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Unimolecular Decomposition of $CF_3CHClCCl_2$ Radicals Chemically Activated by the Reaction of TCE and CF_3 Radicals.

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Abstract

Trichloroethylene ($CHCl=CCl_2$) or TCE was widely used in the chemical industry due to its versatility and properties. TCE was eventually banned by the Environmental Protection Agency (EPA) due to its carcinogenic properties, yet tons of TCE unused remained in the environment. A reaction between TCE and CF_3 radicals was studied in order to determine possible pathways that TCE can react to form various, less toxic products as a potential starting point for novel methods of safely degrading discarded TCE. Photolysis of CF_3I was the source of CF_3 radicals that subsequently added to the CHCl end of TCE producing chemically activated $CF_3CHClCCl_2$ radicals in the gas phase. The addition of CF_3 radicals to the CCl_2 end of TCE would produce CF_3CCl_2CHCl radicals, but quantum chemical calculations using Gaussian verified that this reaction was not important, in agreement with experimental findings. The chemically activated $CF_3CHClCCl_2$ radical decomposed by loss of atomic Cl to form $CF_3CH=CCl_2$ or was stabilized by collision with reactant molecules. The stabilized $CF_3CHClCCl_2$ radical combined with CF_3 radicals yielding $CF_3CHClCCl_2CF_3$. The atomic Cl added to TCE forming the $CHCl_2CCl_2$ radical that subsequently combined with CF_3 radicals producing $CHCl_2CCl_2CF_3$. Gas chromatography and mass spectra analysis were used to determine products that were formed in the reaction vessel. Three main products that formed were positively determined to be $CF_3CHClCCl_2CF_3$, $CF_3CH=CCl_2$, and $CF_3CCl_2CHCl_2$. Future studies include determining reaction pathway and characterizing final products of the reaction between $CFCl=CFCl$ and CF_3 radicals as well as trans-$CHCl=CClCF_3$ and CF_3 radicals.

1. Introduction

Volatile organic compound (VOC) emissions such as that of trichloroethylene (TCE) have been a major public health issue due to their toxic, often carcinogenic, properties. Many countries have implemented emission controls on TCE, one of the most noxious sources of VOC emissions.[1-2] TCE is a carcinogenic chemical that was widely used in industries as a degreaser agent.[1-2] Factories that used or produced metal products used large amounts of TCE, such as hearing aid factories.[1-2] Through leakage and poor disposal practices, TCE has become the most common water and land pollutant in the United States. During the last several decades, numerous studies have been done to investigate various techniques that can be used to remove or decompose TCE from contaminated soil and water.[1-2] A recent study investigated the use of nanoparticles in the photocatalytic oxidation (PCO) reaction of TCE and showed some promise of improving TCE cleanup techniques.[1] More studies are needed to find a TCE remediation technique that will be cost affective and efficient in removing all trace of TCE from the contaminated medium.

More research into the photocatalytic oxidation (PCO) reaction of TCE and nanoparticles such as TiO_2 will increase the chance of finding an efficient and the proper way to dispose of TCE and clean up contamination site. Heterogeneous photocatalysis utilizing semiconductor particles such as TiO_2 in combination with ultraviolet (UV) irradiation proves to be an effective treatment for TCE.[1] Some byproducts of the reactions include hydrogen chloride, carbon dioxide, and water, all non-toxic or significantly less toxic than TCE. Some other byproducts that are deemed toxic to the environment and human health includes phosgene ($COCl_2$), chloroform ($CHCl_3$), and carbon monoxide

(CO).[1] Due to the production of some toxic byproducts, the PCO technique is not a common way to degrade TCE and other halogenated compounds, which necessitates further research in this area.

A new potentially effective method of decomposing TCE and other similar compounds utilizes gas phase kinetics studies to force TCE to undergo radical reactions to produce several products that are non-toxic to humans and the environment. If this novel method proves to product non-toxic products, it could be a viable alternative to the PCO method. The initial hypothesis for the reaction route that TCE with undergo is a disproportionation-combination pathway that would result in the production of various HCFC molecules as main products and byproducts. Scheme 1 shows the initial reaction of TCE and CF_3 radicals to produce chemically activated $CF_3CHClCCl_2$ molecules.

$$\dot{C}F_3 + CHCl{=}CCl_2 \longrightarrow CF_3CHCl\dot{C}Cl_2^* \qquad (2\text{-}1)$$

$$\longrightarrow CF_3CCl_2\dot{C}HCl^* \qquad (2\text{-}2)$$

Scheme 1: Reaction between TCE and CF_3 radicals

The chemically activated $CF_3CHClCCl_2$ molecules are predicted to further undergo a reaction with CF_3 radicals to form products through disproportionation-combination pathways. Scheme 2 shows the disproportionation-combination reaction of the chemically activated $CF_3CHClCCl_2$ molecules, where k_c in reaction (3-1) is the combination rate constant and k_d in reaction (3-2) and (3-3) is the rate constant for disproportionation. The main products of the predicted scheme above are $CF_3CHClCCl_2CF_3$, $CF_3CH{=}CCl_2$, CF_3Cl and CF_3H.

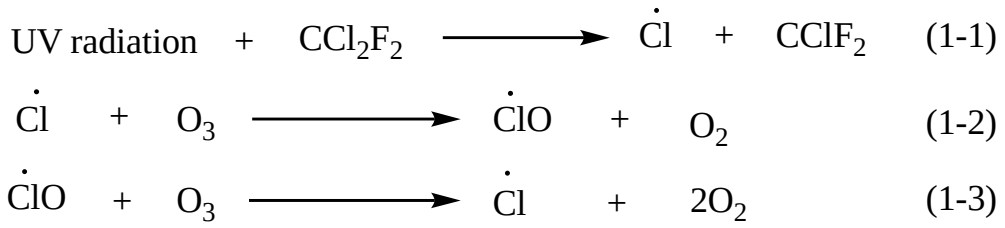
$$CF_3CHCl\dot{C}Cl_2 + \dot{C}F_3 \xrightarrow{k_c} CF_3CHClCCl_2CF_3 \qquad (3\text{-}1)$$

$$\xrightarrow{k_d} CF_3Cl + CF_3CH{=}CCl_2 \qquad (3\text{-}2)$$

$$\xrightarrow{k_d} CF_3H + CF_3CCl{=}CCl_2 \qquad (3\text{-}3)$$

Scheme 2: Disproportionation-Combination reaction of chemically activated $CF_3CHClCCl_2$ molecules

The motivation of this research is to look at the disproportionation-combination pathway of TCE, which can be created from the elimination reaction of CFC compounds. Chlorofluorocarbons or CFCs are gases that contribute to global climate change and cause depletion of the earth's ozone layer. These gases were developed in the 1930s as a safe, non-toxic substitute to compounds such as ammonia for the purpose of refrigeration.[3] CFCs are very stable except under ultraviolet light, unreactive, and nontoxic. Due to its characteristic and physiochemical properties, CFCs were very common in industrial uses and commercial products.[3] When the ultraviolet light from the sun hit CFCs or hydrochlorofluorocarbons (HCFCs), the molecules decompose into halide radical, which will react with the ozone layer and decompose it into O_2 (g). Scheme 3 shows the reaction mechanism of CFCs decomposition under ultraviolet light.



Scheme 3: Depletion of the ozone layer by CFCs

The Montreal Protocol was created in 1987 to eliminate all use of CFCs in first-world counties by the year 2000 due to its potential to greatly impact the ozone layer.[4] Hydrochlorofluorocarbons or HCFCs and Hydrofluorocarbons or HFCs are common subclasses of CFCs that includes a hydrogen atom in addition to the fluorine and chlorine atoms. HFCs and HCFCs were used as a suitable replacement for CFCs after its worldwide ban in 1987.[4] HCFC compounds react differently from CFCs because they contain a hydrogen atom, which causes them to decompose by reaction with OH radicals before they reach the stratosphere. HFC compounds do not contain chlorine and thus do not attack the ozone layer. HFCs and HCFCs survive in the atmosphere for 2 to 40 years, compared to CFCs that can last as long as 150 years in the atmosphere. Both HFCs and HCFCs still have a detrimental impact on the atmosphere, as they are greenhouse gases.

Previous research explore the reaction pathway of 1,1-HX (X=halogen) elimination reaction and the characteristics of intermediate molecules, such as chemically activated $CHCl_2CHCl_2$, depicted as $CHCl_2CHCl_2^*$, which produce TCE as a product of the elimination. The 1,1-HX elimination reaction is a type of reaction that eliminates a hydrogen atom and a halogen atom from the same carbon atom in the molecule, which then produces a carbene and hydrogen halide as products.[5] A carbene is a molecule containing a neutral carbon atom with a valence of two and two unshared valence electrons. In order to find efficient ways to decompose TCE, one need to further understand the characteristics of the products that are produced through the elimination reaction, this research focuses on identifying and characterizing the reaction pathways that TCE and similar halogenated alkenes will undergo when reacted with CF_3 radicals. The understanding of the characteristics of the product is vital in

Little to no work has been done on the characteristics of the 1,1 elimination reaction of HCFCs or HFCs. There have been many studies on the unimolecular reaction of 1,2-dichloroethane[3] and $CHCl_2CHCl_2$[4]. Previous research has been focused on the 1,2-elimination, which included the study of intermediates; the rate constant of the reaction under different conditions, such as varying pressure or temperature; the threshold energy of different elimination reactions; and multiple reaction pathways that the reactants can undergo. A study has been done on the characteristics of CD_3CHFCl and its reaction pathway. The 1,1-HF elimination and 1,1-HCl elimination were found to be two of the four possible reaction pathways for the decomposition of CD_3CHFCl. The other two pathways were 1,2-elimination of DF and DCl. Electronic structure calculations were used to create models for the transition states of the reaction and to calculate the threshold energies of those transition states.

Another study was done on the kinetics of CH_2ClO radical reaction with O_2 and NO by a chemistry research team from the University of Minnesota.[6] The CH_2ClO radical was formed from decomposition of CH_2ClO_2 while CH_2ClO_2 was formed from the CH_2Cl and O_2 reaction. The reaction of CH_2ClO_2 and NO produce the chemically activated CH_2ClO radicals. The CH_2ClO radical has sufficient energy for 1,1-HCl elimination.[6] These findings provide the foundation for comparison with the research of a new molecule; similar methods will be used to conduct a new experiment that will go deeper into understanding the pathways of the reaction.

In a more recent study, the data were coupled with the calculations from the Rice-Ramsperger-Kassel-Marcus (RRKM) method to determine the rate constants and threshold energy for the transition state.[7] The experimental rate constant is compared to the calculated rate constant and assign the threshold energy for the pathway.[3-11] Computational programs such as Gaussian 09 and multi-well are used to calculate the RRKM reaction rates. Vacuum apparatus was used as a medium to hold the gaseous reaction. The method of chemical activation experiment was used to conduct the experiment with the use of an ultraviolet lamp to form CF_3 radicals. Once the photolysis reaction formed products, the gas chromatography/mass spectrometry was used to separate and analyze the products. In order to confirm the compound identify in the mass spectra, the ion fragments of the compound will be used to compare to the mass ratio in the mass table.

2. Methodology

The reaction between TCE and CF_3I took place in a 2.588 cc, 7.481 cc, and 14.85 cc Pyrex vessel with a small amount of Hg_2I_2 in the vessel, which acts as a catalyst and an iodine scavenger in the reaction. CF_3I were used to create the CF_3 radicals. Scheme 4 shows the reaction between CF_3I and Hg_2I_2 to produce CF_3 radicals.

$$2CF_3I\,(g) + Hg_2I_2\,(s) \longrightarrow 2\dot{C}F_3 + 2HgI_2 \qquad (4\text{-}1)$$

Scheme 4: Reaction between CF_3I and Hg_2I_2

A vacuum apparatus was used to store gas molecule and transfer gas molecules into the reaction vessel. An MKS electronic manometer pressure gauge and a Hasting gauge were used to determine the pressure of the compound in the reaction. A pressure gauge was used to determine high-pressure readings and a Hasting gauge was used to determine a more accurate low-pressure readings. The liquid nitrogen bath was utilized as a freezing agent that can freeze the movement of gas compounds into the vessel. The Pyrex vessel was placed onto the vacuum apparatus to bring the pressure in the vessel down to approximately 0 torr. Then, the TCE gas vessel on the apparatus was opened and let the pressure stabilize at approximately 1 torr. The TCE gas was then trapped in a calibrated vessel. The calibrated vessel was used to determine the actual amount of reactant gas that was used in the reaction through the ideal gas law calculation. The remaining TCE gas was frozen back into its original vessel. The 1 torr of TCE gas in the calibrated vessel was transferred to the reaction vessel. The same procedure was repeated for the transfer of approximately 5 torr CF_3I molecules into the reaction vessel. Temperature of the room was recorded after every sample creation.

A high pressure UV lamp was used to photolyze the reaction with wavelength ranging from 300 nm to 400 nm. The photolysis time for the reaction is 5 minutes. After photolysis, the vessel was placed onto a separate Gas Chromatography-Mass Spectrometry (GC-MS) vacuum apparatus. The sample was frozen into the injection loop of the GC-MS for 10 minutes, and then the pressure was stabilized after the 10-minute period. After the pressure has stabilized, the sample was unfroze from the injection loop using hot water as the sample was injected into the GC-MS. Table 1 shows GC-MS operational parameters for the experiment.

Table 1. GC-MS Parameters

Column and Carrier Gas Information	
Column Name	Rtx-624
Column serial #	204585
Column Length	105 m
Column Diameter	0.25 mm
Column Thickness	1.4 μm
Column Inlet Pressure	172.4 kPa
Column Flow	1 mL/min
Linear Velocity	19.2 cm/sec
Split Ratio	10

Total Flow	17.4 mL/min
Temperature	30°C

Density Functional Theory was used to calculate the energies of two initial radicals that were formed in reaction between TCE and CF_3 radicals and the radicals that were formed from the side reaction between atomic chloride and TCE. The method M06-2X with the basis set of cc-aug-pvtz was used specifically to calculate the minimum energies of those radicals. The Boltzmann population formula was used to calculate the population of all intermediate radicals that were formed both in the main reaction and the side reaction. The samples were analyzed by looking at the mass spectra and comparing the ion fragments of individual compound to the mass on the mass table. Some products in the reaction were compared to a commercially purchased sample of the same compound by injection into the GC-MS and comparing retention time of the compound peak.

3. Data and Discussion

The reaction mechanism for TCE and CF_3I was determined and studied. Three dominant products were positively identified in the reaction. Scheme 5 below shows the proposed reaction mechanism.

$$CF_3CHCl\dot{C}Cl_2^* \longrightarrow CF_3CH{=}CCl_2 + \dot{Cl} \quad (5\text{-}1)$$

$$\xrightarrow{[M]} CF_3CHCl\dot{C}Cl_2 + M^* \quad (5\text{-}2)$$

$$CF_3CHCl\dot{C}Cl_2 + \dot{C}F_3 \longrightarrow CF_3CHClCCl_2CF_3 \quad (5\text{-}3)$$

$$\dot{Cl} + CHCl{=}CCl_2 \longrightarrow CHCl_2\dot{C}Cl_2 \quad (5\text{-}4)$$

$$\longrightarrow \dot{C}HClCCl_3 \quad (5\text{-}5)$$

$$CHCl_2\dot{C}Cl_2 + \dot{C}F_3 \longrightarrow CF_3CCl_2CHCl_2 \quad (5\text{-}6)$$

$$\dot{C}HClCCl_3 + \dot{C}F_3 \longrightarrow CF_3CHClCCl_3 \quad (5\text{-}7)$$

Scheme 5: Reaction mechanism for decomposition of the chemically activated $CF_3CHClCCl_2$ radicals

The initial decomposition reaction, reaction (5-1), generates the alkene product that was seen as the most dominant product in the reaction vessel. The first reaction also produced a byproduct of atomic chlorine that will later on react with TCE in reaction (5-4). The chemically activated $CF_3CHClCCl_2^*$ molecules can also collide with a third body molecule and transfer its energy to the third body, causing $CF_3CHClCCl_2^*$ to be stabilized in reaction (5-2). The side reaction between the atomic chlorine and TCE could produce two intermediate radicals that will continue on to react with CF_3 radicals as seen in reaction (5-4) through (5-7). The end product of the combination reaction (5-6) between $CHCl_2CCl_2$ radicals and CF_3 radicals was found to be the second dominant product in the reaction vessel. The third most dominant product was formed from the combination reaction of $CF_3CHClCCl_2$ radicals and CF_3 radicals in reaction (5-3) after the chemically activated $CF_3CHClCCl_2$ radicals collide a third body molecule and loses its energy. The alkene product was positively identified in the experimental reaction through comparing the mass spectra with

that of a commercially purchased sample. The retention time for $CF_3CH=CCl_2$ was determined to be at 27.5 minutes. Figure 1 shows the mass spectra of the $CF_3CH=CCl_2$ compound.

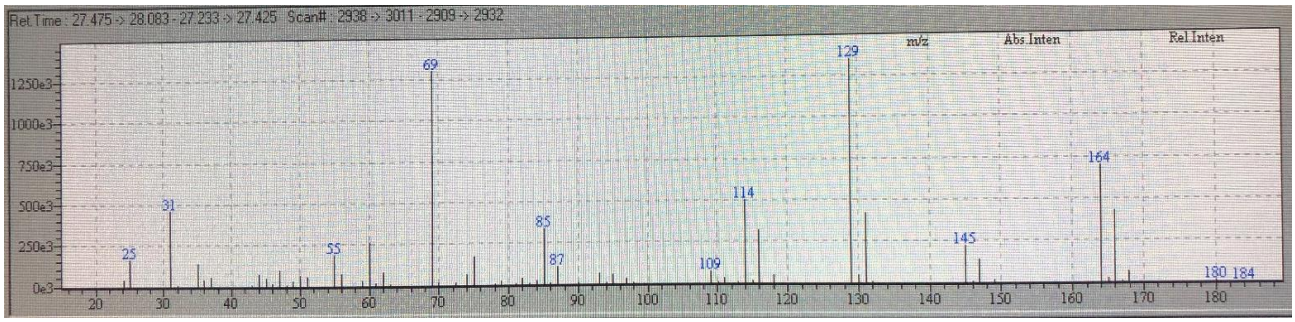


Figure 1: $CF_3CH=CCl_2$ mass spectra

Moreover, a mass table was used to identify the ion mass of individual fragments in the mass spectra. Table 2 shows the mass table for $CF_3CH=CCl_2$ and its fragmented ions.

Table 2. Mass table with fragmented ion masses for $CF_3CH=CCl_2$

Retention Time: 27.60 minutes		
Molar Mass: 164 g/mol		
m/z	Relative Intensity	Ions
129	100.00	$CF_3CH=C^{35}Cl^+$
69	99.09	CF_3^+
164	46.58	$CF_3CH=CCl_2^+$
131	31.43	$CF_3CH=C^{37}Cl^+$
145	17.74	$CF_2CH=CCl_2^+$

The molar mass of $CF_3CH=CCl_2$ is 164 g/mol. Mass 129 with 100 relative intensity in the mass spectra was determined to be the mass of $CF_3CH=C^{35}Cl^+$. Different chlorine isotopic masses were also found in the spectra. Mass 131 was the mass of the same molecule but with a different isotopic mass of chlorine in the molecule. The ratio of isotopic mass chlorine 35 and 37 have a ratio of 3:1, which correspond with the relative intensity of each isotopic mass in the mass table. Mass 69 is the mass of CF_3 cation. Mass 164 was determined to be the parent ion mass of the molecule $CF_3CH=CCl_2$. Mass 145 was the mass of $CF_2CH=CCl_2^+$, which resulted from a carbon fluorine bond breakage. All five fragmented ions were determined to be formed from the parent ion of $CF_3CH=CCl_2$.

The second most dominant product that was formed in the reaction was determined to be $CF_3CCl_2CHCl_2$. $CF_3CCl_2CHCl_2$ was positively identified in the experimental reaction through mass spectral analysis. The retention time for $CF_3CCl_2CHCl_2$ was determined to be at 50 minutes. Figure 2 shows the mass spectra for the $CF_3CCl_2CHCl_2$ compound.

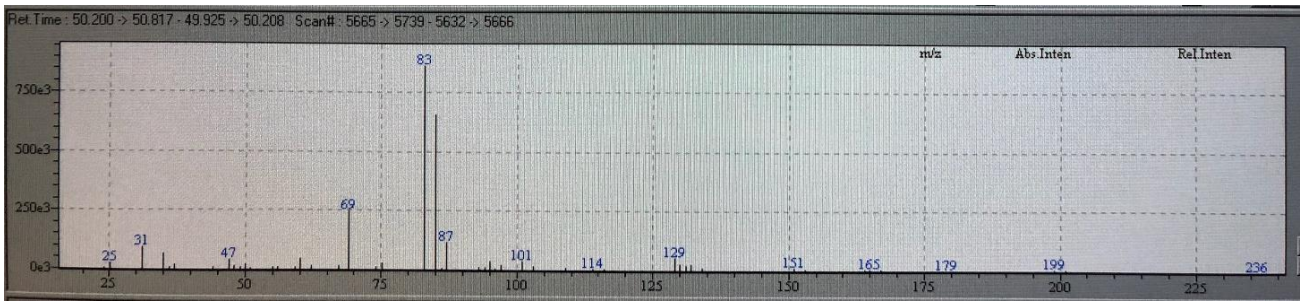


Figure 2: $CF_3CCl_2CHCl_2$ mass spectra

Mass table that correspond to the mass spectra of $CF_3CCl_2CHCl_2$ was used to positively determine the identity of the compound that correspond to the mass spectra. Table 3 shows the mass table that corresponds to the mass spectra in figure 2.

Table 3. Mass table for $CF_3CCl_2CHCl_2$

Retention Time: 50.40 minutes		
Molar Mass: 234 g/mol		
m/z	Relative Intensity	Ions
83	100.00	$CH^{35,35}Cl_2^+$
85	75.10	$CH^{37,35}Cl_2^+$
69	27.26	CF_3^+
87	13.51	$CH^{37,37}Cl_2^+$
199	2.54	$CF_3CClCHCl_2^+$

The molar mass of $CF_3CCl_2CHCl_2$ is 234 g/mol. The m/z of 83, 85, and 87 are the ion mass that came from the different isotopic mass of chlorine in the compound. All three masses resulted from the breakage of the carbon number two and carbon number three bond in the compound. Mass 69 is the mass of CF_3^+. Mass 199 was found to be the mass of $CF_3CClCHCl_2^+$, which resulted from the breakage of the carbon chlorine bond in carbon number two. All ion masses in the table were positively identified to form from the fragmentation of the $CF_3CCl_2CHCl_2$ molecule, which is the parent ion. Mass spectra in Figure 2 can be said to come from the $CF_3CCl_2CHCl_2$ molecule.

The third most dominant product that was formed in the reaction was positively determined to be $CF_3CHClCCl_2CF_3$ through analysis of mass spectra and mass table. Figure 3 shows the mass spectra for $CF_3CHClCCl_2CF_3$ compound. The retention time for $CF_3CHClCCl_2CF_3$ was determined to be at 40.75 minutes. The mass table that correspond to the mass spectra above was used to analyzed the ion fragments and its corresponding mass. Table 4 shows the mass table for $CF_3CHClCCl_2CF_3$ compound.

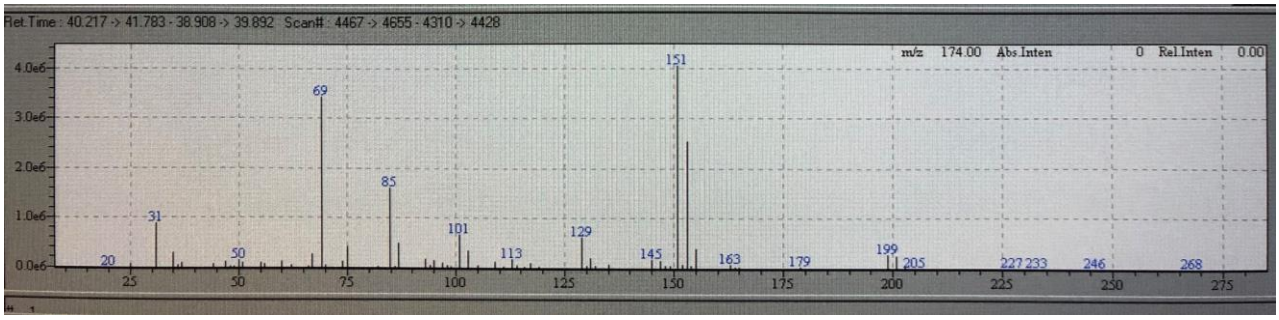


Figure 3: $CF_3CHClCCl_2CF_3$ mass spectra

Table 4. Mass Table for $CF_3CHClCCl_2CF_3$

Retention Time: 40.75 minutes		
Molar Mass: 268 g/mol		
m/z	Relative Intensity	Ions
151	100.00	$CF_3CCl_2^+$
69	84.92	CF_3^+
85	39.62	$CHCl_2^+$
199	7.20	$CF_3CHClCCl_2^+$
268	1.63	$CF_3CHClCCl_2CF_3^+$

The molar mass of $CF_3CHClCCl_2CF_3$ is 268.00 g/mol. Mass 151 was the mass of $CF_3CCl_2^+$, which resulted from the carbon number two and three bond breakage. Mass 69 is the signature mass of CF_3^+. Mass 85 was found to be the mass of $CHCl_2^+$ due to the bond breakage of carbon number one/two and carbon number two/three. The ion formed

from the chlorine rearrangement that happened after the bond breakage. Mass 199 was the mass of $CF_3CHClCCl_2^+$, which formed from the carbon number three and number four bond breakage. Mass 268 was determined to be the parent ion mass of $CF_3CHClCCl_2CF_3$. With the parent ion mass of $CF_3CHClCCl_2CF_3$ and the ion fragments identified, the mass spectra in Figure 3 were identified to be the mass spectra of $CF_3CHClCCl_2CF_3$ molecule.

Furthermore, the energies of the two intermediate radicals in the reactions (2-1) and (2-2) and the two intermediate radicals in the reactions (5-4) and (5-5) were calculated via Density Functional Theory and M06-2X with the basis set of cc-aug-pvtz calculating method. The energies of the four intermediate radicals were calculated to determine the relative stability of each radical compared to the other radical that was formed in the same reaction. Table 5 shows the energies and the difference in energies between two intermediate radicals in the same reaction.

Table 5. Calculated Energies and Differences for Intermediate Radicals in the Reaction

Radical	Enthalpy Energy (kcal/mol)	Difference (kcal/mol)
$CF_3CHClCCl_2$	-1126387.521	5.371
CF_3CCl_2CHCl	-1126382.150	
$CHCl_2CCl_2$	-1203276.549	1.785
$CHClCCl_3$	-1203274.764	

The difference between the energy of $CF_3CHClCCl_2$ and CF_3CCl_2CHCl radical was calculated to be 5.371 kcal/mol. Radical $CF_3CHClCCl_2$ have the lesser energy between the two radicals, which means that $CF_3CHClCCl_2$ radical is more thermodynamically stable than CF_3CCl_2CHCl radical. The same can be said for the energy comparison between $CHCl_2CCl_2$ and $CHClCCl_3$ radicals. The difference between the two radicals was calculated to be 1.785 kcal/mol. The $CHCl_2CCl_2$ was calculated to have the lesser energy between the two radicals, thus $CHCl_2CCl_2$ is more thermodynamically stable than $CHClCCl_3$ radical.

Boltzmann population was also calculated for the four intermediate radicals in the reaction. A comparison of the population between each two radicals that formed in the same reaction was done for the purpose of confirming the reaction pathway that is more dominant in the reaction as a whole. Table 6 shows the calculated Boltzmann population ratio between of $CF_3CHClCCl_2$ and CF_3CCl_2CHCl radical as well as $CHCl_2CCl_2$ and $CHClCCl_3$ radicals.

Table 6. Boltzmann Population of $CF_3CHClCCl_2$ and CF_3CCl_2CHCl as well as $CHCl_2CCl_2$ and $CHClCCl_3$ Radicals

Radical	Population Ratio
$CF_3CHClCCl_2$ and CF_3CCl_2CHCl	8700/1
$CHCl_2CCl_2$ and $CHClCCl_3$	20/1

Since $CF_3CHClCCl_2$ radical is more probable in the reaction vessel, the major pathway that the reaction undergoes was through the reaction between the intermediate $CF_3CHClCCl_2$ radical and CF_3 radicals. The same can be said for the yield of the $CHCl_2CCl_2$ radical compare to the $CHClCCl_3$ radical. Since the population of $CHCl_2CCl_2$ radical is higher than that of $CHClCCl_3$ radical, the main pathway that happens in the side reaction between atomic chlorine and TCE was the reaction between the intermediate $CHCl_2CCl_2$ radical and CF_3 radicals. The higher populations between

all the intermediate radicals also correspond to the energies and the stability between all four radicals. The more stable the radical is, the more it will form in the reaction and become the dominant radical.

4. Conclusion

A total of three dominant products were found in the experiment reaction between TCE and CF_3I. The results from the experiment prove that the disproportionation-combination reaction mechanism that was proposed initially was false. The reaction was determined to undergo a unimolecular decomposition reaction instead of disproportion-combination reaction. Mass spectra were used to determine the identity of each products peak in the gas chromatogram of the reaction. Three peaks were determined to be the peak of $CF_3CH{=}CCl_2$, $CF_3CHClCCl_2CF_3$, and $CF_3CCl_2CHCl_2$ compound. Through identification of all the product peaks in the gas chromatogram, the unimolecular decomposition pathway can be supported to be a possible pathway that the reaction can undergo under the experimental condition. The Boltzmann population of the initial intermediate radical and the side reaction intermediate radicals was also studied.

With a better knowledge of the TCE reaction pathway with radicals such as CF_3, one can further understand other, potentially safer and more effective, possibilities that TCE can be remediated. Since TCE is a carcinogenic compound that cannot be disposed of in the nature, a non-harmful way to dispose of the compound either mechanically or chemically is necessary. This experiment provides a possible way to dispose of TCE chemically through a chemical reaction with CF_3I to produce less harmful products. The study of the chemical mechanistic pathway of TCE and CF_3I reaction has never been done before. Future studies can be done with different compounds that is similar to TCE such as $CCl_2{=}CCl_2$. The results of those studies can be used to compare to the results in this experiment in further understand the properties and behavior of alkenes in a reaction with radicals.

5. Acknowledgements

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6. References

1. Li, K.; Stefan M. I.; Crittenden J. C. Trichloroethene Degradation by Uv/H_2O_2 Advanced Oxidation Process: Product Study and Kinetic Modeling. *Environmental Science Technology* **2007**, 41, 1696-1703.
2. Jung, B.; Farzaneh, H.; Khodary A.; Abdel-Wahab, A. Photochemical degradation of trichloroethylene by sulfite-mediated UV irradiation. *Journal of Environmental Chemical Engieering 3* **2015**, 2194-2202.
3. Duncan, J. R.; Solaka, S. A.; Setser, D. W.; Holmes, B. E. Unimolecular HCl and HF Elimination Reactions of 1,2-Dichloroethane, 1,2-Difluoroethane, and 1,2-Chlorofluoroethane: Assignment of Threshold Energies. *The Journal of Physical Chemistry A* **2010**, 114 (2), 794–803.
4. Larkin, A. C.; Nestler, M. J.; Smith, C. A.; Heard, G. L.; Setser, D. W.; Holmes, B. E. Chemical Activation Study of the Unimolecular Reactions of $CD_3CD_2CHCl_2$ and $CHCl_2CHCl_2$ with Analysis of the 1,1-HCl Elimination Pathway. *The Journal of Physical Chemistry A* **2016**, 120 (42), 8244-8253.
5. Rossabi, S. M.; Smith, K. C.; Heard, G. L.; Holmes, B. E. Unimolecular Rate Constants for the HF and HCl Elimination Reactions from Chemically Activated CF_2ClSH. *International Journal of Chemical Kinetics* **2015**, 47 (6), 379–388.
6. Wu, F.; Carr, R. W. Kinetics of CH_2ClO Radical Reactions with O_2 and NO, and the Unimolecular Elimination of HCl. *The Journal of Physical Chemistry A* **2001**, 105 (9), 1423–1432.
7. Brown, T. M.; Nestler, M. J.; Rossabi, S. M.; Heard, G. L.; Setser, D. W.; Holmes, B. E. Characterization of the 1,1-HCl Elimination Reaction of Vibrationally Excited CD_3CHFCl Molecules and Assignment of Threshold Energies for 1,1-HCl and 1,2-DCl plus 1,1-HF and 1,2-DF Elimination Reactions. *The Journal of Physical Chemistry A* **2015**, 119 (36), 9441–9451.
8. Rajakumar, B.; Reddy, K. P. J.; Arunan, E. Unimolecular HCl Elimination from 1,2-Dichloroethane: A Single Pulse Shock Tube and Ab Initio Study. *The Journal of Physical Chemistry A* **2002**, 106 (36), 8366–8373.

9. Wu, F.; Carr, R. W. The Chloromethoxy Radical: Kinetics of the Reaction with O_2 and the Unimolecular Elimination of HCl at 306 K. *Chemical Physics Letters* **1999**, 305 (1-2), 44–50.
10. Dubnikova, F.; Lifshitz, A. Formation of Van Der Waals Complexes in Concerted Unimolecular Elimination Processes. *Physical Chemistry* **2012**, 2012, 1–7.
11. Zhu, L.; Bozzelli, J. W. Kinetics and Mechanism for the Thermal Chlorination of Chloroform in the Gas Phase: Inclusion of HCl Elimination from $CHCl_3$. *International Journal of Chemical Kinetics* **2003**, 35 (12), 647–660.