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PROGRESS REPORT

DEPARTMENT OF ENERGY
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"RESEARCH IN CHEMICAL KINETICS"

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**Progress Report on work carried out during the contract period from
January 1, 1991 to December 31, 1991**

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DISCLAIMER

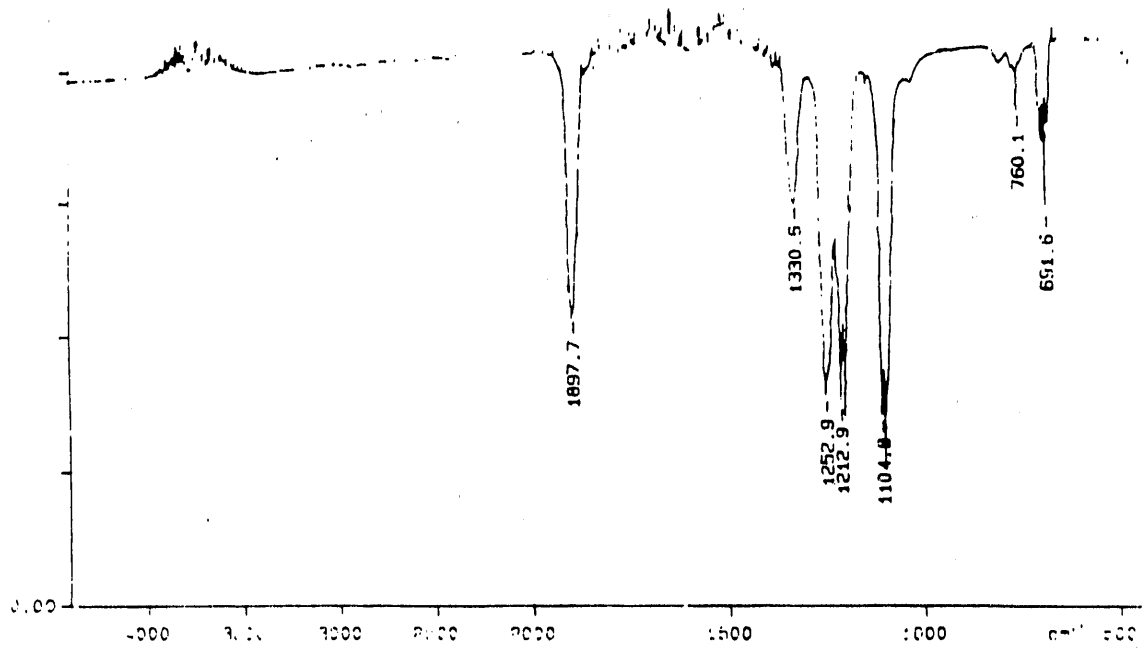
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FIGURE 1

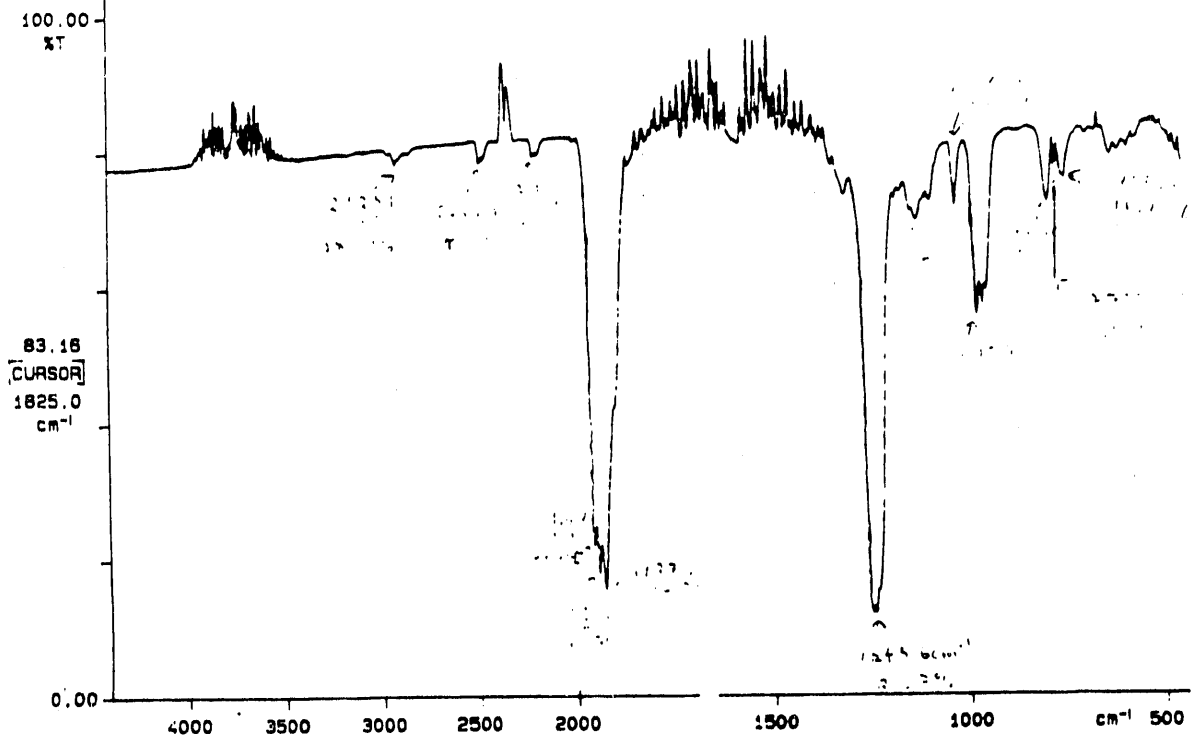
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16 scans, 2.0cm-1
CF₃CFD, @ 0.60 torr

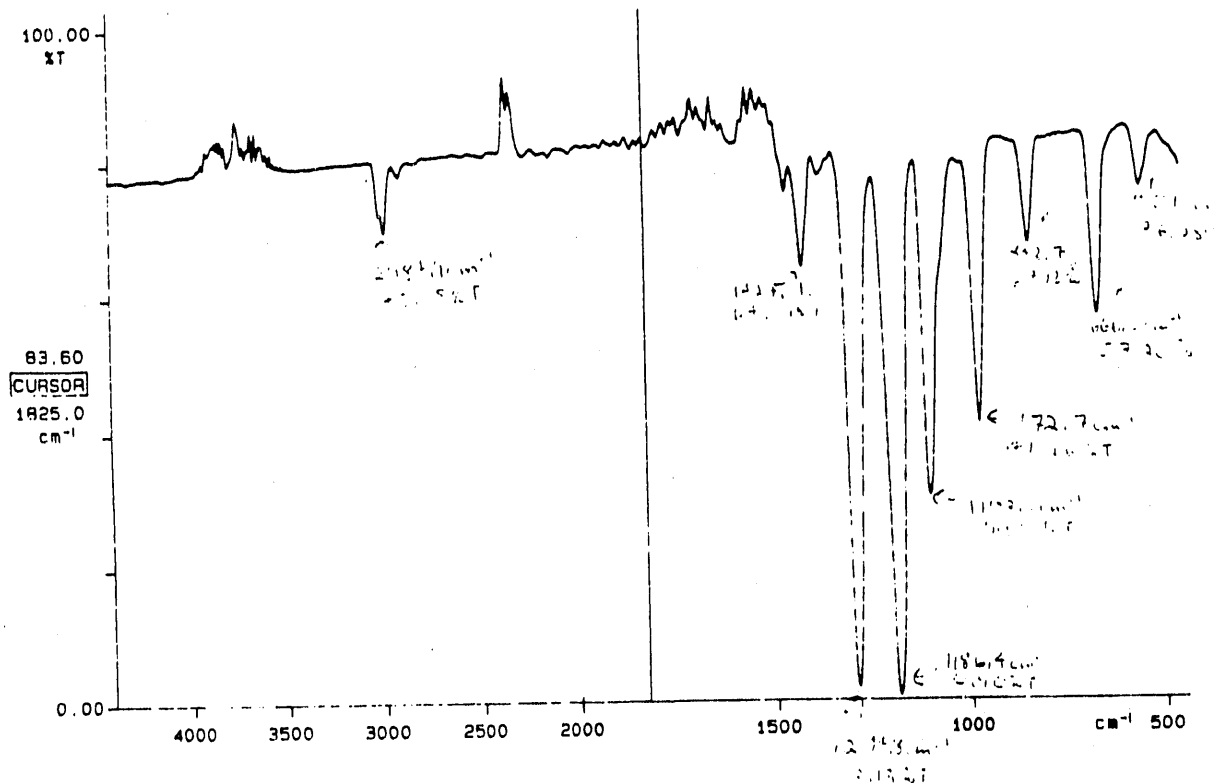
FIGURE 2

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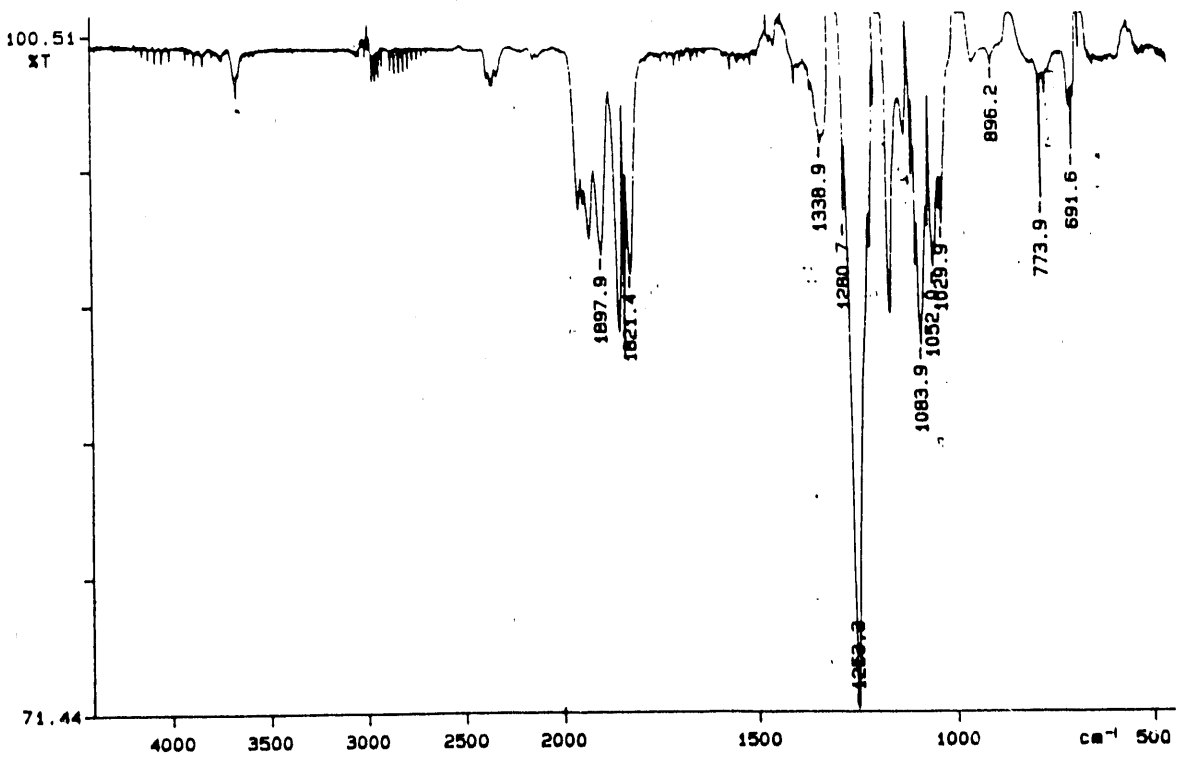
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Y: 16 scans, 4.0cm-1
Carbonyl Fluoride (CF₂O), 6.7 torr

PERKIN ELMER **FIGURE 3**



91/04/02 11:52 benzylamine
Y: 16 scans, 16.0cm⁻¹. apod weak
1, 1, 1, 2 tetrafluoroethane

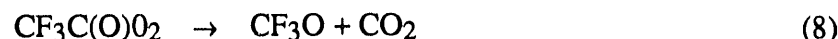
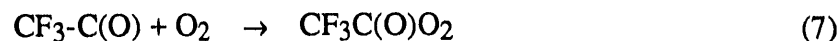
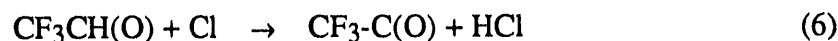
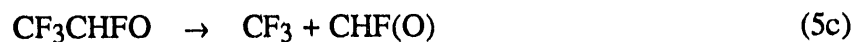
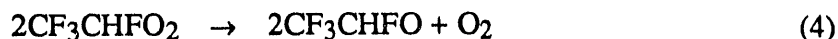
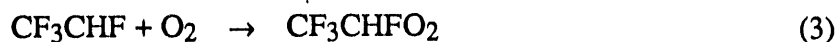
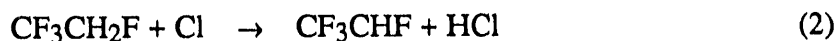
PERKIN ELMER **FIGURE 4**



These same products are seen at
smaller irradiation times in
smaller quantities

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Z: 64 scans, 2.0cm⁻¹. diff
Run 18e Sample run t = 60min irradiation

The expected reactions are as follows (analogous mechanism to reference):³



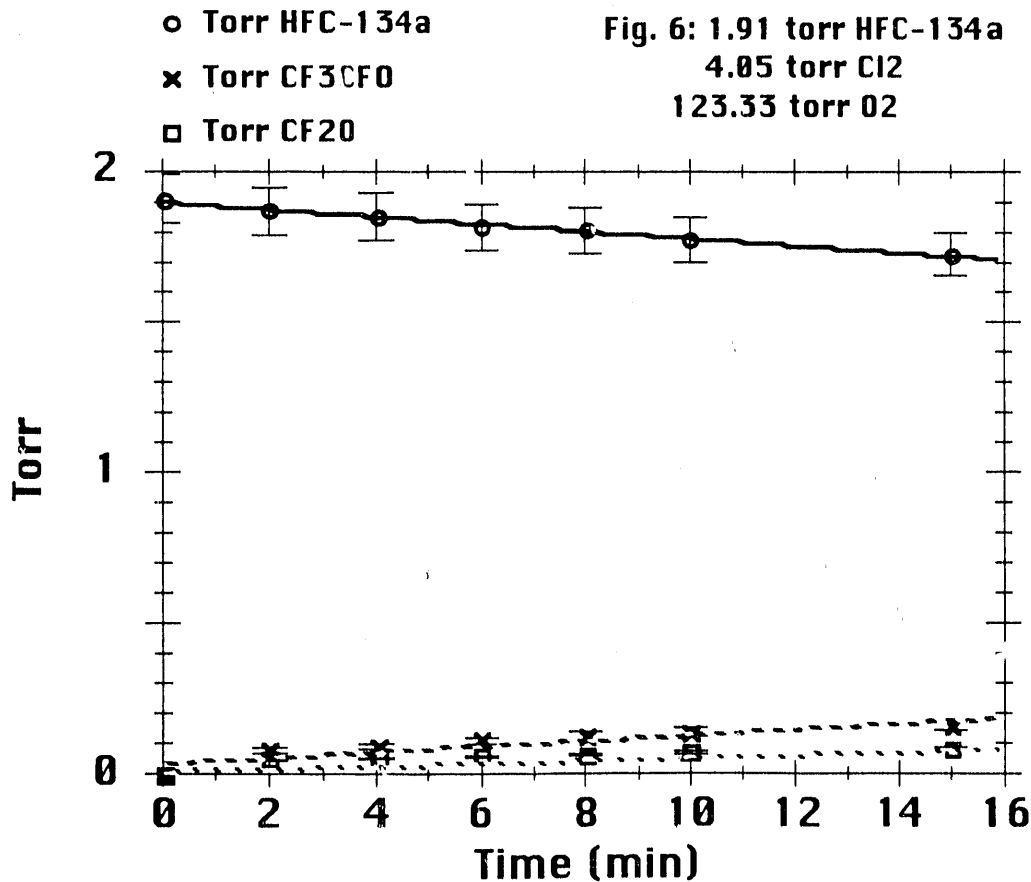
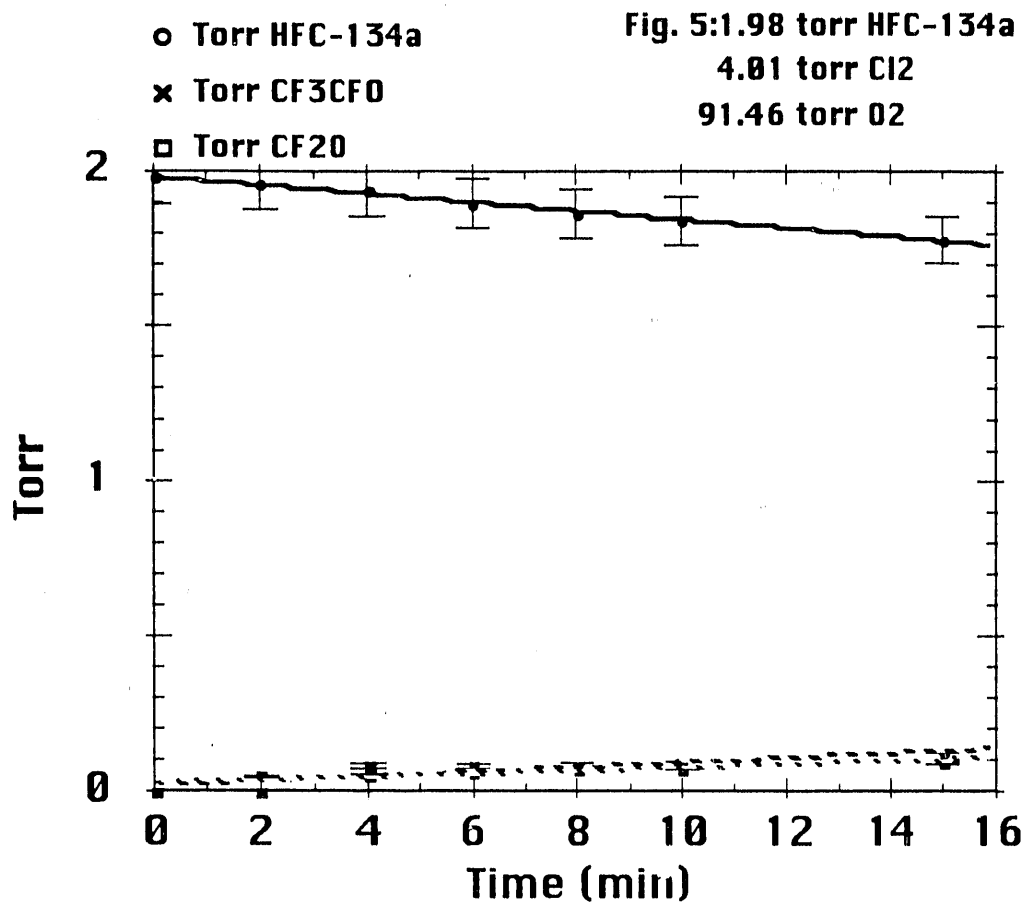
Preliminary studies show $\text{CF}_3\text{CF}(\text{O})$ and $\text{CF}_2(\text{O})$ to be products of this reaction. The effect of varying the irradiation time on the yields of these two products is shown in Figures 5 and 6 for two samples with different O_2 concentrations. The presence of $\text{CF}_2(\text{O})$ suggests that $\text{CF}_3\text{CH}(\text{O})$ might also be a product, as shown in the possible mechanism. The FTIR spectrum of $\text{CF}_3\text{CH}(\text{O})$ has not yet been obtained due to the extreme difficulty in handling the material. Attempts will be made to prepare an authentic sample of $\text{CF}_3\text{CH}(\text{O})$ for spectral measurement. $\text{CHF}(\text{O})$, expected from reaction 5c, was not observed as a product in these runs.⁴

Wavelengths Identified and Assumed in Figure 4

<u>Wavelength (cm-1)</u>	<u>Compound</u>
691.6	$\text{CF}_3\text{CF}(\text{O})$
760.1	$\text{CF}_3\text{CF}(\text{O})$
773.9	$\text{CF}_2(\text{O})$
896.2	To be identified
1029.9	$\text{CF}_2(\text{O})$
1052.0	To be identified
1083.9	To be identified
1212.2	$\text{CF}_3\text{CF}(\text{O})$
1253.3	$\text{CF}_3\text{CF}(\text{O})$
1280.7	To be identified
1338.9	To be identified
1821.4	$\text{CClF}(\text{O})^a$
1835.6	$\text{CClF}(\text{O})^a$
1849.6	$\text{CClF}(\text{O})^a$
1897.8	$\text{CF}_3\text{CF}(\text{O})$

^a By undetermined mechanism. See Reference 3.

Subsequent experiments will involve the influence of O_2 concentration, the impact of the presence of N_2 , and a pressure study. This study may also be expanded to other hydrofluorocarbons and hydrochlorofluorocarbons.

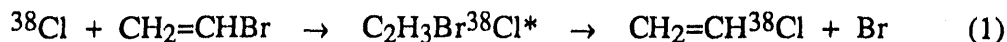


REFERENCES FOR SECTION I

1. Sukornick, B. "Potentially Acceptable Substitutes for the Chlorofluorocarbons: Properties and Performance Features of HFC-134a, HFC-123, and HCFC-141b", *Int. J. Thermo.*, **1989**, *10*, 553-561.
2. Gillotay, D.; Simon P. "Temperature Dependence of Ultraviolet Absorption Cross-Sections of Alternative Chlorofluoroethanes", *J. Atmos. Chem.*, **1991**, *12*, 269-285.
3. Edney, E.O.; Gay, B.W., Jr.; Driscoll, D.J. "Chlorine-Initiated Oxidation Studies of Hydrochlorofluorocarbons: Results for HCFC-123 (CF₃CHCl₂) and HCFC-141b (CFC₁₂CH₃)", *J. Atmos. Chem.*, **1991**, *12*, 105-120.
4. Olah, G.A.; Kuhn, S.J. "Formylation with Formyl Fluoride: A New Aldehyde Synthesis and Formylation Method", *J. Am. Chem. Soc.*, **1960**, *82*, 2380-2382.

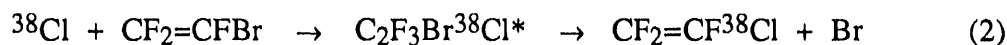
II. ABSTRACTION REACTIONS BY THERMAL CHLORINE ATOMS WITH HFC-134a

Thermalized ^{38}Cl atoms from the neutron irradiation¹ of CClF_3 were used to determine the relative rate constants for HFC-134a and other alkanes and haloalkanes versus a common competitor, vinyl bromide, at 4000 torr, with measurement of the decomposition product, $\text{CH}_2=\text{CH}^{38}\text{Cl}$, formed following ^{38}Cl addition to $\text{CH}_2=\text{CHBr}$.²⁻⁵ Alkanes and haloalkanes with



well-known rate constants for reactions⁶ with chlorine atoms are chosen as the competitor molecules for the conversion of the measured relative rate constants onto an absolute scale.

Vinyl bromide proved to react too quickly with chlorine atoms to allow accurate measurement of the rate constant for Cl atom reaction with HFC-134a (Fig. 1). The common competitor was therefore changed to bromotrifluoroethylene. It was found by using ethane as a competing reagent that the formation of $\text{CF}_2=\text{CF}^{38}\text{Cl}$ from $\text{CF}_2=\text{CFBr}$ at a total pressure of 4000 torr of CClF_3 is about three times slower than the corresponding reaction with $\text{CH}_2=\text{CHBr}$ to form $\text{CH}_2=\text{CH}^{38}\text{Cl}$.



The reciprocal yields of $\text{CF}_2=\text{CF}^{38}\text{Cl}$, with allowance for a 5% loss of total ^{38}Cl through hot reactions, are plotted against competitor ratios (see Fig. 2). These lines provide slopes whose ratios give the ratios of the respective rate constants. Methane and methyl chloride, whose rate constants for reaction with chlorine atoms are well-known, were used as the reference reactants.

Measured Slopes and Rate Constants for Reactions of Chlorine Atoms with the Competing Reagents

<u>Competing Reagent</u>	<u>Measured Slope</u>	<u>k(298)</u>	<u>Reference</u>
CH_4	$.029 \pm .002$	$(1.0 \pm 0.10) \text{E} - 13$	6
CH_3Cl	$.159 \pm .013$	$(4.9 \pm 0.98) \text{E} - 13$	6
CH_3F		$(3.61 \pm 0.10) \text{E} - 13$	7
CH_3F		$3.4 \text{E} - 13$	8
CH_3F	$.063 \pm .005$	$(2.17 \pm 0.31) \text{E} - 13$	this work ^a
HFC-134a	$.0039 \pm .0003$	$(1.33 \pm 0.20) \text{E} - 14$	this work ^a

^a Using methane as the reference line.

As seen from the above table, the ratio (5.48 ± 0.59) of the respective slopes measured for CH_4 and CH_3Cl agree within experimental error with the ratio of their respective rate constants (4.9 ± 1.1). However, the rate constant determined for CH_3F in our experiments is about 40% lower than the value reported in the literature.⁷ For chlorine atom reaction with HFC-134a, the present study indicates a rate constant of $(1.33 \pm 0.20) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298K. Additional confirmation of the rate constants determined for CH_3F and HFC-134a is being sought from further experiments using H_2 as a reference reactant. As can be seen in Figure 2, the data points for $\text{RH}=\text{CH}_4$, CH_3F and CH_3Cl appear to show a slight upward curvature suggesting lower measured yields of $\text{CF}_2=\text{CF}^{38}\text{Cl}$ (than would be expected for a linear fit) at the higher $[\text{RH}]/[\text{CF}_2=\text{CFBr}]$ ratios. Whether this curvature is caused by the involvement of non-thermal ^{38}Cl reactions is currently being checked through a temperature study⁹ of the different competitive systems.

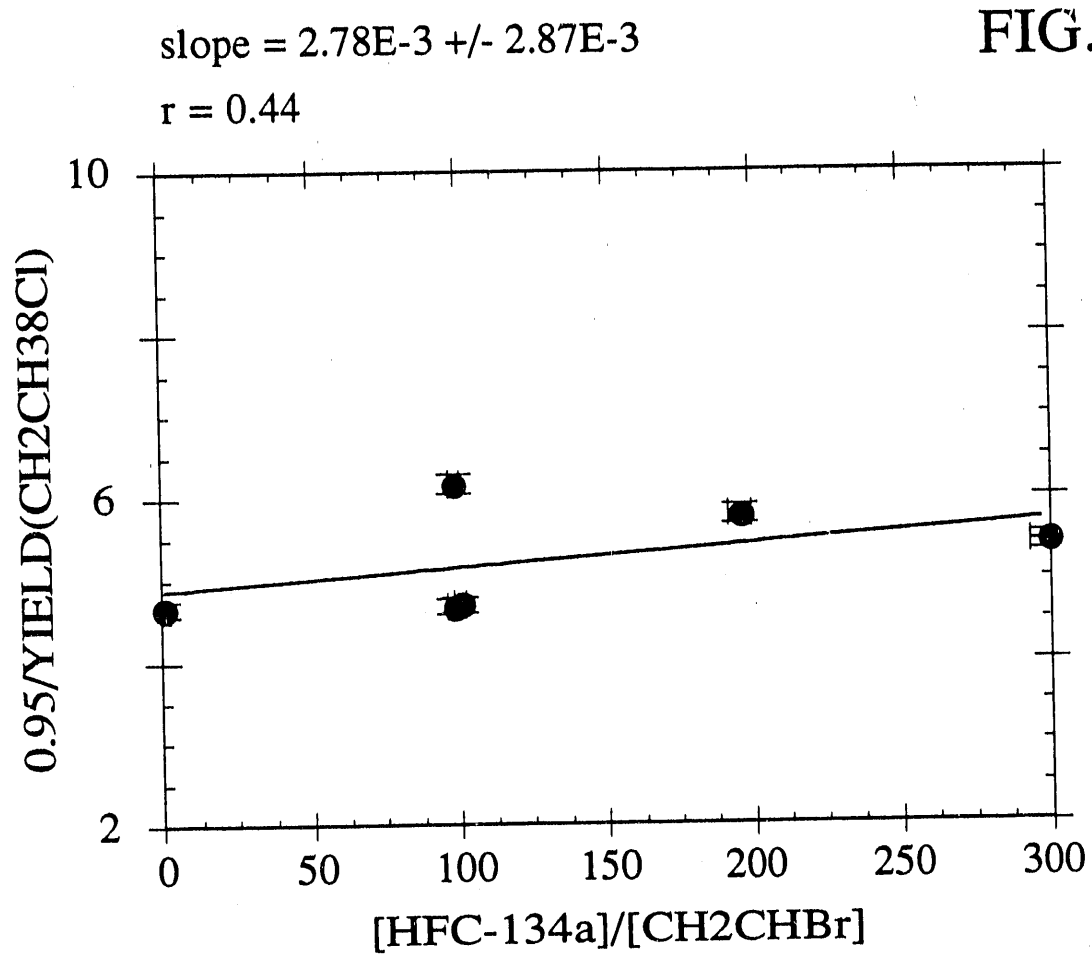
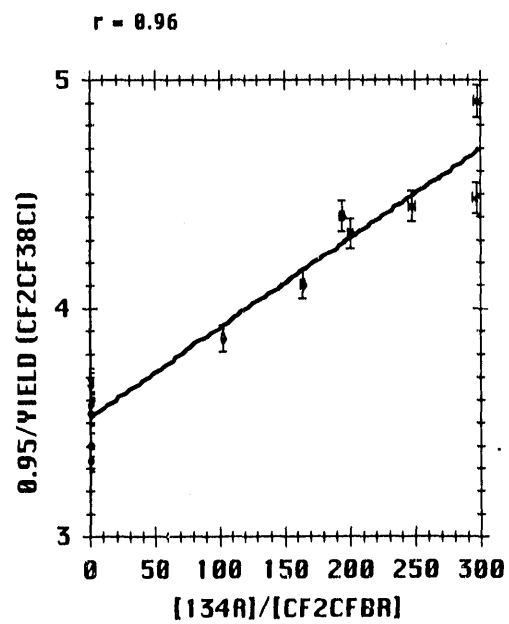
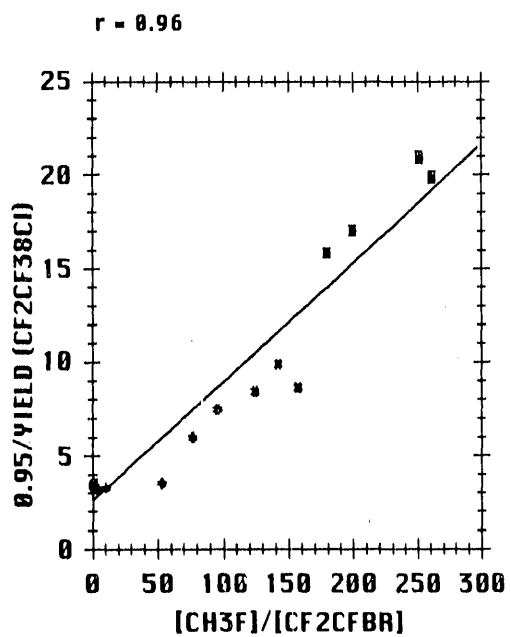
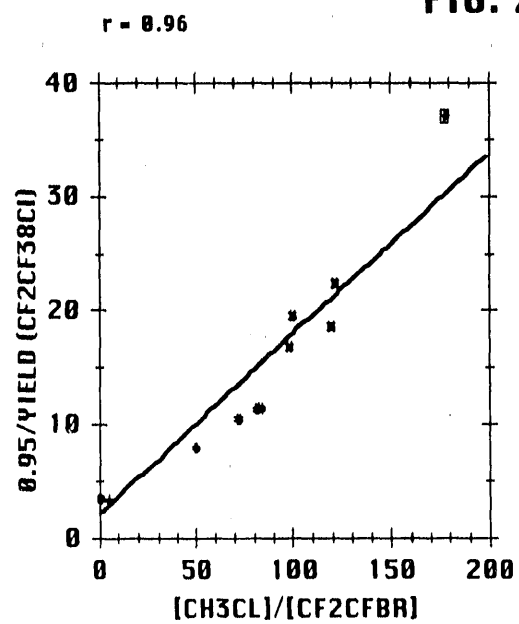
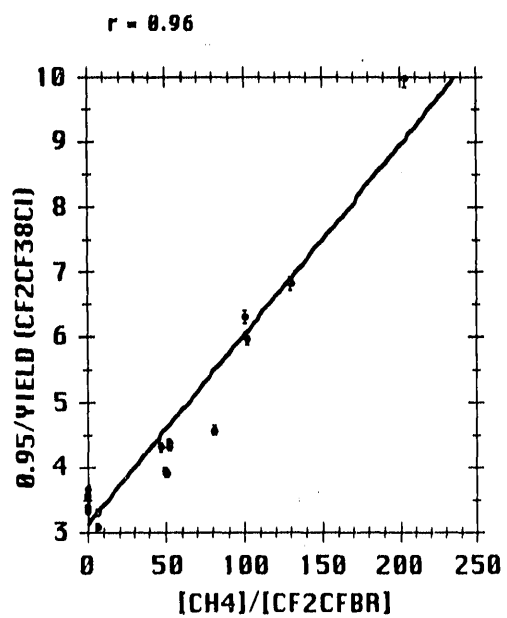


FIG. 2

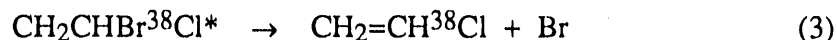
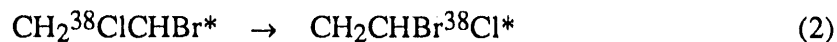
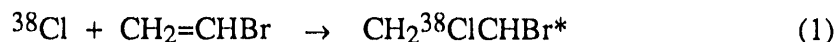


REFERENCES FOR SECTION II

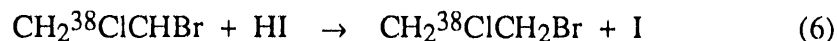
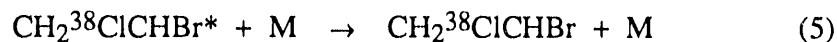
1. Lee, F.S.C.; Rowland, F.S. "Thermal Chlorine-38 Atom Sources: Neutron Irradiation of CClF_3 and CCl_2F_2 ", *J. Phys. Chem.*, **1977**, *81*, 1229-1235.
2. Lee, F.S.C.; Rowland, F.S. "Competitive Radiotracer Evaluation of Relative Rate Constants at Stratospheric Temperatures for Reactions of ^{38}Cl with CH_4 and C_2H_6 vs. $\text{CH}_2=\text{CHBr}$ ", *J. Phys. Chem.*, **1977**, *81*, 86-87.
3. Iyer, R.S.; Rowland, F.S. "A Long-Lived $\text{C}_2\text{H}_3\text{ClBr}^*$ Radical from the Reaction of Atomic Chlorine with Vinyl Bromide", *Chem. Phys. Lett.*, **1983**, *103*, 213-218.
4. Iyer, R.S.; Rogers, P.J.; Rowland, F.S. "Thermal Rate Constant for Addition of Chlorine Atoms to Ethylene", *J. Phys. Chem.*, **1983**, *87*, 3799-3801.
5. Lu, E.C.-C.; Iyer, R.S.; Rowland, F.S. "Reaction Rates for Thermal Chlorine Atoms with H_2S from 232 to 359K by a Radiochemical Technique", *J. Phys. Chem.*, **1986**, *90*, 1988-1990.
6. Demore, W.B.; Sander, S.P.; Golden, D.M.; Molina, M.J.; Hampson, R.F.; Kurylo, M.J.; Howard, C.J.; Ravishankara, A.R. "Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling", Evaluation 9, NASA Panel for Data Evaluation, *Publ. 90-1*, Jet Propulsion Laboratory, Pasadena, CA, **1990**.
7. Manning, R.G.; Kurylo, M.J. "Flash Photolysis Resonance Fluorescence Investigation of the Temperature Dependencies of the Reactions of $\text{Cl}(^2\text{P})$ Atoms with CH_4 , CH_3Cl , CH_3F , $\text{CH}_3\text{F}^\dagger$, and C_2H_6 ", *J. Phys. Chem.*, **1977**, *81*, 291-296.
8. Atkinson, R. private communication, unpublished rate constant (without a reported error) for $\text{CH}_3\text{F} + \text{Cl}^\cdot$ at 298K, **1991**.
9. Lu, E.C.-C. Thesis Dissertation, "Kinetics of Some Reactions of Atmospheric Interest: Hydrolysis of Carbonyl Sulfide and Reaction Rates of Thermal Chlorine Atoms with Carbonyl Sulfide, Methanol, Hydrogen Sulfide, and Methyl Chloride", **1987**.

III. CHLORINE ATOM REACTIONS WITH VINYL BROMIDE

The addition of thermal chlorine atoms to $\text{CH}_2=\text{CHBr}$ has been previously studied by us using radioactive ^{38}Cl atoms.¹ In those experiments carried out in the pressure range 50-4000 torr, CClF_3 was used as the bath gas and HI as the scavenger for collisionally stabilized radicals. $\text{CH}_2^{38}\text{ClCH}_2\text{Br}$ was observed as the chief product at high pressures with yields exceeding 75% at 4000 torr, while at low pressure, the major product was $\text{CH}_2=\text{CH}^{38}\text{Cl}$. The obvious precursor for $\text{CH}_2=\text{CH}^{38}\text{Cl}$ in these experiments is the vibrationally excited $\text{CH}_2\text{CHBr}^{38}\text{Cl}^*$ radicals. Collisional stabilization of these radicals, followed by reaction with HI, would be expected to form $\text{CH}_3\text{CHBr}^{38}\text{Cl}$. However, the yield of this product was always $<0.1\%$. The observed dependence of the yields of $\text{CH}_2^{38}\text{ClCH}_2\text{Br}$ and $\text{CH}_2=\text{CH}^{38}\text{Cl}$ on total pressure and $[\text{HI}]/[\text{CH}_2=\text{CHBr}]$ ratios in these experiments could be fitted with either one of two proposed mechanisms. In mechanism (A), ^{38}Cl atoms added predominantly to the CH_2 end of the olefin-forming $\text{CH}_2^{38}\text{ClCHBr}^*$ as in Reaction 1. Isomerization of these radicals to form $\text{CH}_2\text{CHBr}^{38}\text{Cl}^*$ by a 1,2-Cl atom shift



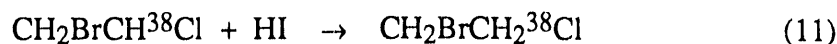
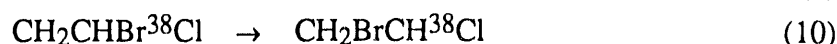
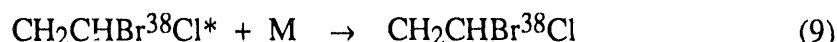
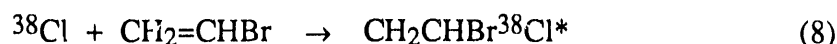
(Reaction 2), followed by the rapid loss of Br (Reaction 3) resulted in the formation of the product $\text{CH}_2=\text{CH}^{38}\text{Cl}$. This "anti-Markovnikov" addition of Cl followed by Reactions 2 and 3 has been previously proposed to explain the formation of $\text{CH}_2=\text{CHCl}$, observed as a product in molecular beam^{2,3} and infrared chemiluminescence⁴ studies. However, the product yield data observed in our ^{38}Cl experiments could not be explained by Reactions 1-3 alone, and we found it necessary to include the additional reaction steps, 4-6, in order to obtain quantitative fits to the yield data.



In these experiments, besides serving as a radical scavenger, HI functioned also as a competitor for thermal ^{38}Cl through Reaction 7. In mechanism (A), the loss of Br from $\text{CH}_2\text{CHBr}^{38}\text{Cl}^*$ (Reaction 3) is very rapid such that no collisional stabilization of these radicals occurred in the pressure range studied.



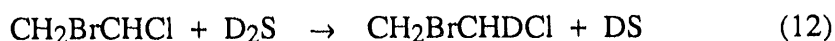
The alternative mechanism (B) involved the postulate that ^{38}Cl atoms reacted to form both $\text{CH}_2^{38}\text{ClCHBr}^*$ and $\text{CH}_2\text{CHBr}^{38}\text{Cl}^*$ in generally comparable initial yields. No 1,2-Cl atom shift occurs in this mechanism, and $\text{CH}_2\text{CHBr}^{38}\text{Cl}^*$ radicals formed in (8) either lose the bromine as in (3) or are collisionally stabilized as in (9). The stabilized radicals are postulated to undergo a 1,2-bromine atom shift (10) prior to reaction with HI (11).



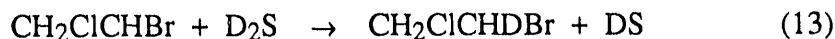
This 1,2-bromine shift satisfactorily explained the absence of $\text{CH}_3\text{CHBr}^{38}\text{Cl}$ as an observed product, while the measured $\text{CH}_2^{38}\text{ClCH}_2\text{Br}$ could be formed in this mechanism from reaction with HI of either $\text{CH}_2^{38}\text{ClCHBr}$ as in (6) or $\text{CH}_2\text{BrCH}^{38}\text{Cl}$ as in (11).

Of these two proposed mechanisms, the mechanism (B) involving ^{38}Cl addition to both the carbon atoms of $\text{CH}_2=\text{CHBr}$ was preferred by us because in the parallel experiments with $\text{CH}_2=\text{CHF}$, both $\text{CH}_2^{38}\text{ClCH}_2\text{F}$ and $\text{CH}_3\text{CH}^{38}\text{ClF}$ were observed with only a weak "anti-Markovnikov" preference of 2:1 favoring addition to the CH_2 end.⁵ Furthermore, the direction of the 1,2-bromine shift postulated in (B) is consistent with the observations reported earlier that such halogen shifts occur away from a multiple-halogen substituted carbon atom toward the CH_2 end of the radical.^{6,7}

The present experiments are being carried out with the goal of obtaining confirmation as to which of these two mechanisms is operative. The photolytic method for generating Cl atoms has been used in these experiments, and D_2S served as the radical scavenger. The products formed were separated by gas chromatography and analyzed by mass spectrometry. The critical postulate in mechanism (B) is the 1,2-bromine atom shift (10) to form CH_2BrCHCl radicals. With D_2S as the radical scavenger, these radicals would form $\text{CH}_2\text{BrCHDCl}$ as in (12).



The reaction with D_2S of CH_2ClCHBr radicals formed from (1) plus (5) would lead to $\text{CH}_2\text{ClCHDBr}$ as in (13) and would be distinguishable from the isomer formed in (12). If any



CH_2CHBrCl radicals react with D_2S prior to the 1,2-bromine atom shift, the product formed, $\text{CH}_2\text{DCHBrCl}$ is gas chromatographically separable from the isomers formed in (12) and (13). Therefore, if $\text{CH}_2\text{BrCHDCl}$ is present in the reaction products, there will be evidence for the existence of Reaction 10. In addition, the percent of the stabilization product with the structure $\text{CH}_2\text{BrCHDCl}$ will determine to what degree "anti-Markovnikov" addition is appropriate in describing the system.

Several well known chlorine atm sources include Cl_2 , *t*-butyl hypochlorite ($[\text{CH}_3]_3\text{COCl}$) and phosgene (COCl_2). Cl_2 photodissociates at ~ 500 nm to give two near-thermal Cl's. *t*-Butyl hypochlorite has a weak absorption at 334 nm and yields one near-thermal Cl. The third dissociates at 253.7 nm to give $\text{Cl} + \text{COCl}^*$. COCl^* then dissociates to provide overall 2Cl and one CO. All three of these were applied in the present study.

Initial work with Cl_2 showed this reagent could not be used. In the dark, reaction between Cl_2 and the vinyl bromide produced only $\text{CH}_2\text{ClCHClBr}$. The product was the result of a heterogeneous reaction seen by Knox.⁸ Vinyl chloride was not observed in the product spectrum. If atomic chlorine had been generated in the reaction system, then vinyl chloride should have been seen. It was concluded that, due to the fast rate for the heterogeneous reaction, all the Cl_2 had reacted before the system could be photo-irradiated. It was thought that Halocarbon wax or Teflon-coated cells could slow down this reaction, but these cells displayed the same problems as bare quartz.

The next set of reactions using *t*-butyl hypochlorite were more successful. Non-irradiated reaction mixtures displayed traces of $\text{CH}_2\text{ClCHClBr}$, thought to be the result of Cl_2 impurity in the *t*-butyl hypochlorite. The irradiated samples showed vinyl chloride so Cl was generated. However, this yield was very low due to the small cross section for *t*-butyl hypochlorite at 253.7 nm.

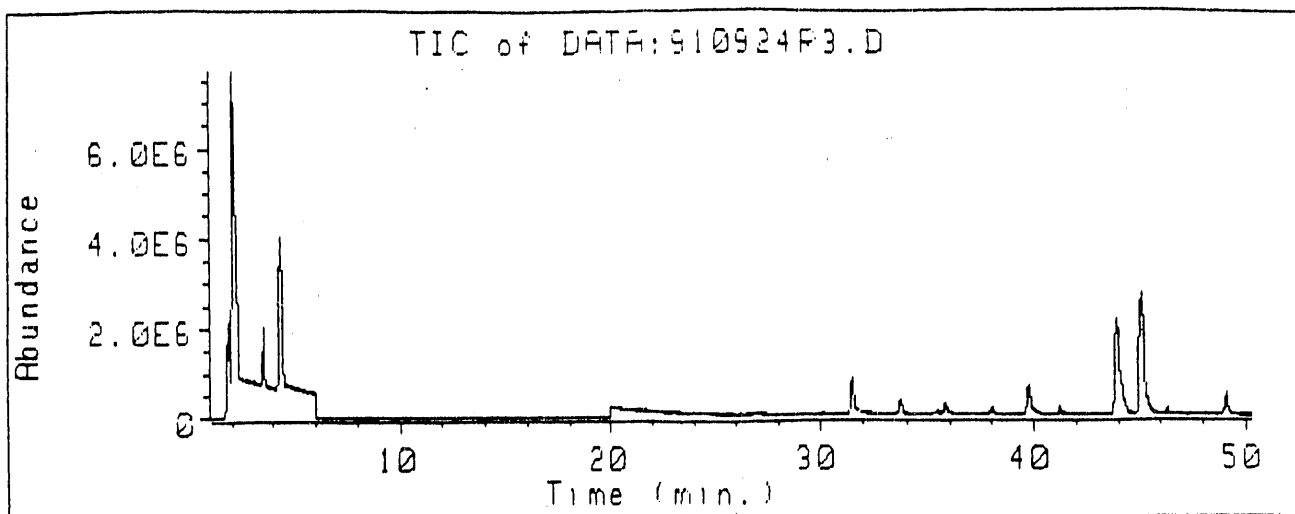
The next set of experiments used COCl_2 . This source did not have any of the problems associated with the first two. At 253.7 nm, the absorption cross section is large, $9.1 \times 10^{-4} \text{ torr}^{-1} \text{ cm}^{-1}$ (base 10), and the quantum yield of CO is unity.⁹ In addition, work by Hecklen has shown that this reagent only reacts by a free radical mechanism.¹⁰

The reactions were carried out with equal concentrations of D_2S , vinyl bromide and phosgene (~ 0.1 torr). These gases were measured into a vacuum line and then condensed in the reaction cell using liquid nitrogen. A balance of N_2 was then added between 105 and 450 torr.

The cells were removed from the liquid nitrogen and allowed to warm to room temperature. Correcting for temperature effects, the final pressures were between 406 and 1742 torr. The samples were irradiated for 5 minutes at 253.7 nm using a low pressure Hg lamp. The condensable products were then collected with liquid nitrogen and analyzed using gas chromatography followed by mass spectroscopy. A typical gas chromatogram is shown in Figure 1. The decomposition product, vinyl chloride, identified by its retention time and mass spectra, was quantified using $m/e = 62$. The two deuterated stabilization products, $\text{CH}_2\text{BrCHDCl}$ and $\text{CHDBrCH}_2\text{Cl}$, identified by mass spectra, co-eluted and were quantified together using $m/e = 64$. In addition, some fully protonated stabilization product, $\text{CH}_2\text{BrCH}_2\text{Cl}$, co-eluted. The D_2S used in these experiments had a specified isotopic purity of $> 97\%$. It appears that HDS is formed in the reaction vessel by isotopic exchange reactions of D_2S on the glass surface, and the observed $\text{CH}_2\text{BrCH}_2\text{Cl}$ is presumably formed by H abstraction from HDS by the bromochloroethyl radicals. $\text{CH}_2\text{BrCH}_2\text{Cl}$ was quantified using the fragment peak at $m/e = 63$. When the yield of decomposition divided by stabilizations plotted versus the reciprocal pressure (Figure 2), a linear fit is seen. This pressure effect is consistent with an addition-decomposition mechanism occurring in the system.

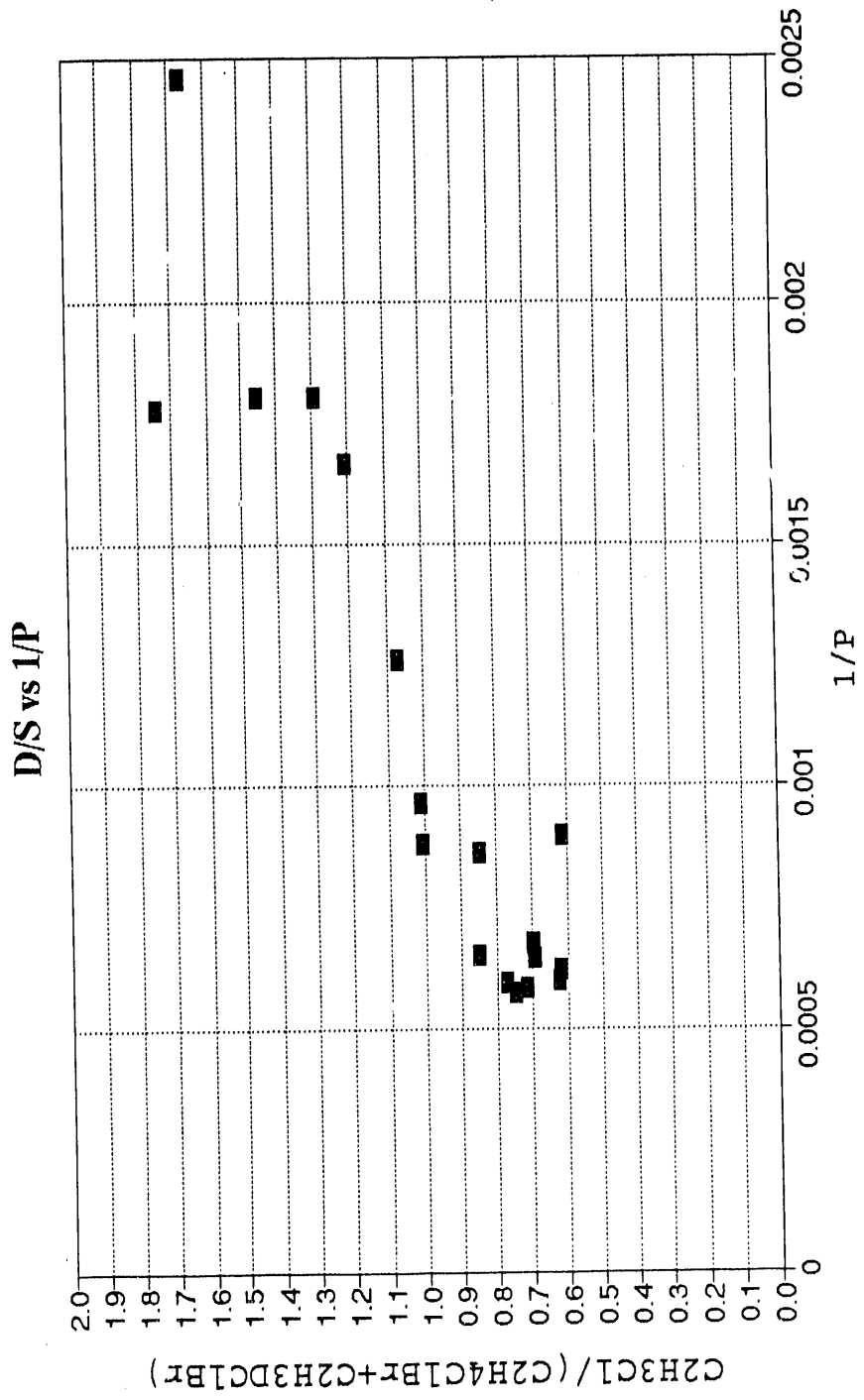
Due to the co-elusion of the three stabilization products, determination of the ratio of $[\text{CH}_2\text{BrCHDCl}]$ to $[\text{CH}_2\text{ClCHDBr}]$ required a great deal of data reduction. Treating the stabilization products as a single compound, the percent deuterium was determined on the CH_2Br end, then used to find the ratio. First, a standard was run of the fully protonated product, $\text{CH}_2\text{BrCH}_2\text{Cl}$, and each peak in the mass spectra was assigned. Then the mass spectra generated during the elution of the stabilization products were integrated. Using the assignment of peaks made with the protonated standard, the percent deuterium on the brominated side of the molecule was then determined by the change in relative peak intensities. The chlorinated side could not be used to confirm the results due to the interference of doubly charged ions. This number was then added to the percent of product that was fully protonated. The average value over the 19 runs made, 73%, represents the percent of the deuterated stabilization product with the deuterium on the brominated end. The percent of the product that was the result of bromine migration is then $100 - 73 = 27\%$.

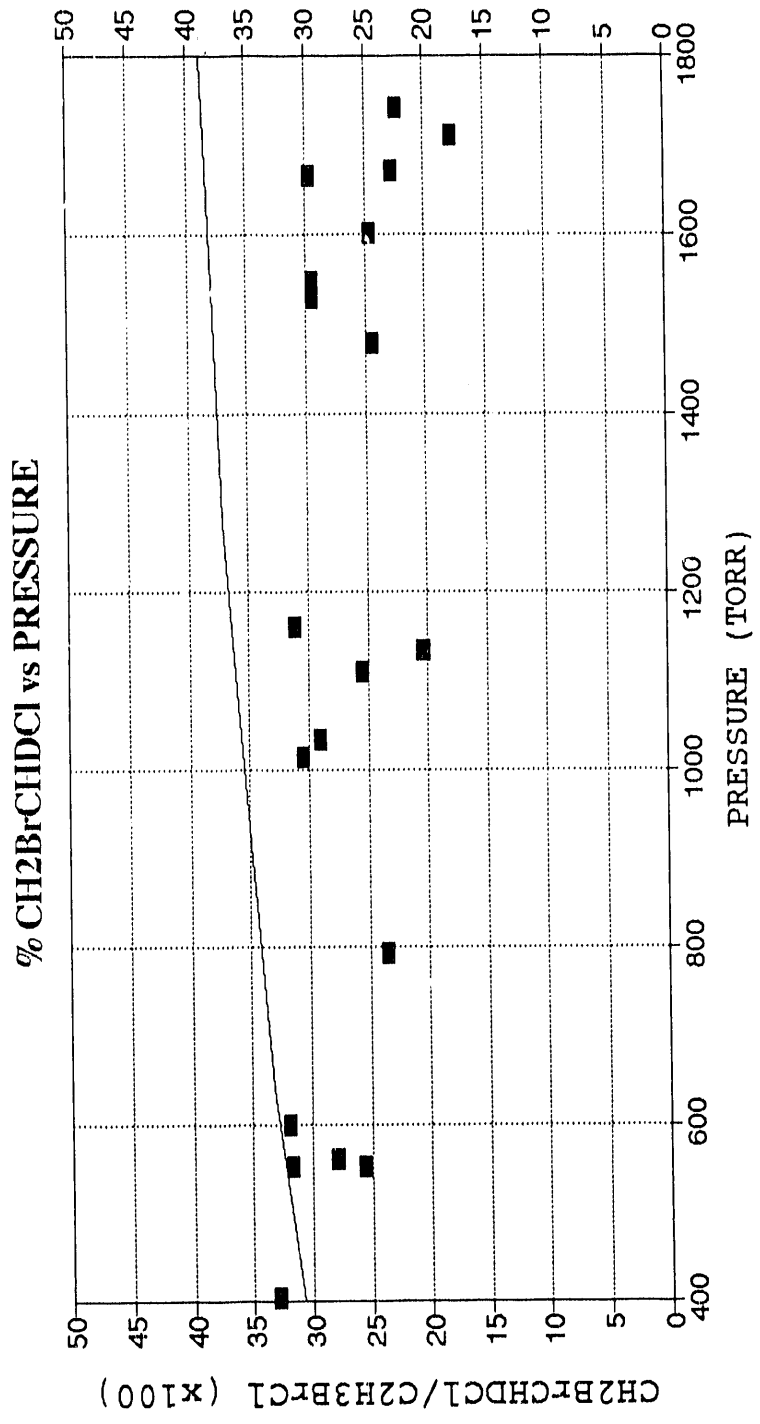
Using the rate constants derived in our previous studies, a computer model was developed to estimate the percent of stabilization product resulting from bromine migration in CH_2CHBrCl as a function of pressure. A plot of these results, along with our experimental data, are shown in Figure 3. Our data do not show the pressure dependence predicted by the model, and more model calculations are currently being carried out to examine this. However, our average value for the percent bromine migration agrees with the model within the error of the experiment. Most importantly, this result supports the existence of a 1,2-bromine migration in the radical intermediate postulated in mechanism B of our previous work.



<u>TIME(MIN)</u>	<u>COMPOUND</u>
1.86*	CO ₂
2.06*	D ₂ S, HDS
3.55	SO ₂
4.34*	CH ₂ CHCl
6.00 to 20.00*	COCl ₂ , CH ₂ CHBr (ion-multiplier off)
31.48	CH ₂ BrCl
33.71	C ₂ H ₂ BrCl
35.44	CH ₂ ClCHDCl, CH ₂ ClCH ₂ Cl
35.81	CH ₃ CHBrCl (and deuterated form)
38.04	C ₂ H ₂ Br ₂
39.76	C ₂ H ₂ BrCl
41.19	CH ₂ Br ₂
43.99*	CH ₂ BrCHDCl, CHDBrCH ₂ Cl, CH ₂ BrCH ₂ Cl
45.09	C ₂ H ₃ DBr ₂ , C ₂ H ₄ Br ₂
46.30	C ₂ H ₂ Cl ₂ O
49.21	C ₂ H ₂ Br ₂

*Confirmed with standards (all other assignments made by mass spectra alone)





■ EXPERIMENTAL — MODEL B CALCULATION

REFERENCES FOR SECTION III

1. Iyer, R.S.; Rowland, F.S. "A Long-Lived $C_2H_3ClBr^*$ Radical from the Reaction of Atomic Chlorine with Vinyl Bromide", *Chem. Phys. Lett.* **1983**, *103*, 213.
2. Cheung, J.T.; McDonald, J.D.; Herschbach, D.R. "Molecular Beam Chemistry. Unimolecular Decomposition of Chemically Activated Chlorobromoalkyl Radicals", *J. Am. Chem. Soc.* **1973**, *95*, 7889.
3. Buss, R.J.; Coggiola, M.J.; Lee, Y.T. "Molecular Beam Studies of Unimolecular Reactions $Cl, F + C_2H_3Br$ ", *Faraday Discussions Chem. Soc.* **1979**, *67*, 162.
4. Durana, J.F.; McDonald, J.D. "Infrared Chemiluminescence Studies of Chlorine Substitution Reactions with Brominated Unsaturated Hydrocarbons", *J. Chem. Phys.* **1976**, *64*, 2518.
5. Iyer, R.S.; Chen, C.-Y.; Rowland, F.S. "Gas-Phase Reactions of Atomic Chlorine with Vinyl Fluoride", *J. Phys. Chem.* **1985**, *89*, 2042.
6. Skell, P.S.; Parks, R.R.; Lewis, D.C.; Shea, K.J. "Bridged Bromine and Chlorine Free Radical Intermediates, Free-Radical Halogenations of 2-Halobutanes", *J. Amer. Chem. Soc.* **1973**, *95*, 6735.
7. Friedlina, R.Kh. Advances in Free Radical Chemistry, Vol. I, Ed. Williams, G.H., Academic Press, New York, **1965**, p. 211.
8. Knox, J.; Waugh, K.C. "Activated Chloroalkyl Radicals in the Chlorination of Trichloroethylene and other Olefins", *Trans. Faraday Soc.* **1969**, *65*, 1585.
9. Okabe, H. Photochemistry of Small Molecules, Wiley-Interscience, New York, **1978**, p. 289.
10. Heicklen, J. "The Photolysis of Phosgene-Ethylene Mixtures", *J. Amer. Chem. Soc.* **1965**, *87*, 445.

PROGRESS REPORT
DEPARTMENT OF ENERGY
RESEARCH CONTRACT DE-FG03-86ER13469

I. GAS PHASE OXIDATION STUDIES OF HYDROFLUOROCARBONS AND HYDROCHLOROFLUOROCARBONS BY FTIR

There is considerable interest in substitutes for CFC-11 and CFC-12 and their subsequent reactions in the earth's atmosphere. The proposed substitutes for the CFCs are hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). In the troposphere, these molecules are expected to react with OH radicals resulting in the formation of haloalkyl radicals. Very little information is available at the present time on the subsequent reactions of such haloalkyl radicals under atmospheric conditions. We have initiated a series of photochemical experiments with product identification and measurement by FTIR for understanding the oxidation mechanism of these haloalkyl radicals.

Our initial experiments have involved HFC-134a (CF₃CH₂F), which has been proposed as a possible substitute for CFC-12, used for air-conditioning and refrigeration.¹ The U.V. absorption cross section data² indicate that solar photolysis cannot be a tropospheric removal process for CF₃CH₂F. Hence, oxidation initiated by OH radicals is the expected tropospheric removal process for CF₃CH₂F. The production of CF₃CHF radicals from this compound can be accomplished by reaction with either OH (Equation 1) or with Cl (Equation 2).



Because of the greater ease of production of Cl atoms as compared to OH radicals, our initial experiments have involved the use of reaction 2 to produce CF₃CHF radicals and examination of their subsequent oxidation in the presence of O₂. The photodissociation of Cl₂ at 340 nm was used to generate Cl atoms. Small amounts (2 to 4 torr) of HFC-134a and Cl₂ are mixed with 80 to 100 torr of O₂ in an FTIR cell (with potassium bromide windows) also equipped with windows (Suprasil) enabling ultraviolet (UV) radiation to pass through the cell. The cell and its contents are then subjected to UV radiation (using an Oriel 1000 watt Xe-Hg arc lamp and a Bausch & Lomb Monochromator) at a wavelength of 340 nanometers for incremental time intervals. After each exposure to radiation, the cell is carried to a Perkin-Elmer Model 1600 FTIR and analyzed by FTIR. The percent transmission of infrared radiation by the products is determined by subtracting the spectrum of the non-irradiated sample from the spectrum of the irradiated sample. The percent transmissions are converted to torr by use of calibration curves. Figures 1-3 show sample spectra of the parent compound (HFC-134a) and two of the products (CF₂(O) and CF₃CF(O)). Figure 4 shows the difference spectrum obtained following a 60-minute irradiation of a mixture of HFC-134a (3.98 torr), Cl₂ (2.06 torr), and O₂ (81.72 torr).

Wavelengths used in Calibration Curves

<u>Compound</u>	<u>Wavelength (cm⁻¹)</u>
HFC-134a	666.7
CF ₂ (O)	691.6
CF ₃ CF(O)	773.9

NOTE: These wavelengths were chosen because of minimum absorption by the other components in the cell at these wavelengths.

END

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