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Experimental Measurement of the Branching Ratio for the Competitive 1,2-DF/1,1-HF and the E/Z-$CD_3CD=CHF$ and $CD_3CD=CDF$ for the Unimolecular Elimination of HF/DF from $CD_3CD_2CHF_2$

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Abstract

Chlorinated Halocarbons and chlorofluorocarbons (CFCs) have become synonymous with environmental destruction, ozone depletion and the greenhouse effect. HCFCs (hydro chlorofluorocarbons) and HFCs (hydro fluorocarbons) became the interim replacements for CFCs when the Montreal Protocol banned them in 1987. However, these molecules have their own hazardous implications, specifically as greenhouse gases. It is for these reasons that HCFC and HFC compounds will be phased out by 2020 in developed countries and 2030 in developing nations. The cleanup or conversions of these molecules into feedstock are therefore a major priority and point of study. The in lab study of these numerous compounds to determine their degradation processes and how they react in the atmosphere has become vital to the preservation of the environment and the future of our planet. $CD_3CD_2CHF_2$ is the focus of this study because it is a suitable model for many HFC's that will be banned in 2020. Photolysis of CD_3CD_2I and CHF_2I in Pyrex vessels with some Hg_2I_2 using an ultraviolet lamp forms HgI_2 and the CD_3CD_2 and CHF2 radicals that combine to produce chemically activated $CD_3CD_2CHF_2$. Reaction vessels, over a range of pressures, contained approximately a 4:1.5 ratio of CD_3CD_2I and CHF_2I were prepared. A Gas Chromatographer Mass Spectrometer was used for product analysis. The 1,2-DF elimination forms E and Z-$CD_3CD=CHF$ favoring the E-isomer. The 1,1-HF elimination reaction forms the CD_3CD_2CF: carbene that may transfer a D giving E and Z-$CD_3CD=CDF$ also favoring the E formation at certain pressures. It was also found that not all carbene has the energy to undergo D migration and stays in the unstable form. Trapping the unstable carbene with a scavenger was also studied. The competition between the 1,2- and 1,1-HF/DF elimination, the results from DFT calculations for the various reaction channels, and the molecules carbene chemistry will be discussed.

1. Introduction

Chlorinated Halocarbons (CFCs) are culprits of environmental destruction, ozone depletion and the greenhouse effect. The study of these molecules and their various degradation processes are of great interest in the quest to preserve the environment. CFCs were used as pesticides, pharmaceuticals, disinfectants, degreasing agents, coolant fluids, in the cleaning of organic contaminants and as intermediates to chemicals in many industrial processes. These compounds eliminate atomic chlorine which reacts in the atmosphere and are the cause for some Eco-toxicity; they are also implicated in human health defects. HCFCs, Hydro chlorofluorocarbons, became the interim replacements when CFCs were banned by the Montreal Protocol in 1987. However, they offer their own share of problems. The major concern with CFCs is that they undergo degradation in the atmosphere and react with and deplete the stratosphere when they are de-chlorinated, eliminating a protective layer for the earth and increasing the amount of UV radiation that is allowed access to the surface of earth. Atomic chlorine from these molecules reacts in the atmosphere producing harmful substances such as chlorinated aromatic species. HCFCs are actually considered less harmful than CFCs because they are more reactive. These molecules photo-dissociate, or react with OH radicals, in the lower levels of the atmosphere; meaning they absorb light and eliminate a hydrogen and a halogen – either Chlorine, Fluorine, or Bromine. They react more readily with hydroxyl radicals in the troposphere, a lower level of the atmosphere, therefore protecting the stratosphere – a far more protective layer. As they are more reactive, HCFCs have a shorter atmospheric lifetime than CFCs so they were deemed a replacement for the more harmful CFCs.[1] However, they still have hazardous implications, specifically as greenhouse gases. These molecules directly contribute to the re-warming of earth as they absorb in the window that would usually allow infrared radiation to leave the atmosphere. They are also considered more harmful than common greenhouse gases – carbon dioxide, water vapor, and methane – because they more strongly absorb infrared radiation. It is for these reasons that HCFC compounds are planned, by the Montreal protocol, to be phased out by 2020 in developed countries and 2030 in developing nations. The cleanup or conversions of these molecules into feed-stock are therefore a major priority and point of study. For this reason, the study of the reaction of these compounds in the atmosphere, and their degradation processes has become vital to the future of our planet.

The cleanup of CFCs has been a long term project. The main pathways to treat these substances are incineration – burning in the presence of oxygen, pyrolysis – heating without oxygen until breakdown, or conversion of reactants into feedstock to be used in other chemical processes. Most commonly these molecules are treated using pyrolysis or are recovered as organic vapors. The recovery of organic vapors is through adsorption. This is a technique employing micro or macro pores to adsorb the organics from a solid state, based on the van der Waals interaction between molecules. Organic vapors were exempt from the US Clean Air Act of 1990, as they did not contribute to the production smog; however these compounds have been found to react with ozone and have possible implications in human health and therefore a cleanup attempt was made, utilizing primarily adsorption and condensation techniques. However, because many molecules cannot be disposed of in this way, pyrolysis and incineration were also employed, essentially the burning of the molecules. Pyrolysis is a cleanup technique that results in the stimulation of the elimination pathways of these HCFCs. The products of these various eliminations then react in the atmosphere. For this reason, research in the degradation pathways of these molecules is of interest.

Pyrolysis or incineration of these compounds results in elimination mechanisms. To accurately obtain kinetic parameters of these elimination mechanisms, gas kineticists must be able to recreate said molecules and the degradation mechanisms that follow – stabilization, elimination, and interchange. The in-lab re-creation of these processes is completed using a variety of experimental methodology. To recreate the molecules found in the atmosphere, radicals are created synthetically in the lab, they then combine to form the target molecule of the study. These radicals can be created using several different techniques, including but not limited to production of haloalkyl radicals from iodohaloalkanes, mercury photolysis and laser induced chemistry. In production of haloalkyls radicals from iodohaloalkanes, iodate reactants are combined in a Pyrex vessel containing Mercury 1 iodide. Ultra Violet radiation stimulates the Mercury 1 iodide to Mercury 2 iodide when the reactants lose their Iodide to the mercury and become radical species. They are then free to combine to form the target molecule. In Mercury photosensitization, quartz vessels containing mercury drops are photolyzed under a high pressure germicidal lamp for varying time periods (depending on vessel size). In this process mercury is excited from the singlet to the triplet state and then passes this energy to the gas phase reactants – normally with the formula R-I – also present in the vessel, prompting these reactants to eliminate their Iodide and form radicals. These energized radicals then spontaneously combine and form an energized target molecule which is then equipped with enough energy to undergo the various degradation mechanisms kineticists seek to study.[2] Another methodology is radical recombination reactions by laser-induced decomposition technique. In this technique, laser radiation from a CO_2 laser is focused on the center of a reaction cell, creating radicals from the reactants. Radicals then combine forming the chemically activated/reactant. The experimentation is carried out at a fixed pressure and a controlled concentration of reactants, a specific software program was developed for this methodology.[3] Computational kinetics studies using Density Functional Theory (DFT) and a variance of levels of theory and basis sets are also employed in order to study the plausible transition mechanisms of these molecules, as well as theorize threshold energies and zero point vibrational frequencies for these mechanisms.[4] Multi-configurational self-consistent field (CASSCF) is also a technique utilized to investigate the 1, 1 elimination mechanisms.[5] From these we are also able to determine the competiveness of these processes based on energy levels and what halogen is being manipulated.[6]

Regardless of the methodology for radical formation, the instrumentation of analysis and the mechanisms of interest remain generally consistent in this area of kinetic study. It is known that HCFC and HFC molecules undergo several degradation processes. The mechanisms for these processes include but are not limited to 1, 1 HX elimination, 1, 2 HX elimination, and interchange.[7,5] The eliminations from the energized target molecule are determined by the ratio of masses as yielded by the Gas Chromatographer Mass Spectrometer (GCMS). A Gas Chromatographer Mass Spectrometer is the most common instrumentation for these studies, similar instruments such as the Flame Ionization Detector (FID) are also utilized for analysis. From these mass ratios, stabilization vs. Decomposition plots and branching ratios can be developed at various pressures in order to determine the ratios and rates of the various degradation processes. From this information kineticists are able to theorize the most plausible mechanisms of degradation and their rates, and translate this data into determining what may be formed, atmospheric lifetime, and how these molecules may react in the atmosphere.

Significant interest in these molecules as feedstock is arising in the scientific community.[8] The degree of feedstock conversion depends on each individual molecule and its specific decomposition pathways. In general, the molecule is recovered and recycled in its entirety, essentially avoiding the environmental impact of the feedstock. Finding viable pathways to convert HCFCs and HFCs into commercially useful products has become a trending area of study because these molecules contain valuable C-F bonds that are expensive when manufactured. Specifically, HCFCs and HFCs that undergo competitive 1, 1-HX and 1, 2 elimination are of interest to our research group. A study of the 1, 1-HX elimination is important because there is little known comprehensive understanding of the expected reaction mechanism. It is important to complete experimental studies on these molecules in order to obtain accurate kinetic parameters for all decomposition pathways available to the molecule. As seen in table 1, several HCFCs and HFCs are currently in use that could show competitive 1, 1-HX elimination.

Table 1. HCFCs and HCFs in use that will decompose by 1,1-HX elimination

Formula	Designation	Uses
$CHClF_2$	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
CF3CHF2	HFC-125	Refrigerant
CHF3	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 amounts in adhesives, coatings, and inks
CF_2ClCF_2CHFCl	HCFC-225cb	
$(CF_3CH_2CHF_2)$	HFC-245fa	Foam Blowing Agent
$CHFCl_2$	HCFC-21	Refrigerant, Solvent, and Aerosol Propellant
CF_3CF_2H	HFC-125	Refrigerant and Air Conditioning

Holmes/Heard Research NSF Grant Proposal

$CD_3CD_2CHF_2$ is a model system for competitive 1,1 and 1,2 elimination because it has been found that adding two halogens to the same terminal carbon substantially increases the chance for 1,1 elimination. $CD_3CD_2CHF_2$ is similar to several propanes on the above list, and is therefore expected to also decompose via competitive 1,1 elimination. $CD_3CD_2CHF_2$ is the focus of this study, in an attempt to add it to the list of HFCs that undergo 1, 1-HX elimination and can be used as a commercially feasible material.

When 1, 1 elimination occurs, an unstable carbene is formed. When there is enough internal energy available the unstable carbene undergoes hydrogen or deuterium migration to form a stable alkene. Studies show that due to the energy it takes for a molecule to undergo the stabilization mechanism, it is often the case that the molecule is unable to stabilize.[9] As in the case of the study, a side product is formed when the CHF_2 and CD_3CD_2 radicals are formed via photolysis, CHF_2 self combines to form CHF_2CHF_2. It also undergoes competitive 1, 1 and 1, 2 elimination. It does not have the available energy to undergo Hydrogen migration after 1, 1 elimination results in an unstable carbene. Studies show that the unstable carbene can be trapped for analysis using a scavenger. In this study, cis-2 butene is used as the scavenger in order to determine what percent of the carbene was able to stabilize. This is a re-creation of the work done by Hazeldine et al., in order to reanalyze their ratios and data.[10]

2. Methods

Chemically activated $CD_3CD_2CHF_2$ with approximately 90 kcalmol^{-1} of internal energy was created by photolysis of gaseous CD_3CD_2I and CHF_2I in Pyrex vessels with some Hg_2I_2 using a low-pressure mercury lamp to form HgI_2 and CD_3CD_2 and CHF_2 radicals that combined to produce the target product. The CHF_2 radical also self-combines to form chemically activated CHF_2CHF_2 as an additional product. Reaction vessels had a volume range from 14.85 to 1168 cc and contained approximately a 4:1.5 torr ratio of CD_3CD_2I and CHF_2I. All samples were prepared on a grease-free vacuum with electric manometer to measure pressures. Photolysis times under the ultra-violet lamp ranged from 2 to 8 minutes, depending on vessel size.

Shown in figure 1, chemically activated $CD_3CD_2CHF_2$ undergoes unimolecular 1,2-DF elimination, directly forming $CD_2CD=CHF$, 1-fluoropropene-d_4 (E/Z). This molecule also undergoes 1, 1-HF elimination which forms the CD_3CD_2CF: carbene that subsequently transfers a deuterium yielding $CD_3CD=CDF$, 1-fluoropropene-d_5 (E/Z).

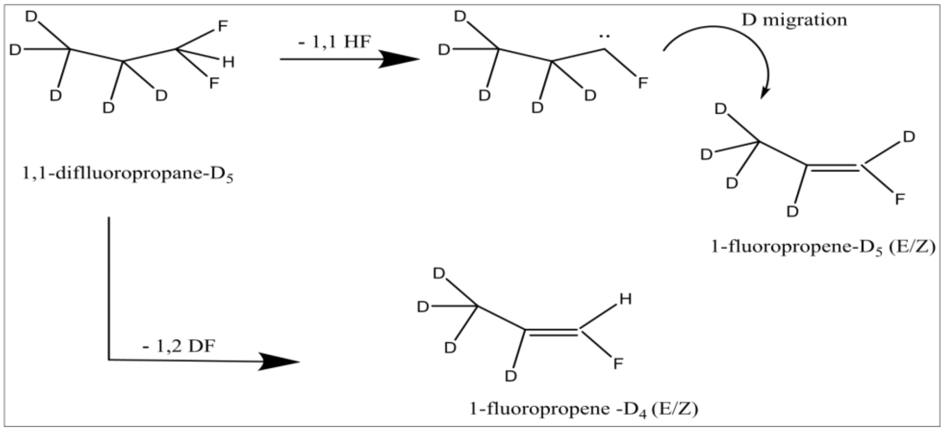


Figure 1. Reaction Mechanism for 1,2-DF and 1,1HF elimination from chemically activated $CD_3CD_2CHF_2$.

The abundance of each product is dictated by the relative energies for each pathway, as shown in figure 2.

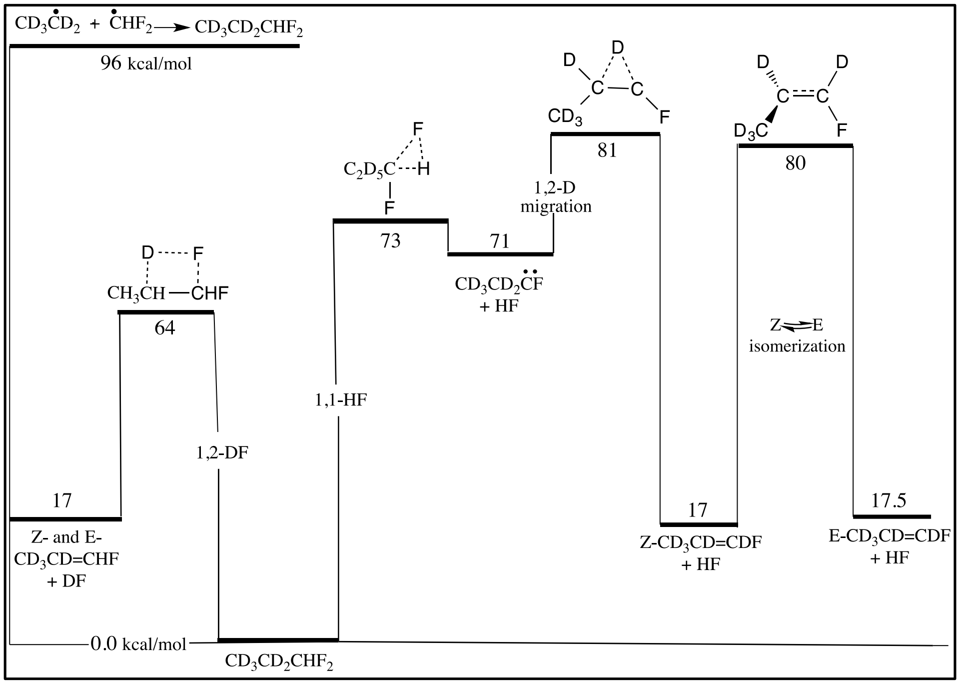


Figure 2. $CD_3CD_2CHF_2$ Energy Schematic for hypothesized degradation pathways.

A Shimadzu GC-MS QP2010 with a Restek RTX-200 column was used for product analysis. Retention times were $CD_2CD{=}CHF$ (product of 1,2-DF elimination) 16.6 minutes and $CD_3CD{=}CDF$ (product of 1,1-HF elimination) 16.5 minutes. Products were identified by comparison of GC retention times with authentic samples. Purity and identity of the authentic samples were established using a Shimadzu Gas Chromatograph GC-14A equipped with flame ionization detector and MXt-624 column. Calibration of the system was completed using a GC-FID because an authentic sample of 1fluoropropene was not able to be obtained, but 2-propene and 3-propene, available authentic samples, should burn the same as 1-propene.

Threshold energy for 1, 2-HF elimination from $CH_3CH_2CHF_2$ was computationally determined using the B3PW91 level of theory and 6-311+g (2df, 2p) basis set. Gauss View computational computer software was utilized to create the molecules. Calculations on 1,1-HF elimination were calculated my research colleague Meghan McGreal using multi-reference CasSCF software.

Two Isodesmic reaction calculations were completed in order to determine the enthalpy of reaction for the formation of target product $CH_3CH_2CHF_2$, table 2. Isodesmic reactions are those where there are the same bonds in the reactants and the products. Therefore, using cancellation of the two-body problem, the reaction enthalpies may be calculated simply by subtracting energies of products minus reactant energies. These were calculated twice using known energies, once using energies from DFT larger basis set and again from MP2 larger basis set.

Table 2. Isodesmic Reactions used to calculated ΔH_{rxn} for formation of $CH_3CH_2CHF_2$.

Isodesmic Reactions
$CH_3CHF_2 + CH_3CH_2CH_3 \rightarrow CH_3CH_3 + \mathbf{CH_3CH_2CHF_2}$
$CH_3CHF_2 + C_2H_6 \rightarrow CH_4 + \mathbf{CH_3CH_2CHF_2}$

In addition to $CD_3CD_2CHF_2$ formation, CHF_2CHF_2 is formed from the self-combination of CHF_2 radical. It is theorized that this molecule also undergoes both 1,1-HF and 1,2-HF elimination, much in the same way as the $CD_3CD_2CHF_2$ system, through carbene formation, as shown in figure 3. However, it is also theorized that not all the carbene isomerizes into the stable alkene. A portion of the carbene may add across a double bound to form a cyclopropane, as shown in the top portion of figure 3.[9] To study this mechanism, excess cis-2-butene was added to this reaction in order to determine the percent of carbene that was able to stabilize. Analysis of the cyclopropane isomers formed from the carbene addition of the scavenger was analyzed on the Shimadzu GC-MS QP2010. Calibration of CHF_2CHF_2 was completed on the Shimadzu GCMS as an authentic sample of 1, 1, 2-trifluroethene could be purchased.

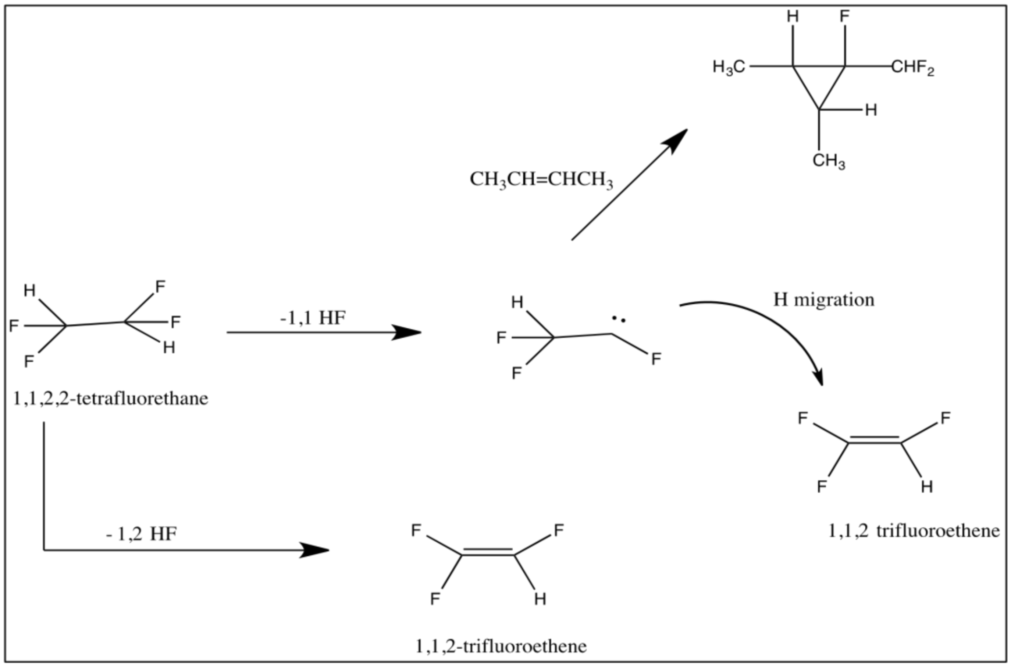


Figure 3. Reaction Mechanism for 1,2-HF and 1,1HF elimination from chemically activated CHF_2CHF_2.

3. Results and Discussion

The ratios of 1, 1-HF ($CD_3CD=CDF$) and 1, 2-DF ($CD_2CD=CHF$) elimination products versus stabilization product ($CD_3CD_2CHF_2$) were plotted versus the inverse pressure and are shown in figure 4. This shows the overall likelihood to the target molecule to undergo a decomposition pathway versus forming the stabilized compound. The calibration factor for detector response for the D/S plot was calculated to be 1.38. The ratio of the likelihood of 1,1 vs. 1,2 elimination in both the E peak and the Z peak, over a range of inverse pressures was also plotted in figure 5; 1,2 elimination is the preferred pathway at all pressures. The 1,2-DF elimination forms E and Z $CD_3CD=CHF$ in a 1.2 ratio favoring the Z-isomer. The 1,1-HF elimination reaction forms the CD_3CD_2CF: carbene that subsequently transfers a D giving an E/Z-$CD_3CD=CDF$ ratio that is near 4 at the highest pressures and declines to 2.5 at the lowest pressures. This pressure effect suggests that the 1,1HF elimination process preferentially forms the Z-isomer that isomerizes to the E-geometry as the pressure is lowered. The ratio of $CD_3CD=CHF/CD_3CD=CDF$ is the relative rates for the 1,2DF/1,1-HF pathways and it is constant at 3.0 for the cis-isomer. (Peak 1) The ratio of E-$CD_3CD=CHF/CD_3CD=CDF$ (peak 2) declines from about 8 at the highest pressures to a low-pressure limit approaching 6. Figure 6 shows the overall Z (cis) formation calculated from the additive abundance of both the mass produced from 1,1-HF and 1,2-DF eliminations vs. the E (trans) formation, plotted over the inverse pressure. The branching plot confirms the preference of Z isomer formation for both 1,1 and 1,2 elimination with the ratio slightly decreasing form 1.8 to 1.4 as pressure increases. Figure 7 is the branching ratio plot for Z versus E formation in the peak formed from 1, 1 elimination (mass 65) and Z versus E formation in the peak formed form 1, 2 elimination (mass 64). Again, it is confirmed that E is preferentially formed in both decomposition pathways. The ratio of preference for E isomer formation in slightly decreased from 1.8 to 1.3 as pressure decreases in 1,2-DF elimination. The ratio of preference for E isomer formation decreases from 4 to 2.5 in 1,1-HF elimination. Through experiment and results from DFT calculations, competition between the 1,2- and 1,1-HF/DF elimination with a preferential formation of the Z isomer was confirmed. The reaction rate of the unimolecular elimination reactions were computationally determined by research colleague Meghan Megreal.[10]

Isodesmic Calculations for Enthalpy of reaction were completed and shown in Table 3. Threshold energy for 1,2-HF elimination from $CH_3CH_3CHF_2$ was computationally determined using the B3PW91 basis set to be 59.00 kcal/mol for the E isomer and 59.60 kcal/mol for the Z geometry, confirming the system's preference for the E-isomer formation. Those for 1, 2-DF from $CD_3CD_2CHF_2$ were computed to be, as previously shown in figure 2, 64 kcal/mol. Competitive 1,1 and 1,2 elimination for the $CD_3CD_2CHF_2$ system was evident in the experimental testing.

Table 3. ΔH_{rxn} (kcal/mol) calculated from Isodesmic Reactions

Isodesmic Reactions	ΔH_{rxn} (kcal/mol)	
	DFT	MP2
$CH_3CHF_2 + CH_3CH_2CH_3 \rightarrow CH_3CH_3 + \mathbf{CH_3CH_2CHF_2}$	0.06275	0.04832
$CH_3CHF_2 + C_2H_6 \rightarrow CH_4 + \mathbf{CH_3CH_2CHF_2}$	-1.86932	-3.39415

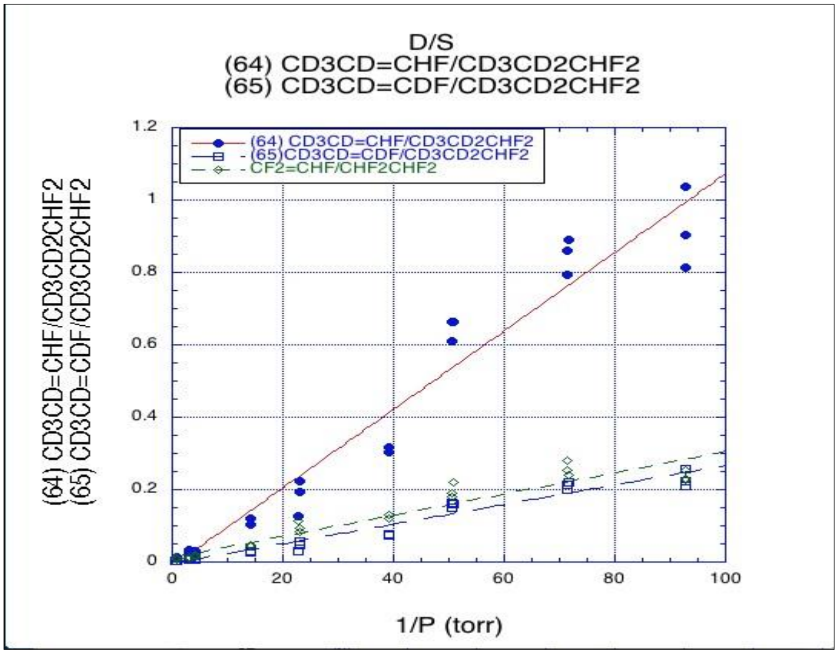


Figure 4. D/S vs. 1/P plot of the unimolecular eliminations from $CD_3CD_2CHF_2$.

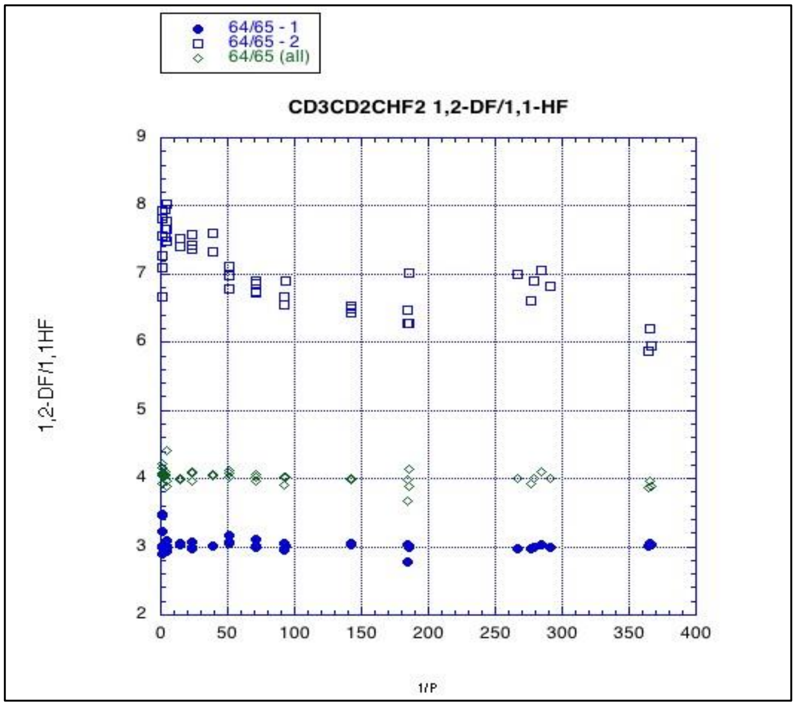


Figure 5. Branching Plot of the ratio of 1,2 vs. 1,1 elimination in the E peak (1), the Z peak (2), and overall (all).

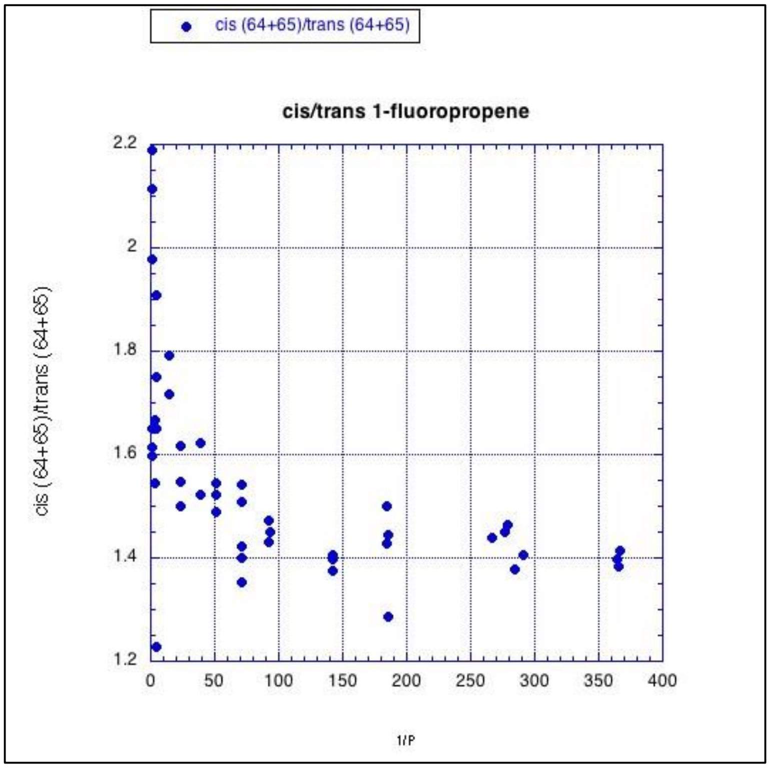


Figure 6. Branching ratio of total Z (cis) formation for both 1,1 and 1,2 elimination vs. E (trans) formation for both 1,1 and 1,2 elimination (abundances added)

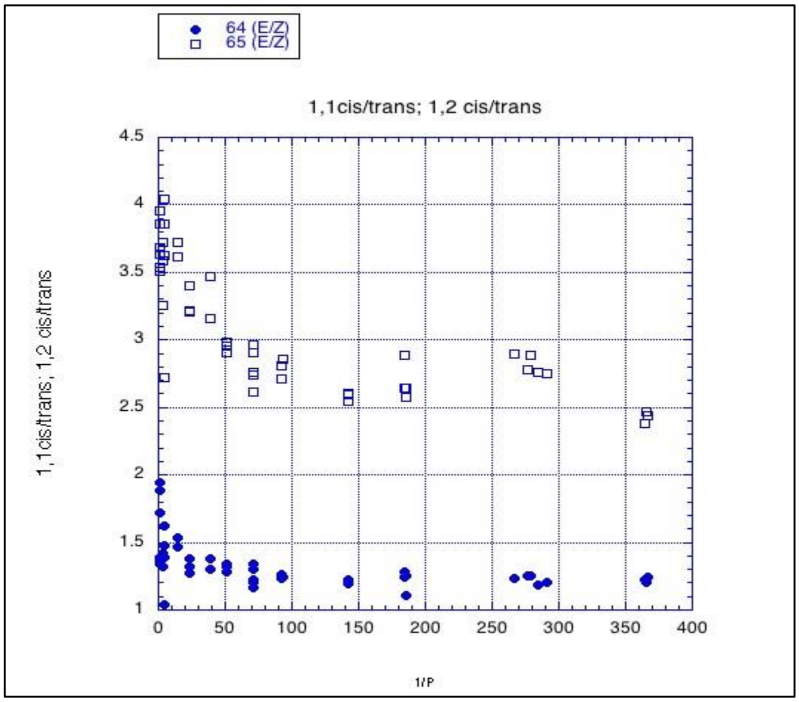


Figure 7. Branching ratio for E/Z formation in the 1, 1 elimination pathway and the 1, 2 elimination pathway

Results from the self-recombination of radical CHF_2 were also of interest to the study.

The decomposition versus stabilization ratio from 1,1,2,2 – tetrafluoroethane is shown in figure 8. The calibration factor for this system was found to be 1.48. The molecule was also found, by GCMS analysis to have a portion of its carbene stay in the unstable form and add across the C=C double bond of our alkene. The portion of non-stabilized carbene seemed to be constant, regardless of the ratio of that to the alkene. This finding signifies that as hypothesized, none of the carbine from the tetrafluuro system has enough energy to overcome the barrier to for the stable alkene. All the carbine is trapped by the scavenger, cis 2-butene, and forms the expected cyclopropanes. The identification of two isomers of the cyclopropanes were confirmed by comparison of mass spec tables obtained in our lab and those form the study conducted by Haszeldine et.al. The mass spec of the cyclopropanes found by that group are essentially identical to those found in our group, Figures 9 and 10. The study of carbene trapping in cyclopropane chemistry is unfinished.

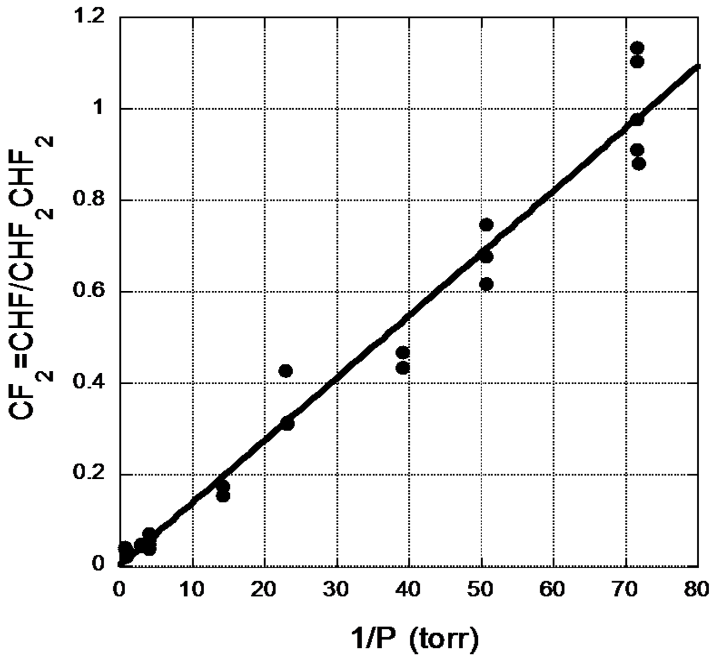


Figure 8. D/S vs. 1/P plot of the unimolecular eliminations from CHF_2CHF_2

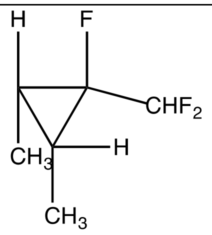
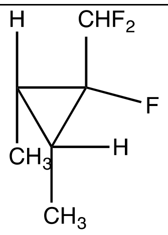
Mechanism	**Products**	**Retention Time (min)**
Radical Addition to Cis-2-butene	 	40.2 46.5

Figure 9. Retention times for two isomers of the product of radical addition to cis-2-butene

m/e	Relative Abundance	Ion	Comment
55	100	C_4H_7 *	
106	24	$C_5F_2H_8$	M* - CHF
29	19	C_2H_5 *	
39	16	C_3H_3 *	
27	15	C_2H_3*	
51	13	CHF_2*	Radical elimination
91	12	$C_3H_2FCHF_2$*	M* - methyl

Figure 10. Mass spec table of cyclopropane at retention time 40.2 minutes

4. Conclusion

The study of $CD_3CD_2CHF_2$ found that the molecule undergoes energetically competitive 1, 1-HF and 1, 2-DF elimination. GCMS analysis showed that the Z-isomer of the propene is preferentially formed. These findings support the kinetic calculations that propose that the molecule would do such. The findings also support previous studies completed on molecules with two halogens on the terminal carbon that suggest a higher likelihood to undergo 1, 1 elimination. Experimental data of this elimination pathway verified $CD_3CD_2CHF_2$'s ability for viable feedstock conversion. This verification insinuates that molecules with similar structures will also be able to be converted into feedstock. Study of the side product, CHF_2CHF_2, shows that this molecule also undergoes competitive 1, 1 and 1, 2-HF elimination. Analysis confirms that not all carbene has the internal energy to stabilize. In this case it was found that none of the carbene has enough energy to stabilize, and all the stable alkene observed was from 1, 2, elimination. All unstable carbene from 1, 1-HF elimination was trapped using cis-2-butene. Two isomers of cyclopropane were formed via carbene addition over the double bond of cis-2-butene. The carbene trapping experimentation confirms the findings of Hazeldine et al. More work must be done on this mechanism, however primary findings coincide. Overall, this studies confirms the necessity to explore 1, 1-elimination pathways in order to be able to correctly predict all degradation pathways and the rates and ratios of the decompositions that HCFC's and HFC's undergo in the atmosphere. This will allow for proper cleanup of these molecules and the preservation of our atmosphere.

5. Acknowledgements

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