Determination of Rate Constants for the Decomposition of Dichloropropane

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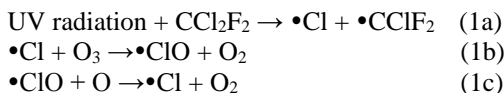Faculty Advisors: Dr. Bert E. Holmes and Dr. George L. Heard

Abstract

Hydrochlorofluorocarbons (HCFCs) have become ubiquitous in the chemical industry and in many commercial operations since they replaced chlorofluorocarbons (CFCs). The Montreal Protocol requires HCFCs to be phased out by 2030 worldwide. Therefore HCFCs need to be discarded and destroyed or converted into feedstock useful to the chemical industry. Computational models can be developed to evaluate the synthetic utility of potential conversion processes of halocarbons to commercially feasible materials. For these calculations of complex kinetic schemes to be reliable, accurate kinetic parameters are needed for all decomposition pathways. Degradation mechanisms of HCFCs include: interchange, stabilization and elimination (1,1-HX and 1,2-HX, where X = F or Cl). The 1,1-HX elimination pathway has not been widely studied. Therefore the contribution of 1,1-HX elimination to the formation of a carbene is unknown for most HCFCs. This research focuses on the model compound 1,1-dichloropropane and will determine ratios of the molecule's degradation pathways. Vibrationally excited $CD_3CD_2CHCl_2$ molecules were generated via recombination of CD_3CD_2 and $CHCl_2$ radicals prepared from CD_3CD_2I and $CHCl_3$. 1,1-HCl and 1,2-DCl elimination were observed and their individual rate constants were measured for production of both *cis-* and *trans-*1-chloropropene for each pathway. The four major products were Z-$CD_3CD=CHCl$ and E-$CD_3CD=CHCl$ (both the result of 1,2-DCl loss), and Z-$CD_3CD=CDCl$ and E-$CD_3CD=CDCl$ (both the result of 1,1-HCl loss), with a total experimental rate constant of 3×10^7 s^{-1}. The 1,1-HCl elimination reaction initially formed the CD_3CD_2CCl carbene that underwent D-migration to give either Z- or E-$CD_3CD=CDCl$. The branching fraction for the 1,1-HCl versus 1,2-DCl elimination reactions was 0.15. The Z/E-$CD_3CD=CHCl$ branching ratio for 1,2-DCl loss is 1.8. However, the Z/E-$CD_3CD=CDCl$ declined from 3 at the highest pressures to 1.8 at lower pressures as the Z-isomer was preferentially formed from the carbene and some of the Z-$CD_3CD=CDCl$ had sufficient energy to isomerize to the E-isomer.

Keywords: Gas Phase Kinetics, Hydrochlorofluorocarbons, Environment

1. Introduction

Chlorofluorocarbons (CFCs) were used as refrigerants, foam blowing agents, cleaning agents, and propellants.[1] In 1987, the Montreal Protocol required their use to be eliminated by 2000 in developing countries due to their environmental hazards.[2] CFCs are highly stable and unreactive in nature. They have low boiling points, low permeation rates, low surface tension, low viscosity and long atmospheric lifetimes—some reaching to over 300 years. Although these properties have proven useful in the industrial sector, they allow for CFCs to diffuse into and rise to the upper levels of the atmosphere. Once in the earth's upper atmosphere, the sun's ultra violet radiation decomposes CFCs into atomic chlorine (1a). Concurrently, O_2 molecules are interacting with UV, yielding atomic oxygen that then interacts with O_2 producing ozone molecules.[3] These atomic particles (denoted with an •) deplete the stratospheric ozone, a layer of the atmosphere that shields the earth from harmful ultraviolet radiation from the sun, through a chain reaction (1b, 1c).
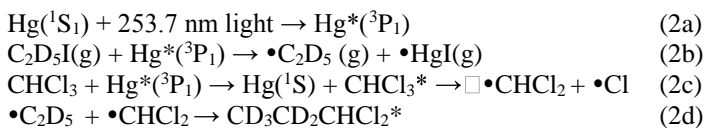
$$\text{UV radiation} + CCl_2F_2 \rightarrow \bullet Cl + \bullet CClF_2 \quad (1a)$$
$$\bullet Cl + O_3 \rightarrow \bullet ClO + O_2 \quad (1b)$$
$$\bullet ClO + O \rightarrow \bullet Cl + O_2 \quad (1c)$$

Each atomic chlorine is estimated to undergo 100,000 reactions before being removed from the chain reaction seen in Equation 1.[1] In addition to destroying the ozone, CFCs may also affect the reflection of infrared radiation from the earth's surface causing global climate change.[2]

Hydrochlorofluorocarbons (HCFCs) have been used as an interim replacement for CFCs due to their similar physiochemical properties. HCFCs are less harmful to the environment than CFCs because HCFCs react with hydroxyl radicals in the troposphere[2] and the presence of a carbon hydrogen bond results in a shorter life span, ranging from 2-25 years.[1] In addition, HCFCs photo-dissociate, absorb light and eliminate an HX species (X=halogen), in lower levels of the atmosphere.[4] Therefore, HCFCs were deemed a suitable replacement due to releasing an smaller amount of atomic chlorine into the stratosphere, a comparatively higher protective level of the atmosphere. Unfortunately, HCFCs still pose a threat to the environment. The chlorine substituent is still present, thus the small amount that does reach the stratosphere depletes the ozone. HCFCs are also potent greenhouse gases. HCFCs tend to be more harmful than the common greenhouse gases- water vapor, methane, and carbon dioxide- because they are much stronger absorbers of IR radiation. According to the Montreal Protocol, HCFCs are to be phased out by 2020 in developed countries and 2030 world wide.[2] Therefore the understanding of the reactions of CFCs and HCFCs with the atmosphere, as well as their degradation processes or methods to convert them into useful feedstock, is critical.

Due to their environmental hazard, methods to destroy and to recover organic vapors of CFCs have been widely studied. Methods to destroy CFCs include: using sodium naphthalenide to dehalogenate,[6] incineration-burning in the presence of oxygen,[7] pyrolysis- heating in the absence of oxygen,[1] catalytic oxidation,[8] and decomposition with water vapor.[1] Methods to recover organic vapors from CFCs include: condensation-chilling a gas to a saturated liquid by heat transfer, absorption- transferring organic vapors to a designated liquid solvent, in which the organics are soluble, adsorption-the adhesion of the organic vapors to a solid surface, most common being coal or coconut shells, and membrane separation.[2] Research is also being conducted on how to covert CFCs, HCFCs, and HFCs into useful chemical feedstocks. One reason is because these molecules contain carbon fluorine bonds, which have a high manufacturing cost.[9] Models have been developed[8,10,11] to evaluate the potential of converting halocarbons into feedstock. In some cases, these research teams are using a combinatorial chemistry approach, testing a variety of co-reactants and measuring the product distributions,[5] rather than relying on a fundamental understanding of the expected mechanisms. However, in order for these models to be reliable in their kinetic calculations, accurate kinetic parameters for all possible degradation mechanisms need to be determined.

Both incineration and pyrolysis of CFCs result in elimination pathways ending in one of two degradation mechanisms: elimination of HX, or interchange. These pathways can be studied experimentally multiple ways. Combination of radicals is used to create the target molecule for study. Radical species can be created a variety of ways,[12-17] including, but not limited to, photolysis of haloacetones and alkyl iodides, photolysis with a laser or mercury lamp, or mercury photosensitization. $CD_3CD_2CHCl_2*$, the target molecule of this study, was created via mercury photosensitization through the process seen in Equation 2. The asterisk (*) denotes the molecule or atom is chemically or photo-activated.

$$Hg(^1S_1) + 253.7 \text{ nm light} \rightarrow Hg*(^3P_1) \quad (2a)$$
$$C_2D_5I(g) + Hg*(^3P_1) \rightarrow \bullet C_2D_5 \ (g) + \bullet HgI(g) \quad (2b)$$
$$CHCl_3 + Hg*(^3P_1) \rightarrow Hg(^1S) + CHCl_3* \rightarrow \square \bullet CHCl_2 + \bullet Cl \quad (2c)$$
$$\bullet C_2D_5 + \bullet CHCl_2 \rightarrow CD_3CD_2CHCl_2* \quad (2d)$$

Mercury photosensitization is the photolysis of Hg vapor with a germicidal lamp, 253.7 nm photons, producing Hg $(^3P_1)$ (2a). Hg $(^3P_1)$ is then quenched by interaction with a haloalkane, typically with a Cl or I atom, forming mercury halide and a radical (2b).[17] In addition Hg $(^3P_1)$, can transfer its energy to a haloalkane, resulting in two radicals and Hg $(^1S_1)$ (2c). Radicals can then recombine into the energized target molecule (2d). In this study, the energized $CD_3CD_2CHCl_2*$ may react by 1,2-DCl elimination (3a), 1,1-HCl elimination (3b) (Figure 1), or be collisional stabilized through a vibrational energy transfer from $CD_3CD_2CHCl_2*$ to a bath molecules, M (3d). The singlet carbene formed through 1,1-HCl elimination (3b) may retain vibrational energy and isomerize to $CD_3CD=CDCl$, via a deuterium migration (3c).

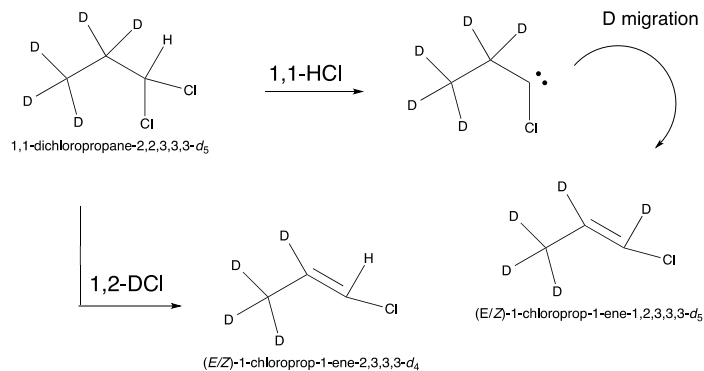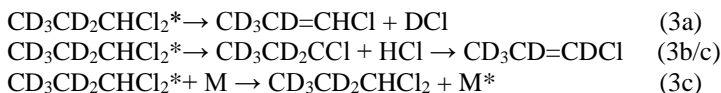$CD_3CD_2CHCl_2* \rightarrow CD_3CD=CHCl + DCl$ (3a)

$CD_3CD_2CHCl_2* \rightarrow CD_3CD_2CCl + HCl \rightarrow CD_3CD=CDCl$ (3b/c)

$CD_3CD_2CHCl_2* + M \rightarrow CD_3CD_2CHCl_2 + M*$ (3c)

Figure 1. Elimination pathways of $CD_3CD_2CHCl_2*$

When studying the stabilization and degradation mechanisms of CFCs and HCFCs—interchange and elimination (1,1-HX and 1,2-HX)—the energized target molecule is commonly measured using a Gas Chromatograph Mass Spectrometer (GC/MS),[12] or a Flame Ionization Detector (FID).[13] These instruments allow for ratios of products to be obtained. From these, experimental rate constants can be measured for each reaction channel by comparing the ratio of decomposition product (D) to the collisionally stabilized (S) molecule, $CD_3CD_2CHCl_2$, as a function of pressure (Eq. 4). The use of deuterium allows for the 1,1-HX pathway to be distinguished from the 1,2-HX pathway when analyzed with GC/MS.[12]

$k_{1,2-DCl}[CD_3CD_2CHCl_2*]/k_M [M][CD_3CD_2CHCl_2*] = [CD_3CD=CHCl]/[CD_3CD_2CHCl_2]$ (4)

If a small fraction of reactants are converted to the product then [M] equals the pressure (P) in the reaction vessel and Eq. 4 becomes the following:

$(k_{1,2-DCl}/k_M) (1/P) = D/S = [CD_3CD=CHCl]/[CD_3CD_2CHCl_2]$ (5)

A plot of the D/S vs. 1/P should be linear with a zero intercept and a slope equal to k_{exp}, which is also equivalent to $k_{1,2-DCl}/k_M$. Collision theory calculation gives the k_M. These plots along with the standard collision rate constant, k_M value, allow for reaction rates to be determined by multiplication of k_M by the slope.[12] This method also allows for the effects of different electron withdrawing and donating groups on rates to be measured.[13]

For parallel unimolecular reactions whose rates differ by more than a factor of ten, Eq. 5 is not reliable. Therefore a branching ratio plot should be made for the two decomposition pathways using data at low pressures, where D is maximized and S is essentially zero.

$k_{1,2-DCl}/k_{1,1-HCl} = [CD_3CD=CHCl]/[CD_3CD=CDCl] = $ Branching Ratio (6)

This data should be independent of pressure and the measured product ratio gives the rate constant for the slower channel relative to the rate constant for the dominant channel that has been determined using D/S data.

A scavenger molecule, $CF_3CH=CH_2$, was added to the vessel to remove the atomic Cl that would otherwise attack

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the alkenes formed from the elimination reactions (3a, 3b). Alkene removal by atomic chlorine would cause Eq. 5 and 6 to be invalid; therefore, the use of a scavenger is necessary for accurate determination of rate constants.[18] Knowing the rate of reactions of CFCs and HCFCs leads to a better understanding of likely products formed during degradation or during the conversion processes into useful feedstocks.

For the past decade, the Holmes/Heard research group has focused on understanding the 1,2-halogen interchange reaction for gas phase haloalkanes, both experimentally and computationally.[12,13] In addition, the research group has extensively studied 1,2-HX and 1,2-DX eliminations (X=F, Cl, or Br).[19] They have reinterpreted the decomposition mechanism for neopentyl chloride, neopentyl bromide,[19] CF_3CH_2Cl,[20] and 1,1-dichloroacetone[20] to be a 1,2-halogen interchange reaction followed by a 1,2-HX elimination reaction, whereas prior studies used 1,1-HX elimination to explain their observations. The group is currently studying 1,1-HX elimination reactions, both experimentally and computationally, utilizing many techniques described above. This research will be of interest to those attempting to develop viable pathways for converting HCFCs and HFCs into chemical feedstock and to those attempting to develop computational models for their destruction.

Table 1 lists ten HFCs and HCFCs that are in use or are produced as by-products during manufacturing of halocarbons.[21-24] The four halomethanes in Table 1 will only decompose by 1,1-HX elimination or bond rupture. The ethanes and propanes can undergo 1,1-HX and 1,2-HX elimination and halogen interchange but due to a high halogen content, the E_0s for the later two processes will be elevated. Thus, the decomposition of the halo-ethanes and propanes in Table 1 will likely contribute a significant amount to the formation of the carbene product. The majority of HCFCs in use range from one to three carbons with two terminal halogens. The three major options for the halogen placement is two terminal chlorines, two terminal fluorines, or a terminal chlorine and fluorine. It is also possible for there to be two terminal halogen sets, one on each end of the carbon chain.

Table 1. HFCs and HCFCs that are in use or are produced as by-products during manufacturing of halocarbons.

Formula	Name	Use
$CHClF_2$	HCFC-22	Refrigerant and Air Conditioners
CF_3CHCl_2	HCFC-123	Centrifugal chillers and portable fire extinguishers
CF_3CHFCl	HCFC-124	Some heat pumps and special air conditioning equipment
CF_3CHF_2	HFC-125	Refrigerant
CHF_3	HFC-23	By-product during production of HCFC-22
CF_2H_2	HFC-32	Refrigerant and air conditioning
$CF_3CF_2CHCl_2$	HCFC-225ca	Cleaning solvent/aerosol solvent, small amount in
CF_2ClCF_2CHFCl	HCFC-225cb	adhesives, coatings, and inks
$CF_3CH_2CHF_2$	HCFC-245fa	Foam Blowing Agent
$CHFCl_2$	HCFC-21	Refrigerant, solvent, and aerosol propellant

Using these trends, the Holmes/Heard research group is able to study model compounds, in order to obtain a comprehensive understanding of the role of the 1,1-HX elimination reaction in the degradation of HCFCs. 1,1-Dichloropropane ($CD_3CD_2CHCl_2$), a model compound for two terminal chlorines on a three carbon chain, is the focus of this study. The main objectives of this study include the following: (1) To determine the rate of decomposition to form Z and E isomers of 1-Chloropropene for both 1,1-HCl and 1,2-DCl elimination, (2) the ratio of Z versus E from 1,1-HCl elimination, as well as the ratio of Z versus E for the 1,2-DCl elimination, and (3) the ratio of 1,2-DCl versus 1,1-HCl elimination for Z-1-Chloropropene and the ratio for E-1-Chloropropene.

2. Experimental Methods

Samples of C_2D_5I, $CHCl_3$, and $CF_3CH=CH_2$ were placed into a quartz vessel, ranging from 9-1050 cm^3, with a droplet of Hg. The molar ratio of reactants were 5:2:4 respectively. All samples were prepared on a grease-free vacuum with an electronic manometer to measure the pressures to the nearest thousandth of torr, with error of ±0.05%. A calibrated volume of 13.02 cm^3 was used. With a known temperature, calibrated volume, and pressure, the pressure in the reaction vessel can be determined. The reaction vessels were irradiated with 253.7 nm resonance line of a Hg germicidal lamp. Irradiation times ranged from five minutes to four seconds, depending on the vessel size. Once

irradiated, the $\bullet CD_3CD_2$ and $\bullet CHCl_2$ combined to form the chemically activated target molecule, $CD_3CD_2CHCl_2^*$, as seen in the Equation 2d. The chemically activated molecule underwent elimination as seen in Figure 1.

The contents of the vessel were then transferred to the vacuum line of a gas chromatograph. Two gas chromatographs were used during this study. Each were attached to a mass spectrometer (Shimadzu QP5000 and Shimadzu GC-MS QP2010) as a detector and analyzed with a Restek RTX-624 and a RTX-200 column, respectively. Commercial samples were obtained of $CH_3CH=CHCl$ and $CH_3CH_2CHCl_2$ and analyzed to determine identification of products and a calibration factor of 0.55. Retention times and masses of the products can be seen in Table 2.

Table 2. GCMS retention times and analyzed mass of major products.

(*E/Z*) Product	Mass (m/z) for analysis	Mass (m/z) of parents	Retention Time (min)
Z-CD$_3$CD=CHCl	80	80/82	22.2
E-CD$_3$CD=CHCl	80	80/82	23.5
Z-CD$_3$CD=CDCl	81	81/83	22.2
E-CD$_3$CD=CDCl	81	81/83	23.5
CD$_3$CD$_2$CHCl$_2$	84	117/119/121	39.4

3. Results and Discussion

Experimental measurements were taken for 22 samples over a pressure range of 0.770-15.4 torr, in order to determine the decomposition and stabilization product ratios. The D/S ratios were plotted and are presented in Figure 2, 3 and 4. The total unimolecular rate constant was determined in pressure units by plotting the sum of the yields of the four decomposition products divided by the stabilized product, $CD_3CD_2CHCl_2$, verses 1/P (Figure 2), and found to be 2.30 ± 0.094 torr. The experimental rate constant for 1,2-DCl elimination pathway is 1.96 ± 0.083 torr and for 1,1-HCl elimination pathway is 0.34 ± 0.011 torr (Figure 3). Experimental rate constants for the individual pathways were determined by plotting the yield of each decomposition product against the stabilized product (Figure 4). The individual rate constants can be found in Table 3 and are defined as $k_{exp}= (P)(D/S)$.

Table 3. Rate constants of elimination pathways of 1,1-Dichloropropane.

Elimination Pathway	Product	k_{exp} (torr)
1,2-DCl	*Z*-CD$_3$CD=CHCl	1.01 ± 0.04
1,2-DCl	*E*-CD$_3$CD=CHCl	0.76 ± 0.04
1,1-HCl	*Z*-CD$_3$CD=CDCl	0.229 ± 0.010
1,1-HCl	*E*-CD$_3$CD=CDCl	0.106 ± 0.004

Experimental measurements were taken for 32 samples over a pressure range of 0.135-15.4 torr, in order to find the product ratios. The branching ratio for the 1,2-DCl pathway (*Z*-CD$_3$CD=CHCl/*E*-CD$_3$CD=CHCl), the 1,1-HCl pathway (*Z*-CD$_3$CD=CDCl/*E*-CD$_3$CD=CDCl), and for the comparison of the 1,2-DCl/1,1-HCl for each of the isomers (*Z*-CD$_3$CD=CHCl/*Z*-CD$_3$CD=CDCl and *E*-CD$_3$CD=CHCl/*E*-CD$_3$CD=CDCl) can be seen in Figure 5. The branching ratio for the total 1,2-DCl verses 1,1-HCl elimination products can be seen in Figure 6. No calibration factor is needed to compare the rates of decomposition directly.

At high pressure, the ratio of their individual rates, as noted in Table 4, closely resembles the product ratios from Figure 5. At low pressures, the product ratio of *Z*-CD$_3$CD=CHCl/*Z*-CD$_3$CD=CDCl decreases to 4.9 and *E*-CD$_3$CD=CHCl/*E*-CD$_3$CD=CDCl decreases to 5.6. At low pressures the molecule has enough energy to undergo 1,2-DCl or 1,1-HCl elimination, whereas at high pressures there are more collisions occurring, thus decreasing energy available to the molecules.

Therefore, either at high pressure the majority of the molecules only have enough energy to undergo 1,2-DCl elimination, since it has a lower energy transition state. Or the 1,1-HCl elimination forms CD_3CD_2CCl and at high pressures the carbene is stabilized by collision before isomerizing to *E* or *Z* CD$_3$CD=CDCl. This correlation can be

seen in Figure 6. The branching ratio for 1,2-DCl/1,1-HCl is 5.75. In addition, the *Z* confirmation is lower in energy and at high pressures the product does not have enough energy to isomerize to *E*. This causes the decrease in the product ratio of *Z/E*-CD₃CD=CHCl and *Z/E*-CD₃CD=CHCl both to 1.8 at low pressures.

Table 4. Ratios of 1,2-DCl and 1,1-HX elimination products at high and low pressure.

Ratio of Products	High Pressure (Branching Ratio Plot)	Low Pressure (Branching Ratio Plot)	Ratio of Slopes (D/S Plot)
Z/E-CD₃CD=CHCl	2.1	1.8	1.34
Z/E-CD₃CD=CDCl	3	1.8	2.15
Z-CD₃CD=CHCl/ *Z*-CD₃CD=CDCl	6.2	4.9	4.4
E-CD₃CD=CHCl/ *Z*-CD₃CD=CDCl	7.2	5.6	7.1

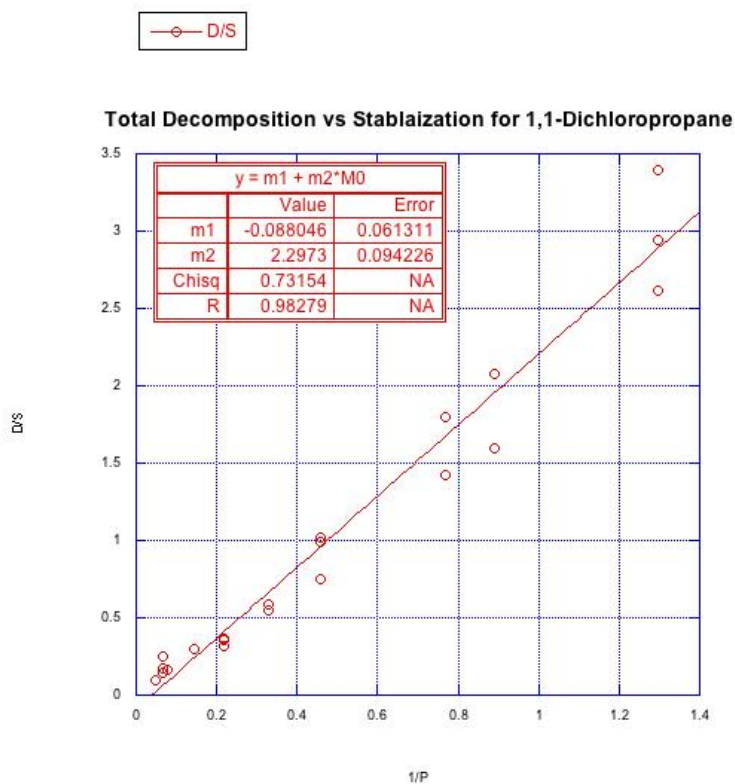Figure 2. Total decomposition versus stabilization plot for 1,1-Dichloroprane.

Note: y = m1 + m2*MO, is in the format of y = b + mx where m1 is the x-intercept, m2 is the slope, and MO is x. Chisq is the Chi-squared value and R is the correlation coefficient. This holds true for Figures 2-6.

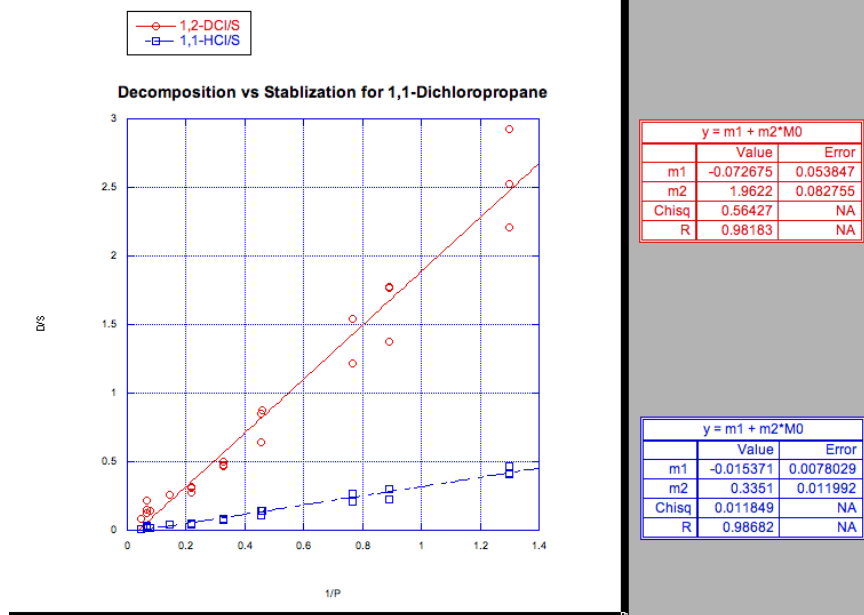Figure 3. Decomposition versus stabilization plot for 1,1-Dichloroprane for the two major pathways 1,2-DCl elimination forming CD$_3$CD=CHCl and 1,1-HCl elimination forming CD$_3$CD=CDCl.
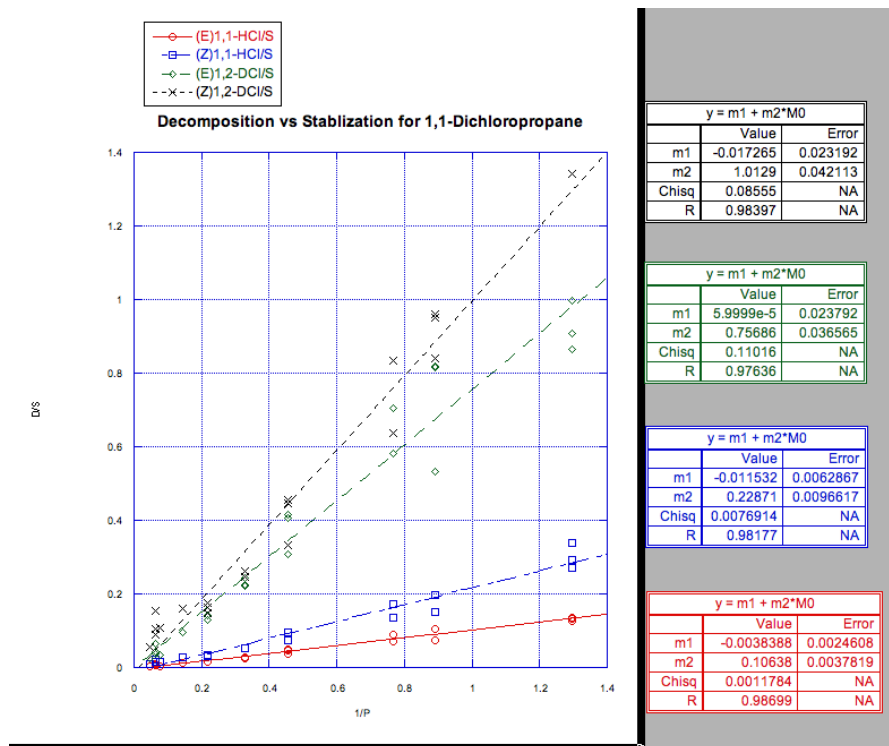

Figure 4. The decomposition versus stabilization plot for the four major elimination products of 1,1-Dichloropropane.
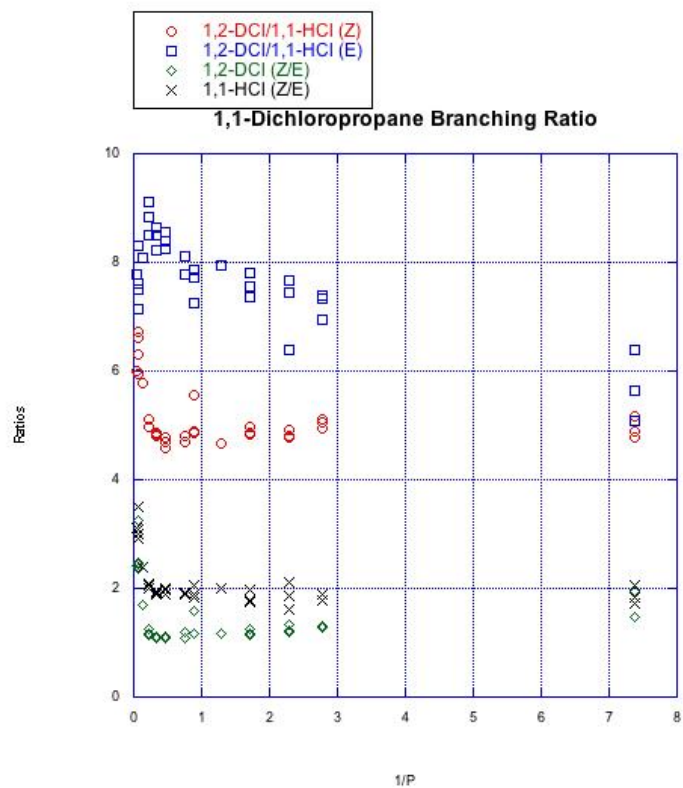
Figure 5. The branching ratio plot for the four major elimination products of 1,1-Dichloropropane.
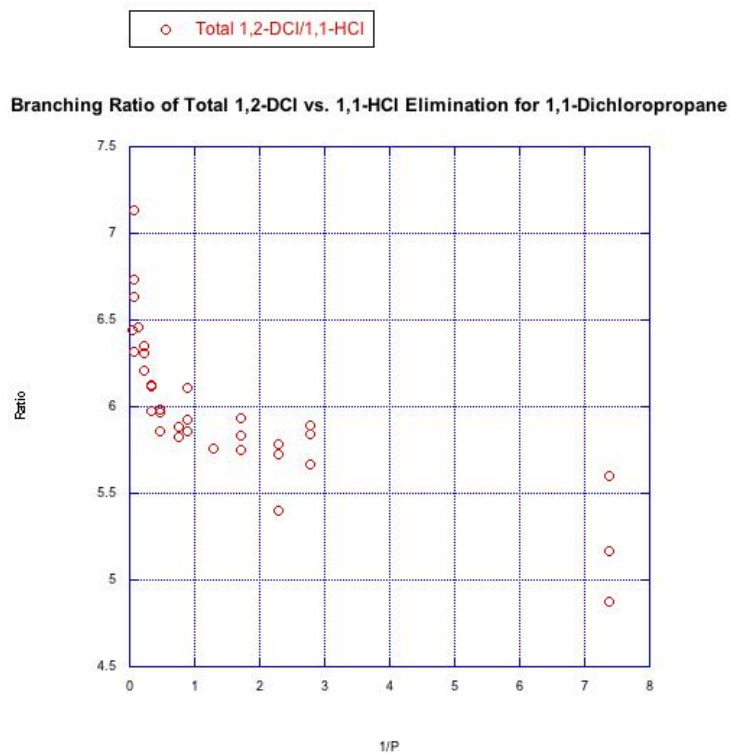

Figure 6. The branching ratio plot for 1,2-DCl versus 1,1-HCl elimination.

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4. Conclusion

Although HCFCs are a better alternative to CFCs, they still deplete the ozone layer and are greenhouse gases with long atmospheric lifetimes. Due to HCFCs environmental hazard, methods to recover and either destroy or to convert HCFCs into useful chemical feedstock. However, fundamental understandings of HCFCs' degradation pathways are not fully understood. In order to reliably evaluate the potential of converting halocarbons into feedstock via computational models, there needs to be a fundamental understanding of the kinetic parameters of each degradation pathway.

The 1,2-HX elimination has been extensively studied by the Holmes/Heard research. The 1,1-HX elimination has not been as widely studied and is the current main focus of the research group. Determining the rates of all possible degradation pathways, 1,2-HX and 1,1-HX included, is vital to those attempting to develop viable pathways for converting HCFCs and HFCs into chemical feedstock and to those attempting to develop computational models for their destruction.

1,1-Dichloropropane ($CD_3CD_2CHCl_2$) is a model compound for two terminal chlorines on a three-carbon chain. Rate constants for the four unimolecular reaction channels of $CD_3CD_2CHCl_2^*$ were measured by the chemical activation technique. The rate of the four decomposition products versus stabilization is 2.30 ± 0.094 torr. The four decomposition products are Z-$CD_3CD=CHCl$, E-$CD_3CD=CHCl$, Z-$CD_3CD=CDCl$, and E-$CD_3CD=CDCl$, with unimolecular rate constants of 1.01, 0.76, 0.229, 0.106 torr, respectively. The branching fractions for the Z/E-1,2-DCl pathway products, Z/E-1,1-HCl pathway products, Z-$CD_3CD=CHCl$/Z-$CD_3CD=CDCl$, and E-$CD_3CD=CHCl$/E-$CD_3CD=CDCl$ are 2.1, 3, 6.2, and 7.2 at high pressure, respectively, and 1.8, 1.8, 4.9, and 5.6 at low pressures, respectively. The Z-isomer of each elimination reaction is lower in energy; therefore, the molecules are only able to isomerize to it at low pressures. The 1,2-DCl elimination is favored over the 1,1-HCl, due to lower activation energies. The calculated rate constants for this model compound will lend to a better understanding of likely products formed during the destruction or conversion of HCFCs.

5. Acknowledgements

6. References

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