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The Decomposition Behavior of HCFC-123 and Related Products

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Abstract

CHCl2I was synthesized to use in a photocatalysis reaction facilitated by Hg2I2. The CHCl2I and CF3I was used to generate chemically activated CF3-CHCl2 from radical CHCl2 and radical CF3. This was done by the combination of photosensitization and photolysis using a high-pressure mercury lamp with catalytic Hg2I2. The unimolecular decomposition reactions were qualified by identifying the products, and the rates of reaction will be quantified based on the ratio of decomposed products using a 2010 Shimadzu gas chromatograph mass spectrometer, GC-MS QP2010. The intent of this study was to expand data on the reactions that hydrochlorofluorocarbons (HCFCs) will undergo, as they are a commercially important class of greenhouse gases, which are in the process of being re-engineered to be more environmentally friendly. Understanding these reactions is key to the efficient recycling of HCFCs. To date, CF3-CHCl2 (HCFC-123) has been formed by the aforementioned process and identified. Both CF2=CCl2, which is the product of the 1,2 HF elimination and the carbene product CF3C:Cl, which is the result of the 1,1 HCl elimination pathway have been located. CF3C:Cl can be trapped with either *cis*-2-butene or *trans*-2-butene. The resulting three-member ring seems to decompose into various alkene products, the mass spectrums of which are presented. It is thought that the 1,1 HCl elimination pathway is dominant over the 1,2 HF elimination pathway, but quantitative data derived from the rates of these reactions is still needed for verification.

1. Introduction

Hydrochlorofluorocarbons (HCFCs), a commercially important class of chemicals, are gradually being phased out of use due to their potential to exacerbate climate change.[1] Therefore, to ease the transition to other, less harmful compounds, understanding the reactions that HCFCs undergo is imperative. By having a strong command of HCFC reaction pathways, companies that have a large supply of chemicals containing these compounds or that could recover HCFCs from existing equipment, which will soon no longer be usable, will have the option to convert their stock into more useful forms, rather than simply incinerate it. As the Montreal Protocol requires all HCFCs and CFCs in use to be recalled and either destroyed or recycled, this is of paramount importance.[1] Ultimately, by determining more efficient ways to recycle HCFC compounds, we hope to mitigate the wasted effort and cost of simple destruction, thereby contributing to environmental stewardship and economic efficiency.

Table 1. Industry reported stocks and production of HCFCs.[2,3]

Name	Formula	Purpose	Production (t)
HCFC-123	CF_3-$CHCl_2$	refrigerant, extinguishing agent, solvent	between 37,000 and 67,000 total inventory
HCFC-22	$CHClF_2$	refrigerant	28,000
HCFC-141b	CH_3CCl_2F	blowing agent	unknown, 35% of total production
HCFC-142b	CH_3CF_2Cl	blowing agent or refrigerant	35
HCFC-225ca	$CHCl_2CCF_2CF_3$	aerosol solvent	production ceased in 2015

The reaction pathway classes under investigation for this project are the elimination pathways 1,1 HCl, 1,2 HF, and the FCl interchange pathway in HCFC-123, or CF_3-$CHCl_2$. In previous years, the focus has been the chloro-fluoro interchange reaction and the 1,2-HX elimination reaction, both of which are also relevant to current research. An elimination reaction is when a compound loses two groups, typically a halogen atom and a hydrogen, either simultaneously or stepwise. This reaction class is well understood when the two groups are on adjacent carbons, but in the case of HCFCs, there are large gaps in the scientific literature that need to be bridged by further research. For example, the rate constants for the 1,1-HX elimination reactions of HCFCs are not well known.

For industrial repurposing of chemicals, efficient, high percent yield reactions are important; hence, determining these rate constants, and how they are affected by factors such as temperature, pressure, and the effects of adding different substituents is of paramount importance to their reprocessing. To determine these facts about reaction pathways, chemicals can be reacted so that all primary products and side products can be identified. These reactions are conducted under various constraints, such as high or low pressure. Subsequent work focuses on determining the ratio of products in order to find the reaction rate constants. Lastly, data is recorded, and specific reactions are categorized accordingly.

Previous work in this field has covered the 1,1 HCl elimination pathway. In early 2016, one of the University of North Carolina at Asheville's research groups, led by Dr. Holmes and Dr. Heard, in collaboration with Dr. Setser, published an article that examined the elimination of HCl from $CHCl_2CHCl_2$ and $CD_3CD_2CHCl_2$.[4] The experiment was conducted by photolysis of reactants with a drop of mercury. $CF_3CH{=}CH_2$ was added to act as a scavenger of free chlorine, and after a reaction period between 10 seconds and ten minutes, the gas was frozen, and then injected into a GC-MS and analyzed.[4] The research resulted in the successful determination of the threshold energies for six possible reactions of $CHCl_2CHCl_2$ and $CD_3CD_2CHCl_2$, along with a characterization of the vibrational frequencies of the transition states associated with the 1,1 HCl elimination of $CD_3CD_2CHCl_2$, which was of primary interest in that project.

This research group has consistently used the mercury photocatalysis method for their work and has successfully repeated the general process for other reactions important to HCFC chemistry. For example, in 2015, they examined the competition between 1,1-HF and 1,2-DF elimination pathways for $CD_3CD_2CHF_2$.[5] This data is useful to the broad area of research because it can be used to get a rough idea of the relative prevalence of a particular reaction pathway among competitive pathways, furthering our knowledge of how these compounds can be converted efficiently into something useful.

In a related vein of research, Holmes' group in 2014 determined the threshold energies for the unimolecular reactions of 1,1,1-trichloroethane and 1,1,1-trichloropropane, using a similar methodology, but with different starting reagents and the inclusion of GC-MS instrumentation with flame ionization.[6] This is relevant to HCFC synthetic chemistry for reasons already listed. Further back in this group's research history, the field of inquiry broadens, but ranges from examining the threshold energies of 1,2 FCl interchange reactions in chlorofluoroethanes[7] to finding the rate constants and threshold energies for the elimination of HCl and HF from a trio of HCFCs.[8]

Surprisingly, there are not any other prominent research groups investigating this area of chemistry at the moment, despite its importance to ensuring an economical transition away from HCFCs in the coming years. However, other research groups have contributed to the field of inquiry of our research group by providing background information. An article written in 1994 by Dr. Wallington, an atmospheric chemist, is particularly interesting, as it discusses a pulse radiolysis method for characterization of second order CFC radical reaction rates and Arrhenius parameters. He notes that no research was done before on the self-reaction kinetics of CFCs.[9] Although Wallington's methodology is quite different than that of the Asheville research group, his general goal of characterizing CFC kinetics by examining the products of reaction is similar enough to current HCFC research that it is worth mentioning.

Another research group which touched upon HCFC decomposition but with radically differing methods is that of Sekhar, Millward, and Tschuikow-Roux, who in 1973 decomposed HCFC-123 in high-pressure environments via shock tube.[10] They worked between 1120 K and 1260 K, and between 2800-3600 Torr. They identified the decomposition products to be CF_2CClF, perhaps produced by the FCl-interchange reaction discovered by the Holmes Research group, whereby CF_3CCl_2H converts to $CF_2ClCHFCl$ and undergoes a 1,2-HCl elimination reaction to yield CF_2=CFCl. They deduced the rate of formation of CF_2CClF to be represented by Equation

$$\log_{10}\left(\frac{K_1^{\infty}}{s}\right) = (13.4 \pm 0.7) - \left[\frac{(61.3 \pm 3.8\ \text{Kcal})}{2.303RT}\right] \quad (1)$$

It was noted that at higher temperatures, it was possible to induce a 1,2 HF elimination, but at those energies, it was just as likely to destroy the carbon bond holding HCFC-123 together, and thus became intractable. This work has been mentioned last as it is the most germane to our specific research, since it actually deals with CF_3-$CHCl_2$.

An additional area of research will be to determine the presence or absence of predicted side reactions, as well as the rate constants of those reactions. This study addresses this inquiry by examining the chemical activation and reaction of the HCFC CF_3-$CHCl_2$, paying special attention to the 1,1-HCl Elimination, along with the better understood 1,2 HF elimination. By categorizing this reaction pathway, and others, the raw data on HCFC reactivity will be increased, while also providing chemists the tools to use these reactions in a high-yield synthesis as a means to recycle compounds that are being phased out of use.

2. Research Methods

2.1 $CHCl_2I$ Synthesis

First, 37.5328 g of KOH was added to 75 mL of water, producing a 50% KOH solution. The KOH solution was added to a 500 mL round bottom flask, then 1.4374 g 18-crown-6, 50.0149 g NaI and 107.38 mL chloroform. The solution was allowed to sit in a refrigerator at 0°C for two days while being stirred by a magnetic bar. The product was then poured into a 1 L separation funnel. The round bottom flask was washed twice with ice water. The flask was inverted and vented several times before the heavier organic layer was drained off into an Erlenmeyer flask. The product was dried with sodium sulfate. The product was filtered through cotton and placed into a round bottom flask for concentration by rotary evaporation.

After concentration, the product was transferred into a gas rack by placing it under a vacuum, and heating the donor vessel with warm water, while cooling the accepting vessel with liquid nitrogen. This caused the product to evaporate out of the reaction vessel and condense into the permanent storage vessel attached to the vacuum gas rack. To remove excess chloroform, the vessel was chilled to 0 °C with ice water that was fully saturated with NaCl; next, the vessel was opened and allowed to equilibrate into the sealed vacuum rack. The vessel was closed, and the gas was frozen into a waste container. This was repeated until the natural pressure of the gas was ~2.5 Torr, at which point it was nearly pure $CHCl_2I$, as shown by GC-MS analysis, and the waste vessel contained nearly pure chloroform. This target pressure was estimated to be ~5 Torr, as given by Trouton's rule (Equation 2), the Clausius-Clapeyron equation (Equation 3), and the exact pressure found by trial and error.

$$\Delta\overline{S} \approx 10.5R \quad (2)$$

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \quad (3)$$

Whenever $CHCl_2I$ supply was depleted, this procedure was repeated. Approximate yield was 2 grams.

2.1 Sample Preparation

A Pyrex® reaction vessel containing Hg_2I_2 was placed on the rack and allowed to pump down to vacuum pressure. The vessel's stopcock was closed, and therefore isolated from the system. The vacuum stopcock was closed, creating a stable, low pressure system. A gas was allowed to fill the vacuum, by slowly opening its containers stopcock, and when a desired pressure was reached, the gas's container was closed. A calibrated container, with a known volume, had its stopcock closed; then the gas's pressure and volume, as well as the temperature of the room, was recorded. By using the ideal gas law (Equation 4), the moles of gas can be determined.

$$PV = nRT \quad (4)$$

The remaining gas in the main vacuum rack was then frozen with liquid nitrogen back into its storage vessel, and the vacuum was reopened, removing any remaining gas particles. The gas's container was closed again, and after a few minutes, the vacuum was closed as well. The reaction vessel was reopened, and frozen. The calibrated volume, which by then contained the gas we were interested in reacting, was opened, and the gas flowed from its calibrated container into our reaction vessel, where it was then frozen. After a few minutes, the reaction vessel was closed. If multiple gases were needed in the same reaction vessel, as they often are, then the process was repeated for each gas, with the added step of allowing the vacuum to pump out the vacuum rack between each gas's transport, to avoid contamination. Samples were then placed under a high-pressure mercury lamp. After a set duration of exposure under the lamps, they were ready for GC-MS analysis.

Closed sample containers were then joined to the gas rack that leads to a GC-MS and pumped to vacuum pressures. The vacuum stopcock was closed, creating a stable vacuum environment. The gas's vessel was then opened, allowing the gas to flow into the gas rack. Afterward, it was frozen with liquid nitrogen into the GC-MS injection loop; the loop was set to inject, warmed with hot water, and the instrument activated nearly simultaneously, so that the warm gas was pushed into the instrument for analysis.

When using high volume sample vessels, an extra step of freezing the gas into a temporary low volume trap was introduced, whereby the gas would be frozen into a low volume trap, and then the vacuum opened, so that excess gas would be pulled towards the vacuum through the frozen trap. This was done to ensure that the volume discrepancy between large volume containers and the very small volume of the injection loop of the GC-MS did not cause a significant portion of the gas to remain in the large sample vessel, and instead was forced into the injection loop for analysis. Many samples were prepared using this method described above and later run through GC-MS for analysis.

3. Results & Discussion

$CHCl_2I$ was formed and its H-NMR was taken. Comparison to existing literature shows successful synthesis at acceptable purity.[11] Specifically, there exists a peak at 8.0 ppm which appears to be $CHCl_2I$, and a peak at 7.6 ppm which appears to be from chloroform. Our product was also analyzed with a 2010 Shimadzu GC-MS, GC-MS QP 2010, on a vacuum rack by injecting 1.75 Torr from a 3.88 mL container.

Figure 1 shows a peak appearing at 45 minutes with mass signatures of 210, 127, and 83 m/z. The 210 mass matches $CHCl_2I^+$, while the 127 mass matches I^+, and the 83 mass matches $\bullet CHCl_2^+$. This corresponds exceedingly well with what one would expect from an MS of $CHCl_2I$; see Figure 9 for reference in the Supplemental Materials. Table 2 shows the aforementioned MS in a quick-reference table form.

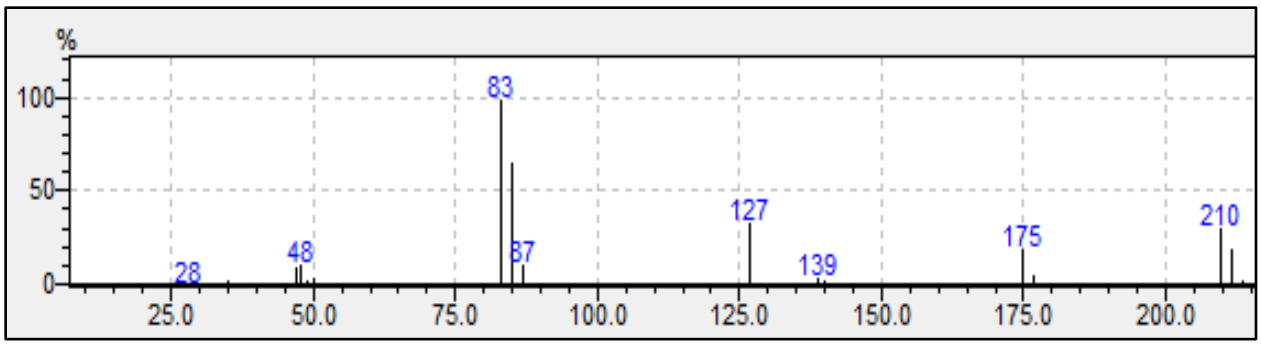

Figure 1. Experimental Spectrum $CHCl_2I$ via GC-MS Q2010 at 45 minutes.

Table 2. A $CHCl_2I$ mass table.

Mass	**Source Ion**	**Source**
210	$CHCl_2I^+$	Parent Ion
175	$CHCl^{\bullet+}$	Removal of a chlorine
127	I^+	Liberated Iodine
83	$CH^{35}Cl_2^{\bullet+}$	Loss of Iodine
85	$CH^{35}Cl^{37}Cl^{\bullet+}$	Loss of Iodine
87	$CH^{37}Cl_2^{\bullet+}$	Loss of Iodine

Both H-NMR and the 2010 Shimadzu GC-MS show a ratio of approximately 5:1 product to unreacted chloroform. Therefore, synthesis has been considered successful. After the final purification procedure using the vacuum rack described in the methods section, the integrated $CHCl_2I$ peak is 96% of total visible peaks. Below, a brief description of the methodology and results discovered with each method is described. Full run data and sample gas ratios can be found in Table 7 of the Supplemental Materials.

The first six runs were used to locate unreacted compounds, as well as to briefly test what sort of gas ratio would produce a good heterochemical reaction yield (where CF_3 and $CHCl_2$ interacted) (Table 7). A high ratio of CF_3I to $CHCl_2I$ was noted to give better yield of CF_3-$CHCl_2$, but its appearance at this point was sporadic. It was noted that lower ratios tended to have little to no heterochemical reaction, as it seems that $CHCl_2I$ reacts with itself very quickly, while CF_3I takes longer to form radicals. Thus, at 3:1 or lower ratios, by the time CF_3I has formed a reasonable population of radical species, all $CHCl_2$ radicals have been formed and finished reacting with themselves. Shortly thereafter, a peak at 23.7 minutes was found on Shimadzu GC-MS QP2010 runs in samples 2d, 3a, 3f, and all later runs with anything greater than a 4:1 CF_3I to $CHCl_2I$ ratio (Table 7). This peak is nearly identical to mass spectrometry signatures for CF_3-$CHCl_2$ from established literature, which can be located in Figure 10 of the Supplemental Materials section.

Notably, Figure 2 shows a peak at 152 and 154, which matches the nominal mass for CF_3-$CHCl_2$. There is also a peak at 133, which corresponds to the loss of a fluorine, with a characteristic 9:6:1 ratio of intensity for the 83:85:87 mass signatures. This agrees with literature spectra, an example of which can be found in Figure 10 of the Supplemental Materials. It is therefore thought that the peak was actually caused by CF_3-$CHCl_2$, which is the intended analyte. A quick-reference mass table for CF_3-$CHCl_2$ (HCFC-123) is presented in Table 3.

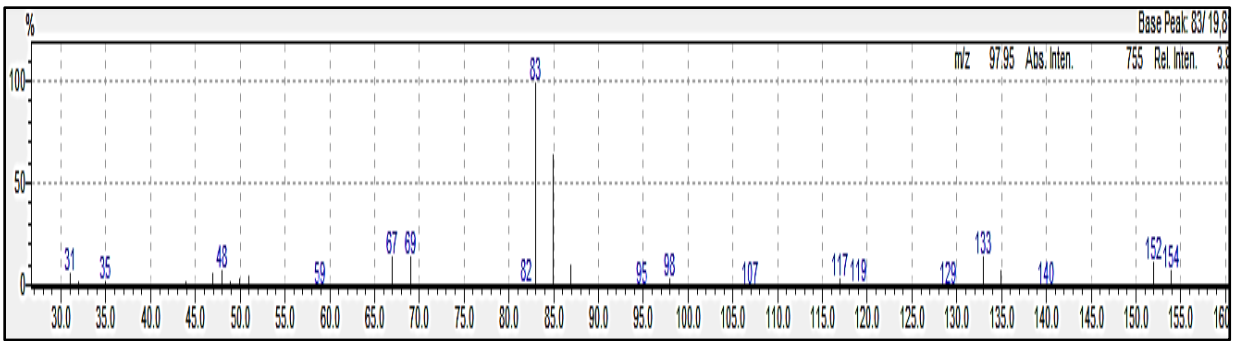

Figure 2. CF_3-$CHCl_2$ Experimental Spectrum via GC-MS Q2010 at 23.7 minutes.

Table 3. A mass table for HCFC-123 (CF_3-$CHCl_2$).

Mass	**Source Ion**	**Relative Abundance**	**Source**
152	CF_3-$CHCl_2^+$	12.27%	Parent Ion
133	$CF_2CHCl_2^+$	14.30%	Removal of a fluorine
117	CF_3CHCl^+	3.97%	Removal of a chlorine
83	$CHCl_2^{\bullet+}$	100%	Main carbon bond scission
85	$CHCl^{37}Cl^{\bullet+}$	66.82%	Main carbon bond scission
87	$CH^{37}Cl_2^{\bullet+}$	11.20%	Main carbon bond scission
69	$CF_3^{\bullet+}$	15.21%	Main carbon bond scission

It was noted that we had a seemingly random detection of CF_3-CHCl during experimentation, and as a possible fix, mercury photosensitization was tested with a germicidal lamp. This did not alleviate the problem, but exclusively using the Shimadzu QP2010 GC-MS did (instead of using both the aforementioned instrument as well as the older Shimadzu GC-MS Qp5000). Therefore, the high-pressure mercury lamp and Hg_2I_2 photosensitization was selected as the standard method, as the mercury photosensitization had no advantage, and once the instrument standardization was implemented, this method produced consistent results.

During low pressure runs, it was noted that the intensity of the 23.7-peak associated with CF_3-$CHCl_2$ decreased, so we were not able to locate a peak that matched literature spectra for the expected product CF_2=CCl_2. The shrinking of the 23.7-peak indicates that more of the product CF_3-$CHCl_2$ is undergoing decomposition; however, as it was not possible to locate the expected product CF_2=CCl_2, even with a reference spectrum as a guide. It was not until amending the analytic procedure to allow for a greater pressure of our sample to be sent to the GC-MS that CF_2=CCl_2 was found. By freezing an intermediary vacuum chamber between the sample vessel and the GC-MS and allowing gas to freeze to its walls, and then to gently apply suction to the system, so that gas residing in the sample chamber is sucked through the frozen intermediary chamber, it is thought that a great amount of very low pressure sample can be sequestered into a smaller environment, where its total pressure will be increased.

After performing this technique, it was discovered that at 20.45 minutes, a peak containing 132, 134, and 136 masses, in a 9/6/1 ratio was discovered, which matches the literature spectrum presented in Figure 11 of the Supplemental Materials. See Figure 3 for the spectrum, as well as evidence of neighboring products obfuscating a clean view of CF_2=CCl_2. These masses tracked well, but they were coincident to nearby peaks, obscuring the tracking of other masses, this is thought to be CF_2=CCl_2. The spectrum shown in Figure 3 was generated by setting the MS to display specific mass signature intensities over time, so that a chart was generated which shows the intensity and time of mass

signatures. Once relative intensities have been manually set in the instrument, if these mass signatures overlap with each other, that can be taken as evidence that these signatures come from the same compound and are not coincidental or the result of overlap from an unrelated compound. Thus, the purple 132 mass signature tracks with the blue 134 and green 136 mass signatures.

Figure 3. Mass tracking spectrum thought to correspond to CF_2=CCl_2.

There exists some evidence that the 1,1 HCl elimination will occur in HCFC-123[10], and so a search for the carbene product CF_3C:Cl, which is formed when HCl is eliminated from HCFC-123, was initiated. Since there exists no literature spectrum of the three-membered ring that is formed when the carbene CF_3C:Cl joins with *trans*-2-butene, isolating the peak corresponding to it was difficult. While a full spectrum does not exist for this product, it is known that the parent ion of the trapped carbene will be seen, and the dominant fragment will be a 137-peak corresponding to a loss of a chlorine.[12] This pattern is observed in a peak at 44.1 minutes, which likely corresponds to this ring. The following masses are observed: 172, 137, 69, 55, as can be seen in Figure 4 and in a quick-reference mass table in Table 4.

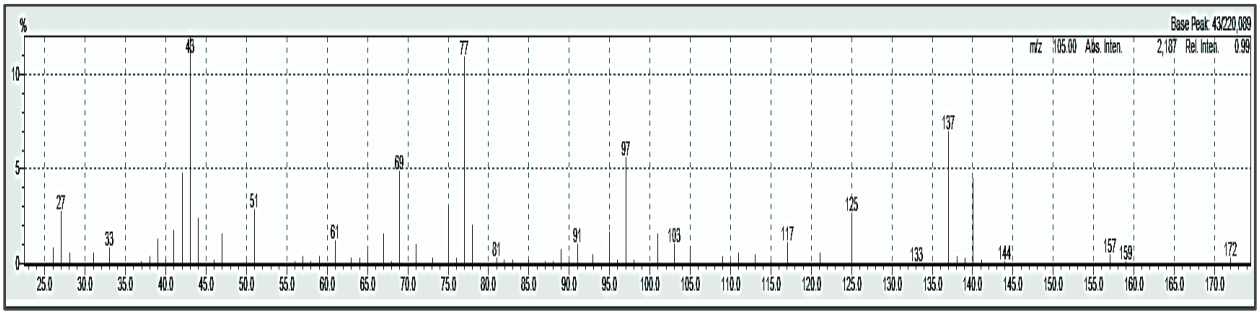

Figure 4. *cis*-2-Butene trapped carbene adduct spectrum via Shimadzu GC-MS Q2010 at 44.1 minutes.

Table 4. Mass table for *cis*-2-butene trapped adduct.

Mass	**Source Ion**	**Source**
172	$C_6ClF_3H_8^+$	parent ion
137	$C_6F_3H_8^+$	adduct loses a chlorine
69	$CF_3\bullet^+$	CF_3 radical is fragmented from adduct
55	C4H7+	carbon scission

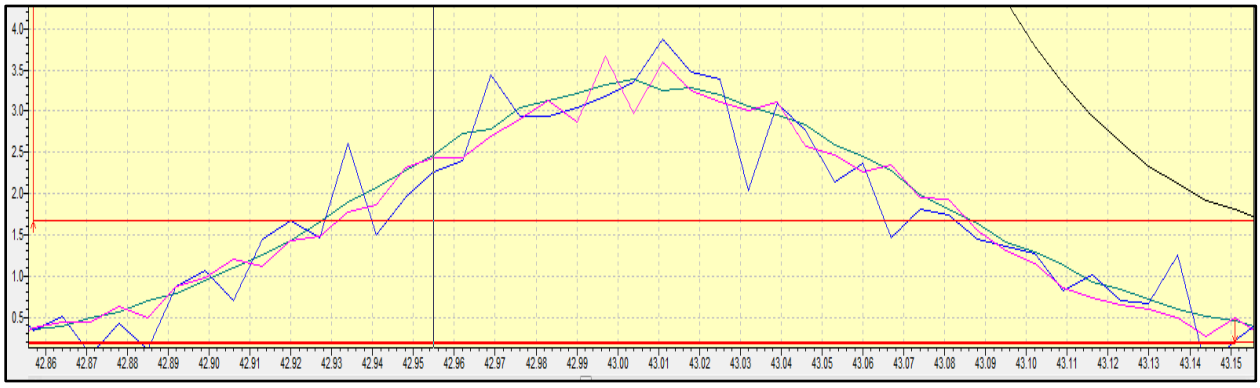

Figure 5. Mass tracking of *trans*-2-butene trapped carbene via Shimadzu GC-MS Q2010. 43 mins.

Further evidence this peak belongs to our trapped carbene comes in the form of mass tracking seen in Figure 5. Mass vs Time is displayed; note that blue represents 172, purple 174, and green 137.

Another result to note are the 172/174 3:1 ratio masses appearing after our analyte, and lacking a 137-mass signature, as seen in Figure 6. It is thought that these peaks are due to the three-membered rings generated from trapping our carbene opening, and rearranging into alkenes.

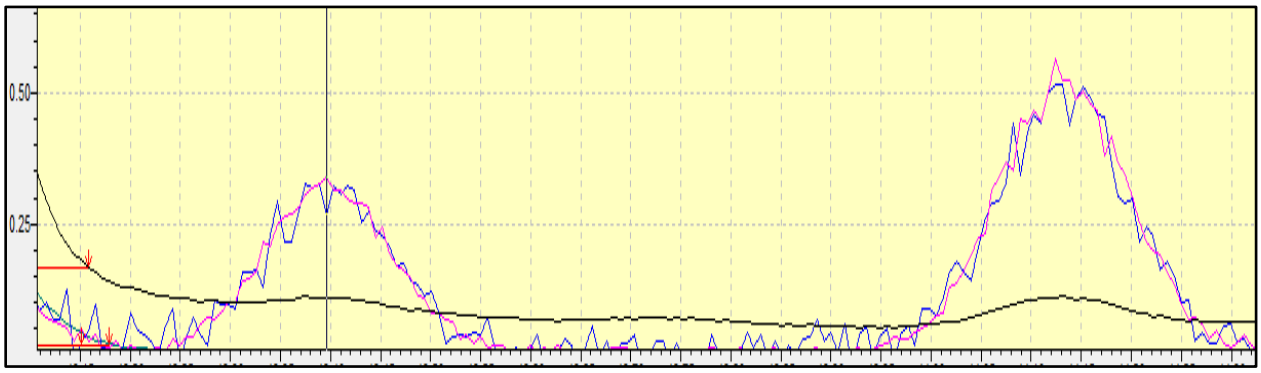

Figure 6. Tracking of Opened-ring alkene adduct via Shimadzu Q2010 GC-MS.

There have been 5 detected products when *cis*-2-butene is used as a trap, with retention times of 39, 41, 42.3, 44.1, and 46, as well as 3 products which have retention times of 41, 42.3, and 44.1 when *trans*-2-butene is used as a trap. This is likely due to the fact that the *cis*-2-butene has two isomers, as shown on the left two depictions in Figure 7,

and therefore, two of these products are likely unbroken rings in different configurations, while the other three products are thought to be alkenes generated from the strained three-member ring opening.

Presented in Table 5 are the mass tables and retention times of compounds detected in the *cis*-2-butene system. Note that the 42.5 and 43 minute retention time compounds display a 137-peak (Table 5a-b), suggesting that these spectra probably indicate the left and middle three-membered rings shown in Figure 7; further, the 43 minute retention time peak was so heavily overlapped with another interfering compounds peak that only three masses can be shown to track closely with it (Table 5b). Lastly, the compounds presented after 43 and 42.5-minute retention time lack a 137-peak (Table 5c-e) and are likely alkenes that are generated from the three-membered ring opening.

Table 5a-e. Masses detected when *cis*-2-butene is used to sequester $CF_3C{:}Cl$.

(a) 42.5 Minute Retention Time

M/z	**%**	**Fragment**
73	84	$C{:}F\text{-}CH\text{-}CH_2CH_3^+$
94	40	$CFCClCH_4^+$
113	38	$CF_2CClCH_4^+$
137	34	$CF_3C_5H_8^+$
172	8	Parent Ion

(b) 43 Minute Retention Time

M/z	**% (not detectable for this peak)**	**Fragment**
172	N/a	Parent Ion
174	N/a	Parent Ion Isotope
137	N/a	$CF_3C_5H_8^+$

(c) 39 Minutes Retention Time

M/z	**%**	**Fragment**
55	74%	$CH_3CH{=}CHCH_2^+$
29	59%	$CH_3CH_2^+$
43	47%	$CH_3CH_2\text{-}CH_2^+$
27	34%	$CH_2{=}CH_1^+$

(d) 44 Minute Retention Time

M/z	**%**	**Fragment**
55	100	$CH_3CH=CHCH_2^+$
29	12	$CH_3CH_2^+$
172	11	Parent Ion
81	9	$CF_2HCH_2CH_3^+$
39	8	C_3H_3?
69	7	CF_3^+

(e) 46 Minute Retention Time

M/z	**%**	**Fragment**
55	100	$CH_3CH=CHCH_2^+$
67	28	$CH_3CH=CHCH_2C:^+$
39	25	$C_3H_3^+$
172	14	Parent Ion
91	12	CH_3CH_2-CH_2CHCl^+
41	12	$CH_2=CH_1CH_2^+$
65	9	$CF_2CH_3^+$

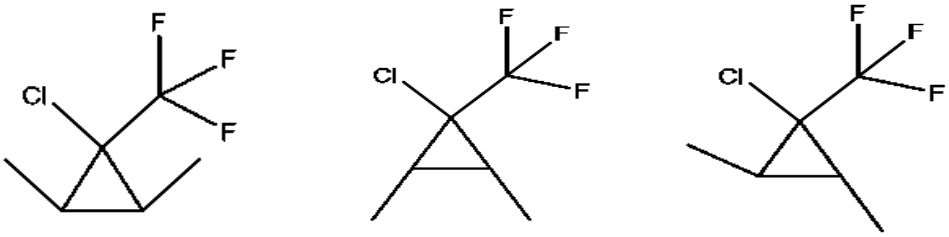

Figure 7. Possible structures of trapped carbene adduct conformers.

Presented in Table 6 are the masses detected for the peaks observed in the *trans*-2-butene system. The rightmost three-membered ring shown in figure 7 likely corresponds to the peak observed at 42.5 minutes retention time (Table 6a), as it shows a strong 137-peak, and the peaks at 43 and 44 minutes (Table 6b-c) likely correspond to alkenes from the three-membered ring opening.

Table 6a-c. Masses detected when *trans*-2-butene is used to sequester CF_3C:Cl.

(a) 42.5 Minutes Retention Time

M/z	**%**	**Fragment**
137	100	$CF_3C_5H_8^+$
97	24	CF_2CCl^+
117	14	CF_3CHCl^+
157	7	$CF_3CClCHCHCH_3^+$
138	6	$CF_3C_5H_9^+$
172	5	Parent Ion
174	1.8	Parent Ion Isotope

(b) 43 Minutes Retention Time

M/z	**%**	**Fragment**
55	100	$CH_3CH{=}CHCH_2^+$
67	49	$CH_3CH{=}CHCH_2C:^+$
39	31	$C_3H_3^+$
65	20	$CF_2CH_3^+$
102	20	$ClCC_4H_8^+$
172	13	Parent Ion

(c) 44 Minutes Retention Time

M/z	**%**	**Fragment**
55	100	$CH_3CH{=}CHCH_2^+$
172	10	Parent Ion
81	9	$CF_2HCH_2CH_3^+$
69	5	CF_3^+
174	3	Parent Ion Isotope

Although the aforementioned analysis and the data presented in Tables 6-7 suggest alkene rearrangement occurs, it is not obvious which pathway(s) this rearrangement takes. Figure 8 shows the most likely possible pathways. Literature shows that the chlorine migration pathway is likely preferred, as it is known that when CCl_2 binds to

Cl_3CSiCl_3 to form a three-membered ring, the chlorine migration pathway is preferred, showing a 7:1 chlorine to hydrogen migration ratio.[13] Further, when 1,1-dichlorocyclopropane is thermally decomposed, while the hydrogen and chlorine migration take place in parallel channels, at 610 K, the chlorine migration is preferred 20:1, while at 725 K, it is preferred 15:1.[14] In keeping with the trend of higher energy states showing less selectivity towards the chlorine migration, when high-energy chemical activation of 1,1-dichlorocyclopropane is investigated by addition of CH_2 to 1,1-dichloroethylene, hydrogen migration is preferred to chlorine migration, but these results are obfuscated by side reactions and the introduction of 1,2 HCl elimination into the system of parallel pathways.[15]

It is useful to consider chlorocyclopropane as well. In 1978 Heydtmann reported the rate constant for the isomerization of chlorocyclopropane to 3-chloroprop-1-ene was $8.7*10^8 S^{-1}$ and had an activation energy of 324 KJ/Mol.[13] In Heydtmann's 1984 paper it is reported that 2-chloropropene was not observed under varying conditions with chemical activation; as this product can only be formed by hydrogen migration, it was concluded that hydrogen migration did not occur. The author notes that in an analogous system, wherein chlorine was substituted for fluorine, 2-fluoropropene was generated.[13] This is contradicted by a more recent 1984 study, which reports that under oxygen-free conditions, chemically activated chlorocyclopropane may yield products dependent on hydrogen migration.[15] Depending on which bond breaks in a chlorocyclopropane system, hydrogen migration may be observed, and with it *cis*-1-chloropropene and *trans*-1-chloropropene as well. These products may only be produced if a bond adjacent to the chlorine atom breaks. If the bond opposite the chlorine atom breaks, no hydrogen migration occurs, and 3-chloropropene is a reported product, indicating chlorine migration. It should be noted that when an adjacent bond breaks, chlorine migration is not possible, thereby necessitating hydrogen migration; however, when the opposite bond breaks, both chlorine migration and hydrogen migration are possible. As only chlorine migration was observed in Heydtmann's 1984 study, it is clear that when in direct competition with hydrogen migration, chlorine migration is preferred. The product ratios reported are 2.59:1 for 3-chloropropene: (*cis*-1-chloropropene + *trans*-1-chloropropene), indicating that scission of the bond opposite the chlorine atom is the favored pathway.

It is unclear which system is a more germane model to our system, as it is unclear what effect the CF_3 group contributes. Regardless, in both systems, hydrogen migration is observed, which indicates that pathways which incorporate hydrogen migration are likely present in our system, further expanding the number of possible rearrangement pathways. These are illustrated in Figure 8; pathway 1 shows chlorine migration, while Pathways 2 and 3 demonstrate the possibility of H migration. Note that in this scheme, *cis* and *trans* isomers exist for each product, for a total of six possible rearrangements. Without further experimental work, identifying which of these products are present in our system is not feasible, but it seems likely that Pathway 1 of Figure 8 would be dominant, since in the model systems previously discussed, a similar system was dominant.

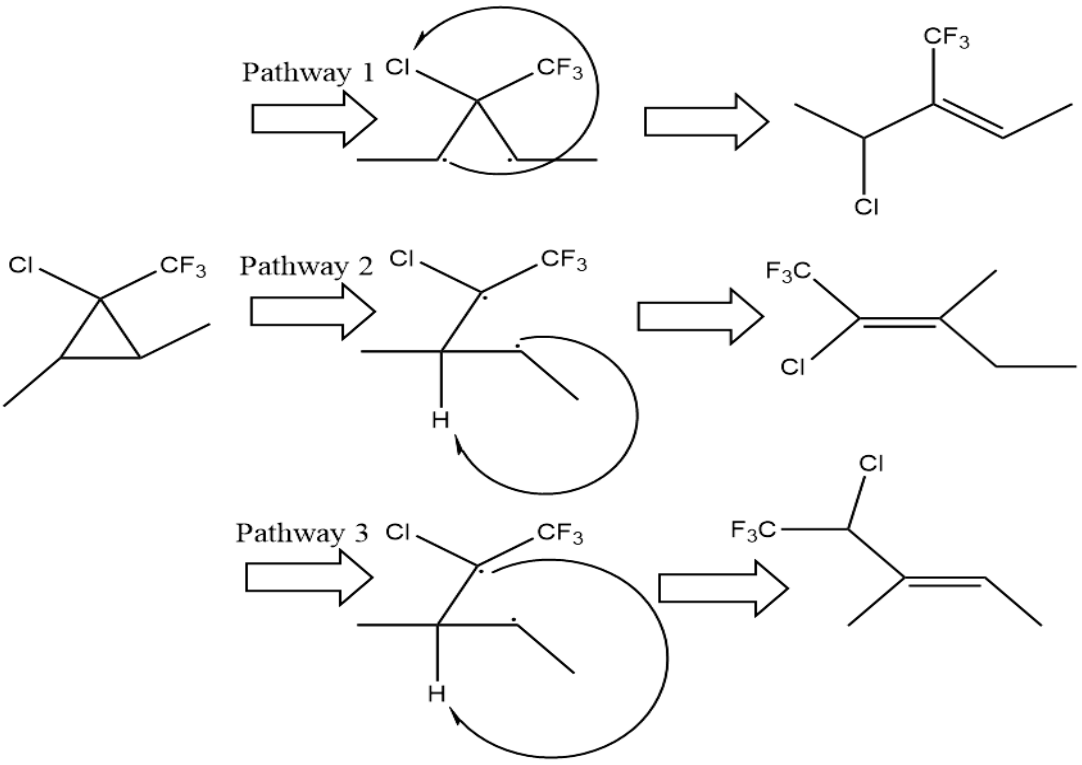

Figure 8. Adduct Rearrangement Pathways.

4. Conclusion

Work to date has been qualitative rather than quantitative, and also experimental with respect to developing a working methodology for consistent results. Much of this methodological work was based off of previous research. For example, in the study "Characterization of the 1,1-HF Elimination Reaction from the Competition between the 1,1-HF and 1,2-DF Unimolecular Elimination Reactions of $CD_3CD_2CHF_2$,"[5] Holmes' research group used mercury photolysis with a high-pressure mercury lamp to elicit heterochemical reaction. This method was tested in our study as a possible way to normalize the initially sporadic appearance of CF_3-$CHCl_2$, before settling on instrument standardization, whereby only the Shimadzu GC-MS QP2010 was used instead.

Other methodological steps taken include the introduction of a low volume trap as an intermediary holding vessel to combat the effect of trying to move a small mol of gas from a 1168 CC vessel into a very small injection loop with any real efficacy. Further, the purification procedure of $CHCl_2I$ proved very successful, and was another example of strategic innovation. These methodological concerns are of course relevant to others who are interested in the broader area of research, who are also trying to work with these understudied and often uncooperative HCFC compounds.

Results to date are surprising. The 1,2 HF elimination is a well-studied pathway, and was assumed to be dominant, since the product is a stable alkene, and not a carbene. In general, reactions that produce stable products are thought to be prevalent. Further, we have seen the 1,2 HF elimination, and 1,2 DF elimination before in HCFC compounds, and categorized them as dominant pathways, if only slightly, as the 1,1 HF elimination was noted to have an activation energy 1 kcal/mol higher than that of the 1,2 HF elimination.[5] While calibrations have not yet been done, it is thought that the 1,1 HCl elimination is in fact dominant, as there are visible peaks present associated with both the stabilized three-membered rings and the alkene rearrangement products, as shown in Figure 6. No such peak can be seen in Figure 3.

Future work will be to verify the predictions made in the Results & Discussion section regarding adduct rearrangement. While there is good reason to believe that the *cis*-2-butene or *trans*-2-butene trapped carbene

undergoes isomerization into an alkene, what pathways it takes is unknown. Having a clear identification of products is necessary to gather total pathway yields, and to subsequently derive reaction rates. Therefore, investigating a parallel system is recommended, whereby either methene or propene would be used as a trap, rather than *cis*- or *trans*-2-butene. The products of this system should be compared to pure compounds produced by chemical vendors, so that products can be verified in these similar systems, shedding light on what would be expected in our novel system. Following this, quantitative data ought to be gathered for reaction rates so that activation energies can be calculated.

5. Acknowledgements

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18. from *Scifinder*, 2017; Chemical Abstracts Service: Columbus, OH, 2017; RN 79-35-6 (accessed May 18, 2018).

7. Supplemental Materials

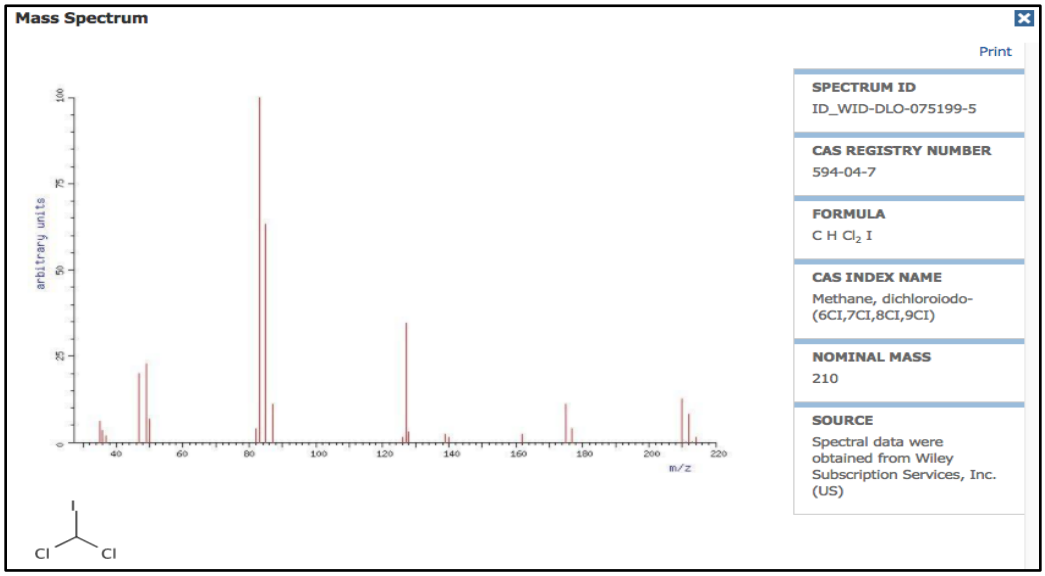

Figure 9. $CHCl_2I$ Literature Spectrum.[16]

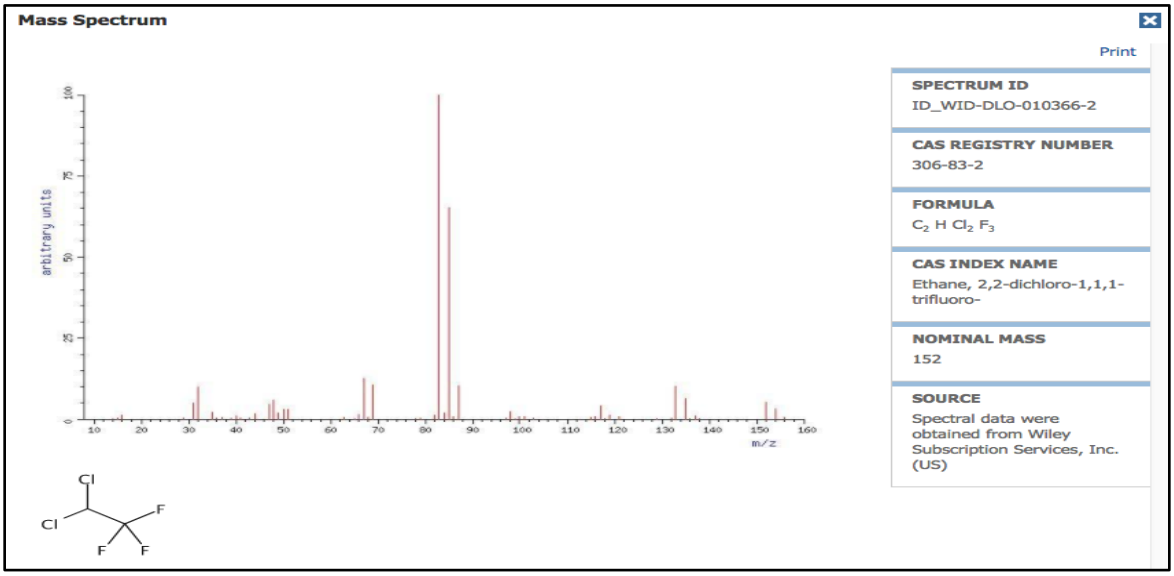

Figure 10. CF_3-$CHCl_2$ (HCFC-123) Literature Spectrum.[17]

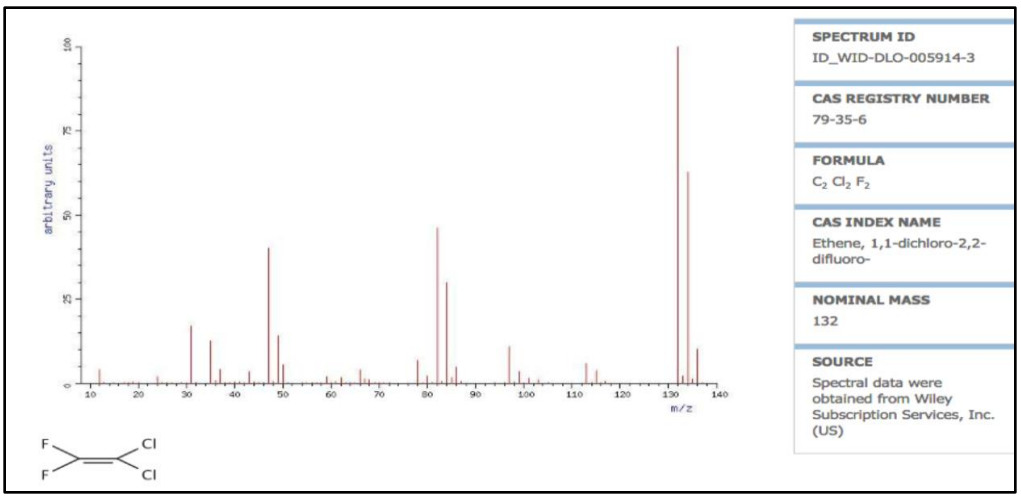

Figure 11. CF_2=CCl_2 Literature Spectrum.[18]

Table 7. Total sample run data presented in chronological order.

Run ID	**CF_3I Pressure (Torr) (if another gas, identity included)**	**$CHCl_2I$ Pressure (Torr)**	**Volume Rxn vessel (cc)**	**Volume calibrated vessel (cc)**	**Photolysis duration and type (mins)**	**3rd gas identity and pressure (if applicable) (Torr)**
2-6/5/17	.5	.5	4.149	13.02	0	
2-6/5/17 B	.5	.5	22.47	13.02	5 HgI	
2-6/5/17 C	.5	.5	22.47	13.02	5 HgI	
2-6/5/17 D	1.9	.5	22.47	13.02	5 HgI	
2-6/5/17 E	20	1	22.47	13.02	5 HgI	
3a	10	.5	22.47	13.02	20 HgI	
3b	0.5	0	22.47	13.02	0	
3c	.5 HFA	.5	22.47	13.02	10 Hg	
3d	3	.5	22.47	13.02	5 Hg	
3e	3	.5	22.47	13.02	15 Hg	
3f	15	.5	22.47	13.02	15 HgI	
4a	3	.5	22.47	13.02	15 Hg	
4b	3	.5	22.47	13.02	15 Hg	
4c	3	.5	22.47	13.02	15 Hg	

4d	2	.45	22.47	13.02	10 HgI	
4e	2	.43	22.47	13.02	15 Hg	
4f	2	.42	22.47	13.02	15 Hg	
4g	2	.42	22.47	13.02	5 HgI	
4i	2	.42	22.47	13.02	5 HgI	
6a	0	.45	22.47	13.02	0	
8b	10	0	7	4.122	0	10 *trans*-2-butene
8c	10	0	7	4.122	0	10 *trans*-2 butene
8d	1	0	7	4.122	15	1 *trans*-2- butene
8e	1	0	7	4.122	15	1 *trans*-2- butene
9a	1	0	7	4.122	15	1 *trans*-2- butene
9b	1	.1	7	4.122	0	1 *trans*-2- butene
9c	10	1	7	4.122	15	10
9d	10	1	1168	13.02	15	10
9f	2	.2	1168	13.02	15	2
9g	2	.2	1168	13.02	15	2
9h	4	.4	1168	13.02	15	4