be applied to a sample mixture containing less polar compounds. Its significance lies in the fact that it can fractionate molecules of similar nature (fatty acids), and this was clearly illustrated in the current work.

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Chapter 3

Optimization of the dechlorination method

3.1 INTRODUCTION

The aim of the work in this chapter is to develop and optimize a method to perform complete dechlorination in supercritical CO₂ for three chlorinated compounds. The compounds being studied are chlorinated fatty and resin acids commonly found in pitch deposits as well as a chlorinated hydrocarbon as a simplified form of chlorinated fatty acid. The intent to perform dechlorination of these compounds comes from the idea that dechlorination of chlorinated wood resins would simplify the resulting chromatogram upon analysis, therefore leads to easier identification of wood resins causing pitch deposition. In the previous chapter, the ability of supercritical CO₂ to selectively extract wood resins in pitch deposits was clearly presented. In this chapter, the possibility of performing simultaneous dechlorination in supercritical CO₂ is also being pursued. If this is possible, then the characterization of pitch deposits (and ultimately their elimination) may be simplified by reducing the number of chlorinated isomers. Much time and effort was spent on the experimental system design although many parts of this will not be discussed in detail.

Optimization of the method included choosing the dechlorination reaction and the appropriate catalyst and support, studying the reaction in liquid phase, and finally applying the knowledge gained in a liquid system to a supercritical fluid system.

3.1.1 Catalytic Hydrodechlorination of Organochlorines

The research was based on the work reported by Ukisu et al on dechlorination of PCBs under mild refluxing conditions [1]. PCBs were effectively dechlorinated to biphenyl and a trace amount of phenylcyclohexane in isopropanol in the presence of NaOH and Pd/C (or Rh/C) at 82°C. Varying the amounts of these two reagents resulted in different degrees of completion, however, in all cases 2 to 3 hours were required to complete a reaction.

It was found that a molar excess of NaOH relative to Cl atoms was required to obtain complete dechlorination. The role of NaOH was considered not only to neutralize the HCl produced but also to facilitate catalytic dehalogenation although the exact mechanism of such process was not investigated. The hydrodechlorination of PCBs should include hydrogen-transfer from isopropanol to PCBs as shown below for monochlorobiphenyl.

Overall,

H* indicate hydrogen-transfer species in some form. Most of NaCl is precipitated due to its low solubility in isopropanol (<10 ppm).

The obvious advantage of this dechlorination method is that the reaction does not require high pressure in the presence of explosive H₂ gas as conventionally performed. In the case of aromatic halides, the substitution of a halogen by hydrogen occurs preferentially so that hydrogenation of the aromatic ring rarely takes place.

As it is the case in this dechlorination system, the presence of base has shown to promote a reaction rate. In the studies of hydrodechlorination of chlorophenols over Pd/C, ammonium hydroxide was found to work better than sodium hydroxide, sodium acetate or triethylamine [2]. However, use of such inorganic base leads to the formation of NaCl which is not desirable. It can accumulate on the catalyst surface and cover the active sites and /or catalyst support and thereby reduces the catalytic activity. The presence of NaCl was confirmed by the X-ray photoelectron spectroscopy (XPS) analysis in the work of Ukisu, et al [3]. Chlorine by itself can also act as a strong inhibitor either by blocking the adsorption sites or by attracting the electrons of the metal particles via an inductive effect [4]. HCl is also known to inhibit the overall reaction rate [5].

Although many studies have been done on catalytic hydrodechlorination and on various reactions in supercritical fluids, there has been no work reported on the combination of the two procedures, i.e. catalytic hydrodechlorination in supercritical fluids. Many advantages of carrying out reactions in supercritical fluids were described previously, and to perform such reactions in carbon dioxide, would represent a new contribution to supercritical fluid research as well as that of heterogeneous catalysis.

3.1.2 Palladium Catalyst

Palladium is one of the most commonly used catalysts for various hydrogenation and hydrodehalogenation reactions of many groups of compounds. In heterogeneous catalysis, palladium is usually used supported. It is occasionally used as palladium oxide or the finely divided palladium black, however, the activity of these catalysts are considerably lower than the supported palladium [6]. Palladium catalysts are known for their general resistance to catalyst poisoning. They can be effectively used in acidic or basic medium although a slight deactivation by base is known.

From the studies of Ukisu et al [1], it is reasonable to choose Pd/C from the four carbon supported noble metal catalysts used in their studies (Pt, Ru, Pd, and Rh). The

dechlorination using Rh was very fast, while Pt and Ru did not show high activity. For the current studies, not only the yield but also the kinetics of the reaction is of interest as will be discussed in Chapter 4 and 5. Therefore it is important to be able to easily follow the progress of the reaction and the use of the fastest catalyst is not of primary importance.

Following their previous reaction using Rh, a successful dechlorination of chlorotoluene (>90%) was achieved at ambient temperature (27°C) by Ukisu, et al. [7]. Different catalyst supports resulted in significant differences in the catalyst activity. Dechlorination completed on active carbon or TiO₂ while it only proceeded to 5 % with SiO₂ and MgO. With the Al₂O₃ support, the yield reached 35 % then leveled off.

It was also reported that high H₂ partial pressures were required to prevent deactivation of Pd/γ-Al₂O₃ for the hydrodechlorination of 1,1-dichlorotetrafluoroethane [5]. Therefore, the catalyst activity not only depends on the nature of the catalyst itself, but also on other factors such as the type of support and the type of reaction system (i.e., solvent, hydrogen donor, etc.).

The activity of the catalyst is generally proportional to the surface area. The surface area of the catalyst must therefore be known. This can be readily measured by the well established procedures associated with the adsorption of gases and vapors. The BET (Brunauer-Emmett-Teller) surface area analysis is normally used by determining the maximum capacity of a non-porous solid.

The aim of the studies in this chapter was to establish a system for complete dechlorination of 1-chlorooctadecane (C₁₈-Cl), 9,10-dichlorostearic acid (Stearic-Cl₂), and 12,14-dichlorodehydroabietic acid (DHA-Cl₂) in supercritical CO₂. The most extensive studies in this work were done on the dechlorination of 1-chlorooctadecane. Stearic-Cl₂ and DHA-Cl₂ were selected to represent the chlorinated fatty and resin acids commonly found in wood resins present in pitch deposits. Structure of these compounds

are shown in Figure 3.1-1. Further investigation into a dechlorination mechanism in supercritical CO₂ will be discussed in the following chapters.

Figure 3.1-1: Molecular structure of the selected compounds used for studies of dechlorination in supercritical CO₂; 1-chlorooctadecane (top), 9,10-dichlorostearic acid (middle), and 12,14-dichlorodehydroabietic acid (bottom)

1-Chlorooctadecane (C₁₈H₃₇Cl); MW 298

9,10-Dichlorostearic acid (C₁₈H₃₄O₂Cl₂); MW 352

12,14-Dichlorodehydroabietic acid (C₂₀H₂₆O₂Cl₂); MW 368

3.2 METHODS AND MATERIALS

3.2.1 Materials

1-chlorooctadecane (96%), octadecane (99%) and stearic acid (95%) were obtained from Aldrich Chemical Co., 9,10-dichlorostearic acid (95 – 99 %) and 12,14-dichlorodehydroabiatic acid (95 – 99 %) were obtained from Helix Biotech. Carbon dioxide (zero grade) was obtained from BOC Gases. 5% Pd/C and 5% Pd/ γ -Al₂O₃ (reduced) were obtained from Alfa *AESAR*. Optima grade isopropanol was purchased from Fisher Scientific.

3.2.2 Synthesis Of Dehydroabiatic Acid

Dehydroabiatic acid was synthesized by the following procedure.

A standard solution of DHA-Cl₂ in isopropanol (25 mL, 19.8 ppm), 53.3 mg of NaOH and 85.1 mg of 5% Pd/ γ -Al₂O₃ were added in a 30 mL Erlenmeyer flask. The reaction mixture was stirred and 4.0 mL of the reaction mixture was transferred every 10 minutes into a 10 mL vial. The solvent was evaporated to dryness followed by addition of 4 mL of 0.054 M H₂SO₄ (aq). Liquid-liquid extraction with 4 mL of hexane was performed on the aqueous phase, and the organic layer was analyzed by a GC/MS after methylation.

3.2.3 Characterization Of Catalyst

The catalyst used for most of the experiments was 5% (w/w) palladium on γ -Al₂O₃. 5% (w/w) palladium on active carbon was also used for the earlier studies.

The surface area of the catalyst was determined by BET measurement using a high speed surface area analyzer (Model 2200, Micromeritics Instrument Co.).

3.2.4 Dechlorination Under Atmospheric Conditions

Choice of Catalyst Support

Dechlorination of C₁₈-Cl was performed by refluxing a 40 mL solution of C₁₈-Cl in isopropanol (3983 ppm) with 0.159 ± 0.001 g of NaOH and 0.9910 ± 0.0001 g Pd/C under nitrogen atmosphere. The reaction mixture was refluxed at 82°C with a heating mantle. One milliliter of a reaction mixture was sampled every hour for 4 hours. The initial time was taken when reflux had started. The sample was transferred into a 2 mL vial, dried under a stream of N₂, then mixed well with 1 mL of hexane. The mixture was then centrifuged, and the supernatant was analyzed by GC/MS. The same procedure was repeated for 20 ppm C₁₈-Cl solution.

The adsorption of octadecane to alumina powder (Al₂O₃) was determined by varying the mass of alumina powder in 40 ppm octadecane solution either in isopropanol or hexane. The mixture was equilibrated at room temperature for 15 minutes and quantified by GC/FID.

Kinetic Studies of Dechlorination at Room Temperature

A typical experiment for the determination of the rate of dechlorination at room temperature was performed as follows. Into a 10 mL vial, 5.00 mL of 51 ppm C₁₈-Cl in isopropanol was pipetted with a desired amount of 5% Pd/ γ -Al₂O₃ and 0.050 ± 0.001 g of NaOH. The reaction mixture was stirred for 60 min and 0.5 mL of the reaction mixture was sampled every 10 min into a 2 mL vial. Ten drops of H₂O were added and the mixture was mixed well followed by addition of hexane (0.5 mL). After the solution was separated well, the organic phase was taken out for analysis by GC/MS or FID. The same procedure was repeated with Pd/c₁₈ ratios of 50, 101, 201, 291, and 358.

3.2.5 Dechlorination In Supercritical Carbon Dioxide

Dechlorination System

Prior to the construction of the reaction cell (autoclave), dechlorination of $C_{18}\text{-Cl}$ was performed using the supercritical fluid extraction cell described in Chapter 2. Although results were not useful to extract much kinetic data, some mechanistic information was obtained.

All stainless steel fittings and tubing were purchased from Chromatographic Specialties, Inc. The inlet of the cell was connected to a Suprex SF-50 syringe pump. Shutoff valves were placed at both inlet and outlet to be able to isolate the system. The cell was filled with dechlorination reagents and a standard solution of $C_{18}\text{-Cl}$ in isopropanol (51 ppm). The optimized packing order of this cell is shown in Figure 3.2-1. The cell inlet was opened to fill the cell with CO_2 , equilibration was established for 20 minutes at 40 or 80°C, then the contents were extracted for 10 minutes. The extract was collected in isopropanol and analyzed by GC/MS.

A stainless steel reaction cell with an internal volume of 2.0 mL was constructed at the Science Technology Centre at Carleton University. A brief schematic diagram of this cell is shown in Figure 3.2-2, and the detailed engineering diagram is shown on Appendix I and II. This cell was built to allow filling and emptying via sampling valves. The inlet tube was extended to the bottom of the cell just above a magnetic stir bar. A frit (2 μm , 1/8" o.d.) at the outlet prevented the solid catalyst from escaping. Dechlorination in supercritical CO_2 was performed in this reaction cell mounted atop a magnetic stirrer and placed in the oven of a Suprex MPS/225 supercritical system. Sufficient stirring was achieved to disperse all the catalyst in isopropanol at atmospheric pressure ($\rho = 0.78 \text{ g/mL}$), which suggests sufficient stirring in supercritical CO_2 of comparable density. Optimized reaction system diagram is shown Figure 3.2-3. Sample injection was done through the sampling valve (4), which was introduced to the system at the inlet of the reaction cell. Solvent introduction to recover undesorbed reaction products from the cell was done by introduction of a solvent pump through a valve which allows 1 mL of solvent injection at a time. The solvent shown on Figure 3.2-3 is isopropanol, however,

Figure 3.2-1: Optimized packing order for dechlorination of 1-chlorooctadecane in supercritical CO_2 using the pre-analysis reaction cell

Figure 3.2-2: A brief schematic diagram of a reaction cell designed by Science Technology Centre (refer to Appendix I and II for an engineering diagram)

different solvents including hexane, acetone, and acetonitrile were also used. Another sampling loop was introduced near the outlet of the pump to allow sampling of the fluid phase (13: sample loop) with a 6-port valve (14). For the most experiments, collection of the reaction products were done directly into a collection vial (12) into collecting solvent.

Dechlorination in Supercritical CO₂

In order to determine the effect of different bases, 0.0181 ± 0.0001 g 5% Pd/ γ -Al₂O₃ (0.017 mmol Pd) was weighed into the reaction cell followed by addition of 0.0106 g NaOH (0.265 mmol) or 30 μ L triethylamine (0.207 mmol) and a magnetic stir bar. The reaction cell was heated for 10 min to the desired temperature, then stirred for 5 min, followed by the introduction of 50 μ L of the standard solution (1000 ppm in isopropanol) by switching the 6-port valve (refer to valve 4 in Figure 3.2-3) at the inlet of the cell. The composition of isopropanol in CO₂ was 1.4 mole % and thus the fluid phase system consisted of only one phase according to Radosz [8]. The cell was charged with CO₂ to the desired pressure, and the reaction mixture was stirred for the desired time. The outlet and inlet of the reaction cell were opened for 5 min to purge the cell contents into 3 mL of isopropanol in a 5 mL vial. A 6-port valve (valve 6 in Figure 3.2-3) was switched when the inlet was opened to allow isopropanol to enter the cell with CO₂. All the other experiments were performed in the absence of base and the extracts were analyzed by GC/FID.

3.2.6 Analytical Methods

Solutions of C₁₈-Cl were concentrated under a stream of N₂ to 0.5 mL, and analyzed by GC/FID. For Stearic-Cl₂ and DHA-Cl₂, the extract was dried under a stream of N₂, methylated, then dissolved in 0.5 mL of isopropanol and analyzed by GC/FID. The GC column was a 30m Megabore DB-5 (0.5mm i.d., 0.25 μ m film thickness). The temperature program used for the analysis of C₁₈-Cl was 160°C for 3 min, followed by a ramp at 12°C/min to 300°C, held for 1 min. Total analysis time was 15.7 min. C₁₈-Cl and octadecane eluted at the 7.8 min and 10.2 min, respectively. The GC temperature

Figure 3.2-3: Optimized system diagram for dechlorination in supercritical CO₂
 (1: CO₂ pump, 2: isopropanol pump, 3: pressure gauge for isopropanol, 4: 1/16" 6-port valve for standard injection, 5: pressure gauge for the system, 6: 1/8" 6-port valve for isopropanol loop, 7: inlet of the reaction cell, 8: outlet of the reaction cell, 9: reaction cell, 10: magnetic stir bar, 11: restrictor, 12: glass vial with isopropanol, 13: sample loop, 14: 1/16" 6-port valve for product isolation)

program used for Stearic-Cl₂ and DHA-Cl₂ was 190°C for 3 min followed by a ramp at 12°C/min to 300°C held for 1 min. Total analysis time was 13.7 min, and methyl esters of stearic acid, Stearic-Cl₂, dehydroabietic acid, DHA-Cl₂ eluted at 4.2 min, 7.1 min, 5.9 min, and 8.5 min, respectively.

For dechlorination at atmospheric conditions and analysis of dehydroabietic acid were done using GC/MS with the following temperature program. The initial temperature was 120°C held for 3 min, then ramped at 5°C/min to 230°C, followed by a second ramp at 20°C/min to 300°C held for 6.5 min. Total analysis time was 35 min. The injector temperatures were 280°C and the column was a 30m microbore DB-5 (0.25mm i.d., 0.25µm film thickness). With this program, octadecane, C₁₈-Cl, dehydroabietic acid, DHA-Cl₂ eluted at 15.7 min, 21.4 min, 27.4 min, and 33.8 min, respectively. The mass spectrometer was under the same conditions as in section 2.2.4.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis of Dehydroabietic Acid

The synthesis of dehydroabietic acid was done by dechlorination of DHA-Cl₂. Protonation of the acid was required as it formed the sodium salt under the reaction conditions. The use of hydrochloric acid as a protonating agent resulted in re-chlorination of the dechlorinated product, yielding monochlorodehydroabietic acid. This problem was eliminated by using H₂SO₄. The dechlorination scheme for DHA-Cl₂ is shown in Figure 3.3-1. The complete dechlorination was obtained after 10 minutes as is evident by the chromatogram in Figure 3.3-2.

Figure 3.3-1: Dechlorination of 12,14-dichlorodehydroabietic acid to dehydroabietic acid followed by methylation with diazomethane

Figure 3.3-2: Gas Chromatograms of 12,14-dichlorodehydroabiatic acid methyl ester and dehydroabiatic acid methyl ester before dechlorination and after 10 minutes dechlorination of 12,14-dichlorodehydroabiatic acid

3.3.2 Characterization of Catalyst

Scanning electron microscope analysis of the catalyst showed a large variation in a particle size. The mean catalyst support particle size is 25 μm , which is distributed widely from 120 to 20 μm (90 % < 120 μm , 50 % < 50 μm , 10 % < 20 μm) [9].

Table 3.3-1 shows the results from the BET measurements. The catalyst analyzed after use was from dechlorination in supercritical CO_2 without addition of NaOH. The surface areas measured were the same within the standard deviation before and after the use, indicating that there were not significant physical changes of the catalyst during the reaction. The same effect would not be expected if the dechlorination was carried out in the presence of NaOH and a noticeable decrease in surface area would be expected [3, 10].

Table 3.3-1: Surface Area of 5% Pd/ $\gamma\text{-Al}_2\text{O}_3$ by BET measurement
(Triplicate measurements was done for each analysis)

	Before Use	After Use
Mean area/g catalyst (m^2/g)	139.4	138.9
Standard Deviation	10.1	4.6
RSD (%)	7.3	3.3

3.3.3 Dechlorination under Atmospheric Conditions

Choice of Catalyst Support

When the reaction was performed at higher concentration (3983 ppm) the dechlorination was 98% complete within 3 hours as indicated in Figure 3.3-3. However, no response was obtained by GC analysis neither before nor after the dechlorination when the concentration was reduced to 20ppm. At such low substrate concentration, neither the chlorinated nor the dechlorinated substrate was detected suggesting a strong adsorption of

Figure 3.3-3: Dechlorination of 1-chlorooctadecane (reflux at 82°C, 3983 ppm 1-chlorooctadecane in isopropanol, Pd:NaOH:1-chlorooctadecane =0.9:0.7:1)

both reactant and product to the activated carbon support of the catalyst. The catalyst support was changed to Al_2O_3 from active carbon in order to alleviate this problem. To be sure that adsorption of the substrate would not be a problem, a hexane or isopropanol solution of octadecane was equilibrated with a wide range of masses of Al_2O_3 , and the concentration of octadecane was determined by GC/FID. The results using each solvent are presented in Table 3.3-2, and clearly show that the Al_2O_3 support does not adsorb appreciable quantities of octadecane. The concentrations in both solvents are also plotted versus time in Figure 3.3-4. No downward trend was evident.

Table 3.3-2: Adsorption of octadecane to Al_2O_3

$\text{C}_{18}\text{H}_{38}$ in isopropanol		$\text{C}_{18}\text{H}_{38}$ in hexane	
Mass of Al_2O_3 (g)	Area (cnts)	Mass of Al_2O_3 (g)	Area (cnts)
(± 0.0001 g)		(± 0.0001 g)	
0.0000	617816	0.0000	609036
0.0305	624098	0.0299	580474
0.0708	613884	0.0712	600253
0.1058	599762	0.1020	615059
0.1304	632749	0.1316	611513
0.1512	641932	0.1513	596415
0.1716	657819	0.1689	610929
0.2052	630564	0.2021	623725
Mean Area (cnts)	627328	Mean Area (cnts)	605898
Std dev (cnts)	17826	Std dev (cnts)	13284
RSD (%)	2.8	RSD (%)	2.2

The same experiment at the low concentration of $\text{C}_{18}\text{-Cl}$ with $\text{Pd}/\text{Al}_2\text{O}_3$ resulted in successful dechlorination as indicated in Figure 3.3-5 a). A kinetic plot shown in Figure 3.3-5 b) confirmed that dechlorination of $\text{C}_{18}\text{-Cl}$ followed a first order kinetics.

Figure 3.3-4: Adsorption of octadecane on Al_2O_3 in isopropanol (●) and hexane (▲) with different amounts of alumina

Figure 3.3-5: a) Dechlorination of 1-chlorooctadecane ($C_{18}\text{-Cl}$) on 5% $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ (● Octadecane, ■ 1-Chlorooctadecane); 10 ppm $C_{18}\text{-Cl}$ in isopropanol, $\text{Pd}:\text{NaOH}:\text{C}_{18}\text{-Cl} = 36:3228:1$)

Figure 3.3-5: b) A plot of $\ln [C_{18-Cl}]_t/[C_{18-Cl}]_0$ versus time; $y = -0.013x - 0.038$, $r^2 = 0.98$

Kinetic Studies of Dechlorination at Room Temperature

As the reaction at lower temperature was expected to be slower than at 82°C, the amount of catalyst was increased and the reaction was allowed to proceed for 24 hours by stirring at room temperature (24°C). This condition although slow completely dechlorinated all C₁₈-Cl into octadecane. The rate of dechlorination was determined at various concentrations of catalyst. A typical gas chromatogram is shown for Pd/C₁₈-Cl molar ratio of 201 at time zero, and at 60 minutes in Figure 3.3-6.

The first order kinetics was followed for all the Pd/C₁₈-Cl ratios as shown in Figure 3.3-7. Table 3.3-3 summarizes the rate constant at each Pd/C₁₈-Cl molar ratio, as well as normalized rate constant per unit surface area of catalyst. The normalized rate constant was 0.0004 min⁻¹m⁻² with 20.0 % RSD.

Table 3.3-3: Rate constant (k) for dechlorination of C₁₈-Cl at 24°C

Pd/C ₁₈ -Cl (molar)	Surface area (m ²)	k (min ⁻¹ m ⁻²)	r ²
50	13.1	0.0004	0.995
101	26.6	0.0004	0.980
201	52.7	0.0003	0.998
291	78.8	0.0004	0.977
358	94.1	0.0005	0.996

A clear linear relationship between the rate constant and Pd/C₁₈-Cl ratio is shown in Figure 3.3-8, indicating that the reaction rate is proportional to the catalyst concentration, indicating that the reaction is first order in catalyst concentration.

Figure 3.3-6: Gas Chromatograms obtained from dechlorination of 1-chlorooctadecane ($C_{18}\text{-Cl}$); showing only the reactant 1-chlorooctadecane at 0 min, both $C_{18}\text{-Cl}$ and octadecane at 60 minutes ($\text{Pd}/C_{18}\text{-Cl}$ or $\text{Pd}/\text{Cl} = 201$, $T = 24^\circ\text{C}$, $P = 1\text{ atm}$)

Figure 3.3-7: Rate of dechlorination of 1-chlorooctadecane ($C_{18}\text{-Cl}$) at 24°C

Figure 3.3-8: Rate Constant (k) versus Pd/C₁₈-Cl for dechlorination of C₁₈-Cl
 $y = 0.0001x - 0.004$ ($r^2 = 0.94$)

3.3.4 Dechlorination In Supercritical Carbon Dioxide

Optimization of dechlorination method

The focus of the study in this section is to optimize experimental conditions in order to ensure complete dechlorination of all three standard chlorinated compounds in supercritical CO₂. This will meet the practical purpose of destruction of chlorinated compounds.

Using the extraction cell described in Chapter 2, different ways of packing the extraction cell with dechlorination reagents resulted in the optimum order of packing as described in Figure 3.2-1 and the following observations were made.

1. Reducing the area for interaction between the reactants and the catalyst resulted in lower dechlorination yield.
2. Higher dechlorination yields were obtained when the reactant solution was well sorbed into the rest of the system before being pressurized.
3. The dechlorination yield was always higher at higher temperature.

It was apparent that lack of physical contact between the catalyst and the reactant lead to the lower dechlorination yield. This was unavoidable with the given geometry of the cell which resulted in non-homogeneous mixture of the reaction reagents. The major cause of non reproducibility was due to not obtaining the maximum contact between the reactants and the catalyst.

Considering the above, a reaction cell (autoclave) was designed and built at the Science Technology Centre at Carleton University. A schematic diagram of the cell is shown in Figure 3.2-2 and a detailed engineering diagram is shown in Appendix I and II. After many modifications, the system design was optimized as shown in Figure 3.2-3.

A 6-port valve (6 on Figure 3.2-3) was inserted at the inlet of the cell so as to increase the recovery at the end of the reaction. It was determined that at least 10 ml of CO₂ (liq) was required to obtain a recovery higher than approximately 75% which took about 10 min at

a flow rate greater than 1.0 mL/min. When the flow rate was increased to 2.2 mL/min with introduction of isopropanol, the recovery was increased to higher than 91 %.

Effect of different bases

The dechlorination of C₁₈-Cl in supercritical CO₂ resulted in 7.0 ± 0.9 % yield in the presence of NaOH at 40°C and 350 atm. This low yield and low reproducibility was considered to be due to the low solubility of NaOH in supercritical CO₂. The solubility of polar NaOH is very low even in isopropanol and likely to be significantly less in a solvent as non-polar as supercritical CO₂. The high pressure of the system could also contribute to the low yield as discussed in a later section. The first attempt to increase the solubility of base was the use of an organic base instead of NaOH, which was expected to have higher solubility in both isopropanol and supercritical CO₂. Table 3.3-4 shows dissociation constants of some of the stronger organic bases.

Table 3.3-4: Dissociation constants of some organic base in aqueous solution

	K _b	pK _b	@ T (°C)
Triethylamine	1.02×10^{-3}	2.99	18
Trimethylamine	6.45×10^{-5}	4.19	25
Pyridine	1.77×10^{-9}	8.75	25

Triethylamine a strongest base on Table 3.3-4. In its presence at a low concentration, dechlorination proceed less than one percent. Increase in the concentration of triethylamine was expected to increase the dechlorination yield, however, the yield was decreased and no dechlorination proceeded at a 1200 molar ratio of triethylamine to Cl. Two interpretations of this result were taken into account; 1) triethylamine was too weak a base to initiate the reaction, or 2) the strong adsorption of the polar triethylamine on the catalyst surface prevented adsorption of other reaction reagents. The latter interpretation is reinforced by the fact that the dechlorination yield was 4.4 % even in the absence of base (Table 3.3-5). Earlier work showed the catalyst was being deactivated, possibly by

adsorption of NaOH or NaCl on its surface. Although triethylamine is soluble in CO₂, it may have also adsorbed irreversibly on the catalyst resulting in the deactivation of the catalyst. The addition of base was thus considered not just unnecessary but undesirable for completion of dechlorination in supercritical CO₂, contrary to the results under atmospheric conditions. In the absence of NaOH then, neutralization of HCl (equation 3.1.1-3) would not proceed and the overall reaction becomes;

The fact that there were no byproducts observed on the chromatograms confirmed that the chlorine did not form any other organic species. HCl would most likely be adsorbed on the catalyst surface or precipitated on the wall of the reaction cell due to its very low solubility in CO₂. The possibility of catalyst poisoning due to adsorption of HCl on the catalyst surface exists, but is unlikely to be a problem since the quantity of HCl that could be produced in these experiments is so low.

Table 3.3-5: Effect of different bases on dechlorination yield
(Pd/Cl=100, T=40°C, P=350 atm) N.D. (not determined)

Base	Base/Cl (mol/mol)	Dechlorination yield (mol %)	RSD (%)
NaOH	1900	7.0	13.9
Triethylamine	1200	0.0	N.D.
No Base	0	4.4	18.3

The possibility of increasing the low dechlorination yield, in the absence of base to complete dechlorination was sought by altering the other experimental parameters; pressure, concentration of isopropanol, concentration of catalyst, and temperature. The following section discuss the effect of each parameter on the final dechlorination yield.

Variation of Pressure

Effect of pressure was determined at 80°C for all standard compounds and the results are shown in Figure 3.3-9. Dechlorination of C₁₈-Cl resulted in a significant increase in the yield as pressure was decreased that dechlorination essentially completed at pressures at or lower than 100 atm. On contrary, the dechlorination yield of either Stearic-Cl₂ or DHA-Cl₂ was not affected by pressure variation and complete dechlorination yield was attained at all pressure ranging from 1 to 350 atm.

A clear difference between C₁₈-Cl and the other two molecules was considered due to the nature of the molecule. C₁₈-Cl is a non-polar molecule, while both Stearic-Cl₂ and DHA-Cl₂ are quite polar. At higher pressure, adsorption of CO₂ may be significant enough that CO₂ competes effectively with the non-polar C₁₈-Cl for adsorption sites on the catalyst, preferentially occupying more sites, and thereby inhibiting the adsorption of the C₁₈-Cl. The same inhibiting effect by the non-polar CO₂ may not play a role for Stearic-Cl₂ or DHA-Cl₂ as they are much more polar than CO₂. Therefore they would have more preferential adsorption towards polar catalyst surface than CO₂ does and competition for the vacant site would not likely to take place.

Variation of Temperature

The temperature for dechlorination in CO₂ was selected based on the boiling point of isopropanol. The effect of temperature was determined for the range of 24°C to 80°C for C₁₈-Cl. The dechlorination yield generally increased with increasing temperature at all pressures as indicated in Figure 3.3-10. However, it should be noted that this figure only provides a general idea. More precise determination should be done at a constant density of a fluid as it varies significantly within the range of the measurement performed. Appropriate conditions will be used for determination of activation energy which will be discussed in Chapter 4.

For the purpose of this chapter, the dechlorination was complete at 60°C or higher while pressure was kept between 1 atm and 100 atm.

Figure 3.3-9: Effect of pressure on dechlorination yield of 1-chlorooctadecane (●), 9,10-dichlorostearic acid (▼), and 12,14-dichlorodehydroabiatic acid(Δ) in CO₂ (T = 80°C, Pd/reactant =50 (molar), reaction time = 20 min)

Figure 3.3-10: Effect of temperature on dechlorination yield of 1-chlorooctadecane in CO₂ at different pressures (◆ 350 atm, ■ 200 atm, ▼ 100 atm, and ● 1 atm)

Variation of Isopropanol Concentration

The effect of isopropanol on dechlorination yield was determined for $C_{18}\text{-Cl}$. The dechlorination yield reached its optimum of near 100% at an isopropanol fraction of 2.5 % (v/v) as indicated in Figure 3.3-11. At higher isopropanol concentrations, the dechlorination yield decreased significantly, likely due to more extensive adsorption of the polar isopropanol on the surface of the catalyst preventing the adsorption of the reactant, in a similar manner as described for CO_2 at high pressure. In this case, pressure does not need to be high to observe the same effect, as it would already be more preferentially adsorbed on the catalyst surface than $C_{18}\text{-Cl}$. No dechlorination was obtained when isopropanol was absent in the system, indicating that isopropanol is the hydrogen donor for the hydrodechlorination reaction.

One of the many advantages of using supercritical fluids as reaction media is increased mass transport properties compared to a liquid phase reaction. When the dechlorination was performed in liquid isopropanol at atmospheric pressure, isopropanol was used both as a hydrogen donor and a solvent. On contrary, isopropanol plays an only role of a hydrogen donor in supercritical CO_2 , and the bulk of the solvent (the CO_2) serves to increase the mass transfer of reagents, potentially increasing the overall rate of the reaction. Figure 3.3-11 is in agreement of such arguments.

Variation of Catalyst Concentration

Variation of dechlorination yield as a function of palladium to reactant ratio is shown in Figure 3.3-12 for $C_{18}\text{-Cl}$, Stearic- Cl_2 , and DHA- Cl_2 . All plots clearly show that an increase in the amount of catalyst increases the dechlorination yield for all three compounds in almost an exact same manner. The molar ratio of palladium to the reactant molecule was optimized to be 50, i.e., complete dechlorination was obtained above this value.

Figure 3.3-11: Effect of isopropanol fraction variation on dechlorination yield of 1-chlorooctadecane in CO₂ (Pd/Cl = 100, T = 80°C, P = 100 atm, reaction time = 20 min)

Figure 3.3-12: Effect of the Pd/Cl ratio (mole/mole) on dechlorination yield for 1-chlorooctadecane (●), 9,10-dichlorostearic acid (■), 12,14-dichlorodehydroabiatic acid (▼) ($T = 80^{\circ}\text{C}$, $P = 100\text{ atm}$, $[\text{isopropanol}] = 1.4\% \text{ molar}$)

3.5 CONCLUSIONS

OPTIMIZED SYSTEM AND CONDITIONS

When the conditions indicated in Table 3.3-6 are met, dechlorination in supercritical CO₂ was completed for the three compounds studied in this work; C₁₈-Cl, Stearic-Cl₂, and DHA-Cl₂. The fact that there was essentially no difference between the optimized conditions for Stearic-Cl₂ and DHA-Cl₂ the same conditions would most likely apply to other chlorinated fatty and resin acids.

The effect of base was consistent with the earlier studies where the presence of NaOH or NaCl blocks the catalyst surface leading to the catalyst deactivation. The fact that dechlorination still proceeded in its absence implied that the role of base is only to enhance the reaction. Its addition was eliminated and other experimental parameters were optimized to obtain complete dechlorination yield.

The effects of pressure and concentration of isopropanol were indicative of surface adsorption being a limiting factor for a reaction to proceed, i.e., increasing either parameters resulted in the lower dechlorination yield for non-polar C₁₈-Cl. On contrary, Stearic-Cl₂ and DHA-Cl₂ were not affected by increase in pressure. This was consistent with the idea that interaction between polar compounds as for Stearic-Cl₂ and DHA-Cl₂ and the catalyst surface is more preferential than for non-polar C₁₈-Cl. At higher pressure, adsorption of CO₂ would be significant enough that CO₂ competes effectively with the non-polar C₁₈-Cl for adsorption sites on the catalyst, preferentially occupying more sites, thereby inhibiting the adsorption of the C₁₈-Cl.

As opposed to the liquid phase reaction, only the minimum amount of isopropanol was required for the reaction to proceed in CO₂. The role of isopropanol as a hydrogen donor was also evidenced as the reaction did not proceed in the absence of isopropanol.

Hydrodechlorination of $C_{18}\text{-Cl}$, Stearic- Cl_2 , and DHA- Cl_2 in supercritical CO_2 was completed under the conditions summarized in Table 3.3-6. Some insights into the reaction mechanism were also achieved and further analysis and discussion will be the focus of the next chapter in order to understand the mechanism.

Table 3.3-6: Optimized experimental parameters for dechlorination of $C_{18}\text{-Cl}$, Stearic- Cl_2 , and DHA- Cl_2 in supercritical CO_2 with 5 min reaction time (N.D. $\equiv$ not determined)

Experimental Parameter	Optimized Conditions		
	$C_{18}\text{-Cl}$	Stearic- Cl_2	DHA- Cl_2
Base	No addition	N.D.	N.D.
Isopropanol fraction (% v/v)	2.5	N.D.	N.D.
Temperature ($^{\circ}\text{C}$)	> 60	> 60	> 60
Pressure (atm)	< 100	No effect	No effect
Pd / Reactant (mole/mole)	> 50	> 50	> 50

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Chapter 4

Kinetic and Thermodynamic Studies of the Dechlorinations of C₁₈-Cl, Stearic-Cl₂, and DHA-Cl₂ in Supercritical Carbon Dioxide

4.1 INTRODUCTION

In this chapter, kinetic and thermodynamic studies of the hydrodechlorination of 1-chlorooctadecane (C₁₈-Cl), 9,10-dichlorostearic acid (Stearic-Cl₂), and 12,14-dichlorodehydroabiatic acid (DHA-Cl₂) in supercritical CO₂ will be discussed in order to understand the reaction mechanism. The focus will be placed on the determination of rate-determining step of the reaction as well as the activation energy, and enthalpy of desorption at atmospheric conditions. Some values are compared between the two fluid systems; supercritical CO₂ and liquid isopropanol to understand the difference in the reaction mechanism due to the solvent system.

The selected compounds for this study have different physical and chemical properties; the functionality of the molecules, polarity, and molecular shape and size (surface area and volume) can all contribute how the molecules behave under the reaction conditions. C₁₈-Cl is a simple aliphatic molecule while Stearic-Cl₂ and DHA-Cl₂ have carboxylic acid groups, which make the molecules very polar compared to C₁₈-Cl. While C₁₈-Cl and Stearic-Cl₂ are in the form of an aliphatic chain, DHA-Cl₂ is an aromatic molecule with two chlorine atoms on the ring. The dehalogenation of aliphatic halides have been shown to proceed much faster than those of aromatic halides and the C-Cl bond on the aromatic ring is considered to have much higher strength than C-Cl bond on the aliphatic molecule [1]. The structural differences between DHA-Cl₂ and other two molecules (C₁₈-Cl and

Stearic-Cl₂) may affect the orientation of these molecules in supercritical CO₂ and how they move through CO₂ and adsorb on the catalyst surface.

All of these differences affect the interaction of the reacting molecule with a fluid and with a catalyst surface. Differences in their behavior during the reaction are expected to give us a clue as to how the reaction takes place.

Heterogeneous catalytic reactions are generally assumed to follow Langmuir-Hinshelwood (LH) type kinetics, where adsorption of the reactants are on dual sites.

Some studies have shown that hydrogenation reactions follow LH theory with the surface reactions as the rate limiting steps and that two different active sites exist on the catalyst [1]. While a similar process may take place with the compounds studied here, it needs to be remembered that each catalytic system behaves in a different manner. Therefore a precise analysis of the reaction mechanism specific to the current reaction system is required.

4.1.1 Reaction Mechanism and Rate-limiting Step

The process of heterogeneous catalytic reactions can be broken down into the following individual steps as introduced in Chapter 1 [2]. The conceptual view of the steps are illustrated in Figure 4.1-1.

1. External diffusion: Diffusion of the reactants from the bulk fluid to the external surface of the catalyst pores.
2. Internal diffusion: Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
3. Adsorption of a reactant (A) onto the catalyst surface.
4. Reaction on the surface of the catalyst ($A \rightarrow B$)
5. Desorption of the products (B) from the surface.
6. Internal diffusion: Diffusion of the products from the interior of the pellet to its external surface.

7. External diffusion: Diffusion of the products from the external pellet surface to the bulk fluid.

Figure 4.1-1: Cross section of solid catalyst indicating the steps involved in heterogeneous catalytic reactions [2]

The overall rate of reaction is equal to the rate of the slowest step in the mechanism and this step is called the rate-limiting step. When the diffusion steps (1,2,6 and 7) are much faster than the reaction steps (3,4 and 5), the concentrations in the immediate vicinity of the active sites are same as those in the bulk fluid phase. In such a case, the overall rate of the reaction is not affected by the diffusion steps. However, if the reaction steps are much faster than the diffusion steps, the reaction rate is affected by the diffusion and becomes diffusion-controlled. When external diffusion affects the rate, changes in the flow of fluid should change the overall reaction rate. In porous catalysts, internal diffusion may limit the rate of reaction and the overall rate will not be affected by external flow conditions.

The following discussion will be made for the cases where both external and internal diffusion are considered very fast and only the reaction steps of adsorption, surface reaction, or desorption are responsible for the observed rate of reaction [2].

Adsorption Isotherm

Adsorption should be discussed prior to the catalytic reaction rates since chemisorption is usually required in heterogeneous catalysis. Adsorption of species A on an active site S is represented by;

The rate of adsorption of A to the surface is proportional to the number of collisions that these molecules make with the surface per unit time. The collision rate is directly proportional to the concentration of A (C_A). Since A adsorbs only on vacant sites, the rate of attachment is directly proportional to the concentration of vacant sites, C_v . Combining these two facts leads to the following rate equation.

$$\text{rate of adsorption} = k_A C_A C_v \quad (4.1.1-2)$$

The rate of desorption of molecules from the surface is directly proportional to the concentration of the sites occupied by the molecules; C_{AS} .

$$\text{rate of desorption} = k_A C_{AS} \quad (4.1.1-3)$$

Thus the net rate of adsorption is equal to;

$$r_A = k_A C_A C_V - k_{-A} C_{AS} \quad (4.1.1-4)$$

The ratio $K_A = k_A / k_{-A}$ is the adsorption equilibrium constant and substituting this term into equation 4 leads to;

$$r_A = k_A \left(C_A C_V - \frac{C_{AS}}{K_A} \right) \quad (4.1.1-5)$$

The adsorption rate constant k_A for molecular adsorption is essentially independent of temperature while the desorption constant k_{-A} increases exponentially with temperature increase. Consequently, K_A decreases exponentially as temperature increases.

Since A is the only species adsorbed on the catalyst, the total concentration of sites is the sum of the vacant site and the occupied site concentrations.

$$C_t = C_v + C_{AS} \quad (4.1.1-6)$$

The net rate of adsorption equals zero at equilibrium ($r_A = 0$) and solving equation (4.1.1-5) for C_{AS} ,

$$\begin{aligned} C_{AS} &= K_A C_V C_A \\ &= K_A C_A (C_t - C_{AS}) \end{aligned} \quad (4.1.1-7)$$

Rearrangement of equation (4.1.1-7) gives

$$C_{AS} = \frac{K_A C_V C_A}{1 + K_A C_A} \quad (4.1.1-8)$$

This equation shows C_{AS} is a function of the concentration of A, and is called the Langmuir isotherm.

One method of checking whether a model predicts the behavior of the experimental data is to linearize the equation and plot the indicated variables against one another. For example, equation (4.1.1-8) may be rearranged to

$$\frac{C_A}{C_{AS}} = \frac{1}{K_A C_t} + \frac{C_A}{C_t} \quad (4.1.1-9)$$

and the linearity of a plot of C_A/C_{AS} as a function of C_A will determine if the data correspond to a Langmuir single-site isotherm.

Dissociative adsorption

When species A dissociates upon adsorption, the process is referred to as dissociative adsorption.

where A is a molecule consisting of B and C atoms which adsorbed on the active site to produce BS and CS. The rate of adsorption is proportional to the concentration of A in the system because the concentration controls the number of collisions with the surface. Two adjacent vacant sites are required for a molecule to dissociate as it adsorbs. The probability of having two vacant sites adjacent to one another is proportional to the square of the concentration of vacant sites. Therefore the rate of adsorption is proportional to the product of the concentration of A and the square of the vacant site concentration, $C_A C_V^2$. On the other hand, two occupied sites must be adjacent for desorption to occur, or that the rate of desorption is proportional to the product of the occupied-site concentration, $C_{BS} C_{CS}$. The net rate of adsorption can then be expressed as

$$r_A = k_A C_A C_V^2 - k_{-A} C_{BS} C_{CS} \quad (4.1.1-11)$$

which is

$$r_A = k_A (C_A C_V^2 - \frac{C_{BS} C_{CS}}{K_A}) \quad (4.1.1-12)$$

where $K_A = k_A / k_{-A}$ and for dissociative adsorption both k_A and k_{-A} increase exponentially with increasing temperature while K_A decreases with increasing temperature. Since $r_A = 0$ at equilibrium,

$$k_A C_A C_V^2 = k_{-A} C_{BS} C_{CS} \quad (4.1.1-13)$$

For $C_{BS} = C_{CS}$,

$$(K_A C_A)^{1/2} C_V = C_{CS} \quad (4.1.1-14)$$

From balancing the active sites,

$$C_V = C_t - C_{BS} - C_{CS} = C_t - 2C_{CS} \quad (4.1.1-15)$$

Substituting equation (4.1.1-15) into equation (4.1.1-14) results in;

$$C_{CS} = \frac{(K_A C_A)^{1/2} C_t}{1 + 2(K_A C_A)^{1/2}} \quad (4.1.1-16)$$

which by taking the inverse of both sides and then multiplying through by $(C_A)^{1/2}$ yields

$$\frac{(C_A)^{1/2}}{C_{CS}} = \frac{1}{(K_A)^{1/2} C_t} + \frac{2(C_A)^{1/2}}{C_t} \quad (4.1.1-17)$$

If dissociative adsorption takes place, a plot of $(C_A^{1/2} / C_{CS})$ versus $C_A^{1/2}$ should be linear.

In obtaining the Langmuir isotherm equations, several assumptions are made of the system. The most important and questionable of these is a uniform surface, which assumes that any active site has the same attraction for an adsorbing molecule as does any other.

Surface reaction

Once a reactant has been adsorbed onto the surface, it can react in different ways to form the product.

The first way is a single-site mechanism, where only the site with the adsorbed reactant is involved in the reaction.

Since in each step the reaction mechanism is elementary, the rate law is

$$r_s = k_s(C_{AS} - \frac{C_{BS}}{K_s}) \quad (4.1.1-19)$$

where K_s is the surface reaction equilibrium constant; $K_s = k_s / k_{-s}$

The second, is the dual-site mechanism. The adsorbed reactant interacts with another site to form the product. When adsorbed A reacts with an adjacent vacant site:

the corresponding rate law is

$$r_s = k_s(C_{AS}C_v - \frac{C_{BS}C_v}{K_s}) \quad (4.1.1-21)$$

When the reaction occurs between two adsorbed species:

the corresponding rate law is

$$r_S = k_S(C_{AS}C_{BS} - \frac{C_{CS}C_{DS}}{K_S}) \quad (4.1.1-23)$$

When two reacting species are adsorbed on different types of sites S and S':

the corresponding rate law is

$$r_S = k_S(C_{AS}C_{BS'} - \frac{C_{CS}C_{DS}}{K_S}) \quad (4.1.1-25)$$

Reactions involving either single- or dual-site mechanisms described above are referred to as an Langmuir-Hinshelwood mechanism.

And the third is an adsorbed molecule reacting with a molecule in the fluid phase:

the corresponding rate law is

$$r_S = k_S(C_{AS}C_B - \frac{C_{CS}C_D}{K_S}) \quad (4.1.1-27)$$

This type of mechanism is referred to as an Eley-Rideal mechanism.

Desorption

In each of the cases above, the products of the surface reaction adsorbed on the surface are subsequently desorbed into a fluid phase.

the corresponding rate law is

$$r_D = k_D(C_{CS} - \frac{C_C C_V}{K_D}) \quad (4.1.1-29)$$

where K_D is the desorption equilibrium constant. The desorption of C is just the reverse of the adsorption of C and that the rate of desorption of C, r_D is just opposite in sign to the rate of adsorption of C, $r_{A,C}$

$$r_D = -r_{A,C} \quad (4.1.1-30)$$

In addition, the desorption equilibrium constant; K_D is just the reciprocal of the adsorption equilibrium constant for; K_C .

$$K_D = 1 / K_C \quad (4.1.1-31)$$

The Rate Limiting Step

When heterogeneous reactions are carried out at steady state, the rates of each of the three reaction steps in series (adsorption, surface reaction, and desorption) are equal to one another:

$$-r_{\text{reactant}} = r_A = r_S = r_D \quad (4.1.1-32)$$

However, one particular step in the series is usually found to be rate-limiting since its rate is smaller than those of the other steps.

Determination of a Reaction Mechanism

Determination of a rate-limiting step and a rate law which is consistent with experimental observation is an essential step in order to understand a reaction mechanism. The reaction currently being studied, dechlorination of $C_{18}\text{-Cl}$ to form octadecane, is used as a model in deriving the kinetic equations on the assumption that the reaction is not diffusion controlled. The overall reaction is;

In order to simplify the discussion, each molecule is given the following symbol; $C_{18}H_{37}Cl$ ($C_{18}-Cl$) $\equiv$ C, $(CH_3)_2CHOH$ (isopropanol) $\equiv$ I, $C_{18}H_{38}$ (octadecane) $\equiv$ O, $(CH_3)_2CO$ (acetone) $\equiv$ A, and HCl (hydrochloric acid) $\equiv$ H.

The reaction is considered to occur between two adsorbed species; $C_{18}-Cl$ and isopropanol, following Langmuir-Hinshelwood kinetics. The primary assumption before deriving the kinetic equations is that since isopropanol is present in such a large excess compared to $C_{18}-Cl$, the rate of adsorption of isopropanol on the vacant sites is much greater than the rate of adsorption of $C_{18}-Cl$. Thus, once the adsorption of isopropanol reaches equilibrium, the overall reaction becomes pseudo first order in $C_{18}-Cl$ concentration. It is therefore assumed that the moment $C_{18}-Cl$ is adsorbed on the vacant site, there already exists adsorbed isopropanol adjacent to the adsorbed $C_{18}-Cl$.

The reaction scheme is divided into adsorption, surface reaction, and desorption, each of which consists of more than one reaction as shown below. For these derivations, hydrogen is assumed to be produced via homolytic dissociation of the alcohol.

Adsorptions

Surface Reactions

The overall surface reaction can then be written as

Desorptions

The surface reaction is of a dual-site mechanism, in which the reaction occurs between two adsorbed species as described by equation (4.1.1-22) earlier.

The rate expression for the adsorption of C is;

$$r_A = k_A C_C C_V - k_{-A} C_{CS} \quad (4.1.1-34)$$

or,

Adsorption: $r_A = k_A \left(C_C C_V - \frac{C_{CS}}{K_A} \right) \quad (4.1.1-35)$
--

where C_{CS} is a site occupied by $\text{C}_{18}\text{-Cl}$ and K_A is an adsorption equilibrium constant for C and defined as; $K_A = k_A / k_{-A}$. Since C_V is very high compared to the concentrations of adsorbed species, its value remains constant during the reaction and can be incorporated into the rate constant k_S . Here, the assumption is made that the adsorption of isopropanol results in a number of vacant sites adjacent to an adsorbed isopropanol. The concentration of these vacant sites (C_V) is thus equal to the concentration of adsorbed isopropanol molecules (C_{IS}) as long as C_{IS} is less than a half of the total sites.

The rate law for the surface reaction step is therefore;

$$r_s = k_s C_{CS} - k_{-s} C_H C_{OS} C_A \quad (4.1.1-36)$$

or,

Surface Reaction: $r_s = k_s \left(C_{CS} - \frac{C_H C_{OS} C_A}{K_s} \right)$	(4.1.1-37)
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with surface reaction equilibrium constant; $K_s = k_s / k_{-s}$, where k_s incorporates the high and constant concentration of the vacant sites.

The rate of desorption of O is;

$$r_D = k_D C_{OS} - k_{-D} C_O C_V$$

$$r_D = k_D \left(C_{OS} - \frac{C_O C_V}{K_{DO}} \right) \quad (4.1.1-38)$$

Since the desorption of O is just the reverse of its adsorption, it is easily shown that the O adsorption equilibrium constant K_O is the reciprocal of its desorption constant: K_{DO} ; $K_O = 1 / K_{DO}$, and so equation (4.1.1-38) becomes;

Desorption: $r_D = k_D (C_{OS} - K_O C_O C_V)$	(4.1.1-39)
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In order to determine which of the three steps is rate-limiting, one of the steps is assumed first to be rate-limiting and the reaction rate law is formulated in terms of the partial pressures of the species present. If the predicted rate varies with pressure in the same manner as the rate observed experimentally, the implication is that the assumed mechanism and rate-limiting step are correct.

When adsorption is the rate-limiting step

By assuming that adsorption is rate-limiting, k_A is small compared to specific rates of the other steps (k_s and k_D). So the rate of disappearance of $C_{18}\text{-Cl}$ (r_C) becomes;

$$-r'_C = r_A = k_A \left(C_C C_V - \frac{C_{CS}}{K_A} \right) \quad (4.1.1-40)$$

C_V and C_{CS} are not measurable and these variables need to be replaced with measurable quantities for the equation to be useful. Applying a steady-state approximation (as there is no accumulation of reacting species on the surface and the rates of each step in the sequence are all equal),

$$-r'_C = r_A = r_S = r_D \quad (4.1.1-41)$$

Here, k_A is smaller than k_S and k_D , and thus the ratios r_S / k_S and r_D / k_D are very small (approximately zero), while the ratio of r_{AD} / k_{AD} is relatively large.

Substitution of $r_S / k_S \approx 0$ into equation (4.1.1-37) gives

$$C_{CS} = \frac{C_H C_{OS} C_A}{K_S} \quad (4.1.1-42)$$

In a same manner, applying $r_D / k_D \approx 0$ to equation (4.1.1-39) gives

$$C_{OS} = K_O C_O C_V \quad (4.1.1-43)$$

Combining equation (4.1.1-42) and (4.1.1-43) gives the expression for C_{CS} in terms of C_V ;

$$C_{CS} = K_O \frac{C_H C_O C_A}{K_S} C_V \quad (4.1.1-44)$$

Combining equation (4.1.1-40) and (4.1.1-44) leads to,

$$r_A = k_A \left(C_C - \frac{K_O C_O C_H C_A}{K_S K_A} \right) C_V \quad (4.1.1-45)$$

The concentration of vacant sites; C_V can be eliminated by utilizing the site balance to give the total concentration of sites; C_t which assumed constant. It should be emphasized that the total concentration of reactive sites is equal to the concentration of adsorbed isopropanol molecules (C_{IS}) (as long as C_{IS} is less than half of the total sites on the catalyst surface).

Then,

$$C_t = C_V + C_{CS} + C_{OS} \quad (4.1.1-46)$$

Substituting equation (4.1.1-42) and (4.1.1-43) into the above equation,

$$C_t = C_V + K_O \frac{C_H C_O C_A}{K_S} C_V + K_O C_O C_V \quad (4.1.1-47)$$

Solving for C_V ,

$$C_V = \frac{C_t}{1 + C_O C_H C_A K_O / K_S + K_O C_O} = \frac{C_t K_S}{K_S + C_O C_H C_A K_O + K_S K_O C_O} \quad (4.1.1-48)$$

Combining equations (4.1.1-45) and (4.1.1-48),

$$-r'_C = r_A = \frac{C_t k_A (K_A K_S C_C - K_O C_H C_O C_A)}{K_A (K_S + K_O C_O C_H + K_O K_S C_O)} \quad (4.1.1-49)$$

In order to plot the initial rate as a function of C_C , initially no products are present, therefore, $C_H = C_O = C_A = 0$, and equation (4.1.1-40) becomes;

$$-r'_C{}^0 = C_t k_A C_C{}^0 = k C_C{}^0 \quad (4.1.1-50)$$

Thus, if the reaction is adsorption limited, then the initial rate will be linear with the initial concentration of C_C as shown in Figure 4.1-2.

When the surface reaction is the rate-limiting step

From the surface reaction expressed in equation (4.1.1-37) the rate of surface reaction is;

$$-r'_C = r_S = k_S (C_{CS} - \frac{C_H C_{OS} C_A}{K_S}) \quad (4.1.1-51)$$

From equation 44 and the condition that k_A is large by comparison when surface reaction is controlling (i.e., $r_{AD} / k_A \approx 0$),

$$C_{CS} = K_A C_C C_V \quad (4.1.1-52)$$

In a similar manner, since $r_D / k_D \approx 0$, equation (4.1.1-39) becomes;

$$C_{OS} = K_O C_O C_V \quad (4.1.1-53)$$

Substituting C_{CS} and C_{OS} in equation (4.1.1-51) gives,

$$r_S = k_S (C_C K_A - \frac{K_O C_O C_H C_A}{K_S}) C_V \quad (4.1.1-54)$$

To eliminate C_V using $C_t = C_V + C_{CS} + C_{OS}$,

$$C_V = \frac{C_t}{1 + K_A C_C + K_O C_O} \quad (4.1.1-55)$$

therefore,

$$-r'_C = r_S = \frac{k_S C_t (K_S K_A C_C - K_O C_H C_O C_A)}{K_S (1 + C_O K_O + K_A C_C)} \quad (4.1.1-56)$$

Since no products are present at the initial stage of the reaction,

$$-r'_C = r_S = \frac{k_S C_t K_A C_C}{1 + K_A C_C} \quad (4.1.1-57)$$

If we replace $k_S C_t K_A$ by k , then,

$$-r'_C = r_S = \frac{k C_C}{1 + K_A C_C} \quad (4.1.1-58)$$

and the initial rate is;

$$-r'_C{}^0 = \frac{k C_C{}^0}{1 + K_A C_C{}^0} \quad (4.1.1-59)$$

At low C_C , $1 \gg K_A C_C{}^0$, and the initial rate will increase linearly with $C_C{}^0$.

At high C_C , $K_A C_C{}^0 \gg 1$ and equation (4.1.1-59) becomes;

$$-r'_C{}^0 = \frac{k}{K_A} \quad (4.1.1-60)$$

and the rate becomes independent of the concentration of C_C , producing the plot on Figure 4.1-2.

When desorption is the rate-limiting step

The rate expression for the desorption of O is;

$$r'_C = r_D = k_D (C_{OS} - K_O C_O C_V) \quad (4.1.1-61)$$

Since $r_S / k_S \approx 0$, the surface reaction becomes;

$$C_{OS} = K_S \frac{C_{CS}}{C_H C_A} \quad (4.1.1-62)$$

Similarly, for the adsorption step, $r_{AD} / k_{AD} \approx 0$, and equation (4.1.1-35) becomes;

$$C_{CS} = K_A C_C C_V \quad (4.1.1-63)$$

Combining equations (4.1.1-62) and (4.1.1-63) gives;

$$C_{OS} = K_S \frac{K_A K_S C_C C_V}{C_H C_A} \quad (4.1.1-64)$$

Substituting equation (4.1.1-64) to equation (4.1.1-61) gives;

$$r_D = k_D \left(\frac{K_S K_A C_C - K_O C_O C_H C_A}{C_H C_A} \right) C_V \quad (4.1.1-65)$$

By again applying the site balance, $C_t = C_V + C_{CS} + C_{OS}$,

$$C_V = \frac{C_A C_H C_t}{C_H C_A + K_A C_C C_H C_A + K_A K_S C_C} \quad (4.1.1-66)$$

Combining equations (4.1.1-65) and (4.1.1-66) gives;

$$-r'_C = r_D = \frac{k_D C_t (K_S K_A C_C - K_O C_O C_H)}{C_H C_A + K_A C_C C_H C_A + K_A K_S C_C} \quad (4.1.1-67)$$

By setting $C_O = C_H = C_A = 0$ for the initial condition, equation (4.1.1-67) reduces to;

$$-r'_C{}^0 = k_D C_t \quad (4.1.1-68)$$

So if the desorption was the rate-limiting step, the initial rate will be independent of the initial concentration of C_C as illustrated on Figure 4.1-2.

Determination of reaction order and the rate-limiting step is an essential step in understanding the mechanism of the reaction. A plot of initial rate versus initial concentration of a reactant can determine whether the rate-limiting step is adsorption, surface reaction, or desorption as described above. A dependence of the initial rate of reaction on the concentration (i.e., isopropanol or palladium in this reaction) on the initial rate of the reaction also provides the reaction order with respect to each substrate, which describes how each substrate influences the reaction. The Langmuir-Hinshelwood type kinetics have been applied especially for hydrogenation type reactions and generally included some consideration of the specific reaction system [3, 4, 5]. Comparison of a few reports on the kinetic analysis of catalytic hydrodechlorination indicated that the reaction mechanism is specific to the reaction system being studied. The rate-limiting step was deduced to be a different step in each system although all of them were hydrogenation type reactions using a catalyst under a H_2 atmosphere [1,6]. This reaffirms

the fact that the analysis of surface reaction is not a straight forward process that can be easily generalized.

Figure 4.1-2: Characteristic kinetic curves for determination of the rate-limiting step (Initial rate versus initial concentration of reactant)

4.1.2 Activation Energy

Temperature dependence of the reaction can be illustrated by the Arrhenius equation, where the change in the reaction rate constant is expressed as a function of temperature:

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2} \quad (4.1.2-1)$$

or, in integrated form;

$$k = Ae^{-E/RT} \quad (4.1.2-2)$$

where E is the activation energy, R is the universal gas constant, A is the frequency factor including the steric factor and the overall number of collisions per unit time, and T is the absolute temperature. A plot of $\ln k$ versus $1/T$ gives a straight line with a slope $-E/R$. It was stated earlier in Chapter 1 that catalytic reactions have lower free energy of activation than uncatalyzed reactions and this is shown in Figure 4.1-3 [7].

Figure 4.1-3: Potential Energy Profile for a bimolecular reaction
(a) Uncatalyzed (b) Catalyzed

Diffusion can affect the behavior of the reaction taking place in porous solid catalysts [8]. The reaction order observed experimentally may be different from the true reaction order when internal diffusion is a significant resistance. The experimentally observed (apparent) activation energy of a reaction will be smaller than the true activation energy when the resistance to pore diffusion is significant as illustrated in Figure 4.1-4. Experimental systems to ensure the absence of diffusion can be accomplished by decreasing the size of the catalyst [9].

Figure 4.1-4: Arrhenius plot illustrating the diffusion limited regime at higher temperature

Typical values of the apparent activation energy for a hydrodechlorination reaction using different types of catalyst under H_2 atmospheres ranges from ca. 40 kJ mol^{-1} to 115 kJ mol^{-1} for various substrates including chlorobenzenes, chlorophenols, PCBs, chlorocyclohexane, and chloroclorocarbons [5, 6, 10 - 13].

4.1.3 Adsorption and Desorption Thermodynamics

Thermodynamic aspects of the reaction can provide as important information as kinetic studies. In heterogeneous catalytic reactions, adsorption is the primary step for the reaction to further proceed and therefore its importance cannot be overemphasized. It has also been recognized that this process could prevent the reaction from proceeding when appreciable amounts of any substrates is irreversibly adsorbed. This leads to catalyst deactivation by blocking the active sites of the catalyst. Determination of the adsorption enthalpy can be related to the activation energy of the reaction in order for confirmation of the activated step of the reaction, i.e., if the adsorption or desorption is the activated step, its enthalpy should equal the activation energy of the reaction.

Chemisorption is considered to be the main interaction between the surface (Pd/Al₂O₃) and adsorbed species (chlorinated molecules and isopropanol) in the present system, however the interaction between a substrate molecule and a surface may involve more than one type of interaction depending on the chemical structure of both components [14].

The simple technique for a quantitative measure of adsorption is by mixing a sample of solution with a known weight of catalyst at a constant temperature until adsorption equilibrium is reached (usually several hours), and a sample of the solution is then removed for analysis.

The standard free energy of adsorption is related to the adsorption equilibrium constant by

$$\Delta G^0 = -RT \ln K_{eq} \quad (4.1.3-1)$$

ΔG^0 is assumed to correspond to the free-energy change associated with transfer of solute from a solution of unit concentration to a surface. From the temperature coefficient of the equilibrium constant;

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (4.1.3-2)$$

and equation (4.1.3-1) and (4.1.3-2) can be combined to $-RT\ln K_{eq} = \Delta H^0 - T\Delta S^0$ so that

$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4.1.3-3)$$

Plotting $\ln K_{eq}$ versus $1/T$, ΔH^0 and ΔS^0 can be determined. For dilute solutions, equation (4.1.3-1) may be put in the approximate form;

$$\Delta G^0 = -RT \ln \frac{x^a}{x^s} \quad (4.1.3-4)$$

where x^a and x^s are the moles of analyte, adsorbed and in solution, respectively.

If the activated step of the reaction (the rate-limiting step) is the adsorption/desorption process, then the enthalpy of these processes would correspond to the measured activation energy. When the values of these enthalpies are smaller than the activation energy, it indicates that these processes are not the rate-limiting step of the reaction.

The extent of adsorption at any particular concentration generally decreases with increases in temperature, or in other words, the overall process is exothermic. It has been reported that ΔG^0 for the adsorption of stearic, oleic, and linoleic acids from n-heptane solutions on dry rutile surfaces had similar values (-25 to -29 kJ mol⁻¹), implying that the adsorption took place most likely at the same functional group of the molecule, i.e., via the carboxylic acid group [14]. Such a comparison is an important tool in identifying the interaction site in a molecule with a catalyst surface which is difficult to obtain by any other method.

In this chapter, the reaction mechanism of hydrodechlorination of C₁₈-Cl, Stearic--Cl₂, and DHA-Cl₂ in supercritical CO₂ will be investigated. The kinetic analysis is applied to determine the rate-limiting step of the reaction as well as the reaction order with respect to reaction reagents (isopropanol and palladium). Apparent activation energy and enthalpy of desorption are also discussed as they provide important information on the mechanism. Finally, two fluid systems (supercritical CO₂ and liquid isopropanol) are compared and differences are discussed.

4.2 METHODS AND MATERIALS

4.2.1 Materials

The same materials detailed in section 3.2.1 were used for all studies in this section.

4.2.2 Dechlorination at atmospheric pressure

All the experiments at atmospheric pressure were done in the following manner.

Into a 2mL glass vial, 0.0093 ± 0.0001 g of 5 % Pd/ γ -Al₂O₃ (0.004 mmol Pd), a magnetic stir bar, and 1mL of solvent (isopropanol for all the experiments except for variation of isopropanol concentration in which case hexane was used as the solvent) were added. The vial was then placed inside an oven atop a magnetic stirrer. The mixture was then heated to the desired temperature with stirring for 15 min to ensure temperature equilibration. Then 25 μ L of the standard solution (1000ppm C₁₈-Cl in isopropanol) was added to the vial and the mixture was stirred at the set temperature for desired time. The vial was then removed from the oven and the suspension was filtered out using a syringe filter with a 0.45 μ m pore diameter and analyzed by GC/FID. For the experiments to determine the activation energy, the separation was done by centrifuging the suspension for 2 minutes.

The determination of activation energy was done at temperatures ranging from 30°C to 60°C

4.2.3 Dechlorination in supercritical CO₂

Experiments were done as described in section 3.2.4. For the case of C₁₈-Cl, a 6-port valve (valve 14 in Figure 3.2-3) was rotated at the desired time to allow the reaction mixture to be isolated from the catalyst and the collected reaction mixture was then purged with CO₂ in the same manner as in section 3.2.4.

For the determination of activation energy, isopycnic rates of dechlorination were measured at various temperatures from 30°C to 80°C. The density of the reaction system was maintained at 0.63 ± 0.2 g/mL by adjusting pressure at each temperature.

4.2.4 Enthalpy of Desorption for Dechlorinated Compounds

The enthalpy and entropy of desorption of stearic acid and dehydroabiatic acid were determined by equilibrating 5.0 mL of 50 ppm standard solutions with 0.0050 g of Pd/ γ -Al₂O₃ in a 7 mL glass vial for at least 4 hours at temperatures between room temperature and 80°C. After the equilibration was complete, the solution phase was separated from the catalyst by using a syringe filter (0.45 μ m pore). 200 μ L of the filtered solution was methylated with diazomethane prior to GC/FID analysis.

4.2.5 Analytical Methods

All the analyses were done as described in section 3.2.6.

4.3 RESULTS AND DISCUSSION

4.3.1 Reaction Orders and Rate-Limiting Step

The kinetic curve of the reaction was constructed in order to apply the initial rate method. Figure 4.3-1 is a plot of dechlorination yield versus dechlorination time for $C_{18}\text{-Cl}$ in supercritical CO_2 and in liquid isopropanol, which clearly illustrates that the reaction reaches its final yield much faster in supercritical CO_2 than in liquid isopropanol. This is in agreement with the enhancement of the rate of the reaction due to a reduced viscosity and boundary layer between the bulk fluid and the catalyst surface in supercritical CO_2 . Dechlorination time was then set to 2 minutes in supercritical CO_2 and 15 minutes in liquid isopropanol to ensure the calculated rate reflects the initial rate of the reaction.

Figure 4.3-2 and Figure 4.3-3 were constructed by performing the same experiment for Stearic- Cl_2 and DHA- Cl_2 in supercritical CO_2 , respectively. The concentration of catalyst was reduced from the previous experiments with $C_{18}\text{-Cl}$ in order to slow down the reaction for these compounds. However, the reactions were still so fast that the final yield was reached in less than one minute. Dechlorination of Stearic- Cl_2 reached its final yield of only 3.5 % dechlorination within the initial 4 minutes of the reaction, with a sharp rise in the initial one minute. For DHA- Cl_2 , the reaction proceeded even faster than Stearic- Cl_2 and reached its final yield of 65 % yield within the initial one minute of reaction time. As the final yield is already achieved at this time, the initial slope measurement should be done in smaller increments between 0 and 1 minutes. Unfortunately, with the dechlorination system used for these experiments, it was not possible to measure reaction times of less than 1 minute, and for this reason, the dechlorination time was set to be 1 minutes for the following experiments with DHA- Cl_2 .

Table 4.3-1 summarizes the final yield and the ratio of the catalyst to the reactant.

The final dechlorination yield did not reach 100 % in the previous work by Ukisu, et al. in a similar system with Rh-Pt catalyst on Al_2O_3 support. Dechlorination yielded only up to 35 % on Rh-Pt/ Al_2O_3 and leveled off while other support with the same bimetallic

Figure 4.3-1: Kinetic curve for dechlorination of $C_{18}\text{-Cl}$
($T = 60^\circ\text{C}$, $\text{Pd}/C_{18}\text{-Cl}$ (molar) = 50): $\square$ in supercritical CO_2 ($P = 154 \text{ atm}$),
 $\circ$ in liquid isopropanol ($P = 1 \text{ atm}$)

Figure 4.3-2: Kinetic curve for dechlorination of Stearic-Cl₂ in supercritical CO₂
(T = 60°C, P = 154 atm, Pd/Stearic-Cl₂ (molar) = 20)

Figure 4.3-3: Kinetic curve for dechlorination of DHA-Cl₂ in supercritical CO₂
(T = 60°C, P = 154 atm, Pd/DHA-Cl₂ (molar) = 20)

system did not have the same problem [15]. It is possible then that alumina support may be more susceptible for catalyst poisoning than other types of support, however it only remains as a possibility with the limited information available.

Table 4.3-1: Final dechlorination yield for $C_{18}\text{-Cl}$, Stearic- Cl_2 and DHA- Cl_2 in supercritical CO_2 and in liquid isopropanol

		$C_{18}\text{-Cl}$	Stearic- Cl_2	DHA- Cl_2
Yield (%)	SC- CO_2	20	3.5	65
	i-PrOH	> 45	N.D.	N.D.
Pd/reactant (molar)	SC- CO_2	50	20	20
	i-PrOH	50	N.D.	N.D.

N.D. = not determined

4.3.2 Effect of Reactant Concentration

Figure 4.3-4 shows plots of initial rate of dechlorination versus initial concentration of $C_{18}\text{-Cl}$ in supercritical CO_2 and in liquid isopropanol. The plots show that the reaction is first order with respect to the initial concentration of $C_{18}\text{-Cl}$ in both cases. The plot follows equation (4.1.1-50) and therefore the rate-determining step of the reaction must therefore be adsorption, within the given range of concentration. The difference in the slope of the curves in Figure 4.3-4 is directly reflected to the rate constants in two systems, and clearly indicates that the reaction proceeds much faster in supercritical CO_2 than in liquid isopropanol (i.e., refer to the difference in the order of magnitude) as expected.

Figures 4.3-5 and 4.3-6 also show a linear relationship between the initial rate and the initial concentration of the reactant, indicating that the reaction was adsorption limited also for Stearic- Cl_2 and DHA- Cl_2 in supercritical CO_2 .

Table 4.3-2 summarizes the rate constants calculated from Figure 4.3-4, 4.3-5, and 4.3-6. The rate constant was an order of magnitude higher in supercritical CO₂ than in liquid isopropanol for C₁₈-Cl, as discussed above. A significantly smaller rate constant was also obtained for Stearic-Cl₂. The value of DHA-Cl₂ although calculated does not have much implications except to use only as a minimum value since the reaction time measured was not the true time required but the minimum can be measured within the initial raise of the curve as explained earlier.

The rate constant obtained for C₁₈-Cl was an order of magnitude higher than for that for Stearic-Cl₂ (0.10 min⁻¹m⁻² versus 0.010 min⁻¹m⁻²). The adsorption step of a surface reaction includes the penetration of the molecule through a fluid boundary layer near the surface of the catalyst, then the actual landing of the molecule on the catalyst surface. The first step is of considerable importance as this step is influenced by interaction among the reactant molecule, fluid, and the catalyst surface; reactants – surface, surface – fluid, and fluid – reactants interactions and all of these interactions play a role in the process of adsorption. When the reacting molecule passes through the boundary layer, the interaction between the reacting molecule and the fluid is dominant over the interaction between the reacting molecule and the catalyst surface. The nature of such a boundary is a function of the fluid system which in this case is CO₂ with 2.5 % (v/v) isopropanol. There would be higher concentration of isopropanol on the surface of the catalyst as isopropanol is polar and would interact more preferentially with the catalyst surface than CO₂. Penetration through this non-polar boundary layer should be faster for non-polar C₁₈-Cl than polar Stearic-Cl₂. The same explanation is applied when the fluid system is changed to liquid isopropanol from supercritical CO₂. In this case, the boundary phase is all polar isopropanol and diffusion through such a polar phase, even for non-polar C₁₈-Cl would proceed much slower than it would in non-polar supercritical CO₂, due to the lower viscosity of CO₂. This is in agreement with the observed rate constants of C₁₈-Cl; 0.10 min⁻¹m⁻² in supercritical CO₂ and 0.012 min⁻¹m⁻² in liquid isopropanol.

Figure 4.3-4: Initial rate of dechlorination as a function of the initial concentration of $C_{18}\text{-Cl}$ ($T = 60^\circ\text{C}$, $\text{Pd}/C_{18}\text{-Cl}$ (molar) = 50)

- Axis on left: ● in supercritical CO_2 ($P = 154 \text{ atm}$, reaction time = 2 min); $r^2 = 0.92$
- Axis on right: ▲ in liquid isopropanol ($P = 1 \text{ atm}$, reaction time = 15 min); $r^2 = 0.99$

Figure 4.3-5: Initial rate of dechlorination as a function of the initial concentration of Stearic-Cl₂ in supercritical CO₂ (T = 60°C, P = 154 atm, Pd/Stearic-Cl₂ (molar) = 50, reaction time = 1.5 min); $r^2 = 0.84$

Figure 4.3-6: Initial rate of dechlorination as a function of the initial concentration of DHA-Cl₂ in supercritical CO₂ (T = 60°C, P = 154 bar, Pd/DHA-Cl₂ (molar) = 20, reaction time = 1.5 min); $r^2 = 0.96$

Table 4.3-2: Calculated rate constants for dechlorination of C₁₈-Cl, Stearic-Cl₂ and DHA-Cl₂ in supercritical CO₂ and in liquid isopropanol at 1 atm

	k (min ⁻¹ m ⁻²)	
	Supercritical CO ₂	1atm, isopropanol
C ₁₈ -Cl	0.10 ± 0.001	0.012 ± 0.001
Stearic-Cl ₂	0.010 ± 0.0003	Not determined
DHA-Cl ₂	0.013 ± 0.001*	Not determined

* Note that reaction time of 1 minute was used for calculation for DHA-Cl₂.

4.3.3 Effect of Catalyst Concentration

Referring to Figure 4.3-7, the effect of the amount of catalyst on the initial rate of dechlorination of C₁₈-Cl appears to be different in CO₂ than in liquid isopropanol. In liquid isopropanol, the initial rate is linearly related to the amount of Pd present, i.e., the reaction is first order in palladium concentration. This was expected for a reaction controlled by diffusion to or adsorption of the substrate on to the solid surface, i.e., increasing the amount of catalyst increases the rate of adsorption of substrate, hence increases the rate of the overall reaction. In supercritical CO₂, where the diffusion is much faster, the rate is limited by the amount of Pd available at low concentrations of palladium. At higher palladium concentrations, the rate appears to level off. However, the reaction under these conditions was so fast that it was essentially complete with the shortest reaction time measurable. The true reaction rate was therefore not being measured. There is no reason to believe that the true rate does not actually continue to rise with increasing palladium concentration.

Figure 4.3-7: Initial rate of dechlorination of 1-chlorooctadecane ($C_{18}Cl$) as a function of the initial concentration of palladium

- in SC- CO_2 ($T = 80^\circ C$, $P = 100$ atm, reaction time = 2 min)
 ○ in liquid isopropanol ($T = 60^\circ C$, $P = 1$ atm, reaction time = 15 min)

When the concentration of the catalyst is increased, the equilibrium of the primary step of the reaction, presumed as the adsorption of isopropanol on catalyst surface, is shifted to its right hand side, providing more adsorbed isopropanol. This would increase the rate of the second step of the reaction, adsorption of $C_{18}\text{-Cl}$ to the catalyst surface on a site adjacent to an adsorbed isopropanol, and hence enhance the overall rate of the reaction.

4.3.4 Effect of Isopropanol Concentration

When the dechlorination is performed at atmospheric pressure, isopropanol has the roles of a hydrogen donor and a solvent. In supercritical CO_2 , the role of isopropanol as a hydrogen donor only was explicitly determined by varying its concentration at low enough concentrations that it did not affect the solvent properties. At atmospheric pressure, hexane was used as a solvent and the initial rate of dechlorination was determined as a function of initial concentration of isopropanol. Dechlorination did not proceed in absence of isopropanol in either supercritical CO_2 or in hexane at atmospheric pressure, confirming its role as a hydrogen donor in the reaction mechanism.

Even though a direct comparison cannot be made, the effects of varying the isopropanol concentration in supercritical CO_2 (Chapter 3 Figure 3.3-7) are quite different from those in hexane (Figure 4.3-8). At atmospheric pressure, the rate increases proportionally with the initial concentration of isopropanol while in supercritical CO_2 , increasing the isopropanol volume fraction to more than 2.5 % had a clear inhibiting effect on the dechlorination yield. This was considered due to excessive adsorption of the polar alcohol on the surface of the catalyst preventing the adsorption of the reactant. Pressure had a similar effect on dechlorination yield (significant decrease in the yield at higher pressure). These results both support the proposed mechanism, whereby the rate-limiting step for the reaction is adsorption of the reactant molecule on the catalyst surface.

It should be noted that all the other liquid isopropanol experiments except for the determination of the effect of initial concentration of isopropanol were done in 100%

Figure 4.3-8: Initial rate of dechlorination of $C_{18}\text{-Cl}$ as a function of the initial concentration of isopropanol ($T = 60^\circ\text{C}$, $P = 1\text{ atm}$, $\text{Pd}/C_{18}\text{-Cl}$ (molar) = 50, reaction time = 15 min, solvent: hexane)

(v/v) isopropanol at atmospheric pressure. If we were to keep the volume fraction of isopropanol to 2.5 % as it was in supercritical CO₂, then the corresponding rates in Figure 4.3-4 and Figure 4.3-7 would have been even lower, indicating again how much faster the reaction is in supercritical CO₂ than in a liquid solvent.

The volume fraction of 2.5 % corresponds to a molar fraction of 1.4 % which creates a binary fluid system. The critical point corresponds to 33.6°C and 72.3 atm and a plot of density versus pressure does not differ much from the plot for pure CO₂. When reactions are carried in supercritical fluids, it is important to ensure the homogeneity of a fluid by making sure that the system consists of only one phase. This binary system of 1.4 % isopropanol in CO₂ consists of only one phase according to Radosz [16].

4.3.5 Apparent Activation Energy

The rate constants were found to increase with temperature as expected. Arrhenius plots were constructed to determine the apparent activation energies (E_a) for C₁₈-Cl in supercritical and in liquid isopropanol (Figure 4.3-9), and for Stearic-Cl₂ and DHA-Cl₂ in supercritical CO₂ (Figure 4.3-10). All the values obtained are summarized in Table 4.3-3.

Table 4.3-3: Apparent activation energies (E_a) for dechlorination of C₁₈-Cl, Stearic-Cl₂ and DHA-Cl₂ in supercritical CO₂ and liquid isopropanol

	E_a (kJ/mol)	
	Supercritical CO ₂	1atm, isopropanol
C ₁₈ -Cl	43 ± 5	35 ± 3
Stearic-Cl ₂	40 ± 7	Not determined
DHA-Cl ₂	135 ± 9	Not determined

The values of the apparent activation energy for C₁₈-Cl in supercritical CO₂ and in liquid isopropanol were the same within the experimental errors (Figure 4.3-9). This indicates

that the rate limiting step is the same in both cases, consistent with the earlier results obtained, i.e., adsorption is the rate-limiting step of the reaction in both fluids.

In supercritical CO₂ referring to Figure 4.3-10, C₁₈-Cl and Stearic-Cl₂ also had the same apparent activation energies while the activation energy of DHA-Cl₂ was more than three times greater. As the rate-limiting step was determined to be the adsorption of the reactant molecules, high activation energy indicates that the adsorption of such a molecule to the catalyst surface through the boundary layer is more energetically demanding than the other two compounds. This is likely due to the sizes and shapes of the substrate molecules. C₁₈-Cl and Stearic-Cl₂ are much smaller molecules than DHA-Cl₂ and

diffusion of a larger molecule would be considered more energetically demanding than a smaller molecule, especially in this case where a polar DHA-Cl₂ molecule is going through a non-polar CO₂ fluid phase. Such interaction is not preferred, and high activation energy may be the reflection of enhanced effect by a larger size of a molecule.

Figure 4.3-10 demonstrates a clear linearity obtained for all three compounds indicating that the reaction was not limited by diffusion for all three compounds in supercritical CO₂ for the given range of temperatures (30°C to 80°C). Dechlorination of C₁₈-Cl in liquid isopropanol was only performed in the temperatures up to 60°C. Below this temperature, the Arrhenius plot had a consistent linearity and therefore it was considered that the reaction was not influenced by diffusion. It may be the case when the temperature is increased to higher than 60°C.

Figure 4.3-9: Arrhenius plot of dechlorination of $C_{18}\text{-Cl}$ for determination of apparent activation energy: ($\text{Pd}/C_{18}\text{-Cl}$ (molar) = 50)

□ in SC-CO_2 ($\rho = 0.63 \pm 0.2 \text{ g/mL}$); $E_a = 43 \pm 5 \text{ kJ mol}^{-1}$ ($r^2 = 0.91$)

○ in liquid isopropanol at ($P = 1 \text{ atm}$); $E_a = 35 \pm 3 \text{ kJ mol}^{-1}$ ($r^2 = 0.91$)

Figure 4.3-10: Arrhenius plot for determination of apparent activation energy of dechlorination in supercritical CO_2 ($\rho = 0.63 \pm 0.2 \text{ g/mL}$, $\text{Pd/reactant (molar)} = 50$);
 $\text{C}_{18}\text{-Cl}$: $E_a = 43 \pm 5 \text{ kJ mol}^{-1}$ ($\circ$, $r^2 = 0.91$)
 Stearic-Cl_2 : $E_a = 40 \pm 7 \text{ kJ mol}^{-1}$ (Δ , $r^2 = 0.69$)
 DHA-Cl_2 : $E_a = 135 \pm 9 \text{ kJ mol}^{-1}$ ($\square$, $r^2 = 0.97$)

4.3.6 Enthalpy of Desorption of Dechlorinated Molecules

The rate limiting step of the dechlorination of $C_{18}\text{-Cl}$ was the same under two conditions (supercritical CO_2 and in liquid isopropanol at 1 atm) and therefore the reactions must have the same rate-limiting step; adsorption. This can be further confirmed by eliminating other possible steps to be a rate-limiting step. One step of the reaction where the thermodynamic information is easily obtained is the desorption of the dechlorinated compounds at atmospheric conditions. The enthalpies of desorption of stearic acid and dehydroabiatic acids were therefore determined in liquid isopropanol. A plot of $\ln K_{\text{eq}}$ versus $1/T$ is shown in Figure 4.3-11 and the calculated values were summarized in Table 4.3-4.

The desorption enthalpies of stearic acid and dehydroabiatic acid ($18 \pm 2 \text{ kJmol}^{-1}$ and $12 \pm 2 \text{ kJmol}^{-1}$, respectively) were less than half of the activation energies for their dechlorination ($40 \pm 7 \text{ kJmol}^{-1}$ and $135 \pm 9 \text{ kJmol}^{-1}$, respectively), indicating that desorption of the dechlorinated compounds is energetically less demanding than the activation step. Therefore desorption of the dechlorination products is not the rate-limiting step, in agreement with the earlier results.

Adsorption of octadecane on the catalyst surface was not significant enough to be able to perform quantitative analysis. In this case, the interaction between the polar catalyst surface (due to the polar nature of the catalyst support) and isopropanol is dominant over the interaction between octadecane and the catalyst surface or between octadecane and isopropanol.

Table 4.3-4: Thermodynamic values for desorption of dechlorinated products (stearic acid and dehydroabiatic acid) from $\text{Pd}/\text{Al}_2\text{O}_3$ surface

	$\Delta H \text{ (kJ mol}^{-1}\text{)}$	$\Delta S \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$
Stearic acid	18 ± 2	38 ± 1
Dehydroabiatic acid	12 ± 2	40 ± 1

Figure 4.3-11: Determination of enthalpy of desorption of stearic acid and dehydroabietic acid ($T = 80^{\circ}\text{C}$, $P = 1 \text{ atm}$, $\text{Pd}/\text{analyte (molar)} = 3$, equilibration time $> 4 \text{ hours}$);
 Stearic acid ($\circ$, $r^2 = 0.89$): $\Delta H_{\text{des}} = 18 \pm 2 \text{ kJ mol}^{-1}$
 dehydroabietic acid (∇ , $r^2 = 0.85$): $\Delta H_{\text{des}} = 12 \pm 2 \text{ kJ mol}^{-1}$

4.4 SUMMARY AND CONCLUSIONS

The reaction is considered to follow a Langmuir-Hinshelwood type mechanism which takes place between the adsorbed chlorinated molecule and the adsorbed isopropanol. Isopropanol is in excess compared to the reactant leading to the overall reaction being pseudo first order in the concentration of the substrate.

The rate-limiting step of the reaction was determined to be the adsorption of the reactant molecule in all cases for $C_{18}\text{-Cl}$, Stearic- Cl_2 , and DHA- Cl_2 , as clearly illustrated in Figures 4.3-4, 4.3-5, and 4.3-6, respectively. Further studies of the kinetics of the reaction clearly revealed that the reaction is first order in $C_{18}\text{-Cl}$ both in supercritical CO_2 and in liquid isopropanol. The rate constant was an order of magnitude higher in supercritical CO_2 than in liquid isopropanol, which illustrates a faster diffusion in supercritical fluids than in liquids, and that a boundary CO_2 phase is more easily crossed than a liquid isopropanol phase, especially for a non-polar molecules such as $C_{18}\text{-Cl}$. This was also shown by smaller rate constant for Stearic- Cl_2 in supercritical CO_2 .

In both supercritical CO_2 and in liquid isopropanol, the rate of dechlorination was increased with the catalyst concentration. The effect was more significant in supercritical CO_2 than in liquid isopropanol as shown for $C_{18}\text{-Cl}$ in Figure 4.3-7.

The initial rate of reaction was linearly proportional to the concentration of isopropanol at atmospheric pressure in hexane, but there was a clear inhibiting effect at high concentration above an optimum value in supercritical CO_2 . Together with the effect of pressure discussed in Chapter 3, it supports the argument that the rate-limiting step is the adsorption of the reactant. Excessive amount of either CO_2 or isopropanol results in less vacant sites on the catalyst surface available for adsorption of $C_{18}\text{-Cl}$.

The apparent activation energy of the reaction was also the same in two fluids within experimental errors for $C_{18}\text{-Cl}$, confirming that the rate-limiting step of the reaction was

the same in both fluids. The much higher E_a for DHA-Cl₂ was likely due to its much greater size than the other two substrates.

Enthalpies of desorption of stearic acid and dehydroabiatic acid further confirmed that the rate-limiting step is not desorption of dechlorinated products.

Table 4.3-5 summarizes the experimental data obtained with some physical properties of the molecules studied. Structure of the molecule and the value of activation energy correspond with each other as discussed earlier. The polarities of the molecules are consistent with the observed pressure effect in the supercritical CO₂ system.

Table 4.3-5: Summary of Experimental data obtained for dechlorination of C₁₈-Cl, Stearic-Cl₂, and DHA-Cl₂ in supercritical CO₂ ($\rho = 0.63 \pm 0.02$ g/mL)

	C ₁₈ -Cl	Stearic-Cl ₂	DHA-Cl ₂
Structure	Aliphatic	Aliphatic	Aromatic
E_a (kJ mol ⁻¹)	(43 ± 5)	(40 ± 7)	(135 ± 7)
Functional group	N/A	-COOH	-COOH
Polarity	Non-polar	Polar	Polar
Pressure Effect	Yes	No	No
k (min ⁻¹ m ⁻²)	0.10 ± 0.001	0.010 ± 0.0003	0.013 ± 0.001

In this Chapter, the rate-limiting step of the dechlorination reaction was determined to be the penetration of the substrate through the boundary layer next to the catalyst surface. The effects of other reaction reagents (isopropanol and the catalyst itself) on the rate of dechlorination, activation energies, and enthalpy of desorption were determined and summarized.

One major advantage of performing heterogeneous catalysis in supercritical fluids is the faster reaction which was well demonstrated in this chapter for dechlorination of C₁₈-Cl.

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Chapter 5

Congener Specific Kinetic Studies of the Dechlorination of Polychlorinated Biphenyls in Supercritical Carbon Dioxide

5.1 INTRODUCTION

The molecules of interest in the previous chapters have been rather simple in a sense that they were not extensively chlorinated (i.e., only one or two chlorine atoms per molecule). Dechlorination of such molecules would lead to one or a few dechlorination pathways so that the reaction scheme would not be complex. However, it will not be the case when the molecule is heavily chlorinated, such as in hexachlorobenzenes or higher congeners of PCBs, where there will be such a large number of dechlorination pathways that kinetic analysis of such multiple system becomes very challenging. In this chapter, the focus of the work is to apply the dechlorination method developed in the previous chapters to more complex molecules (i.e., polychlorinated biphenyls) in order to determine the dechlorination pathways and hence the selectivity of the reaction with respect to the nature of the reacting molecule. Further attempts were made to find a tool to predict the selectivity using theoretical calculations.

5.1.1 Dechlorination Pathways and Selectivity

It has been recognized by researchers that only a limited amount of data is available on the surface processes in catalytic dechlorination. This brings about difficulty in applying a direct comparison of the experimental data to the published studies and some assumptions become necessary when comparison is made to a more extensively studied

system. This is especially the case for hydrodechlorination in supercritical CO₂, of which detailed mechanistic studies has not been done extensively.

There has been much development of dechlorination methods for PCBs with obvious practical and environmental purposes, however comparatively little has been done on the congener specific kinetic analysis of the dechlorination of PCBs. The most relevant work was done by Murena on gas phase hydrodechlorination, where selected PCB congeners were individually dechlorinated in a hydrogen atmosphere using sulphided Ni-Mo/ γ -Al₂O₃ [1]. Kinetic analysis of the dechlorination of commercial PCB mixtures is a difficult task due to the presence of many reaction pathways producing many more PCB congeners as intermediates. An attempt to perform the kinetic analysis of the hydrodechlorination processes of a PCB dielectric oil has been reported without a clear insight of the reaction pathway due to the complexity of the reacting mixture [2].

However, it has been shown that a reaction does not follow all possible pathways. Hence, substitution patterns of the reacting chlorinated molecule and the observed intermediates should provide us clues to understand the mechanism of hydrodechlorination [1].

The aim of research in this chapter is to identify dechlorination pathways of some specific PCB congeners in order to understand the selectivity of the reaction which will help to elucidate the reaction mechanism. Once this is established, it will then be possible to predict the kinetics of the hydrodechlorination process of individual PCBs or PCB mixtures for which no experimental data are available.

It has been reported by several authors that the selectivity of hydrodechlorination reactions is controlled by steric and electronic effects (inductive and resonance effects) [1]. Then the rate of dechlorination can depend on both the nature and position of any additional substituent on the ring, which could increase or decrease the rate of C-Cl bond dissociation. The chlorine atom is known to act both as an electron donating and withdrawing substituent, and thus its substitution position becomes an important factor in

determining the selectivity of the reaction. Several authors summarized that the rate of hydrodechlorination depends on the following factors; the structure of the reacting molecule, total number of Cl atoms, the position of the substituted Cl atom, the number and type of atoms adjacent to the C-Cl bond of interest, and the particular carbon atom Cl atoms are bonded to [1,3].

One parameter that clearly distinguishes the reaction mechanism (and hence the selectivity) from one to another is the form of hydrogen transfer. Most hydrodechlorination reactions have been performed with the use of hydrogen gas and in such a case the transferred hydrogen is considered to be in the H^+ form, which leads to the formation of arenium ion as the transition state followed by a loss of Cl^- . In the current study, the source of hydrogen is isopropanol. There are a few studies on the hydrogenation or hydrodehalogenation using alcohol as a hydrogen donor, suggesting that the hydrogen transfer is in the form of a hydride ion [4, 5, 6].

Whether the reaction proceeds in the gas phase or the liquid phase, most catalytic hydrodechlorination reactions proceed sequentially as it has been reported for 1,2,3-trichlorobenzene, CCl_4 and $CHCl_3$, and chlorophenols [7, 8, 9], and the rate of dechlorination has shown to decrease at each succeeding stage [8, 10, 11]. This was consistent with the work of Murena although they expected highly chlorinated compounds to have a higher dechlorination rate both for statistical considerations and for being more strongly adsorbed on the catalyst [1]. The authors did not find such correlation between the dechlorination rate and the total number of chlorine atoms. Moreover, there was a large spread in the values of the kinetic rate constants in correspondence with a fixed number of Cl atoms. It is also reported that in treating a PCB mixture with Ni catalyst within a group of PCB isomers having the same number of chlorine atoms, certain isomers were selectively produced and reacted, indicating that other effects are involved. The postulated mechanism was an electrophilic substitution

with inductive and steric effects being predominant with respect to resonance effects; which was in agreement with the analysis of the selectivity of the reaction products.

Electrophilic Substitution

The reaction mechanism involving a carbocation intermediate known as arenium ion is well described by Hagh and Allen in hydrodechlorination of chlorobenzenes on sulfided NiMo/ γ -Al₂O₃ [12]. The surface anion vacancies exposing Mo³⁺ are presumably bonded to the aromatic nucleus by interaction with its π electrons. This interaction weakens the resonant structure of the benzene ring by donation of electrons to the anti-bonding orbital or removal of electrons from the bonding orbitals. The electrophilic attack of a proton would result in the formation of a delocalized carbocation intermediate known as arenium ion as shown in Figure 5.1-1.

Figure 5.1-1: Electrophilic substitution mechanism of hydrodechlorination of chlorobenzene by arenium ion intermediate

Considering the case of a polychlorinated benzene, the direction of substitution reactions depend on two factors: an inductive effect and a resonance effect. The chlorine substituent withdraws electronegativity from the ring, leading to partial deactivation to electrophilic substitution through the inductive effect. It can also stabilize the arenium ion resulting from ortho and para attack by donating an unshared pair of electrons through the resonance effect. The removal of a Cl atom in positions ortho and para is more favored than the removal in meta position by the delocalization of the positive charge on the phenyl group. On the surface of the catalyst, the aromatic resonance structure is weakened

by the interaction with the Mo^{3+} , the resonance effect of chloro groups are considered to be reduced and inductive effects become a dominant control on the selectivity.

The above theory has been applied by several authors to hydrodechlorination of various chlorinated compounds. One example is on hydrodechlorination of tri- and tetrachlorobiphenyls [1]. The hydrodechlorination of 3,4,5-trichlorobiphenyl only results in 3,4-dichlorobiphenyl, but not 3,5-dichlorobiphenyl. The arenium intermediate of 3,5-dichlorobiphenyl is relatively unstable due to the presence of positive charges next to two chlorine atoms, while that of 3,4-dichlorobiphenyl is relatively more stable as only one Cl atom is involved. Consequently, a general statement can be made that Cl atoms adjacent to the substituted Cl atom would destabilize the arenium ion reducing the rate of hydrodechlorination reaction. The reaction proceeds faster when the substituted Cl atom was between two H atoms.

Substituent Effects

Murena [13] determined that the presence of the phenyl group had an increasing effect on the rate of removal of the Cl by a factor of about two by comparing the hydrodechlorination of monochlorobiphenyls to that of chlorobenzene. The electron donor phenyl group was considered to enhance an electrophilic substitution. The position of the Cl atom of monochlorobiphenyl did not affect the rate of hydrodechlorination. In this case, the phenyl group was considered to hold a high resonance effect dominating over a weak inductive effect due to chlorine substitution position. On contrary to the earlier studies [12], the inductive effect did not result in an observable selectivity except that the presence of the phenyl group stabilizes the arenium ion formed during the electrophilic attack resulting in the higher rate of monochlorobiphenyl than that of chlorobenzene.

Shin and Keane [14] also applied an electrophilic substitution mechanism on the studies of hydrodechlorination of dichlorophenols using a 1.5% (w/w) Ni/SiO₂ catalyst. In the absence of appreciable steric constraints, chlorine removal was more energetically demanding from dichlorophenol than chlorophenol. Most of the observed selectivity was considered due to the inductive and steric effects of the reaction. For example, from resonance stabilization considerations, 2,3-, 2,5- and 3,4-dichlorophenol should result in the preferential formation of 3-chlorophenol, however only 3,4-dichlorophenol follows this criteria. Steric constraints seemed to be dominating over the resonance stabilization. On the other hand, there were some cases where an obvious steric effect was not observed. Dechlorination of 2,4-dichlorophenol and 2,5-dichlorophenol resulted in a preferential removal of *ortho*-Cl indicating that an effect can not be attributed directly to steric constraints.

The dechlorination proceeded both simultaneously and in a step-wise manner for hydrodechlorination of chlorophenols. When two chlorines are adjacent to one another on the ring (2,3- and 3,4-), dechlorination proceeded simultaneously to a greater extent than when two chlorines are separated on the aromatic ring (2,6-, 3,5-). Moreover, the selectivity decreased as the chlorines are separated further apart.

From the observed selectivity on dechlorination, authors suggested that the chlorine component of the reacting molecule or the intermediates must have a direct interaction with the catalyst as hydrodechlorination was the only reaction observed. Interaction of the benzene ring and /or hydroxyl group with the catalyst may assist the orientation of the reactant on the surface but does not lead to ring reduction or deoxygenation.

Nucleophilic Substitution

Despite the use of a variety of alcohols, 2-propanol is most often used as a hydrogen donor, due to its simplicity, availability, and the ease of removal of dehydrogenation

product (acetone) from the reaction system. Potassium hydroxide is often used in this reaction, which is believed to remove a proton from the reacting complex effectively. Many other homogeneous catalyst systems using an alcohol as the hydrogen donor use a base for their activity. Despite the common and extensive use of this system, the full mechanistic details are not understood completely [4].

The function of isopropanol (2-propanol) as a hydrogen donor in the current hydrodechlorination system was discussed in Chapter 3 and 4. It was also confirmed by a use of deuterium-labeled 2-propanol as a solvent for dechlorination of 1,2,4-trichlorobenzene [5]. The transfer of hydrogen from 2-propanol was evident by a production of deuterium containing benzene. On contrary, almost no D-containing benzene was observed in the reaction with $\text{CH}_3\text{CH}(\text{OD})\text{CH}_3$, leading to the conclusion that it is the α -hydrogen of 2-propanol being exclusively transferred to the substrate.

2-butanol and 2-propanol (2° alcohols) resulted in higher yield than 1-propanol or ethanol (1° alcohols) and among all 2-propanol was incomparably high, further supporting this argument. The presence of hydride species on the solid catalysts was also assumed by LaPierre, et al in the gas-phase hydrodechlorination of chlorobenzene with H_2 [6].

Substituent Effects

When hydrogen transfer takes place in the form of a hydride species, the reaction mechanism must become nucleophilic substitution. The inductive effect should then be the opposite of what is observed for an electrophilic substitution reaction as shown for chlorobenzene in Figure 5.1-2.

Figure 5.1-2: Nucleophilic substitution mechanism of hydrodechlorination of chlorobenzene

The substituent effect on the rate of dechlorination of aromatic chlorides (chlorobenzene, *p*-chlorotoluene, and 4-chlorobiphenyl) was studied by Ukisu, et al [15]. Dechlorination rates were lower for 4-chlorobiphenyl and *p*-chlorotoluene than for chlorobenzene due to their electron-donating substituents (phenyl and methyl group). In the homogeneous dechlorination of aryl chlorides catalyzed by palladium complexes, the reaction is retarded by electron-donating substituents (i.e., CH₃, CH₃O, and NH₂) and enhanced by electron-withdrawing substituents (i.e., CHO and CN), in agreement with the observed selectivity. In this work, the reaction mechanism is believed to proceed by nucleophilic substitution with hydrogen transfer in a form of a hydride species.

Parameters that affect the selectivity

Steric Effects

The steric effects stay consistent whether the reaction is described by electrophilic or nucleophilic reaction mechanism.

Murena [13] found that the rate of removal of *ortho*-Cl is lower than that of either *meta*- or *para*- positions for monochlorobiphenyls, however the difference between the rate of *meta*- and *para*- was less clear. The rate constants of monochlorobiphenyls were determined to be the lowest for *ortho*-substitution, in agreement with the observations of LaPierre, et al [6]. These authors observed that *ortho*-substituted Cl atoms were less labile than *meta*- and *para*-substituted ones and suggested that the rate of any PCB mixture could be characterized by the degree of *ortho*-substitution versus combined *meta*- and *para*-substitution only. The same effect was observed for hydrodechlorination of dichlorophenols by Shin and Keane [14] and chlorobenzenes by Suzdorf, et al [9].

Ukisu, et al also found the same effect on dechlorination of chlorotoluene in nucleophilic substitution [15]. However, when a mixture containing an equivalent molar amount of *o*-, *m*- and *p*-chlorotoluene was used as a reactant, no significant difference in the dechlorination rate was observed among the isomers, possibly due to less steric effect on chlorotoluenes than polychlorinated compounds such as PCBs and trichlorobenzene.

Substituent Effects

This effect is obviously opposite in the two mechanisms being proposed. When the substituent is electron donating, it increases the rate in electrophilic reaction by stabilizing the arenium ion intermediate while the rate is decreased in a nucleophilic reaction. When the substituent is electron withdrawing, the opposite becomes true. If the statement made by Hagh and Allen [12] is true and that the resonance effect is minimal in hydrodechlorination of an aromatic halide due to the weakening of the aromatic resonance, then the inductive effect takes over the reaction selectivity. Thus the reaction selectivity should be distinctive between the two mechanisms which should then be the key in determining the reaction substitution mechanism.

Affinity of a Substrate for the Catalyst Surface

The affinity of substrates for the catalyst is an important parameter in understanding heterogeneous catalytic reactions. Chlorobenzenes, for instance, are very difficult to hydrodechlorinate [12]. This suggests that the interaction of chlorobenzenes with a catalyst surface must be very different from how, for instance, PCBs interact with the surface. Another example where such effects are observed is with the hydrodechlorination reactions of chlorobenzene, p-chlorotoluene, and 4-chlorobiphenyl [15]. The order of the reaction rate changed when the experiments were performed individually, as opposed to together. The change in the order indicates a sensitivity of the affinity of the catalyst for the substrate on the substituents on the aromatic ring.

Number of Chlorine Atoms

Murena attempted to show a correlation between the rate constants and the number of chlorine atoms on a ring [1]. The authors expected to see highly chlorinated compounds to have a higher hydrodechlorination rate, however, the correlation was not quite clear between the rate and the total number of chlorine atoms. There was a large spread in the

values of the rate constant for congeners with the same number of chlorine atoms, indicating the presence of selectivity in the dechlorination pathways.

Bond Dissociation Energy

It has been reported that the hydrodehalogenation rate of aryl halides decreases in the order of $\text{C}_6\text{H}_5\text{-I}$, -Br , -Cl and -F and $\text{C}_6\text{H}_5\text{-F}$ does not react in most catalytic systems [5]. This order corresponds to the bond dissociation energies (C-I : $222.6 \text{ kJ mol}^{-1}$, C-Br : $281.4 \text{ kJ mol}^{-1}$, C-Cl : $340.2 \text{ kJ mol}^{-1}$, C-F : $453.6 \text{ kJ mol}^{-1}$), indicating that higher bond energies between the reacting carbon and chlorine atoms results in a lower rate of the hydrodehalogenation reaction. Determination of the bond dissociation energy at each reacting C-Cl bond may be instructive to understand the reaction pathways of hydrodechlorination of polychlorinated compounds.

Molecular Orbitals

The interaction of the substrate and the catalyst surface depends on the overlap of the lowest unoccupied molecular orbitals (LUMOs) of the substrate with atomic orbitals of the catalyst. Considerable differences in the LUMO energy between planar and non-planar PCB congeners has been suggested to explain the selectivity observed in radiolytic dechlorination [16, 17]. While the determination of the actual overlap of orbitals between the substrate and the catalyst surface is more appropriate approach, the analysis of the LUMO of the substrate itself might be instructive. This will provide the information on the bond order of the C-Cl bond of interest and the electron distribution of the molecule which may be related to a preferential orientation of the molecule on the catalyst surface. The calculation of MO coefficients was therefore undertaken to give a measure of how likely one C-Cl bond is to rupture compared to the others.

The main factors that control the reaction rate in catalytic hydrodechlorinations are steric and electronic effects (inductive and resonance effects). The rate and the selectivity of

dechlorination depend on many parameters; the nature of the substrate (i.e., molecular structure, polarity, etc.), substitution position of chlorine atom on the substrate, degree of substitution (i.e., number of chlorine atoms on the substrate), the number and type of atoms adjacent to the dissociating C-Cl bond (i.e., steric effects), and the form of hydrogen transfer (i.e., electrophilic or nucleophilic substitution). It is also important to realize the solvent being employed interacts with the catalyst and with the substrate. Either of these two interactions may influence the rate and selectivity of the reaction.

5.1.2 Determination of Rate Constants for Individual Pathways

Determination of the rate constants of the individual dechlorination pathways is shown using PCB009 (2,5-dichlorobiphenyl, or '9') as an example. Considering that the dechlorination proceeds in a sequential manner, PCB009 dechlorinates to PCB001 (2-chlorobiphenyl, or '1') and PCB002 (3-chlorobiphenyl, or '2'), followed by further dechlorination of PCB001 and PCB002 to biphenyl ('B') as shown in Figure 5.1-3. Each substrate exists either in solution (subscript = 's') and on the catalyst (adsorbed, subscript = 'a'), and the equilibrium is established between the substrate 'in solution' and the substrate 'adsorbed'.

Equilibrium constant for PCB001 is defined as;

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[1_a]}{[1_s]} \quad (5.1.2-1)$$

The rate of change of the concentration of adsorbed PCB001 is then;

$$\frac{d[1_a]}{dt} = k_{9-1}[9_a] - k_{1-B}[1_a] + k_1[1_s] - k_{-1}[1_a] \quad (5.1.2-2)$$

Substitution of equation (5.1.2-1) into equation (5.1.2-2) due to the equilibrium between PCB001 adsorbed ('1_a') and PCB001 in solution ('1_s');

$$\frac{d[1_a]}{dt} = k_{9-1}[9_a] - k_{1-B}[1_a] \quad (5.1.2-3)$$

Figure 5.1-3: Dechlorination Scheme of PCB009 (2,5-dichlorobiphenyl, '9')
 PCB001 (1), PCB002 (2) and biphenyl (B) Subscripts: in solution (s) or adsorbed (a),
 equilibrium constants (K) and rate constants (k)

The rate constant for the dechlorination of PCB009 to PCB001 is then

$$k_{9-1} = \frac{\frac{d[1_s]}{dt} + k_{1-B}[1_s]}{[9_s]} \quad (5.1.2-4)$$

Introducing the equilibrium constant by substituting equation (5.1.2-1) to equation (5.1.2-4) leads to;

$$k_{9-1} = \frac{K_1 \frac{d[1_s]}{dt} + k_{1-B} K_1 [1_s]}{K_9 [9_s]} \quad (5.1.2-5)$$

And extracting the equilibrium constants from equation (5.1.2-5) results in;

$$\therefore k_{9-1} = \frac{K_1}{K_9} \left\{ \frac{\frac{d[1_s]}{dt} + k_{1-B}[1_s]}{[9_s]} \right\} \quad (5.1.2-6)$$

Similarly, the rate of change of PCB002 is

$$\therefore k_{9-2} = \frac{K_2}{K_9} \left\{ \frac{\frac{d[2_s]}{dt} + k_{2-B}[2_s]}{[9_s]} \right\} \quad (5.1.2-7)$$

Equation (5.1.2-6) and (5.1.2-7) can be simplified to;

$$k'_{9-1} = \frac{\frac{d[1_s]}{dt} + k_{1-B}[1_s]}{[9_s]} \quad (5.1.2-8)$$

$$k'_{9-2} = \frac{\frac{d[2_s]}{dt} + k_{2-B}[2_s]}{[9_s]} \quad (5.1.2-9)$$

where $k_{9-1} = \frac{K_1}{K_9} k'_{9-1}$ and $k_{9-2} = \frac{K_2}{K_9} k'_{9-2}$.

In cases where there is no significant difference between the equilibrium constants among the PCB congeners, i.e., $K_1 = K_2 = K_9$, then k'_{9-1} and k'_{9-2} become equal to k_{9-1} and k_{9-2} , respectively.

When dechlorination of PCB001 and PCB002 are considered separately,

The approach is therefore to measure k_{1-B} and k_{2-B} by observing the dechlorination of PCB001 and PCB002 alone, respectively. Then using data collected from the dechlorination of PCB009, and using equations (5.1.2-8) and (5.1.2-9), the rate constants k'_{9-1} and k'_{9-2} can be calculated.

Thus for PCB009,

$$\frac{d[9]}{dt} = -(k'_{9-1} + k'_{9-2})[9] \quad (5.1.2-12)$$

And taking the integral on both sides leads to;

$$\int_0^t \frac{d[9]}{[9]} = - \int_0^t (k'_{9-1} + k'_{9-2}) dt$$

$$\therefore \ln \frac{[9]_t}{[9]_0} = -(k'_{9-1} + k'_{9-2})t \quad (5.1.2-13)$$

And thus a plot of $\ln [9]_t / [9]_0$ versus time gives a slope of $-(k'_{9-1} + k'_{9-2})$.

It should then be true that the rate constant determined from plotting $\ln [9]_t / [9]_0$ versus time has the same value as the sum of the individual rate constants determined using equation (5.1.2-8) and (5.1.2-9).

5.2 METHODS AND MATERIALS

5.2.1 Materials

The reagents used in this section were same as in Chapter 4 except for all PCB neat standards (97+%) which were purchased from UltraScientific. Optima grade acetonitrile was obtained from Fisher Scientific. Table 5.2-1 is the list of all PCB congeners used for this study.

Table 5.2-1: List of PCB congeners used for this study

PCB#	Number of Cl	Chlorine Position
001	1	2-
002	1	3-
003	1	4-
004	2	2,2'-
006	2	2,3'-
007	2	2,4-
008	2	2,4'-
009	2	2,5-
012	2	3,4-
017	3	2,2',4-
018	3	2,2',5-
025	3	2,3',4-
028	3	2,4,4'-
033	3	2',3,4-
048	4	2,2',4,5-
066	4	2,3',4,4'-
101	5	2,2',4,5,5'-
118	5	2,3',4,4',5-

5.2.2 Recovery from Florisil Trap: Solvent Effects

Florisil (0.3 g) was weighed into a 2mL vial with 20 μ L of 2520ppm biphenyl standard solution in isopropanol, and 1.0mL of solvent (hexane, acetone, isopropanol, acetonitrile,

or dichloromethane). The solution was mixed well for 15 minutes, and the suspension was analyzed by GC/MS. The experiment was repeated with hexane and isopropanol two more times. The relative standard deviation resulted in 9.6% and 2.3%, respectively.

5.2.3 Dechlorination of PCBs

In liquid isopropanol

25 μ L of a 500 ppm 4-chlorobiphenyl standard was added to 5 mL of isopropanol in a round-bottom flask of a refluxing system. The solution was heated to reflux (82.5°C) using a hot water bath. 0.034 ± 0.001 g of 5% Pd/ γ -Al₂O₃ was added to the reaction mixture at time zero. A sample (90 μ L) was taken after 1 minute of refluxing and every 3 minutes up to 9 minutes. The sample was centrifuged for 2 minutes (4000 rpm) and the supernatant was analysed by GC-FID.

The activation energy was determined between the temperatures 47.3 and 82.5°C using the same procedure as above.

In supercritical CO₂

The same procedure was followed as for dechlorination of C₁₈-Cl as described in section 4.2.3. The PCB was introduced into the reaction cell as 112.5 μ L of an appropriate 500 ppm solution in isopropanol. The cell was charged with CO₂ to the desired pressure, and the reaction mixture was stirred for 5 min. The outlet and inlet of the reaction cell were opened for 5 min to purge the cell contents into 3 mL of isopropanol in a 10 mL vial through a Florisil trap. The inlet of the reaction cell was closed and the cell was depressurized to 1 atm. The trap and the cell were rinsed out to recover any remaining reaction products as follows. The trap was then washed with ~2 mL hexane (up to 5 mL) followed by ~2 mL isopropanol (up to 7 mL). Approximately 1.5 mL of CH₃CN was added to the cell, transferred to a 2 mL vial, sonicated for 10 min, then centrifuged for 10 min at 4000 rpm. The suspension was transferred into the vial, and this was repeated again with

fresh CH_3CN solution, which made the total volume to 10mL. The collected solution was then mixed well, a portion of it was transferred to a 2mL vial, and centrifuged at the same speed for 5 min to separate any catalyst might have escaped from the cell. The suspension was then analyzed by GC with FID, ECD, or MS-SIM.

For the determination of rate constants, the dechlorinations of PCB congeners were performed in SC-CO_2 as above for various times ranging from 1 minute to 40 minutes. Typical experiments were performed for 1, 5, 10, 15, and 25 minutes. At least duplicate runs were done for each time. Dechlorination rates of the starting PCBs were calculated from the initial slope of concentration versus time. Dechlorination rates of intermediate PCBs were calculated at later times, when their concentrations were closer to their maximum.

Activation energy was determined at temperatures from 60°C to 80°C. The density of the reaction system was maintained at 0.63 ± 0.02 g/mL by adjusting pressure at each temperature. The required pressures were those predicted by the SFSolver program and are summarized in Table 5.2-2. The reaction time of 5 minutes was used for all experiments.

Table 5.2-2: Pressure selected for determination of activation energy at each temperature for $\rho = 0.63$ g/mL

Temperature (°C)	Pressure (atm)
60	155
65	170
70	185
75	200
80	216

5.2.4 Analytical Methods

For GC/FID and ECD, the column was a 30m Megabore DB-5 (0.5mm i.d., 0.25 μ m film thickness). The GC temperature program used was 110°C for 3 min, followed by a ramp at 5°C/min to 220°C, held for 0 min, then ramped at 30°C/min to 300°C and held for 1 minute, giving a total analysis time of 29.20 min.

For GC/MS analysis, temperature program started at 110°C held for 3 minutes, followed by a ramp at 5°C/min to 205°C followed by a ramp at 30°C/min to 280°C, held for 1 minute. The total analysis time was 23 minutes. MS analysis was performed in selective ion mode using the masses shown in Table 5.2-3.

Table 5.2-3: Mass range chosen for MS/SIM

Segment	Analyte Name	Mass Range	Time (min)
1	Biphenyl	150 – 157	11
2	Monochlorobiphenyl	140 – 200	4
3	Dichlorobiphenyl	140 – 230	3
4	Trichlorobiphenyl	225 – 265	5
Total			23

5.2.5 Theoretical Calculations

Rotational Barriers

The AM1 semi-empirical method, as implemented in the Spartan program [18] was used to determine the geometry of all species. Geometry optimizations were performed on the biphenyl structures, both with and without dihedral constraints, to obtain the minimum and maximum energy structures, respectively. In all cases, the maximum energy structures were planar. Single-point energies of these structures were calculated by the

B3LYP/6-31G(d) method, as implemented in Gaussian 98 [19]. The rotational barrier was taken as the electronic energy difference between the maximum and minimum energy structures.

Bond Dissociation Energy

All gas-phase Bond Dissociation Enthalpies (BDEs) were calculated by the lower-level method of DiLabio and Pratt [20]. This method is known to yield C-Cl BDEs to an accuracy of $\approx 8 \text{ kJ mol}^{-1}$. The AM1 method of the Spartan program was used for geometry optimization and frequency calculations for all species [18]. The frequencies were scaled by a factor of 0.973 to obtain zero point energy correction for vibrational enthalpy. The translational, rotational, and vibrational enthalpy components were summed to yield the thermal correction to the enthalpy for each species. Single-point energy calculations were performed using the (RO)B3P86/6-311G(d,p) method, with the Gaussian 98 program [19]. The electronic energy from the density functional theory (DFT) calculation was added to the enthalpy correction from the AM1 step to yield the enthalpy of each species. BDEs for the reaction; $\text{R-Cl} \rightarrow \text{R}\cdot + \text{Cl}\cdot$ then were calculated by the equation;

$$\text{BDE} = \Delta H_{\text{R}\cdot} + \Delta H_{\text{Cl}\cdot} - \Delta H_{\text{R-Cl}}.$$

Molecular Orbitals and Their Coefficients

Molecular orbital coefficients were calculated using the AM1 semi-empirical method of the Spartan program [18] for the minimum energy structure. The geometry optimizations were performed for all species to ensure the minimum energy structure. The coefficient obtained for each atom in the molecule was normalized by taking the squares of each coefficient.

5.3 RESULTS AND DISCUSSION

5.3.1 Selection of PCB Congeners

Two pentachlorobiphenyls were chosen to study the dechlorination pathways of PCBs; PCB101 (2,2',4,5,5'-pentachlorobiphenyl) and PCB118 (2,3',4,4',5-pentachlorobiphenyl). The selection was made based on the difference in the number of *ortho*-chlorines present on the ring while maintaining the same total number of Cl atoms on the ring. PCB101 has two *ortho*-chlorines and PCB118 has one *ortho*-chlorine. As the steric factor is considered to play an important role in catalytic hydrodechlorination, the difference in the rotational energy barrier of the two phenyl rings was expected to change the rate of dechlorination to a significant extent. This is because a rotationally hindered PCB may not interact with the catalyst surface in the same manner as the one which is not as rotationally hindered.

Dechlorination of these two molecules lead to many possible dechlorination pathways which are shown in Figure 5.3-1 and Figure 5.3-2. Although these two figures may seem very complicated, not all pathways are expected to be undertaken in reality considering many factors that controls the reaction. As a matter of fact, when dechlorination of these two congeners were performed, there were only a few congeners that were present at a quantitative level as intermediates. Those are indicated in blue and the major intermediates at each chlorination level (i.e., di-, tri-, or tetra- chlorobiphenyl) are shown in red. The congeners found to be the major dechlorination intermediates were PCB009, 018, 048 for PCB101 and PCB012, 033, and 066 for PCB118, at di-, tri- and tetra-chlorobiphenyl groups, respectively. The rate constants were determined for these intermediate as well as for other congeners which were their intermediates. Most thorough studies were done on PCB001, 002, and 003, as they were the simplest PCBs of all and should give us the very fundamental understanding of the dechlorination scheme.

Figure 5.3-1: Possible dechlorination pathways of PCB101: Observed (blue) and major (red) intermediates

Figure 5.3-2: Possible dechlorination pathways of PCB118: Observed (blue) and major (red) intermediate¹⁵

5.3.2 Recovery from Florisil Trap

Five different solvents were tested for recovery of biphenyl from the Florisil trap; hexane, acetone, isopropanol, acetonitrile, and dichloromethane. Hexane, isopropanol, and dichloromethane showed almost complete recovery of 94, 93, and 101 %, respectively, while acetone and acetonitrile resulted in lower values (79 and 70 %, respectively). This was different from the recovery of biphenyl from the catalyst where acetonitrile showed significantly higher recovery than acetone (63% versus 38% by introduction to the reaction system for dechlorination of Aroclor 1254). Hexane and isopropanol were used for recovery of the products.

The reaction products were collected into isopropanol in a vial through a Florisil trap. Using biphenyl, approximately 55 % was collected in a vial, 25 % was collected in the trap, and 20 % was collected from washing the catalyst after the reaction, indicating the importance of placing the trap at the collection stage. While the ratio of PCB001 to biphenyl collected in the vial and the trap remained consistent, it was only biphenyl that was collected from washing the catalyst, showing its strong affinity towards the catalyst surface. The same observation was made when other monochlorobiphenyls or even Aroclor 1254 were used, indicating that there is not a significant difference among PCB congeners.

When the catalyst was washed with a solvent just by mixing using a Vortex, washing was required 5 times with a fresh solvent to completely desorb all the biphenyl from the catalyst surface. When sonication was applied, it was complete with 3 washings. This is another indication of a strong affinity of biphenyl with the catalyst surface, likely due to the π conjugation of aromatic ring interacting preferentially with the catalyst surface. Attachment of one Cl atom on the ring is apparently significant enough to deactivate the resonance of the conjugation system to change the affinity towards the surface. The

difference among PCB congeners themselves was not large enough to observe the effect, i.e., all congeners were quantitatively desorbed from the catalyst.

5.3.3 Rate-Limiting Step

A plot of rate versus initial concentration of PCB003 (Figure 5.3-3) indicated that the rate limiting step for the reaction is the surface reaction, contrary to the other molecules studied (Chapter 4) where adsorption was shown to be the rate limiting step. Although scattering of data points was quite significant, it is evident that the plot rises initially then levels off, characteristic of the rate-limiting step being a surface reaction.

Since PCB003 is essentially a non-polar species, it would diffuse thorough the boundary layer relatively quickly, as did $C_{18}\text{-Cl}$. The fact that the rate-limiting step in the case of PCB003 is the surface reaction is in agreement with this, i.e., the surface reaction is slower than adsorption. Some of the physical properties of PCB003 and the other compounds as well as their rate constants and deduced rate limiting steps are presented in Table 5.3-1. It has been reported that dechlorination of an aromatic chloride is more energetically demanding than those of an aliphatic chloride [15]. This is in agreement with the difference observed between $C_{18}\text{-Cl}$ and PCB003 where the earlier is adsorption limited with higher rate constant and the latter is surface reaction limited with a lower rate constant.

Table 5.3-1: Physical properties of reacting molecules

	$C_{18}\text{-Cl}$	Stearic- Cl_2	DHA- Cl_2	PCB003
Polarity	Non-polar	Polar	Polar	Non-polar
Structure	Aliphatic	Aliphatic	Aromatic	Aromatic
Rate-limiting step	Adsorption	Adsorption	Adsorption	Surface reaction
Rate constant ($\text{min}^{-1}\text{m}^{-2}$)	0.10	0.010	> 0.013	0.079

Figure 5.3-3: Initial rate of dechlorination as a function of the initial concentration of PCB003 (4-chlorobipenyl) in supercritical CO₂
 (T = 80°C, P = 100 atm, Pd/PCB = 17, reaction time = 5 min)

5.3.4 Kinetic Analysis of the Dechlorinations of PCBs

Typical plots of concentration of reactants and dechlorination products versus time are shown for PCB003 (Figure 5.3-4), PCB009 (Figure 5.3-5), PCB018 (Figure 5.3-6). Generally speaking, the lower chlorinated congeners dechlorinated faster. As the number of chlorines was increased, the number of dechlorination products increased, and therefore it was considered more difficult to quantitatively analyze the concentration of dechlorinated products since the concentration of each product was lower. With a pentachlorobiphenyl (i.e., PCB118), the concentrations of the majority of the intermediate congeners were not detected even with a use of an electron capture detector. For the lower chlorinated congeners which produce less intermediates, an analysis was done to determine the rate constant for each dechlorination pathway. For example, PCB009 loses one chlorine to produce PCB001 or PCB002, then another to produce biphenyl. The rate constant for disappearance of PCB009 should be the sum of the rate constants for the two initial dechlorination steps. These individual rate constants were determined using the slope method. Data analysis for this process was done on a spreadsheet as shown in Table 5.3-2. The concentration of each congener was calculated from the GC analysis at each time, the rate and the mean concentration were calculated between the each successive time intervals, and the rate constants for individual dechlorination pathways to produce each intermediate were calculated using equations introduced earlier (equation 5.1.2-8 and 5.1.2-9). The sum of the all individual rate constants was then calculated (i.e., $k_{9,1} + k_{9,2}$) and compared to the rate constant obtained for the dechlorination of the starting PCB (i.e., PCB009). Some of the networks could be readily excluded as they gave rise to a negative value of one or more of these constants. The time chosen to evaluate the rate constants was typically closer to 50 % dechlorination, when there were easily measurable quantities of the reactant, intermediates, and the product. At that time, the difference between the rate constant of the starting PCB (i.e., k_9 for PCB009) and sum of the rate constants to all the individual intermediates (i.e., $k_{9,1}$ for PCB001 and $k_{9,2}$ for PCB002) was a minimum. The rate of dechlorination of the starting PCB was calculated from the

plot of $\ln [\text{PCB}]_t/[\text{PCB}]_0$ versus time for each congener. An example of such a plot for PCB009 is shown in Figure 5.3-7.

Table 5.3-2: Spread sheet for determination of rate constants for PCB009

Reaction Time	(min)	1	5	10	15	20	25
Concentration	BP	2.1	5.9	9.4	13	23	24
[]	PCB001	0.97	3.9	6.1	8.6	8.9	8.9
($\mu\text{mole mL}^{-1}$)	PCB002	1.1	1.5	2.0	2.4	2.0	2.3
	PCB009	59	52	46	39	29	28
$D[]/dt$	BP	0.93	0.70	0.78	2.0	0.16	
($\mu\text{mole mL}^{-1}\text{min}^{-1}$)	PCB001	0.73	0.45	0.50	0.062	-0.0030	
	PCB002	0.093	0.11	0.076	-0.085	0.070	
	PCB009	-1.8	-1.3	-1.3	-2.0	-0.23	
[] (mean)	BP	4.0	7.6	11	18	24	
($\mu\text{mole mL}^{-1}$)	PCB001	2.4	5.1	7.4	8.8	8.9	
	PCB002	1.3	1.8	2.2	2.2	2.2	
	PCB009	56	49	43	34	28	
Rate Constant: k	k_{9-1}	0.013	0.013	0.020	0.018	0.020	
($\text{min}^{-1}\text{m}^{-2}$)	k_{9-2}	0.0030	0.0040	0.0040	0.0020	0.0060	
Sum	$k_{9-1} + k_{9-2}$	0.015	0.017	0.024	0.019	0.026	
K_9	-slope	0.025	0.025	0.025	0.025	0.025	
$(k_{9-1} + k_{9-2}) - k_9$		-0.010	-0.0080	-0.001	-0.0060	0.0010	
% difference		-38	-31	-3.26	-23	2.6	

The column in bold text shows the time where the difference between the rate of disappearance of the starting PCB and the sum of the rate constants for two intermediates (i.e., $\text{PCB009} \rightarrow \text{PCB002}$ and $\text{PCB009} \rightarrow \text{PCB001}$) is a minimum. It was generally the case that the precise quantitation was difficult at shorter or longer times, as the concentrations of the intermediates were too low.

Figure 5.3-4: Kinetic Curve for dechlorination of PCB003 (4-chlorobiphenyl)
(● Biphenyl, ○ PCB003)

Figure 5.3-5: Kinetic Curve for dechlorination of PCB009 (2,5-dichlorobiphenyl)
(● Biphenyl, ○ PCB001, ▼ PCB002, ▽ PCB009)

Figure 5.3-6: Kinetic Curve for dechlorination of PCB018 (2,2',5-dichlorobiphenyl)
 (○ Biphenyl, ● PCB002, ▼ PCB004, ▽ PCB009, ■ PCB006, △ PCB018)

Figure 5.3-7: Kinetic plot for determination of rate constant for PCB009 (2,5-dichlorobiphenyl): $y = -0.033 - 0.024x$, $r^2 = 0.96$

5.3.5 Rate Constants and Dechlorination Pathways

The rate constant for dechlorination of 3 monochlorobiphenyls, 6 dichlorobiphenyls, 5 trichlorobiphenyls, 2 tetrachlorobiphenyls, and 2 pentachlorobiphenyls are summarized in Table 5.3-3. Most of the values were obtained with good precision indicated by the standard error of estimate. All the rate constants (k) were normalized by the surface area of catalyst used and are presented in units of $\text{min}^{-1}\text{m}^{-2}$ in Table 5.3-3.

Table 5.3-3: Rate constants (k) for dechlorination of PCB congeners

	PCB #	Chlorine Position	k ($\text{min}^{-1}\text{m}^{-2}$)	Std error ($\text{min}^{-1}\text{m}^{-2}$)	r ²
Monochlorobiphenyl	001	2-	0.063	0.004	0.97
	002	3-	0.054	0.003	0.996
	003	4-	0.079	0.006	0.95
Dichlorobiphenyl	004	2,2'-	0.006	0.001	0.88
	006	2,3'-	0.019	0.002	0.95
	007	2,4-	0.022	0.001	0.99
	008	2,4'-	0.016	0.001	0.98
	009	2,5-	0.025	0.002	0.96
	012	3,4-	0.016	0.002	0.90
Trichlorobiphenyl	017	2,2',4-	0.084	0.014	0.81
	018	2,2',5-	0.036	0.001	0.99
	025	2,3',4-	0.094	0.011	0.94
	028	2,4,4'-	0.068	0.024	0.90
	033	2',3,4-	0.034	0.005	0.85
Tetrachlorobiphenyl	048	2,2',4,5-	0.053	0.007	0.93
	066	2,3',4,4'-	0.040	0.008	0.79
Pentachlorobiphenyl	101	2,2',4,5,5'-	0.016	0.002	0.93
	118	2,3',4,4',5-	0.016	0.003	0.89

Generally speaking, the lower chlorinated congeners resulted in the higher rate constants. The discrepancy was observed between di- and tri- congeners where the rate constants of tri-congeners were higher than di-congeners. This was considered due to the increase in the number of pathways possible for dechlorination to proceed. Dechlorination pathways for each group of congeners will be discussed in more detail in later sections. The

relationship between the number of chlorine atoms on the starting PCB and the corresponding rate constants is shown in Figure 5.3-8. The effective rate constants, defined by Murena, which are the rate constants divided by the number of chlorines on the starting PCBs, were also calculated. These values were plotted against the number of chlorine atoms as shown in Figure 5.3-9.

The substitution effect of chlorine atoms in monochlorobiphenyl did not result in any extreme difference in the rate constants, although there was an increasing trend going from *meta*-, to *ortho*- to *para*-substitution, which is different from the earlier work reported by Murena [1]. Steric hindrance at the *ortho*-position did not seem to be a factor in dechlorination of monochlorobiphenyls. The dichlorobiphenyl with the lowest rate constant was PCB004 (2,2'-dichlorobiphenyl) where two *ortho*-chlorines are present, one on each ring. While steric hindrance may play a role, it is also possible that the low rate constant can be attributed to non-planarity of the molecule due to a higher rotational barrier at the center of the molecule. The rate constants for the rest of the dichlorobiphenyls varied significantly from each other. The rate constants of trichlorobiphenyls resulted in rather large differences among them, however a trend in dechlorination pathways was not clear from the data. Tetrachlorobiphenyls and pentachlorobiphenyls resulted in similar rate constants among themselves.

The congeners included in Table 5.3-3 are the major intermediates found from the dechlorination of the two starting congeners (PCB101 and PCB118), as well as possible parents of the major intermediates. The overall trend, that the rate constants were lower for more heavily chlorinated congeners, is in agreement with earlier work [1, 8, 10, 11].

Rate constants versus number of Cl atoms on PCB

The rate constants determined for all congeners studied were plotted against the number of chlorine atoms on the starting PCB as shown in Figure 5.3-8. A general trend of lower

rate constant with increasing number of chlorine atoms is observed with a discrepancy for dichlorobiphenyls as discussed earlier. A clear gap is observed in rate constants for di- and tri-chlorobiphenyl, which will be discussed later in more detail.

The effective rate constants were calculated by dividing the rate constants by the number of chlorine atoms on the starting PCB as described by Murena [1], and plotted against the number of chlorine atoms on the reacting PCB molecule. There was a general trend of decreasing rate constant with increasing number of chlorine atoms although there still is a 'break' at dichlorobiphenyl where the effective rate constants become lower than those of trichlorobiphenyl as shown on Figure 5.3-9, and this was also observed by the earlier study where the effective rate constants of dichlorobiphenyl are lower than those of monochlorobiphenyl and trichlorobiphenyl. The general shape of the plot of averaged values are in agreement with Murena's work. The difference in less scattering at higher number of chlorine atoms simply originates in the fact that a smaller number of congeners were determined in this work.

Figure 5.3-9: Rate constants of dechlorination reaction as a function of the total chlorine number on the starting PCB

Figure 5.3-10: Effective Rate constants of dechlorination reaction as a function of the total chlorine number on the starting PCB (Averaged value indicated as ▲)

5.3.6 Dechlorination Pathways and Selectivity

Monochlorobiphenyls

The rate constants did not show significant differences among the three monochlorobiphenyls. A similar observation was made by [13] under different dechlorination conditions (H_2 atmosphere with Ni-Mo/ γ - Al_2O_3 catalyst). The relative values of the rate constants obtained for monochlorobiphenyls are summarized in Table 5.3-4 for two systems.

Table 5.3-4: Comparison of relative rate constants (with respect to values of PCB001)

PCB#	Cl position	k ($\text{min}^{-1}\text{m}^{-2}$)	This work	Murena
001	<i>Ortho</i>	0.063 ± 0.004	1.0	1.0
002	<i>Meta</i>	0.054 ± 0.003	0.9	1.0
003	<i>Para</i>	0.079 ± 0.006	1.3	1.1

In both systems, *para*-substituted biphenyl has the highest rate constant, while the order of *ortho*- and *meta*-substituted changes. Murena's work showed very similar values between the *meta*- and *ortho*-substituted PCBs while the *meta*-substituted congeners showed slightly lower value in the present work. The steric hindrance of the *ortho*-substitution position may be a reason for its lower values in both systems. The lower value of *meta*-substituted PCB found in the current work may be an indication of the reaction mechanism being an electrophilic substitution where there is no stabilization effect on the carbocation intermediate by hydrogen attack on the *meta*-position as is on *ortho*- or *para*- positions, thus the attack on *ortho*- or *para*-positions is preferred over the *meta*-position. Although this was also the mechanism proposed by Murena, monochlorobiphenyls were shown not to be affected by this inductive effect in their work. The reason as to why monochlorobiphenyls exhibit the observed order of rate constants is not clear. The electrophilic substitution mechanism proposed by Hagh and Allen [12] is

based on the consideration that the inductive effects alone dominate the selectivity of the reaction as the resonance effect is reduced due to the interaction of the π electrons and the anion vacancies on the catalyst surface. Such consideration may not be adequate in the current system as the catalytic system is different and the apparent difference in the affinity towards the catalyst surface was observed between biphenyl and PCB molecules, i.e., strong interaction between the π electrons and the catalyst surface may not take place to the same extent. Therefore both inductive and resonance effects may play significant roles.

Dichlorobiphenyls

The rate constants for a total of 6 dichlorobiphenyls were determined. PCB004 (2,2'-dichlorobiphenyl) had a significantly lower rate constant than any other dichlorobiphenyl. A positive correlation between the number of *ortho*-chlorine atoms and the rotational energy barrier is shown in Figure 5.3-10. The exceptionally high value of the rotational energy barrier obtained for PCB004 was due to the fact that each ring has one *ortho*-chlorine atom. If two *ortho*-chlorines are present both on the same ring, the resulting rotational energy barrier would be much lower than the range of values obtained with one *ortho*-chlorine.

The low rate constant obtained for PCB004 could be attributed to the fact that this molecule is non-planar and therefore would be more difficult to interact with the catalyst surface (i.e., a good overlap of molecular orbitals might not be possible due to its non-planar conformation). Table 5.3-5 shows the rate constants for each dechlorination pathway and the rotational energy barrier.

Figure 5.3-10: Relationship between the number of chlorine atoms on dichlorobiphenyl and corresponding rotational energy barrier calculated on six dichlorobiphenyls studied

Table 5.3-5: Rate constants (k) for dechlorination of dichlorobiphenyls and the calculated rotational energy barrier (E_r) [18]

PCB#	Chlorine Positions	k ($\text{min}^{-1}\text{m}^{-2}$)	E_r (kcal/mol)
004	2,2'-	0.006	33.2
006	2,3'-	0.019	8.5
007	2,4 -	0.022	8.8
008	2,4'-	0.016	8.7
009	2,5-	0.025	9.0
012	3,4-	0.016	2.4

In order to understand the dechlorination pathways, the six dichlorobiphenyls were divided into two groups; PCB004 (2,2'-), PCB006 (2,3'-), and PCB008 (2,4'-) have two chlorine atoms on separate rings and PCB007 (2,4-), PCB009 (2,5-) and PCB012 (3,4-) have two chlorines on the same ring. The observed dechlorination pathways for the former group with the rate constants are shown in Figure 5.3-11 and those of the latter group are shown in Figure 5.3-12, where total value is the rate constant for the disappearance of the starting PCB (dichlorobiphenyl).

All the congeners having one *ortho* chlorine (PCB006, 007, 008, and 009) preferentially dechlorinated to PCB001 (2-). This is also clear by a comparison of the k values shown in Table 5.3-6. The bold text indicates the pathways for dissociation of *ortho*-chlorines, and resulted in much lower rate constants than the pathways to form PCB001 as an intermediate.

It is apparent from Table 5.3-6 that the removal of *ortho*-chlorine is less favored than the removal of a non *ortho*-chlorine. The rate constants between the three monochlorobiphenyls were much higher (0.054 to $0.079 \text{ min}^{-1}\text{m}^{-2}$) than those of dichlorobiphenyls and not significantly different from each other. Thus, it is evident that the higher rate constants for producing PCB001 (0.013 to $0.020 \text{ min}^{-1}\text{m}^{-2}$) than for

PCB002 (0.002 to $0.006 \text{ min}^{-1}\text{m}^{-2}$) or PCB003 ($0.005 \text{ min}^{-1}\text{m}^{-2}$) indicate faster dechlorination process to PCB001 than PCB002 or PCB003, and are not because the monochlorobiphenyl intermediates then dechlorinated at a different rate to biphenyl.

Table 5.3-6: Comparison of rate constants for individual dechlorination pathways for dichlorobiphenyls containing one ortho-chlorine atom

Starting PCB#	Chlorine Position	Dissociated Cl Position	Intermediate Formed	k for individual step ($\text{min}^{-1}\text{m}^{-2}$)
006	2,3'-	3'-	001	0.016
		2 -	002	0.003
007	2,4 -	4 -	001	0.018
		2 -	003	0.005
008	2,4'-	4'-	001	0.013
		2 -	002	0.002
009	2,5-	5 -	001	0.020
		2 -	002	0.006

The results from the dechlorination of PCB012 (3,4-) offer an insight into the mechanism of the surface reaction (Figure 5.3-12, bottom). The rate constant found from the initial slope was $0.016 \text{ min}^{-1}\text{m}^{-2}$. Those of the intermediates of PCB002 (k_{12-2}) and PCB003 (k_{12-3}) were $0.004 \text{ min}^{-1}\text{m}^{-2}$ and $0.003 \text{ min}^{-1}\text{m}^{-2}$, respectively giving the sum of only $0.007 \text{ min}^{-1}\text{m}^{-2}$. The large difference of $0.009 \text{ min}^{-1}\text{m}^{-2}$ obtained between the sum k_{12-2} and k_{12-3} and the total rate constant suggests that a third pathway for dechlorination of PCB012 is possible, i.e., the loss of two chlorines in one step. This would reduce the observed concentrations of both PCB002 and PCB003, and the resulting dechlorination pathway would then be as illustrated in Figure 5.3-12 (bottom), i.e., with an additional pathway to form biphenyl directly from PCB012 with the rate constant being the difference of the total and sum of the individual pathways ($0.009 \text{ min}^{-1}\text{m}^{-2}$).

Figure 5.3-11: Dechlorination pathways for PCB004 (2,2'-dichlorobiphenyl), PCB006 (2,3'-dichlorobiphenyl), and PCB008 (2,4'-dichlorobiphenyl); Total indicates 'total rate constant ($\text{min}^{-1}\text{m}^{-2}$)

PCB004

Total (-slope) = 0.006

PCB006

Total (-slope) = $k_{6-1} + k_{6-2} = 0.019$

PCB008

Total (-slope) = 0.016

$k_{8-1} + k_{8-3} = 0.015$

Figure 5.3-12: Dechlorination pathways of PCB007 (2,4-dichlorobiphenyl), PCB009 (2,5-dichlorobiphenyl), and PCB012 (3,4-dichlorobiphenyl), k ($\text{min}^{-1}\text{m}^{-2}$)

PCB007

Total (-slope) = 0.022

$$k_{7-1} + k_{7-3} = 0.023$$

PCB009

Total (-slope) = 0.025

$$k_{9-1} + k_{9-2} = 0.024$$

PCB012

Total (-slope) = 0.016

$$k_{12-2} + k_{12-3} + k_{12-B} = 0.016$$

This was not observed for any other dichlorobiphenyls (except for PCB004 where loss of either chlorine would result in the same intermediate; PCB001). For example referring to Figure 5.3-12, for PCB007 (2,4-) had the total rate constant of $0.022 \pm 0.001 \text{ min}^{-1}\text{m}^{-2}$ and the sum of the individual rate constants added up to $0.023 \pm 0.002 \text{ min}^{-1}\text{m}^{-2}$. For PCB009 (2,5-) on the same figure, the total rate constant was $0.025 \pm 0.002 \text{ min}^{-1}\text{m}^{-2}$ and the sum of the individual rate constants added up to $0.026 \pm 0.002 \text{ min}^{-1}\text{m}^{-2}$. In both cases, there is no difference between the total rate constant and the sum of the individual steps within the error. Table 5.3-7 summarizes the individual rate constants for each dechlorination pathways for dichlorobiphenyls. The ratio of the sum of the individual rate constants to the total rate constant was calculated as a measure of how much multiple dechlorination takes place before desorption of the product. Much smaller ratio obtained for PCB012 (0.44) compared to other dichlorobiphenyls (approximately 1.00) clearly indicates that PCB012 is the only congener with an extra dechlorination pathway (i.e., a large difference between the total k and the sum of individual rate constants).

Table 5.3-7: Comparison between the total rate constant (k) and the sum of individual rate constants (k_i) for dechlorination of dichlorobiphenyls

Starting PCB#	Cl Position	Total k ($\text{min}^{-1}\text{m}^{-2}$)	k_i ($\text{min}^{-1}\text{m}^{-2}$)			Sum of k_i ($\text{min}^{-1}\text{m}^{-2}$)	k_i / k
			001	002	003		
006	2,3'-	0.019	0.016	0.003		0.019	1.00
007	2,4 -	0.022	0.018		0.005	0.023	1.05
008	2,4'-	0.016	0.013	0.002		0.015	0.94
009	2,5-	0.025	0.020	0.006		0.026	1.04
012	3,4-	0.016		0.004	0.003	0.007	0.44

It is apparent from Table 5.3-7 that PCB012 is the only dichlorobiphenyl that resulted in the large difference between the total rate constant and the sum of the individual rate constants, and therefore this is the only congener among all the dichlorobiphenyls studied that undergo multiple dechlorination. Multiple dechlorination can be more precisely

defined as a subsequent dissociation of another chlorine atom prior to the desorption of the intermediate. Therefore dissociation still occurs in a sequential manner but more than one step can proceed before the intermediate desorbs from the catalyst surface. One apparent structural difference between PCB012 and the rest of the dichlorobiphenyls is that PCB012 does not contain any *ortho*-chlorine atoms. The fact that the pathway to produce PCB001 was always faster than either to produce PCB002 or PCB003 indicates that dissociation of *ortho*-chlorine from dichlorobiphenyl is not a preferred pathway although this was not the case with monochlorobiphenyl (i.e., the rate constants for *ortho*-chlorine dissociation was higher than for *meta*-chlorine dissociation). This suggests then that the addition of another chlorine and which substitution position it takes determines the selectivity in dechlorination pathways. Steric hindrance in *ortho*-substitution position (due to a presence of adjacent ring) may become a dominant factor in the selectivity of dechlorination pathway for dichlorobiphenyls.

The earlier statement regarding the fact that biphenyl was more significantly adsorbed on the catalyst surface than any other PCB congeners, together with the observed trend in the dechlorination of dichlorobiphenyl provides further insight into the mechanism of the surface reaction. A π conjugation system of an aromatic ring in biphenyl interacts preferentially with the surface resulting in the strong adsorption. The fact that this is lost by the addition of chlorine atoms (i.e., for PCBs) suggests that the π conjugation system is disturbed upon addition of chlorine atoms or that the interaction between the molecule (PCBs) and the catalyst surface may also be through other parts of the molecule. (i.e., the molecule may not adsorb flat on the catalyst surface). If it does not adsorb flat on the surface, both of the two chlorine atoms adjacent to each other in PCB012 could have a better interaction with the catalyst surface than the other dichlorobiphenyl congeners where two chlorines are separated by at least one carbon position. In the later case, one chlorine would have more preferential interaction with the catalyst surface while the other would be to the lesser extent. An *ortho*-chlorine having a large phenyl group adjacent is probably less accessible than the chlorines at the other positions.

Shin [14] and Murena [1] related the dechlorination rate to how many adjacent hydrogen atoms are present and that dechlorination proceeds faster when chlorine atom is in between two hydrogen atoms than two chlorine atoms. PCB012 is the only dichlorobiphenyl which always has another chlorine atom adjacent to the one being dissociated while all the other dichlorobiphenyl in Table 5.3-6 has at least one chlorine atom in between two hydrogen atoms, in agreement with the earlier work.

Shin [14] also showed that dechlorination of dichlorophenols proceeded simultaneously to a greater extent when two chlorines are adjacent to one another than when two chlorines are separated, which was evident in this work for dichlorobiphenyls.

Using the approach taken by Shin [3], when the inductive effect is solely considered, the difference in rate constants between PCB006 (2,3'-dichlorobiphenyl) and PCB008 (2,4'-dichlorobiphenyl) to produce PCB001 can be explained in terms of the nucleophilic substitution mechanism. In this case, hydride ion, proposed by Ukisu [5], the nucleophile attacks the PCB, and the intermediate formed will be a carboanion. This carboanion ion intermediate results in a delocalized negative charge on the carbon where the phenyl group is attached. The phenyl group being electron donating will destabilize the intermediate. This would be observed with PCB008 but not with PCB006 as there is neither electron withdrawing or donating group on any carbon where the delocalized negative charge exists as illustrated in Figure 5.3-13.

Figure 5.3-13: Carboanion intermediates for PCB006 and PCB008 to produce PCB001 showing relative stability

Figure 5.3-14 illustrates a similar effect considered for PCB007 (2,4-dichlorobiphenyl) and PCB009 (2,5-dichlorobiphenyl). The intermediate carboanion for PCB009 have Cl atom on the carbon with a negative charge stabilizing the ring while PCB007 have phenyl group destabilizing the ring, leading to higher rate constant for PCB009 than for PCB007 which was observed.

Figure 5.3-14: Carboanion intermediates for PCB007 and PCB009 to produce PCB001 showing relative stability

Inductive effects can not fully explain the size of the difference between the two sets of congeners, i.e., larger difference between PCB006 and PCB008 and smaller difference between PCB007 and PCB009. This nucleophilic substitution mechanism postulated for dichlorobiphenyls is contradictory to the earlier postulation of electrophilic substitution mechanism applied for monochlorobiphenyl. It is unlikely that two sets of congeners undergo different mechanisms of dechlorination as it would be governed by the form of hydrogen transfer from isopropanol not from PCB congeners.

Trichlorobiphenyls

The rate constants for five trichlorobiphenyls (0.034 to $0.094 \text{ min}^{-1} \text{ m}^{-2}$) were higher than those of dichlorobiphenyls (0.006 to $0.025 \text{ min}^{-1} \text{ m}^{-2}$). Dechlorination pathways for PCB017, PCB018, PCB025, PCB028, and PCB033 are shown in Figures 5.3-14, -15, -16, -17, and -18, respectively. With dichlorobiphenyls, PCB012 was the only congener which resulted in the further dechlorination of the intermediate prior to desorption. It was the case for all the trichlorobiphenyl congeners studied as shown in Table 5.3-8. However,

the sum of the individual rate constants were only up to 20% of the total rate constant. This was a clear indication that there was an appreciable amount of multiple dechlorination, leaving only small amounts of the immediate intermediates (dichlorobiphenyls) to be desorbed. Referring back to the earlier argument, the surface reaction takes place by many steps which can be broken down into the following steps; 1 - adsorption of the starting PCB on the catalyst surface in a most preferred orientation, 2 - dechlorination reaction to lose a chlorine atom, 3 - possible desorption resulting in the immediate intermediate (i.e., monochlorobiphenyl from dichlorobiphenyl, dichlorobiphenyl from trichlorobiphenyl, etc.), or loss of another chlorine atom with or without a rearrangement of the orientation of the intermediate on the catalyst surface, then 4 - possible desorption of the next intermediate (i.e., if the starting PCB was trichlorobiphenyl, then monochlorobiphenyl, etc), and so on. Steps 3 and 4 can be repeated as many times until the intermediate loses all chlorine atoms and becomes biphenyl, and the number of repetitions increases as the number of chlorine atoms increases on the starting PCB. As a result, a larger difference in the total rate constant and the sum of the individual rate constants are expected for the higher congeners.

Table 5.3-8: Comparison between the total rate constant (k) and the sum of individual rate constants (k_i) for dechlorination of trichlorobiphenyls

PCB #	Cl Position	k ($\text{min}^{-1}\text{m}^{-2}$)	Sum of k_i ($\text{min}^{-1}\text{m}^{-2}$)	k_i / k
017	2,2',4-	0.084	0.001	0.01
018	2,2',5-	0.036	0.007	0.19
025	2,3',4-	0.094	0.022	0.23
028	2,4,4'-	0.068	0.013	0.19
033	2',3,4-	0.034	0.005	0.15

Referring to Table 5.3-8, much lower values of the rate constants were obtained for PCB018 (2,2',4-) and PCB033 (2',3,4-); $0.036 \text{ min}^{-1}\text{m}^{-2}$ and $0.034 \text{ min}^{-1}\text{m}^{-2}$, respectively, compared to the rest of the congeners (0.068 to $0.094 \text{ min}^{-1}\text{m}^{-2}$). This difference is also

clearly shown in Figure 5.3-8. Although a clear explanation for the difference between these two groups of congeners was not found, the low rate constants for PCB018 and PCB033 may be the reason for these congeners being the major trichlorobiphenyls from the dechlorination of PCB101 and PCB118, respectively. The other trichlorobiphenyl congeners may have been formed as well but dechlorinated faster than PCB018 and 033 and therefore were not detected.

Table 5.3-9: Total and individual rate constants (k and k_i) for dechlorination pathways of trichlorobiphenyls with the rotational energy barrier (E_r)

PCB #	Cl Position	# of <i>Ortho</i> -Cl	k ($\text{min}^{-1}\text{m}^{-2}$)	Loss of Cl	Intermediate Formed	k_i ($\text{min}^{-1}\text{m}^{-2}$)	E_r (kcal/mol)
017	2,2',4-	2	0.084	2'-	007	0.000	32.6
				2 -	008	0.000	
				4 -	004	0.001	
018	2,2',5-	2	0.036	2'-	009	0.000	22.7
				5 -	004	0.007	
				2 -	006	0.000	
025	2,3',4-	1	0.094	4 -	006	0.012	8.8
				2 -	013	0.000	
				3'-	007	0.010	
028	2,4,4'-	1	0.068	4 -	008	0.006	8.5
				2 -	015	0.000	
				4'-	007	0.007	
033	2',3,4-	1	0.034	4 -	006	0.001	8.6
				3 -	008	0.000	
				2'-	012	0.004	

Significantly higher rotational energy barrier of 32.6 kcal/mol and 22.7 kcal/mol were calculated for PCB017 (2,2',4-) and PCB018 (2,2',5-), respectively, containing two *ortho*-chlorine atoms (one on each ring), than 8.5 – 8.8 kcal/mol for PCB025 (2,3',4-), PCB028 (2,4,4'-) and PCB033 (2',3,4-) which have only one *ortho*-chlorine atom (refer to Table 5.3-9). PCB017 and PCB018 both result in the formation of only PCB004 (2,2'-dichlorobiphenyl). The reason for this again may be a combination of *ortho*-chlorines

having greater steric hindrance and these PCB congeners being non-planar so that the interaction of the PCB and the catalyst surface is very limited to certain orientations thus allowing only non *ortho*-chlorines to have better interaction with the catalyst surface.

Dechlorination pathways of PCB017 are shown in Figure 5.3-15. PCB004 (2,2'-dichlorobiphenyl) was the only intermediate detected at a quantitative level. PCB001 (2-monochlorobiphenyl) must have been formed, but was not detected indicating that rearrangement of its orientation on the surface followed by further dechlorination to biphenyl had proceeded prior to desorption to give PCB001 as an intermediate.

Dechlorination pathways of PCB018 shown in Figure 5.3-16 shows somewhat different effect from PCB017. It was the same in that PCB004 (2,2'-dichlorobiphenyl) was the only intermediate detected among dichlorobiphenyl congeners, however in this case, PCB002 (3-monochlorobiphenyl) was also detected. The formation of PCB002 from PCB004 is not likely to occur and this confirms the formation of PCB006 (2,3'-dichlorobiphenyl) and PCB009 (2,5-dichlorobiphenyl), which then lost another chlorine atom to produce PCB002 as an intermediate. PCB001 (2-monochlorobiphenyl) which is the immediate intermediate from PCB004 was again not detected.

Another observation is clear when dechlorination pathways for PCB017 and PCB018 were compared to those of dichlorobiphenyls. Any dichlorobiphenyl intermediates for PCB017 or PCB018 (with the exception of PCB004) were expected to preferentially produce PCB001 from the results obtained earlier with dichlorobiphenyls. However PCB001 was not detected from dechlorinations of neither PCB017 nor PCB018. This then is an indication that a PCB behaves in the different manner depending on whether it is the starting PCB or the intermediate from higher congener, i.e., the initial orientation at the catalyst surface would have a significant effect on how the successive dechlorinations proceed.

Total (-slope) = 0.561
 $k_{17-7} + k_{17-8} + k_{17-4} = 0.001$

Figure 5.3-15: Dechlorination pathways for PCB017 (2,2',4-trichlorobiphenyl): A dotted line – not quantitatively confirmed

Figure 5.3-16: Decchlorination pathways for PCB018 (2,2',5-trichlorobiphenyl); A dotted line – not quantitatively confirmed

Finally the higher difference between the total rate constant and the sum of individual rate constant in PCB017 ($0.083 \text{ min}^{-1}\text{m}^{-2}$) than in PCB018 ($0.029 \text{ min}^{-1}\text{m}^{-2}$) on Table 5.3-8 supports the fact that there were more multiple dechlorination steps for in PCB017 than for PCB018.

PCB025 (2,3',4-), PCB028 (2,4,4'-) and PCB033 (2',3,4-) have one *ortho*-chlorine atom and dechlorination pathways for these three trichlorobiphenyl congeners produced more detectable intermediates than PCB017 and PCB018 (two *ortho*-chlorines, one on each ring). Referring to Figure 5.3-17 (PCB025) and Figure 5.3-18 (PCB028), dechlorination pathways were similar in the two cases where no loss of *ortho*-chlorine was detected to produce dichlorobiphenyls. Thus two dichlorobiphenyl intermediates with one *ortho*-chlorine were formed, and all possible monochlorobiphenyl intermediates were detected.

PCB033 (2',3,4-trichlorobiphenyl) on the other hand produced PCB012 (3,4-dichlorobiphenyl) as the major immediate intermediate, which was a result of loss of an *ortho*-chlorine atom (Figure 5.3-19). PCB033 is the only trichlorobiphenyl congener that contained two chlorine atoms adjacent to each other. No clear insight was gained as to why *ortho*-chlorine dissociates leaving the other two chlorines behind, however, it is conceivable that there is an extra interaction that stabilizes C-Cl bond on the ring where there is adjacent C-Cl bond. This is in agreement with the argument made by Singh [14] and Murena [1] described earlier that the dissociation of such C-Cl bond would be slower.

A clear correlation between the inductive effect and the individual rate constants was not found for any of the intermediates of trichlorobiphenyl congeners which agrees with neither of electrophilic nor nucleophilic substitution mechanism. A steric effect was observed with most congeners indicating that it was dominating the selectivity of dechlorination.

Tetrachlorobiphenyls

A large difference between the total rate constant and the sum of individual rate constants was obtained for PCB048 (2,2',4,5-tetrachlorobiphenyl) and PCB066 (2,3',4,4'-tetrachlorobiphenyl) as indicated in Table 5.3-10. The sum of the individual rate constants only accounted for approximately 5% of the total rate constant in each case. The individual rate constants themselves are much smaller and the errors associated with these values would result in higher uncertainty than with the trichlorobiphenyls. It is nevertheless apparent that multiple dechlorination of the starting PCB was the major pathway for dechlorination of PCB048 and PCB066.

The large difference in the rotational energy barriers calculated did not correspond to the rate constants. This indicates that when the number of chlorine atoms increases for higher congeners, there are many possible C-Cl bonds which can dissociate that the planarity of the congener would not play as significant a role. The same effect was observed even with trichlorobiphenyls where there was no obvious relationship between the rate constants and the rotational energy barrier, i.e., rate constant for PCB017 ($0.084 \text{ min}^{-1}\text{m}^{-2}$) was much higher than for PCB018 ($0.036 \text{ min}^{-1}\text{m}^{-2}$) even though both congeners had similar rotational energy barrier (32.6 kcal/mol and 22.7 kcal/mol, respectively) compared to the rest of the trichlorobiphenyls (8.5 to 8.8 kcal/mol).

Table 5.3-10: Total and individual rate constants (k and k_i) for dechlorination of tetrachlorobiphenyls with the rotational energy barrier (E_r)

PCB #	Chlorine Position	k ($\text{min}^{-1}\text{m}^{-2}$)	Sum of k_i ($\text{min}^{-1}\text{m}^{-2}$)	k_i / k	E_r (kcal/mol)
048	2,2',4,5-	0.053	0.003	0.06	32.3
066	2,3',4,4'-	0.040	0.001	0.03	8.6

Total (-slope) = 0.094
 $k_{25,6} + k_{25,13} + k_{25,7} = 0.022$

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Figure 5.3-17: Dechlorination Pathways for PCB025 (2,3,4-trichlorobiphenyl)

Figure 5.3-18: Decchlorination pathways for PCB028 (2,4,4'-trichlorobiphenyl)

Total (-slope) = 0.034
 $k_{33-6} + k_{33-8} + k_{33-12} = 0.005$

Figure 5.3-19: Dechlorination pathways for PCB033 (2',3,4-trichlorobiphenyl): Dotted line – not quantitatively confirmed

Referring to Figure 5.3-20, it is apparent that the dechlorination pathway of PCB048 was primarily via dissociation of non *ortho*-chlorines, so PCB018 (2,2',4-trichlorobiphenyl) and PCB017 (2,2',5-trichlorobiphenyl) were the major intermediates. The same was also true for PCB066 (2,3',4,4'-tetrachlorobiphenyl) as shown in Figure 5.3-21. In both cases, most of the possible dichlorobiphenyl intermediates were also detected.

Pentachlorobiphenyls

The starting pentachlorobiphenyls PCB101 (2,2',4,5,5'-) and PCB118 (2,3',4,4',5'-) had the same rate constants as one another, and each had only one major intermediate (PCB048 and PCB066, respectively as shown in Figure 5.3-22). The same observation was made as in previous cases where non *ortho*-chlorine dissociates preferentially. As it was for trichlorobiphenyls and tetrachlorobiphenyls, the rate constant did not relate to the rotational energy barrier as shown on Table 5.3-11 (i.e., the same rate constant with a large difference in rotational energy barrier), indicating the low importance of planarity of the reacting PCB at highly chlorinated congeners as there are so many C-Cl bonds to be dissociated.

The idea that the PCBs adsorb via the Cl atoms may also be reflected in the large differences between the rate constants for the disappearance of the parent PCBs and the sum of the rate constants for the individual steps. Since this difference is greater for the more highly chlorinated PCBs, it may suggest that more chlorines lead to higher adsorption energy, which in turn leads to more multiple dechlorinations before the product PCB (or biphenyl) desorbs.

Table 5.3-11: Total and individual rate constants (k and k_i) for dechlorination of pentachlorobiphenyls with the rotational energy barrier (E_r)

PCB #	Chlorine Position	k ($\text{min}^{-1}\text{m}^{-2}$)	Sum of k_i ($\text{min}^{-1}\text{m}^{-2}$)	k_i / k	E_r (kcal/mol)
101	2,2',4,5,5'-	0.016	0.010	0.63	21.4
118	2,3',4,4',5'-	0.016	0.002	0.13	8.3

It is also important to notice that PCB077 (3,3',4,4'-tetrachlorobiphenyl), which is a major dechlorination product of PCB118 in nature is the only intermediate congener which was not produced in the current system. In nature, dechlorination proceeds mostly by photolysis, hydrolysis or biodegradation, and these systems do not require PCB congeners to be adsorbed on the catalyst surface. Hence, the steric hindrance of the *ortho*-chlorine does not play as significant role in controlling these dechlorination pathways. *Ortho*-chlorine being more preferentially dechlorinated in the current system is a great advantage over the environmental systems, since the toxicity decreases as dechlorination proceeds, while in nature toxicity may increase as dechlorination proceeds further.

Figure 5.3-20: Dechlorination Pathways for PCB048 (2,2',4,5-tetrachlorobiphenyl): A dotted line – not quantitatively confirmed

Figure 5.3-21: Dechlorination Pathways for PCB066 (2,4,4',5-tetrachlorobiphenyl): A dotted line – not quantitatively confirmed

Figure 5.3-22: Dechlorination Pathways for PCB101 and PCB118 (penta- to tetra-) Dotted lines – not quantitatively confirmed

In summary of the rate constants and the observed dechlorination pathways, a systematic analysis was only possible for mono- and di-chlorobiphenyl congeners. From the comparison of dechlorination pathways between PCB012 (3,4-dichlorobiphenyl) and the rest of the dichlorobiphenyl congeners studied, the dechlorination was understood to proceed as follows.

- 1 – adsorption of the starting PCB on the catalyst surface in a most preferred orientation,
- 2 – dechlorination reaction to lose chlorine atom,
- 3 – possible desorption resulting in the immediate intermediate (i.e., monochlorobiphenyl from dichlorobiphenyl, dichlorobiphenyl from trichlorobiphenyl, etc.), or further dechlorination of another chlorine atom with or without a rearrangement of the orientation of the intermediate on the catalyst surface, then
- 4 – possible desorption of the next intermediate (i.e., if the starting PCB was trichlorobiphenyl, then monochlorobiphenyl, etc).

Steps 3 and 4 can be repeated as many times until the intermediate loses all chlorine atoms and becomes biphenyl, and the number of repetitions increases as the number of chlorine atoms increases on the starting PCB. Consequently, a larger difference in the total rate constant and the sum of the individual rate constants were observed for the higher congeners. This maybe a reflection of the stronger interaction of the higher chlorinated PCBs with the catalyst surface than of the lower chlorinated PCBs.

A steric effect was consistently observed with most of the dechlorination pathways. The general trend applies at any level of congeners that the *ortho*-chlorine is least likely to be dissociated when there are other chlorine atoms present. The dissociation of non-*ortho* chlorine takes place preferentially with some exceptions in higher chlorinated congeners.

Importance of the planarity of the starting PCB is lost with the higher congeners. This is shown by the lower correlation between the rate constant and the rotational energy barrier at tri- and higher congeners. On the other hand, there clearly is a relation in dichlorobiphenyls, where the rate constant of PCB004(2,2'-dichlorobiphenyl) is

significantly smaller ($0.006 \text{ min}^{-1} \text{ m}^{-2}$) than the rest of rate constants (0.013 to $0.020 \text{ min}^{-1} \text{ m}^{-2}$).

5.3.7 Activation Energy

The reaction was determined to be surface reaction limited and therefore the activation energy corresponds to the surface reaction (from the adsorbed PCB to the dechlorinated but still adsorbed product). Table 5.3-12 (Arrhenius plots are shown in Figure 5.3-23) summarizes the activation energies obtained for each monochlorobiphenyl congener in supercritical CO_2 in comparison to the values obtained in liquid isopropanol. The similar values and trends observed in two fluids suggests that the activated (rate-limiting) step of the reaction is the same in both fluids, which is in agreement with the earlier studies on $\text{C}_{18}\text{-Cl}$. There was a clear difference between PCB002 and the other two, where *meta*-substituted monochlorobiphenyl resulted in the higher activation energy than either *ortho*- or *para*-substituted monochlorobiphenyl. This order in the activation energy is consistent with the inductive effect considered for an electrophilic substitution mechanism as it was discussed earlier for the rate constants. There is no stabilization effect on the carbocation intermediate by hydrogen attack on the *meta*-position as there is in *ortho*- or *para*-positions, so that the attack on *ortho*- and *para*-positions is preferred over the *meta*-position.

Table 5.3-12: Apparent activation energy of monochlorobiphenyls (kJ mol^{-1})

PCB#	Cl position	Supercritical CO_2	Liquid isopropanol at 1
001	<i>Ortho</i>	91 ± 3	105 ± 7
002	<i>Meta</i>	128 ± 6	163 ± 18
003	<i>Para</i>	98 ± 5	86 ± 8

Figure 5.3-23: a) Arrhenius plot of dechlorination of monochlorobiphenyls in supercritical CO₂ ($\rho = 0.63 \pm 0.02$ g/mL, Pd/PCB (molar) = 17, reaction time = 5 min)

Figure 5.3-23: b) Arrhenius plot of dechlorination of monochlorobiphenyls in liquid isopropanol at (P = 1 atm, Pd/PCB (molar) = 50, reaction time = 15 min)

Comparison of Figure 5.3-23 a) and b) clearly indicate that the reaction becomes diffusion limited in isopropanol above 70°C, but not in supercritical CO₂. This was an important observation that illustrates the advantage of performing reactions in supercritical fluids where diffusion limitation is essentially eliminated.

The rate constants of the reactions in the two fluid systems however were very different; the values in supercritical CO₂ were about twice to three times smaller than those in liquid isopropanol at 1 atm as shown in Table 5.3-13. This leads to the conclusion that the surface reaction proceeded much slower in supercritical CO₂. As the diffusion through the boundary layer in supercritical CO₂ is faster than in liquid isopropanol due to the smaller size of the boundary itself and higher diffusivity in supercritical CO₂, the reason for the surface reaction to be the rate-limiting step is most likely not due to slower diffusion through the boundary but due to slower surface reaction. The composition of the adsorbed surface would be different in two fluid systems. In supercritical CO₂, although the concentration of isopropanol on the surface is higher than in the boundary layer or on the catalyst surface, there is also a significant amount of CO₂. The reaction in supercritical CO₂ may be slow due to the fact that there are many CO₂ molecules around the PCB molecule which preventing the hydrogen transfer from isopropanol to PCB. In liquid isopropanol, the only molecules present in the system are the reactant molecule and isopropanol with the catalyst, so that there was no such inhibiting effect possible to slow the reaction.

Table 5.3-13: Rate constants (k) for monochlorobiphenyls in supercritical CO₂ and in liquid isopropanol (min⁻¹m⁻²)

PCB #	Supercritical CO ₂	Liquid isopropanol
001	0.063 ± 0.004	0.20 ± 0.03
002	0.054 ± 0.003	0.18 ± 0.05
003	0.079 ± 0.006	0.19 ± 0.03

5.3.8 Source of Hydrogen

Whether the reaction was a nucleophilic substitution involving the hydrogen transfer in the form of hydride ion or an electrophilic substitution involving the proton was not clearly shown by the data. There also is a possibility that hydrogen from $-OH$ group of isopropanol was involved in the reaction mechanism as the presence of isopropoxy biphenyl was confirmed by mass spectrum in dechlorination of Aroclor 1254 (Appendix III). The earlier studies where $\alpha-H$ was specifically transferred to the chlorinated compounds in liquid isopropanol system was in the presence of base [5]. The reaction may proceed via different mechanism in the absence of base.

Another possibility in relation with electrophilic substitution mechanism is via direct attachment of proton on chlorine to produce hydrochloric acid as shown in Figure 5.3-24.

Figure 5.3-24: Possible dechlorination mechanism for PCB003 via direct formation of HCl

The produced intermediate cation may then react with hydride ion to produce biphenyl. Further investigation is required to determine the source of hydrogen and the form of hydrogen transfer for the current reaction system.

5.3.9 Theoretical Calculations

In order to gain a better understanding of the selectivity of the dechlorination, a few theoretical parameters were calculated using semi-empirical methods. These include rotational energy barrier (already discussed), bond dissociation energies, and molecular orbital coefficients at each reacting C-Cl bond of all the congeners studied. Each of these parameters were considered to give more insights into the mechanism of dechlorination.

Bond Dissociation Energy

As the dechlorination was reaction limited as previously discussed, one of the possibilities of the actual rate-limiting step in the surface reaction may be C-Cl dissociation. Although the suggested mechanisms are in the form of heterolytic dissociation (electrophilic or nucleophilic substitution), a possibility of a homolytic dissociation can also be considered. If the bond dissociation of the C-Cl bond is the rate-limiting step, then the rate constant should increase as the bond dissociation energy (BDE) increases. It has been reported that the dehalogenation rate of aryl halides decreases in the order of increasing BDE [15].

The BDE was calculated using a semi-empirical method for the homolytic cleavage which known to have an accuracy of ≈ 8 kJ/mol [20] and the results are summarized in Table 5.3-14.

Table 5.3-14: Bond Dissociation Energy of Individual Dechlorination Steps:
 $R-Cl \rightarrow R\cdot + Cl\cdot$

PCB#	# of Cl	Cl position	Dissociated @	Intermediate PCB	K ($\text{min}^{-1}\text{m}^{-2}$)	BDE (kJmol^{-1})
001	1	2 -	2 -		0.063	389.5
002	1	3 -	3 -		0.058	400.8
003	1	4 -	4 -		0.079	403.3
004	2	2,2'-	2'-	001	0.006	411.3
006	2	2,3'-	3'-	001	0.016	401.1
			2 -	002	0.003	389.3
007	2	2,4 -	4 -	001	0.018	400.8
			2 -	003	0.005	387.6
008	2	2,4'-	4'-	001	0.013	402.8

Cont'd

PCB#	# of Cl	Cl position	Dissociated @	Intermediate PCB	K ($\text{min}^{-1}\text{m}^{-2}$)	BDE (kJmol^{-1})
008	2	2,4'-	2 -	002	0.002	389.5
009	2	2,5'-	5 -	001	0.020	402.2
			2 -	002	0.004	391.0
012	2	3,4'-	4 -	002	0.004	400.4
			3 -	003	0.003	397.9
017	3	2,2',4'-	2'-	007	0.001	449.9
			2 -	008	0.000	452.1
			4 -	004	0.000	462.7
018	3	2,2',5'-	2'-	009	0.000	437.6
			5 -	004	0.007	447.8
			2 -	006	0.000	482.1
025	3	2,3',4'-	4 -	006	0.012	430.1
			2 -	013	0.000	421.2
			3'-	007	0.010	438.9
028	3	2,4,4'-	4 -	008	0.006	417.5
			2 -	015	0.000	408.7
			4'-	007	0.007	427.9
033	3	2',3,4'-	4 -	006	0.001	404.0
			3 -	008	0.000	406.1
			2'-	012	0.004	401.7
048	4	2,2',4,5'-	2'-	029	0.000	457.7
			2 -	033	0.000	454.1
			4 -	018	0.001	460.5
			5 -	017	0.002	466.1
066	4	2,3',4,4'-	4 -	033	0.000	471.9
			3'-	037	0.000	463.2
			4'-	028	0.000	477.9
			2 -	025	0.001	483.8
101	5	2,2',4,5,5'-	5'-	048	0.010	489.0
			2 -	067	0.000	492.8
			2'-	066	0.000	497.5
			4 -	052	0.000	497.8
			5 -	049	0.000	503.5
118	5	2,3',4,4',5'-	5'-	076	0.000	509.4
			2 -	081	0.000	500.6
			3'-	066	0.002	511.6
			4'-	068	0.000	519.2

Generally speaking, bond dissociation energy increases as the number of chlorines increases. This may be due to the increase in the resonance effects as the number of chlorines are increased and it becomes more difficult to break any C-Cl bonds at higher resonance.

There was no large difference observed in BDE for the three monochlorobiphenyls. The BDE of heterolytic cleavage was also calculated for these congeners using the same method which resulted in approximately twice as high values as for homolytic cleavage; indicated on Table 5.3-15. However, the ratio of the three calculated energies for both homolytic and heterolytic cleavage resulted in essentially the same values. Since the ratios were the same, the correlation between the rate constants and the homolytic cleavage of the C-Cl bond should be consistent even for the heterolytic cleavage.

Table 5.3-15: Bond dissociation energy for monochlorobiphenyl
(homolytic and heterolytic cleavage)

PCB#	$R-Cl \rightarrow R\cdot + Cl\cdot$ (kJ/mol)	BDE/BDE _{PCB001}	$R-Cl \rightarrow R^+ + Cl^-$ (kJ/mol)	BDE/BDE _{PCB001}
001	389.5	1.00	738.2	1.00
002	400.8	1.03	742.6	1.01
003	403.3	1.04	764.2	1.04

For all the dichlorobiphenyls studied, a plot of k versus BDE was constructed as shown on Figure 5.3-25. The labels for each data points indicate the starting PCB to the resulting PCB, with the substitution position of the C-Cl bond dissociation.

All the *ortho*-Cl dissociation (PCB007 to PCB003, PCB009 to PCB002, PCB006 to PCB002, PCB008 to PCB003) except for that of PCB004 (2,2'-dichlorobiphenyl) resulted in the low BDE (Bottom left corner on Figure 5.3-12). This indicates bond

Figure 5.3-25: Bond Dissociation Energy versus Rate Constants (k) for Dichlorobiphenyls (Labels show the parent congener – product congener, position of the C-Cl bond broken)

dissociation of *ortho*-chlorine is not energetically demanding when the molecules are in the gas phase and free of any steric effects or from the surrounding molecules (i.e., CO₂ or isopropanol). This in turn then should indicate that the low rate constants for these congeners are less related to their own electronic structure, but more with the surrounding environment.

Higher BDE for non-*ortho* Cl dissociation was obtained for all the congeners with at least one *ortho*-Cl (PCB004, PCB006, PCB007, PCB008, and PCB009). The data points for those dissociation are gathered at the top right corner of the Figure 5.3-27. When PCB004 (2,2'-), PCB006 (2,3'-) and PCB008 (2,4'-) were compared (i.e., the dichlorobiphenyls which have *ortho*-chlorine on each side of the ring, referring to Figure 5.3-11), there was a clear relation between the rate constants and BDE as shown in Figure 5.3-26; high BDE resulted in a low rate constant. In this case, *ortho*-substitution dissociation resulted in the highest BDE, followed by *para*- then finally *meta*- to be the lowest. It is interesting to note the difference in the order of decreasing BDE in monochlorobiphenyls (*para*-, *meta*-, then *ortho*-) which did not correspond with the order for dichlorobiphenyls. The presence of an extra *ortho*-chlorine in dichlorobiphenyls seemed to play a significant role in changing the orders between monochlorobiphenyls and dichlorobiphenyls.

For the tri- and higher chlorinated PCBs, there was not enough information to make a direct comparison as for PCB004, PCB006, and PCB008, so no definite conclusion could be drawn from these numbers. It would be informative when both rate constant and BDE were available for all possible dechlorination pathways, and only then, direct comparison can be made at or between the each congener levels so it could be related to the specific position of the C-Cl dissociation.

Figure 5.3-26: Bond Dissociation Energy versus Rate Constants (k) for PCB004, 006, and 008 producing PCB001 (Labels show position of the C-Cl bond broken).
 $(y = -0.004x + 0.390, R^2 = 0.93)$

Molecular Orbitals and their coefficients

Molecular orbitals (MO) for each congener was considered to show a correlation to the observed dechlorination pathways of PCBs as the interaction between the reacting molecule and the catalyst surface would be by the overlap of molecular orbitals. The proposed mechanism of interaction include the overlap of palladium d-orbitals with the lowest unoccupied molecular orbitals (LUMO) of the reacting molecule. If the C-Cl bond being dissociated has a bonding character, then a flow of more electrons into these orbital should result in an increased bond strength, while if the C-Cl bond has anti-bonding character, then the bonding strength is expected to decrease. Smaller MO coefficients indicate that the electrons would less likely distributed to that particular bond or atom.

Identifying the bonding character combined with the magnitude of MO coefficient was considered to show some correlation to the measured rate constants for individual dechlorination steps.

Molecular orbital coefficients for the LUMO on the reacting C and Cl atoms were calculated and summarized in Table 5.3-16. The sign on this value indicates bonding character of the C-Cl bond; '+' for occupied and '-' for unoccupied.

Table 5.3-16: Rate constants and molecular orbital coefficients for each possible dechlorination pathways

PCB #	# of Cl	Cl Position	Dissociated @	Intermediate PCB	k (min ⁻¹ m ⁻²)	C-Cl	(C) ²	(Cl) ²
001	1	2 -	2 -		0.063	-	0.32	0.02
002	1	3 -	3 -		0.058	-	0.06	0.00
003	1	4 -	4 -		0.079	-	0.32	0.02
004	2	2,2'-	2'-	001	0.006	+	0.02	0.00
				001		-	0.25	0.01
006	2	1,2'-	2'-	002	0.016	+	0.00	0.00
			1-	001	0.003	-	0.28	0.01
007	2	2,4 -	4 -	003	0.018	-	0.09	0.00
			2 -	001	0.005	-	0.07	0.00
008	2	2,4'-	4'-	002	0.013	-	0.08	0.00
			2 -	001	0.002	-	0.07	0.01
009	2	2,5-	5 -	002	0.020	-	0.11	0.00
			2 -	002	0.004	-	0.16	0.01
012	2	3,4-	4 -	003	0.004	-	0.10	0.01
			3 -	007	0.003	-	0.03	0.00
017	3	2,2',4-	2'-	008	0.001	-	0.00	0.00
			2 -	004	0.000	-	0.03	0.00
			4 -	009	0.000	-	0.06	0.00
018	3	2,2',5-	2'-	004	0.000	+	0.01	0.00
			5 -	006	0.007	-	0.18	0.01
			2 -	006	0.000	-	0.20	0.01
025	3	2,3',4-	4 -	013	0.012	-	0.29	0.01
			2 -	007	0.000	-	0.12	0.01
			3'-	008	0.010	-	0.00	0.00
028	3	2,4,4'-	4 -	015	0.006	-	0.27	0.01
			2 -	007	0.000	-	0.18	0.01
			4'-	006	0.007	-	0.06	0.00
033	3	2',3,4-	4 -	008	0.001	-	0.16	0.01
			3 -	012	0.000	-	0.04	0.01
			2'-	029	0.004	-	0.11	0.01

Cont'd

PCB #	# of Cl	Cl Position	Dissociated @	Intermediate PCB	k (min ⁻¹ m ⁻²)	C-Cl	(C) ²	(Cl) ²
048	4	2,2',4,5-	2'-	033	0.000	-	0.02	0.00
			2 -	018	0.000	-	0.16	0.01
			4 -	017	0.001	-	0.18	0.01
			5 -	033	0.002	-	0.17	0.01
066	4	2,3',4,4'-	4 -	037	0.000	-	0.23	0.01
			3'-	028	0.000	-	0.12	0.01
			4'-	025	0.000	+	0.00	0.00
			2 -	048	0.001	-	0.00	0.00
101	5	2,2',4,5,5'-	5'-	067	0.010	-	0.00	0.00
			2 -	066	0.000	+	0.00	0.00
			2'-	052	0.000	-	0.36	0.02
			4 -	049	0.000	-	0.44	0.02
			5 -	076	0.000	-	0.37	0.02
118	5	2,3',4,4',5'-	4 -	081	0.000	-	0.20	0.01
			2 -	066	0.000	-	0.17	0.01
							0.00	0.01
			3'-	068	0.000	-	0.01	0.00
			5'-	76	0.000	+	0.03	0.00

For all congeners, the coefficients on the Cl atoms were much smaller than those on the C atom, showing the higher electronic distribution on the ring of the molecule rather than the Cl atom. Most of the C-Cl bonds were anti-bonding except for a few congeners (those with '+' for C-Cl).

For monochlorobiphenyls, the coefficients on both C and Cl atoms were about half for PCB002 (C: 0.06, Cl: 0.03) than for PCB001 (C:0.31, Cl: 0.02) or PCB003 (C:0.32, Cl: 0.02). This may have an implication that substitution at the *meta*-position results in less anti-bonding character than in the *ortho*- or *para*-position. This may be interpreted as that it requires more electron input to break the C-Cl at this position, which is in agreement with the trend observed with the determined activation energy where *meta*-substituted monochlorobiphenyl resulted in the highest activation energy. Thus, there may be a correlation obtained between the MO coefficients and the activation energies, however, further analysis was not made as the experimental values of the activation energies were not obtained for di- and higher congeners.

Statistical analysis was applied to the data shown in Table 5.3-14 for the rate constants, and the squares of the MO coefficients on C and Cl atoms, however it did not result in any clear correlation for any sets of congeners except for monochlorobiphenyls. As the MO coefficient only implies the relative electron distribution within a molecule, it is considered more instructive to incorporate the LUMO energy when the comparison is made among the different molecules. For monochlorobiphenyl, the slowest rate constant was consistent with the smallest MO coefficients for *meta*-substituted position.

It is also important to note that all the values calculated are for the molecules in the gas phase and the MOs are expected to change significantly upon the interaction with the palladium orbitals. Therefore it would be more informative if the model of palladium surface and the molecule can be built to calculate the interacting MOs instead of only the reacting MOs. Such information at this point was not available.

It was instructive to calculate MOs as there was a quite difference between the lower and higher chlorinated congeners. One major difference was for tri- and higher congeners containing two ortho-chlorines on each side of the ring. These congeners were PCB017 (2,2',4-dichlorobiphenyl), PCB018 (2,2',5-trichlorobiphenyl), PCB048 (2,2',4,5-tetrachlorobiphenyl) and PCB101 (2,2',4,5,5'-pentachlorobiphenyl) where there was no electron density distributed on one ring containing only one chlorine atom (2'-position) (refer to Figure 5.3-27). This may be related to the fact that this chlorine atom (2'-position) is the least likely to be dissociated as it was observed for PCB017, PCB018, and PCB048.

PCB012

PCB017

PCB028

PCB101

Figure 5.3-27: Lowest Unoccupied Molecular Orbitals (LUMO) calculated for the selected PCBs

Correlation to C₁₈-Cl, Stearic-Cl₂, and DHA-Cl₂

Theoretical calculation of MO coefficients and bond dissociation energy were also applied to the earlier studied molecules which are summarized in Table 5.3-17. The BDE did not show any significant difference between the molecules, as expected for the adsorption limited reactions. The square of the MO coefficients on carbon and chlorine atoms of interest are shown as $MO(C^2/Cl^2)$ in Table 5.3-17. It is noticeable that similar values were obtained for C₁₈-Cl and Stearic-Cl₂ while much larger value was obtained for DHA-Cl₂. Such difference can be correlated to the magnitude of the apparent activation energy calculated as discussed earlier for monochlorobiphenyls. Although the activated step was not determined to be the surface reaction, the difference in the MOs can be conceived to be affecting the adsorption by changing the affinity of the molecule towards the catalyst surface.

It can be clearly seen that MOs of C-Cl bond in C₁₈-Cl and Stearic-Cl₂ has bonding character while that for DHA-Cl₂ has anti-bonding character. Figure 5.3-28 illustrates that MOs are around C-Cl bond in C₁₈-Cl and Stearic-Cl₂ while they are gathered in p system of the aromatic ring and not so much on actual C-Cl bond in DHA-Cl₂. Such a difference correlates to the size of the $MO(C^2/Cl^2)$ in Table 5.3-17.

Table 5.3-17: Summary of experimental values, theoretical calculations, and physical parameters of the molecules studied in Chapter 4

	C ₁₈ -Cl	Stearic-Cl ₂		DHA-Cl ₂	
		C9	C10	C12	C14
BDE (kJmol ⁻¹)	482	466	466	517	514
MO (C ² / Cl ²)	0.38/0.35	0.40/0.26	0.40/0.26	0.12/0.005	0.08/0.004
E _a (kJmol ⁻¹)	(43 ± 5)	(40 ± 7)	(40 ± 7)	(135 ± 7)	(135 ± 7)
Bonding Character	Bonding	Bonding	Bonding	Anti-bonding	Anti-bonding
Structure	Aliphatic	Aliphatic	Aliphatic	Aromatic	Aromatic
k (min ⁻¹ m ⁻²)	0.10	0.010	0.010	0.013	0.013

Figure 5.3-28: Lowest Unoccupied Molecular Orbitals (LUMO) calculated for $C_{18}\text{-Cl}$, Stearic- Cl_2 , and DHA- Cl_2

$C_{18}\text{-Cl}$

Stearic- Cl_2

DHA- Cl_2

5.4 SUMMARY AND CONCLUSIONS

Studies of dechlorination pathways for PCB101 and PCB118 resulted in more detailed understanding of the surface reaction for PCBs.

The rate-limiting step was determined to be the surface reaction, contrary to the earlier studied molecules (i.e., adsorption limited). In a non-polar fluid phase as in supercritical CO₂, a non-polar molecule would diffuse faster than polar molecules. PCB or 1-chlorooctadecane diffuse through a boundary layer faster than 9,10-dichlorostearic acid or 12,14-dichlorodehydroabiatic acid. The difference observed between 1-chlorooctadecane and PCB003, i.e., adsorption limited versus surface reaction limited reaction, is due to the much slower reaction rate of the PCB. PCB being an aromatic chloride is expected to be more energetically demanding than for the aliphatic 1-chlorooctadecane.

High differences between the affinities of biphenyl and the PCBs towards the catalyst surface indicated that the interaction between the PCBs and the catalyst surface are different from the one between the biphenyl and the surface, suggesting that the orientation of adsorption of PCBs on catalyst surface is probably not in a form where the aromatic rings are parallel to the surface to have full interaction as in the case of biphenyls, but rather on an angle where chlorine atoms are present. Observations which support this idea include;

1. PCB004 (2,2'-dichlorobiphenyl) has a very low rate constant compared to the other dichlorobiphenyls. The non-planarity of this molecule is considered to be the reason.
2. PCB012 (2,3-dichlorobiphenyl) is the only dichlorobiphenyl congener that dechlorination of both chlorines occur prior to desorption. PCB012 is also the only dichlorobiphenyl which has two chlorines adjacent to each other, more accessible structure to be adsorbed than two chlorines further apart from each other.
3. For dichlorobiphenyl congeners containing one *ortho*-chlorine atom, the bond dissociation of non *ortho*-chlorine is more preferred. *Ortho*-chlorine is sterically hindered due to the presence of a phenyl group adjacent.

4. Multiple dechlorination is more significant with higher chlorinated congeners.

The selectivities of tri- and higher congeners were not clear enough to support the above idea.

The presence of additional dechlorination pathways for PCB012 (3,4-dichlorobiphenyl) which were absent in any other dichlorobiphenyl dechlorination pathways suggested the multiple dechlorination can occur prior to desorption of the intermediates formed. The reaction mechanism was then broken down to the following steps.

1. adsorption of the starting PCB on the catalyst surface in a most preferred orientation, 2. dechlorination reaction to loses chlorine atom, 3. desorption resulting in the first intermediate (i.e., monochlorobiphenyl from dichlorobiphenyl, dichlorobiphenyl from trichlorobiphenyl, etc.), or further loss dechlorination of another chlorine atom with or without a rearrangement of the orientation of the intermediate on the catalyst surface, then 4. desorption of the next intermediate (i.e., if the starting PCB was trichlorobiphenyl, then monochlorobiphenyl, etc).

Steps 3 and 4 can be repeated until the intermediate loses all the chlorine atoms and become biphenyl, and the number of repetitions generally increases as the number of chlorine atoms increases on the starting PCB.

Multiple dechlorination pathways became more significant as the number of chlorine atoms were increased (for tri- and above), resulting in significant differences between the total dechlorination rate and the sum of the individual rates. Many intermediate congeners were dechlorinated further before desorption, The same explanation of having the adjacent C-Cl bonds did not apply to the tri- and higher chlorinated biphenyls.

For the majority of cases, *ortho*-chlorine was lost at a slower rate independent of the number of chlorine atoms present on the ring. There were a few exceptions, i.e.,

PCB033(2',3,4-trichlorobiphenyl) producing PCB012 (3,4-dichlorobiphenyl) as the major intermediate losing *ortho*-chlorine in preference to *meta*- or *para*-chlorines, which were not explained well.

The significance of planarity / non-planarity due to the presence of two *ortho*-chlorines at each side of the molecule became less significant as the number of chlorine increased. For example, PCB048 and PCB066 resulted in similar rate constants ($0.053 \text{ min}^{-1}\text{m}^{-2}$ and $0.040 \text{ min}^{-1}\text{m}^{-2}$, respectively) although the rotational energy barrier was much higher for PCB048 (32.3 kcal/mol) than for PCB066 (8.6 kcal/mol) indicating that the planarity does not play a significant role in controlling the rate at higher chlorinated congeners. This is likely due to the increase in possible sites of interaction by increasing the number of chlorine atoms and is in agreement with the earlier stated interaction between the PCBs and the catalyst surface (not through π conjugation system of the rings). Similar conclusions were made for PCB101 and PCB118.

Bond dissociation energies for three monochlorobiphenyls were not very different from each other. For dichlorobiphenyls containing one *ortho*-chlorine atom, all the *ortho*-chlorines dissociated and had lower BDE than the non *ortho*-chlorines. This was an indication of bond dissociation of *ortho*-Cl not being energetically demanding and that low rate constants are solely the result of steric hindrance. However, the steric effect might be minimal when the *ortho*-Cl on those congeners was on the other ring from the C-Cl bond dissociated as shown with the dechlorination of PCB004 (2,2'-), PCB006 (2,3'-) and PCB008 (2,4'-). Among these three molecules, the rate constant decreased as the bond dissociation energy increased.

A general trend was observed for all the congeners whereby bond dissociation energy increased as the number of chlorines increased, suggesting that there is an increase in the resonance effect stabilizing the C-Cl bond.

The MO coefficients were related to the activation energy for monochlorobiphenyls. Lower coefficients were understood as requiring more electron input to break the C-Cl

bond of anti-bonding character compared to the one with higher coefficients, in agreement with the activation energy values and for the rate constants obtained. However, a similar relationship was not obtained with di- or higher congeners indicating that this is only one of many parameters possibly contributing to the selectivity of dechlorination and that the effect is not straight forward as in the case of monochlorobiphenyls. A qualitative analysis of MO's shown by Figure 5.3-27 gave some insight into the reaction selectivity; no electron density was present in the LUMO on the ring containing one ortho-chlorine for PCB017, PCB018, PCB048, and PCB101.

The mechanism of the reaction, whether it is a nucleophilic/ electrophilic substitution or a homolytic cleavage of the bond is still not clear. A clear correlation between the rate constants and BDE for dichlorobiphenyls (PCB004, PCB006, PCB008) suggests that the C-Cl bond dissociation may be the activated step, although this was only specific to these sets of molecules and did not apply to the monochlorobiphenyls. The order of activation energy determined for monochlorobiphenyls did not correspond with the order of the calculated bond dissociation energy.

The inductive effect may be dominant for lower chlorinated biphenyls, the steric and resonance effect seemed to control the reaction selectivity more for tri- and higher chlorinated congeners. As for the mechanism of the reaction and the form of hydrogen transfer, it was not possible to draw a clear conclusion. There also exists a possibility that the mechanism involves a homolytic cleavage of C-Cl bond. Dechlorination of Aroclor 1254 resulted in the production of isopropoxy biphenyls, which may indicate that the source of hydrogen was not only the α -H but also from the hydroxyl group of isopropanol.

Parameters obtained from theoretical calculations could only provide partial elucidation of the mechanism and did not apply to the whole system. It may only be useful if all the possible parameters involved in the reaction are considered at the same time. These parameters include number of chlorine atoms, position of each chlorine atom, MO

coefficients, bond dissociation energy, rotational energy barrier, which are then to be correlated to the individual rate constant for each C-Cl dissociation. All of these parameters were individually correlated in this chapter, but the multiple correlation was found to result in essentially no correlations to draw any reasonable conclusions. Obtaining more experimental data should overcome this limitation to some extent.

It is clear that the combination of many factors controls the selectivity of dechlorination and it is difficult to compare only with one independent parameter. Application of an appropriate statistical method would be more appropriate with more experimental data to fully understand the selectivity of the reaction, which one could imagine to be rather complicated as the number of chlorine increases.

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Chapter 6

Summary and Conclusion

The use of supercritical CO₂ as a solvent for the catalytic hydrodechlorination of different classes of organochlorines was illustrated in this work. The molecules of interest included 1-chlorooctadecane, 9,10-dichlorostearic acid, and 12,14-dichlorodehydroabiatic acid, as well as some selected PCB congeners varying in the number of chlorines (monochlorobiphenyl to pentachlorobiphenyl). Their structural differences as well as polarity and size were considered to be important factors controlling the reaction. The important conclusions made for each chapter are summarized in this chapter.

Chapter 2: Selectivity of Supercritical Fluid Extraction

Fatty acids with different carbon numbers were selectively extracted by SFE while no such selectivity was obtained with Soxhlet extraction, even with a range of solvent polarities. The extraction yields obtained by two methods were comparable, yet Soxhlet extraction resulted in slightly higher yield. The selectivity of SFE was temperature dependent and more defined selectivity was observed at higher temperature, which was likely due to differences in the vapor pressures of the analytes with respect to temperature. A significant increase in the extraction yield was observed by an addition of an organic modifier, consistent with the idea that the solvent strength is significantly increased by addition of a organic modifier.

SFE is limited in its ability to extract polar and high molecular weight compounds, and from the practical purposes, it would not be feasible to perform a full analysis of wood

resins in pitch deposits, which contain a lot of polar and high molecular components. However, the significance of SFE lies in the fact that it can fractionate molecules of similar nature (fatty acids), which was clearly demonstrated in the current work.

Chapter 3: Optimization of the Dechlorination Method

The aim of Chapter 3, to establish a system for complete dechlorination, was achieved with $C_{18}\text{-Cl}$, Stearic- Cl_2 , and DHA- Cl_2 in supercritical CO_2 . The effects of the concentration of each reaction reagent were determined in the process of optimization, which provided important information on the surface reaction mechanism.

Completion of dechlorination was obtained in the absence of base. No dechlorination proceeded in the absence of isopropanol also confirmed that the isopropanol was the hydrogen donor for the reaction. In supercritical CO_2 , isopropanol only acts as a hydrogen donor not as a solvent, which was consistent with the fact that a maximum yield of dechlorination was obtained at a small concentration of isopropanol. All the inhibiting effects observed (by increasing pressure or isopropanol, or addition of base) indicated that the adsorption to the catalyst surface is the rate-limiting step in the dechlorination; surface coverage by any means (i.e., adsorption of surrounding CO_2 , isopropanol, or base) inhibits adsorption of the reactant molecules and therefore results in decreased yield. Furthermore, polar Stearic- Cl_2 or DHA- Cl_2 molecules being unaffected by the pressure increase indicated that the nature of interactions among the fluid-catalyst-reactant molecule are all controlling the surface mechanism.

Chapter 4: Kinetic and Thermodynamic Studies of the Dechlorinations of $C_{18}\text{-Cl}$, Stearic- Cl_2 , DHA- Cl_2 in supercritical CO_2

Further kinetic analysis of the reaction determined the rate-limiting step to be adsorption of the reactant molecules for all three compounds. The reactions are considered to follow Langmuir-Hinshelwood type mechanisms where reaction takes place between the adsorbed chlorinated molecule and an adsorbed isopropanol. The overall reaction was

considered to have a pseudo first order since isopropanol was in excess compared to the reactant.

The reaction of C18-Cl was first order in the substrate in both supercritical CO₂ and in liquid isopropanol. The rate constant was an order of magnitude higher in supercritical CO₂ than in liquid isopropanol, which was indicative of less diffusion resistance near the surface of the catalyst in supercritical CO₂ which is more easily crossed especially for non-polar molecules, i.e., C₁₈-Cl.

A clear difference in the effects of in the initial concentration of isopropanol was observed between the two fluid systems; no inhibiting effect by the increasing concentration of isopropanol was observed in hexane at atmospheric pressure. In CO₂, however increasing the concentration of isopropanol inhibited the reaction.

The same apparent activation energy of the reaction for C₁₈-Cl in two fluid systems was evidence that the reactions have the same rate-limiting step. The much higher E_a for DHA-Cl₂ was likely due to its much greater size than the other two substrates, resulting in larger interactions between itself and the species in the boundary layer.

Enthalpies of desorption of stearic acid and dehydroabiatic acid were much smaller than the activation energies confirming that the rate-limiting step was not desorption of dechlorinated products.

Chapter 5: Congener Specific Kinetic Studies of Dechlorination of PCBs in supercritical CO₂

In Chapter 5, the focus of the studies was to determine the selectivity of dechlorination for polychlorinated compounds such as PCBs.

The rate-limiting step was determined to be the surface reaction due to the much slower surface reaction rate of the PCB. Dechlorination of an aromatic chloride such as PCBs

has been reported to be more energetically demanding than for the aliphatic 1-chlorooctadecane.

High differences between the affinities of biphenyl and the PCBs towards the catalyst surface indicated that the interaction with the catalyst surface is different for PCBs and the biphenyl. This may indicate that the aromatic ring does not have a strong interaction with the catalyst surface, i.e., would not lie flat on the surface. The following observations with mono- and dichlorobiphenyls supported this argument.

1. PCB004 (2,2'-dichlorobiphenyl) has a very low rate constant compared to the other dichlorobiphenyls. The non-planarity of this molecule is considered to be the reason.
2. PCB012 (2,3-dichlorobiphenyl) is the only dichlorobiphenyl congener for which dechlorination of both chlorines occurs prior to desorption. PCB012 is also the only dichlorobiphenyl which has two chlorines adjacent to each other.
3. For dichlorobiphenyl congeners containing one *ortho*-chlorine atom, the bond dissociation of the non *ortho*-chlorine is more preferred. *Ortho*-chlorine is sterically hindered due to the presence of an adjacent phenyl group.
4. Multiple dechlorination is more significant with higher chlorinated congeners.

This was also supported by the fact that the significance of non-planarity due to the presence of two *ortho*-chlorines at each side of the molecule became less significant as the number of chlorines is increased. As the number of chlorines increases, there will be more possible sites of interaction by increasing the number of chlorine atoms and so the interaction between the PCBs and the catalyst surface would not likely be through the π conjugation system of the rings.

A steric effect did not seem to be a dominant factor for dechlorination of monochlorobiphenyls. However it was evident for dichlorobiphenyls as observed for the exceptionally slower rate of PCB004.

Bond dissociation energy correlated with the rate constants for PCB004 (2,2'-), PCB006 (2,3'-) and PCB008 (2,4'-) although a general trend was observed for all the congeners

whereby bond dissociation energy increased as the number of chlorines increased, suggesting that there is an increase in the resonance effect stabilizing the C-Cl bond.

The MO coefficients for monochlorobiphenyls were in agreement with the determined activation energy. As much as it is difficult to draw any conclusive statement, more qualitative analysis of MO showed some consistency with the structure of the molecule; no electron density in the LUMO on the ring containing one ortho-chlorine as shown for PCB017 and PCB101.

A steric effect was more dominant effect for congeners with three or more chlorines where preferential dechlorination of non ortho-chlorines was observed. Inductive effects maybe playing a significant role as was proposed by an electrophilic mechanism for dichlorobiphenyls, however, it remains as speculative as the form of hydrogen is still not known in the current reaction system. The production of isopropoxy biphenyl from dechlorination of Aroclor1254 suggests that the hydroxyl hydrogen also can be transferred.

Theoretical calculations were only good for some parts of the explanation of the mechanism, and could not provide a full correlation to the experimental rate constants obtained. As there are many factors which can affect the rate of dechlorinations, more appropriate approach would be to apply statistical methods to all the possible parameters which could affect the rate of dechlorination; number of chlorine atoms, position of each chlorine atom, MO coefficients, bond dissociation energy, and rotational energy barrier, and with all 209 PCB congeners.

In conclusion, supercritical CO₂ performed as a good extracting fluid in terms of selectivity. Dechlorination in supercritical CO₂ has been shown to result in high yield by setting the reaction conditions to its optimum values, which provides a possible destruction method for organochlorines of environmental significance. Further studies of the reaction mechanism of dechlorination in supercritical CO₂ illustrated characteristic

behavior including faster diffusion rates have higher reaction rates in reactions limited by diffusion or adsorption.

Congener specific kinetic analysis of PCBs showed that while dechlorination is likely to occur in a sequential manner, further dechlorination prior to desorption is possible and more likely for highly chlorinated congeners. This is in agreement with the suggested mechanism where the adsorption of the reacting PCB molecules on the catalyst surface via the chlorine atoms.

Appendix I: Engineering diagram of the reaction cell

Appendix II: Engineering diagram of the parts for the reaction cell

Appendix II: Gas chromatogram of Aroclor 1254 before dechlorination (top) and after dechlorination (middle) – first peak corresponds to biphenyl and the following three peaks are isopropoxy biphenyl with mass spectrum confirmation (bottom)