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Characterization of Unimolecular Elimination Reactions for CD_3CD_2CHFCl

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Abstract

Hydrochlorofluorocarbons (HCFCs) are greenhouse gases and can deplete the ozone layer. To stop further adverse effects, the Montreal Protocol requires HCFCs to be collected and destroyed by 2020 for developed countries and 2030 for developing countries. We studied the decomposition reactions of CD_3CD_2CHFCl as a model system to emulate HCFCs currently in use to better understand how they would react when subjected to high temperature in a destruction chamber. The unimolecular reactions of energized CD_3CD_2CHFCl molecule are 1,1-HCl, 1,1-HF, 1,2-DCl and 1,2-DF elimination with a ratio of 0.16: 0.004: 0.82: 0.013. All elimination pathways form cis- and trans-alkenes and the ratio varied from 1 to 3.5. The data collected shows that the 1,1-HX (X=Cl, F) elimination reaction, forming a carbene, can become the dominant degradation pathway at high temperatures. After all results have been collected, they are calibrated to account for the fact that different molecules fragment differently. Calibrations using the stabilized product were done via proxy because some pure samples could not be acquired. Calibration factors are multiplied into the data and ranged from 1.71 to 8.38. By studying these degradation pathways, it can better understood how to destroy them or convert them into feedstock for other industries after they are all banned.

1. Introduction

Chlorofluorocarbons (CFCs) are gases that have the ability to cool down when they expand in the gas phase. It is this property that is the reason why they are used in refrigerators and air conditioners. CFCs have also been known to cause ozone depletion and have been classified as greenhouse gases. Ozone destruction can happen because CFCs can release atomic chlorine, which then starts a chain reaction that depletes ozone in the stratosphere.[1] The destructive potential that these gases have is known as the ozone depletion potential (ODP),[2,3] which tells us the amount of potential harm a gas can do to the ozone layer. CFCs have a large ODP and caused a lot of damage to the ozone layer and because of this, the Montreal Protocol was established in 1987. This agreement stated that CFCs would be phased out by 1995 for developed countries and 2010 for developing countries.[4]

Table 1. Common HCFC's used with $RCHX_2$ structure (X = Halogen)

Designation	Formula
HCFC- 22	$CHClF_2$
HCFC-124	$CHClFCF_3$
HCFC-123	CF_3CHCl_2
HCFC-21	$CHFCl_2$
HCFC-121	$CHFClCCl_3$

Hydrochlorofluorocarbons (HCFCs) and HFC's started to be used as a replacement for CFCs in the late 1980's. Using HCFCs was justified by the fact they are reactive with OH radicals in the lower atmosphere, so that fewer HCFC molecules would reach the stratosphere and react with ozone.[5] The problem with HCFCs is that they are still greenhouse gases that have a major impact on climate change.[5] To stop the further depletion of the ozone layer and the impacts of climate change, the Montreal Protocol also stated that HCFCs would be phased out by 2020 for developed countries and 2030 for developing countries.[4] But the HCFC gases that are already inside air conditioner compressors and refrigerator units have to be collected and destroyed to stop further ozone depletion and climate change.

Some of the ways that HCFCs and HFC's can be destroyed include electrochemical and photolysis reactions.[1,9] We plan to examine the degradation of HCFC/CFCs to form new products by first doing a photolysis reaction with them to make chemically activated molecules that can degrade via unimolecular reactions. Using UV light to perform a photolysis reaction in a closed system for small amounts of time, we can see that radicals can form and react with each other or other molecules to give new products. When two radicals collide with one another, they form a bond and release energy, which is still contained in the product.

$$\mathrm{C_2D_5 + \cdot CHCl_2 \rightarrow CD_3CD_2CHCl_2^*} \tag{1a}$$

$$\mathrm{\rightarrow CD_3CD_2H + CCl_2} \tag{1b}$$

$$\mathrm{\rightarrow CD_2{=}CD_2 + CDHCl_2} \tag{1c}$$

$$\mathrm{CD_3CD_2CHCl_2^* \rightarrow DCl} + Z\text{- and } E\text{-}\mathrm{CD_3CD{=}CHCl} \tag{2a}$$

$$\mathrm{\rightarrow HCl + CD_3CD_2C\text{-}Cl} \tag{2b}$$

$$\mathrm{+ M \rightarrow CD_3CD_2CHCl_2 + M} \tag{2c}$$

$$\mathrm{CD_3CD_2C\text{-}Cl \rightarrow} Z\text{- and } E\text{-}\mathrm{CD_3CD{=}CDCl} \tag{3a}$$

Figure 1. Possible reaction scheme of C_2D_5 and $CHCl_2$ radicals. It also shows how the major product can release energy by colliding with another molecule or the container wall (M) or by undergoing a unimolecular reaction.[6]

To release this energy, the molecule can either collide into another body to transfer that energy or undergo a unimolecular reaction. Unimolecular reactions involve one molecule reacting by itself to form new products as shown in figure 1. One way this reaction can happen is by an elimination reaction where two substituents are removed from the reacting molecule. When HCFCs undergo these unimolecular elimination reactions, they can either have the chlorine and the hydrogen combine and leave or have the fluorine and the hydrogen react and leave. When these two different atoms react, they are usually thought of as two atoms from two adjacent carbons reacting, this is known as a 1,2-HX elimination (X= F, Cl) shown by reaction 2a in figure 1. But this is not the only type of reaction that can occur for certain HCFC's or HFC's. Two atoms from the same carbon can also combine and cause an elimination reaction, this is known as a 1,1-HX elimination (X= halogen) and the other product being formed is a carbene as shown by reaction 2b in figure 1. For 1,1-HX elimination to occur, there needs to be a second halogen on this terminal carbon to stabilize the carbene product because of its electronegativity and lower the threshold energy for the reaction.[6] In complex haloalkanes, halogens can also switch between carbons to form other isomers.[7]

The goal of this research is to look at 1,1-HX eliminations that can happen to chemically activated CD_3CD_2CHFCl molecules. This particular model was chosen because of carbon chain length, presence of deuterium, and the two different halogens present. Mercury photosensitization of CD_3CD_2I and $CHFCl_2$ produced CD_3CD_2 and $CHFCl$ radicals that combine to make the activated CD_3CD_2CHFCl molecules. Using deuterium as a way to differentiate products by weight, 1,1-HX elimination and a 1,2-HX elimination can be determined using a Gas chromatography–

mass spectrometry unit (GCMS). These 1,1-HX elimination pathways can compete with 1,2-HX eliminations at high levels of energy or temperature.[6] By performing experiments at different pressures, the rate constants for these reactions can be experimentally measured and the relative importance of the 1,1-HX versus the 1,2-HX elimination processes determined.

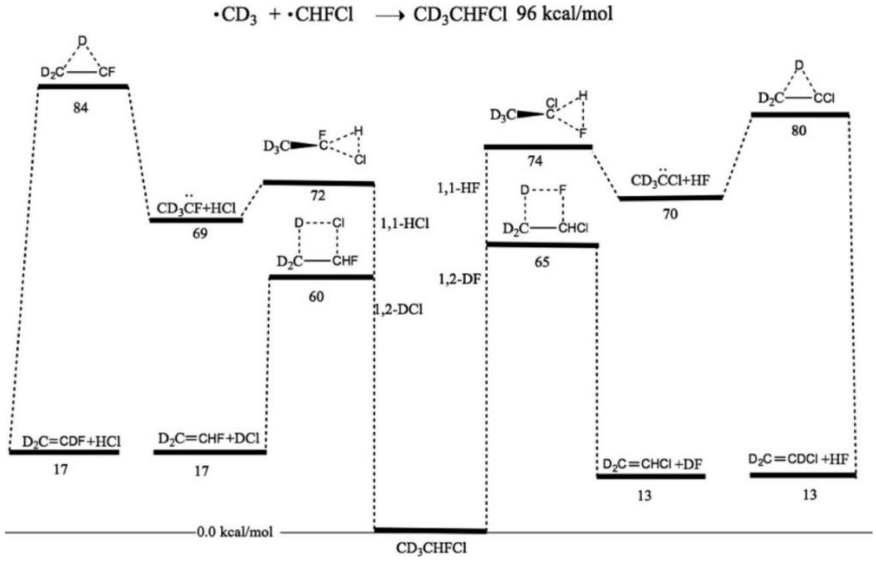


Figure 2. Energies for the products of CD_3 and CHFCl radicals using computational data and observed products using experimental data.[7]

Previous research performed by our research group includes photolysis reactions of haloalkanes, like HCFCs, to determine the amount of 1,1-HX elimination that can happen when pressure is changed. From these experimental systems, computational studies were also done to calculate threshold energies and show possible transition states as shown in figure 2.[6,7] A study done by Larkin et al.[6] showed unimolecular reactions of $CD_3CD_2CHCl_2$ and $CHCl_2CHCl_2$ with experimental rate constants and computational data to corroborate the experimental data. The study of halogen interchange has also been done, showing threshold energies and proposed transitions state by Lisowski et al.[8] The goal of previous studies was to better understand the 1,1-HX elimination and halogen interchange and corroborate with computational results in different systems of interest. This research also provided a better understanding of how changes in substituents affected the amount of 1,1-HX elimination that would happen. This study is to develop a similar understanding of the 1,1-HX elimination reaction, where X = F or Cl.

Previous research also shows decomposition of HCFCs in the presence of O_2 and H_2O gas. Spiess et al.[9] looks at the decomposition of two different species of HCFCs, $CHFCl_2$ and CF_2ClCH_3. Their study only focuses on the complete decomposition of the HCFCs, not looking at the products that can be formed in the process to better understand the decomposition. Another study done by Seo et al.[2] looks at the decomposition of CHF_2Cl in the presence of TiO_2 photocatalyst balls and a microwave discharge electrodeless mercury lamp to react with OH radicals. But again, the products are not observed, in part by the presence of TiO_2 that can trap much of the products. Other studies show computational data regarding (a) bond dissociation energies in HCFCs, done by Shi et al.[10] and (b) geometries of the different transition states some HCFCs may have for 1,1-HX eliminations done by Fu et al.[11] Most of the findings to date do not look at the products of decomposition of HCFCs, but instead look at how well it degrades without looking at any useful products it can make. Theoretical studies help hypothesize possible energies and transition state mechanisms, but without experimental data, the hypothesis cannot be confirmed. The only research group known that is currently looking at the 1,1-HX elimination and interchange products both experimentally and computationally in the gas phase is our research group.

To produce and detect these products, many different instruments are used. Samples are prepared in vacuum vessels, under closed conditions. Radical formation and overall reactions were performed under a germicidal UV lamp. For data collection, a Gas chromatography–mass spectrometry unit is used. This research can shed more light and gain further knowledge of how carbenes form in the gas phase and better understand what products are formed under certain conditions. Carbenes can be used in organometallic and organic chemistry as well as cyclopropanation.

2. Experimental Methods

The model system investigated was CD_3CD_2CHFCl. To make this molecule, CD_3CD_2I, $CHFCl_2$ and $CF_3CH=CH_2$ and a droplet of Hg were loaded into quartz vessels ranging in volume (4 cc to 135 cc vessels) and irradiated with 253.7 nm resonance line of a 15 W Hg germicidal lamp. Using the Hg sensitization technique created atomic chlorine and iodine, so $CF_3CH=CH_2$ was used as a Cl and I atom scavenger.[7] The molar ratios of CD_3CD_2I/ $CHFCl_2$/ $CF_3CH=CH_2$ were 1:1:2 and different irradiation times were tested and the time chosen was 5 minutes. The principle reactions of CD_3CD_2 and CHFCl radicals, which are combination/disproportionation reactions at room temperature, are listed below. The asterisk denotes vibrational excitation.

$$\bullet CD_3CD_2 + \bullet CHFCl \rightarrow CD_3CD_2\text{-}CHFCl^* \qquad (1a)$$

$$\rightarrow CD_3CD_2H + :CFCl$$

$$\rightarrow CD_2{=}CD_2 + CDFCl$$

$$CD_3CD_2 + CD_3CD_2 \rightarrow CD_3CD_2CD_2CD_3^* \qquad (1b)$$

$$\rightarrow CD_3CD_3 + CD_2{=}CD_2$$

$$CHFCl + CHFCl \rightarrow CHFCl\text{-}CHFCl^* \qquad (1c)$$

$$\rightarrow CH_2FCl + :CFCl$$

Scheme 1. Initial radical reaction of CD_3CD_2 and CHFCl radicals

The CHFCl-CHFCl* underwent Cl/F interchange to give $CHF_2\text{-}CHCl_2$, which can also undergo several elimination reactions.[7] Because of the low yield of this reaction, no attempt was made to study and collect data for this unimolecular reaction. The CFCl carbene can recombine, react with the initial radicals or be scavenged by $CF_3CH=CH_2$. These processes should not interfere with the decomposition reactions of $CD_3CD_2\text{-}CHFCl^*$ because of the amount that would be produced is minimal in comparison to the other reactions.

$$CD_3CD_2\text{-}CHFCl^* \rightarrow DCl + CD_3CD{=}CHF \qquad (2a)$$

$$\rightarrow DF + CD_3CD{=}CHCl \qquad (2b)$$

$$\rightarrow HCl + CD_3CD_2CF \rightarrow CD_3CD{=}CDF \qquad (2c)$$

$$\rightarrow HF + CD_3CD_2CCl \rightarrow CD_3CD{=}CDCl \qquad (2d)$$

$$M \rightarrow CD_3CD_2\text{-}CHFCl\ (S) \qquad (3)$$

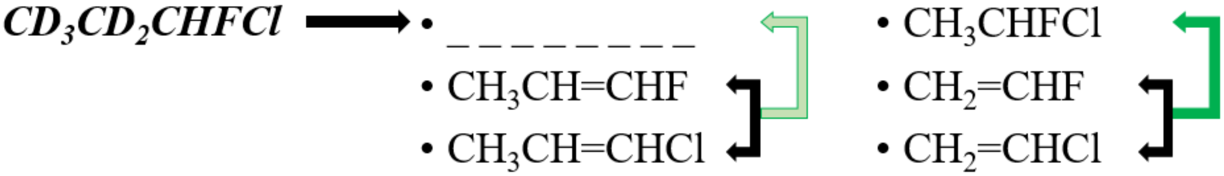
Scheme 2. Decomposition of chemically activated $CD_3CD_2\text{-}CHFCl^*$

The $CD_3CD_2CHFCl^*$ formed the stabilized molecule M by energy transfer or the decomposition product D shown in scheme 2. The CD_3CD_2CF and CD_3CD_2CCl carbenes can isomerize by having D atom migration to give E- or Z- $CD_3CD{=}CDF$ and E- or Z- $CD_3CD{=}CDCl$ respectively. These products were differentiated from $CD_3CD{=}CHF$ and $CD_3CD{=}CHCl$ with a mass spectrometer.

After the data has been collected, it must be calibrated to achieve the true values for the plots. Calibrations are done to compensate for the fact that each molecule fragments differently in the mass spectrometer, so the true integration values can be off because it may not be showing all of the product. To perform calibrations, a pure sample of all the products being observed is needed and compared to each other in the mass spec, then a calibration factor or ratio can be calculated and multiplied to the uncalibrated plots where possible. Pure samples of each product were acquired except for the stabilized product CD_3CD_2-CHFCl due to availability issues. As a solution to this issue, it was decided that the calibrations can still be done via proxy. To do calibrations via proxy, molecules similar to a missing molecule can be used and compared with each other to determine an estimate of the calibration factor that can be used. Once the data is collected, the calibration factor can be calculated using Equation 1. The calibration factor is calculated using the known ratio of the amount of each sample that is put into the vessel and the measured ratio that is observed from the GCMS.

$$(\textit{Calibration Factor}) = (\textit{Known Ratio})/(\textit{Measured Ratio}) \qquad (1)$$

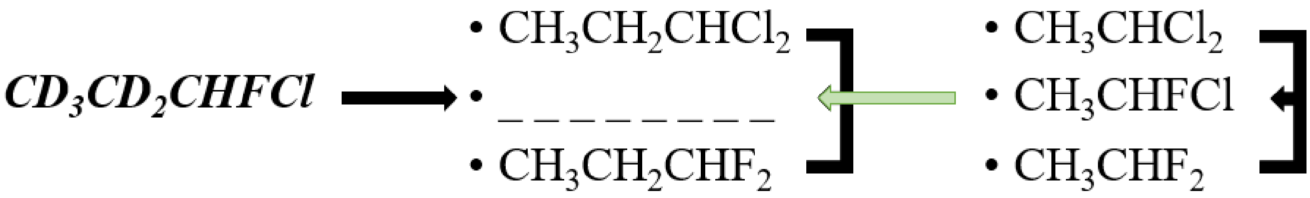
Two Calibration schemes were tested to find a more accurate calibration factor involving the stabilized product CD_3CD_2-CHFCl via proxy. Scheme 3 uses vinyl fluoride, vinyl chloride, and 1,1-chloroflouroethane as a way to predict the calibration factor. To ensure that this system would give us accurate results, the calibration factor of CH_2=CHF to CH_2=CHCl is compared to the calibration factor of CH_3CH=CHF to CH_3CH=CHCl. The calibration ratios would have to be nearly identical to each other to signify that fragmentation patterns for the C3 and the C2 versions would be similar enough and that we could use the ratio of CH_2=CHF to CH_3CHFCl and CH_2=CHCl to CH_3CHFCl as a proxy for CD_3CD_2-CHFCl in the calibration factor for CH_3CH=CHF to CD_3CD_2-CHFCl and CH_3CH=CHCl to CD_3CD_2-CHFCl. Unfortunately, the calibration factors for the ethene variants were not similar enough to the propene variants, so another scheme would have to be used to try at get an accurate calibration factor.



Scheme 3. First calibration proxy, using vinyl chloride, vinyl fluoride, and 1,1-chlorofluoroethane. Other products were also used but not shown above

Scheme 4 uses 1,1-dichloroethane, 1,1-difluoroethane, 1,1-chlorofluoroethane, 1,1-dichloropropane, 1,1-difluoropropane as a way to predict the calibration factor. First the calibration factor of CH_3CHF_2 to CH_3CHCl_2 is compared to the calibration factor for $CH_3CH_2CHF_2$ to $CH_3CH_2CHCl_2$. This is done to ensure that the di-halo-ethane variants fragment the same way as the di-halo-propane variants. If those results are identical, then we can average the calibration factor for CH_3CH=CHCl to CD_3CD_2-CHF_2 and the calibration factor for CH_3CH=CHCl to CD_3CD_2-$CHCl_2$ to arrive at the calibration factor for CH_3CH=CHCl to CD_3CD_2-CHFCl. The same thing can be done to get the calibration factor for CH_3CH=CHF to CD_3CD_2-CHFCl.

An additional calibration factor is also calculated for CH_3CH=CHF to CH_3CH=CHCl. This can be done by dividing the calibration factor for CH_3CH=CHF to CD_3CD_2-CHFCl by the calibration factor for CH_3CH=CHCl to CD_3CD_2-CHFCl.



Scheme 4. Final calibration proxy, using 1,1-Dichloroethane, 1,1-Difluoroethane, 1,1- chlorofluoroethane, 1,1-Dichloropropane, 1,1-Difluoropropane

3. Results and Discussion

Using a Gas chromatography-mass spectrometry unit, all scheme 2 products were identified in a test run. Mass of primary ions produced by the reactants and products were identified in the table below.

Table 2. Primary masses of ions detected for products and reactants.

Molecule	Primary M/Z	Peak Retention Time (min)	Fragment molecule Ions
CD_3CD_2I	161, 34	32	$CD_3CD_2^+ + I^-$
$CHFCl_2$	67, 69	20.4	$CHFCl^+$
$CF_3CH{=}CH_2$	95, 77	15.5	$CF_3C{=}CH_2^+ + CF_2CH{=}CH_2^+$
CD_3CD_2CHFCl	66	29	$CD_3CD_2CHF^+$
$CD_3CD{=}CHF$	64	16.0, 16.5	$CD_3CD{=}CHF^+$
$CD_3CD{=}CHCl$	80	21.7, 23.7	$CD_3CD{=}CHCl^+$
$CD_3CD{=}CDF$	65	16.0, 16.5	$CD_3CD{=}CDF^+$
$CD_3CD{=}CDCl$	81	21.7, 23.7	$CD_3CD{=}CDCl^+$

These masses were chosen because of the percent abundance and little interference with masses of other molecules. Products 2a-d have E/Z isomers that show up separated by the gas chromatograph further providing insight on the amount of each isomer being made.

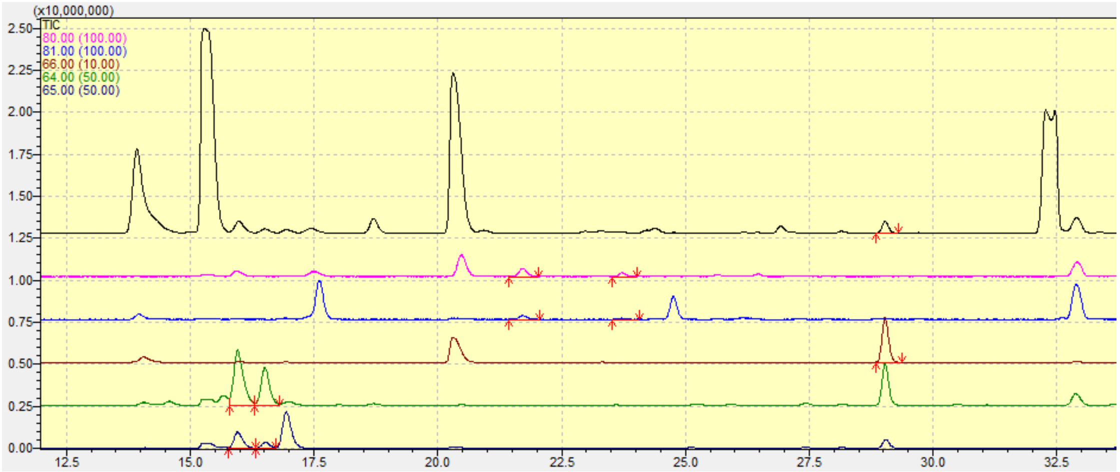


Figure 3. Gas Chromatograph of reaction vessel.

Figure 3 shows the separation, time and integration of the products done by a gas chromatograph. Even with the 5 minute reaction time under UV light, most of material is still left as reactants. Both 1,1-HX and 1,2-DX elimination products come out at nearly the same time because of the similarity in mass and polarity. The time difference between the E/Z products for Cl elimination is not as large as the time difference between E/Z products for F elimination. Both the TIC for the stabilized product and m/z of 66 were integrated for comparison. The reaction of CD_3CD_2I and $CHFCl_2$ in the presence of $CF_3CH{=}CH_2$ formed many products that included 1,1-HX and 1,2-DX elimination. The 1,1-HX elimination products have a D-atom migration to the carbene observed via GCMS. The ratio of concentration of a decomposition product to the stabilized product can equal the ratio of the rate constant of the decomposition product to the collision frequency of the stabilized (k_M) for each elimination product we look at. This can also be done for the E/Z isomers of each elimination.

$$\frac{K^{1,2-HCl}[CD_3CD_2CHFCl*]}{K_M[M][CD_3CD_2CHFCl]} = \frac{{}^{E+Z}[CD_3CD = CHF]}{[CD_3CD_2CHFCl]}$$

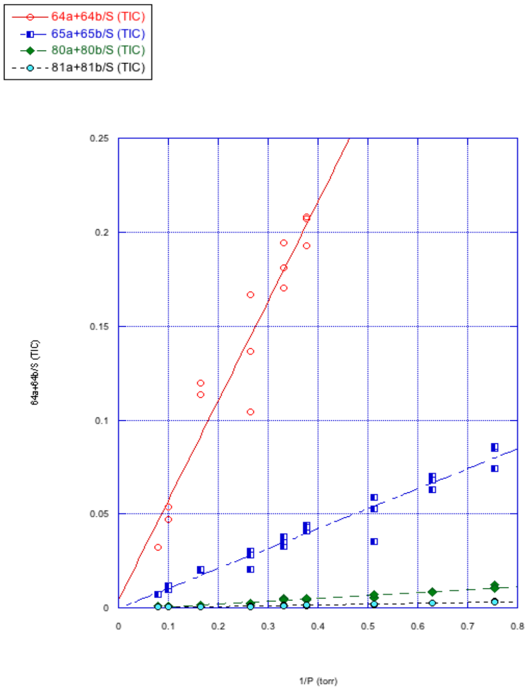
$$\frac{K^{1,2-HCl}}{K_M}\frac{1}{[M]} = \frac{{}^{E+Z}[CD_3CD = CHF]}{[CD_3CD_2CHFCl]}$$

$$\frac{K^{1,2-HCl}}{K_M}\frac{1}{P} = \frac{D}{S} \qquad (2)$$

$$b + mx = y$$

Equation 2. Plotting data using integration values into a standard linear plot

By understanding that the product ratio is equal to the rate ratio, we can use the equation scheme 2 to get a linear line for our D/S plot. The Y-intercept for this plot should be zero, the Y-axis is the ratio of decomposition over Stabilized products, and the Slope will give the ratio of the rates of decomposition over stabilized products. To actually get the rate for each individual decomposition product, the k_M will eventually have to be calculated and multiplied by the slope of the D/S plots. The way k_M is calculated involves using Collision cross-section of the different gas products and average velocity calculations.



y = m1 + m2*M0		
	Value	Error
m1	0.0041163	0.012954
m2	0.52976	0.047379
Chisq	0.004216	NA
R	0.95521	NA

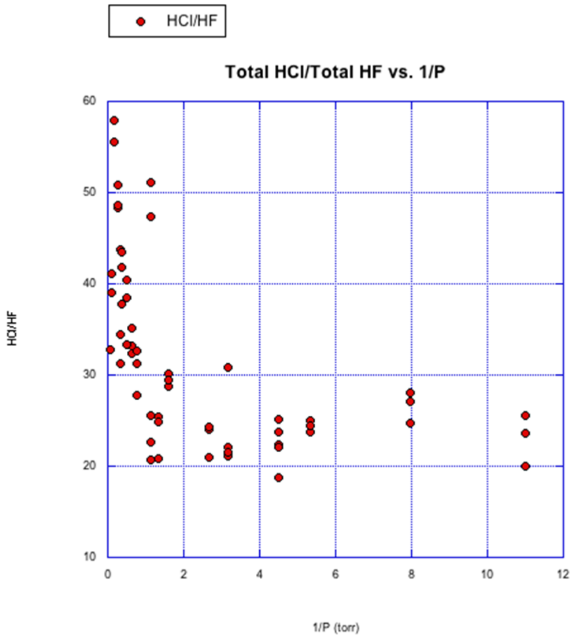
y = m1 + m2*M0		
	Value	Error
m1	-0.00012298	0.0024443
m2	0.10608	0.0053922
Chisq	0.0006309	NA
R	0.97393	NA

y = m1 + m2*M0		
	Value	Error
m1	-0.00092241	0.00035217
m2	0.015163	0.00077689
Chisq	1.3096e-5	NA
R	0.97353	NA

y = m1 + m2*M0		
	Value	Error
m1	-0.00013974	0.00012337
m2	0.0043406	0.00027214
Chisq	1.607e-6	NA
R	0.96112	NA

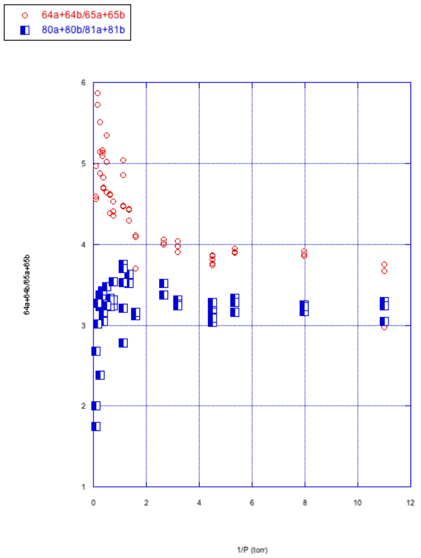
Graph 1. D/S plot for products 2a-d for high pressure runs

Graph 1 shows the degradation products over stabilized product (D/S) verses inverse pressure. The data shows that the amounts of all decomposition products increase at different rates as the pressure decreases. This data can be used to find rate constants for the reaction after the data has been calibrated. We use data under 1/p of less that 1 to avoid data that starts curving upwards due to cascade deactivation, which happens when a collision removes some energy but the molecule can still be reactive. At higher pressures, there are more collisions per second, so the molecule is deactivated before it can react.



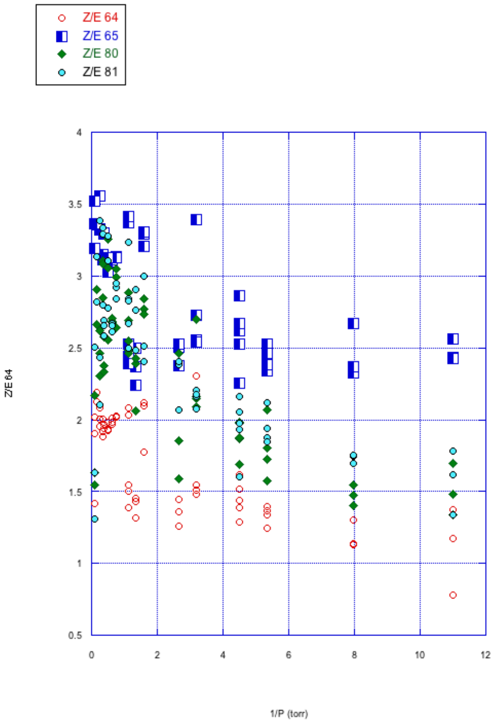
Graph 2. Plot for HCl+DCl/HF+DF ratios at different pressures

Graph 2 looks at how much 1,1-HF and 1,2-DF elimination products are made compared to 1,1-HCl and 1,2-DCl elimination products at different pressures. The data shows that at high pressures, the ratio of HCl to HF increases. At lower pressures, the ratio flattens out at about 25. This data can also be calibrated and used to get the final ratio of rate constant values.



Graph 3. Plot comparing 1,2-DX to 1,1-HX for Fluorine elimination and Chlorine elimination ad different pressures

Graph 3 looks at the difference in the amount of 1,2-DX products and 1,1-HX products relative to each other for both Fluorine and Chlorine elimination pathways verses inverse pressure. The data shows that at high pressure, more 1,2-DCl elimination products (circles) are made in comparison to the 1,1-HCl elimination products and that less 1,2-DF elimination products (squares) are made in comparison to the 1,1-HF elimination products. At lower pressures, the ratios for both F- and Cl-elimination are independent of pressure and come out to be about 3.3 and 3.9 respectively.



Graph 4. Plot compares Z-isomers over E-isomers at different pressures

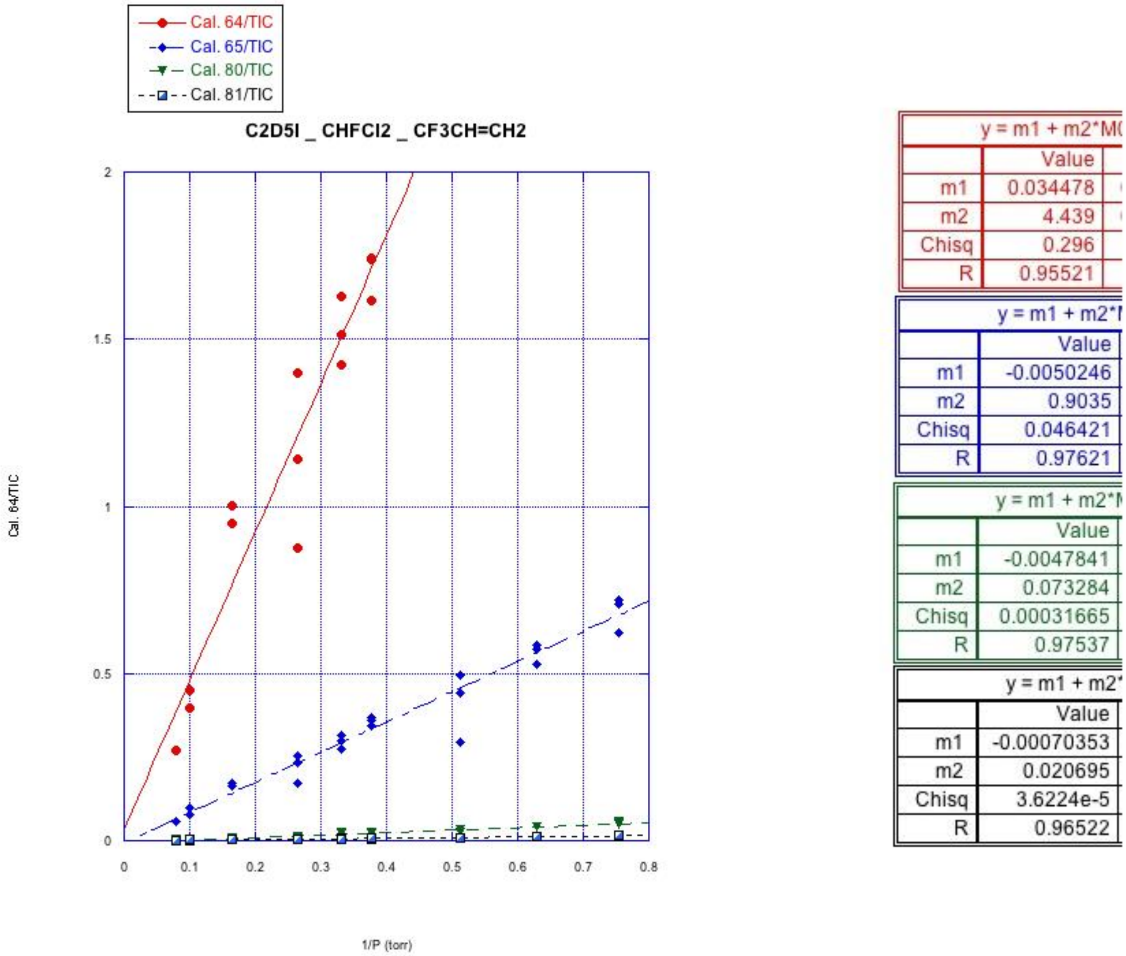
Graph 4 compares how much of Z-isomer and E isomers are made relative to each other at different pressures. All plots show that the ratio of Z- to E- isomers is greater than 1 and is increasing with higher pressure. Cl-elimination data seems to have a step up at higher pressure by about 0.5. That data was collected in the summer of 2016, while lower pressure data was collected in the summer of 2017. The only physical difference between the two summers included replacement of the ion source for the GC-MS. The reason for this difference for the Cl-elimination and why it doesn't seem to affect the F-elimination pathway is still unknown but is being investigated further.

4. Calibrating the data

Only the D/S and the HCl/HF elimination plots can be calibrated because they involve a ratio of different products, every other graph (E vs. Z- alkanes) involves a ratio of the same product but with different isomers or deuterated versions, which we believe should not change the fragmentation patterns between them. Table 3 shows the calibration factors calculated for the final calibration scheme (scheme 4).

Table 4. Calibration factors for the proxy molecules used is scheme 4

Ratio of molecule	*Calibration factor*
CH_3CHF_2 / CH_3CHCl_2	2.3327
$CH_3CH_2CHF_2$ / $CH_3CH_2CHCl_2$	2.3015
$CH_3CH{=}CHCl$ / $CD_3CD_2\text{-}CHF_2$	2.8072
$CH_3CH{=}CHCl$ / $CD_3CD_2\text{-}CHCl_2$	6.6570
$CH_3CH{=}CHF$ / $CD_3CD_2\text{-}CHF_2$	4.9253
$CH_3CH{=}CHF$ / $CD_3CD_2\text{-}CHCl_2$	11.833
$CH_3CH{=}CHCl$ / $CD_3CD_2\text{-}CHFCl$	**4.7321**
$CH_3CH{=}CHF$ / $CD_3CD_2\text{-}CHFCl$	**8.3793**
$CH_3CH{=}CHF$ / $CH_3CH{=}CHCl$	**1.7051**



y = m1 + m2*M	
	Value
m1	0.034478
m2	4.439
Chisq	0.296
R	0.95521

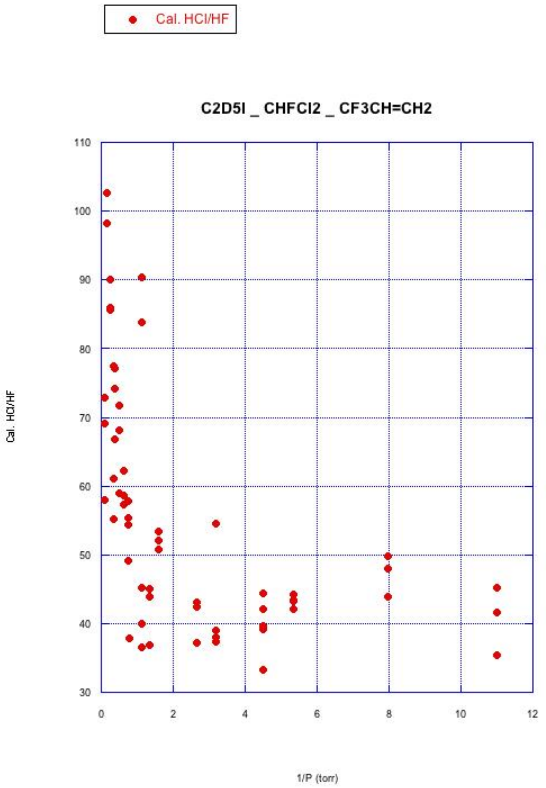
y = m1 + m2*	
	Value
m1	-0.0050246
m2	0.9035
Chisq	0.046421
R	0.97621

y = m1 + m2*	
	Value
m1	-0.0047841
m2	0.073284
Chisq	0.00031665
R	0.97537

y = m1 + m2*	
	Value
m1	-0.00070353
m2	0.020695
Chisq	3.6224e-5
R	0.96522

Graph 5. Calibrated D/S plot for products 2a-d for high pressure runs

Graph 5 takes the original data present on graph 1 and multiplies it with calibration values from table 4. The slope values will later be used for calculating the rate constants for the different pathways. All values are increasing, but still lead to the intercept at higher pressures.



Graph 6. Calibrated Plot for HCl+DCl/HF+DF ratios at different pressures

Graph 6 takes the original data present on graph 2 and multiplies it with calibration values from table 4. It shows that the ratio of Cl-elimination to F-elimination products is even higher at high pressures compared to data in graph 2.

5. Conclusion

HCFCs and CFCs are greenhouse gases and cause ozone destruction. Even though the Montreal protocol will eventually ban HCFCs/CFCs, A/C compressors and refrigerators will still contain them and will have to be collected and destroyed to stop further ozone depletion and climate change.[4] The goal of this research is to investigate CD_3CD_2CHFCl as a model system for HCFCs to the contribution of the 1,1-HX elimination reaction pathway as well as further contribute unimolecular reaction data for the scientific research field. Using a GCMS instrument, reactants and products can be separated and identified. By performing experiments at different pressures, the rate constants for these reactions can be experimentally calculated and the relative importance of the 1,1-HX verses the 1,2-HX elimination processes determined. The results showed that the 1,1-HCl product is about 20% of the 1,2-DCl product and 1,1-HF product is about 25% of the 1,2-DF product. By identifying what products are made at different pressures, specific reactions can be done to get favorable results. Pervious computational research done by the Holmes group has shown that at higher temperatures, 1,1-HX elimination will become more competitive with 1,2-DX elimination, this is due to the fact that 1,1-HX elimination will have a loose transition state, meaning it will have more entropy. The data was then calibrated to compensate for the fact that each molecule fragments differently in the mass spectrometer, so the true integration values can be off because it may not be showing all of the product.

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7. References

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