DOE/ER/13469--79

# Annual Report, 1993

# Grant No. DE-FG03-86ER-13469

# "Research in Chemical Kinetics"

# Principal Investigator, F. S. Rowland

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# PROGRESS REPORT


## DEPARTMENT OF ENERGY
### (DE-FG03-86ER-13469)


# RESEARCH IN CHEMICAL KINETICS


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**Progress Report on work carried out during the contract period from**

**May 1, 1990 to December 31, 1992**


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# RESEARCH IN CHEMICAL KINETICS

## PROGRESS REPORT

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I.  Chlorine Atom Reactions with Vinyl Bromide. Mass Spectrometric Investigations of the anti-Markownikoff Rule.

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## RESEARCH PROPOSAL
### Introduction

I.  Chlorine Atom Reactions With Organometallic Compounds Having Substituents Without Multiple Bond

II.  Chlorine Atom Reactions With Multiply-Bonded Substituents

III.  Competitor Molecules For Rate Constant Determinations

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complex molecule. Our earlier experiments with systems such as the addition of thermal atomic fluorine (using radioactive ^{18}F) to tetrallyl tin had the characteristic that the available pressure ranges for the experiments did not allow extensive decomposition of the resulting radicals. In this instance, possibility always lurked that the observed rapid decompositions (implying non-RRKM behavior because the energy from F addition was confined to only one part of the molecule) were special cases, unrepresentative of the other 90-95% of the additions. Experiments with radioactive 38Cl atoms and substrate molecules have avoided this problem because the rapid decompositions observed here affect essentially all of the molecules involved.

When atomic Cl adds terminally to a tetravinyl metal, the only energetically available process is the reversible loss of Cl. In contrast, when the Cl adds to the second C atom, the breakage of the C-metal bond is usually energetically favorable, and the radical ruptures leaving $CH_2=CHCl$ as a product. The reversible loss of Cl from the terminal position has the substantial advantage that the energetics of the reaction are well-known for the decomposition, i.e. energetically neutral.

Our study of the reactions of thermalized [38]Cl atoms over the past decade has established a very useful technique for measuring the relative rate constants for abstraction of hydrogen atoms from different molecules. Because the quantitative detection of $H^{38}Cl$ in our system is not readily performed, the technique relies on the diminution by competition with RH of the easily-measured yield of some known high yield organic compound labeled with [38]Cl, e.g. $CH2=CH^{38}Cl$ from the reaction of thermal [38]Cl with $CH_2=CHBr$. These relative rates of reaction can then be placed on an absolute scale by measurement of the relative abstraction rate for a compound whose absolute rate constant has been well established by other techniques. This standard competitor is often $C_2H_6$, whose reaction rate constant has been measured by several techniques to be very rapid 5.7 x $10^{-11}$ $cm^3 molecule^{-1}s^{-1}$, with essentially no temperature dependence. This comparison vs. $C_2H_6$ in diminution of $CH_2=CH^{38}Cl$ from $CH_2=CHBr$ has been our standard technique for measuring rate constnats for reactions with olefinic and acetylenic molecules which also react with collision efficiencies exceeding 0.01. This technique has also been applied to measurements of substitution reactions with metallo-organic compounds, e.g. $^{38}Cl + (CH_3)_4M \rightarrow CH_3^{38}Cl + (CH_3)_3M$. In these systems, the major reaction is usually H-atom abstraction, but the attack on the C-M bond to form $CH_3^{38}Cl$ can frequently be observed in low yield. the absolute reaction rate for $^{38}Cl +$ $(CH_3)_4M$ can be measured by the usual competitive techniques, while the rate constant for the substitution reaction is calculated from the fractional yield in the absence of intermolecular competition.

The $C_2H_6/CH_2=CHBr$ competitive system begins to fail when the molecule RH has a rate constant ,0.01 times those of $C_2H_6$ and $CH_2=CHBr$. Under these circumstances, little diminution in $CH_2=CH^{38}Cl$ yield is observed even for amounts of RH large enough to make thermolization of

$^{38}$Cl before reaction problematic. Under these circumstances, standard competitors with slower reaction rates have been sought, and a series of experiments have been run with $CF_2=CFBr$ from which $CF_2=CF^{38}Cl$ is observed. This system has been applied to measurements of the abstraction rate constants for a series of not very reactive molecules, most of them from the class of hydrohalocarbon molecules proposed as technological substitutes for the chlorofluorocarbons banned under the terms of the UNEP Montreal Protocol.

The intensive effort to increase the sensitivity for detection of trace gases in the atmosphere has brought more and more molecules into the range of feasibility for study of their sources and sinks. Often, even the question of whether their formation processes are natural or induced by the activities of mankind is not even qualitatively answered. the general division between biological and non-biological processes, often corresponding to natural vs. anthropogenic, can be investigated through the $^{14}C$ content of the atmospheric traces. In general, all biological activity is closely intertwined with photosynthesis, either in a primary or secondary manner, and this process creates a $^{14}C/^{12}C$ ratio in living things at about the level characteristic of the atmosphere. On the other hand, carbonaceous materials based on fossil fuels have lost their original $^{14}C$ content after about 50,000 years.

The measurement of $^{14}C$ content of trace gases has been successfully carried out for $CO_2$ and $CH_4$, and is now being extended by us to $C_2H_6$, $C_2H_8$ and OCS. The major experimental problem here is simply logistical -- the need to process large amounts of air to obtain the 200 $\mu$grams needed for analysis by accelerator mass spectrometry.

# I. CHLORINE ATOM REACTIONS WITH VINYL BROMIDE. MASS SPECTROMETRIC INVESTIGATIONS OF THE ANTI-MARKOWNIKOFF RULE.

Previous work carried out by us on the addition of thermal $^{38}Cl$ (from reactor neutron irradiation of $^{37}Cl$ in the molecule $CClF_3$ or $CCl_2F_2$) to $CH_2=CHF$ showed that the preference for the addition to the $CH_2$ vs CHF end of the molecule is only a factor of two.[1] This observation was in sharp contrast to the "anti-Markownikoff" rule often used to explain such additions, according to which the addition is qualitively expected to occur at the less-substituted end, i.e. to $CH_2$. We proposed from studies of thermal $^{38}Cl$ atoms added to $CH_2=CHCl$ and $CH_2=CHBr$ that in these cases also, the reaction mechanism possibly involves the addition to both the carbon atoms of the molecule at roughly similar rates, even though the stabilized product seldom from the former and never from the latter, shows $^{38}Cl$ attached the same carbon atom as the initial halogen.[2,3] In those experiments with HI present as a radical scavenger, the pressure-dependent yields for the two observed products, $CH_2=CH^{38}Cl$ and $CH_2^{38}ClCH_2X$ (X=Cl or Br) could be fitted with a kinetic model shown as mechanism B in Table 1 for the reaction with $CH_2=CHBr$. The critical postulate in this mechanism was the 1,2-halogen migration in the $CH_2CHX^{38}Cl$ (reaction 10 for X=Br) prior to reaction with HI as in (11), which explained the absence of $CH_3CHX^{38}Cl$ as an end product. With the use of HI as the radical scavenger, both the $CH_2^{38}ClCHX$ radicals formed from reactions (1) plus (5) as well as the $CH_2XCH^{38}Cl$ radicals formed the 1,2-halogen migration in $CH_2CHX^{38}Cl$ would result in the formation of the identical product, $CH_2^{38}ClCH_2X$. Thus a direct identification and measure of the postulated 1,2-halogen migration was not obtained from the $^{38}Cl$ experiments. Further, the product yield data obtained versus total pressure could be fitted also with an "anti-Markownikoff" addition mechanism followed by a 1,2-chlorine migration in the excited $CH_2^{38}ClCHX^*$ radical. The reaction steps involved in this mechanism are listed under mechanism A in Table 1. Thus, the data from the $^{38}Cl$ experiments did not identify a unique reaction mechanism, although we proposed mechanism B as the preferred one.

In order to determine which of these two mechanisms is operative, we have carried out further experiments on the addition of Cl atoms to $CH_2=CHBr$ using non-radioactive, photochemically produced Cl atoms. While labeling of one of the carbon atoms (e.g. $^{13}CHBr$, CDBr, or CFBr) in principal could allow the two products to be distinguished from one another (i.e. $CH_2^{38}ClCHFBr$ vs. $CH_2BrCHF^{38}Cl$), this distinction has not been detectable for $^{38}Cl$ yields of $10^8$ molecules surviving for an average of one hour before destruction by radioactive decay of $^{38}Cl$. We have instead introduced isotopic labeling through the use of $D_2S$ as a scavenger molecule. The products

formed were separated by gas chromatography and analyzed by mass spectrometry. In mechanism B involving the 1,2-bromine migration (reaction 10), the $CH_2BrCHCl$ radical formed would be scavenged by $D_2S$ to produce $CH_2BrCHDCl$, while the $CH_2ClCHBr$ radical from reaction (1) plus (5) will produce $CH_2ClCHDBr$. The formation of $CH_2BrCHDCl$ as a product would therefore confirm mechanism B. The ionization fragments after C-C bond break, i.e. CH2Br, CH2Cl and the deuterated counterparts, record the distinction between these two molecules.

The chlorine atoms for this study were generated by the 254nm photolysis of $COCl_2$. $N_2$ was used as the bath gas for collisional stabilization of the vibrationally excited radicals formed. The components of the reaction mixture, $COCl_2$, $CH_2=CHBr$, $D_2S$ and $N_2$, were added to a 111ml quartz photolysis cell using standard vacuum line techniques. The mixture was irradiated for 5 minutes with 254 nm radiation from a low pressure mercury lamp (Ultraviolet Products, Inc., Mineralight model R-52). Following the irradiation, the contents of the photolysis cell were passed through a trap maintained at 77K and $N_2$ was pumped out. The fraction collected in the trap was then separated into components by standard temperature programmed gas chromatography using a capillary column (J & W Scientific DB-624, 30 meters long with 1.8m film thickness).
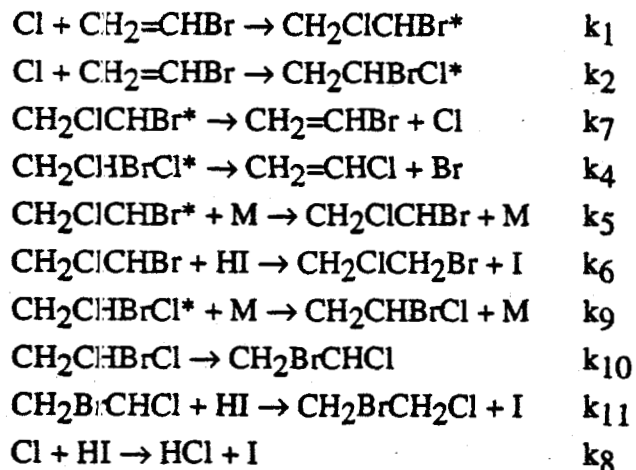
TABLE 1. Proposed Mechanisms for Cl addition to $CH_2=CHBr$ in the Presence of HI.

## MECHANISM A

$$Cl + CH_2=CHBr \rightarrow CH_2ClCHBr^* \qquad k_1$$
$$Cl + CH_2=CHBr \rightarrow CH_2CHBrCl^* \qquad k_2$$
$$CH_2ClCHBr^* \rightarrow CH_2CHBrCl^* \qquad k_3$$
$$CH_2CHBrCl^* \rightarrow CH_2=CHCl + Br \qquad k_4$$
$$CH_2ClCHBr^* + M \rightarrow CH_2ClCHBr + M \qquad k_5$$
$$CH_2ClCHBr + HI \rightarrow CH_2ClCH_2Br + I \qquad k_6$$
$$CH_2ClCHBr^* \rightarrow CH_2=CHBr + Cl \qquad k_7$$
$$Cl + HI \rightarrow HCl + I \qquad k_8$$
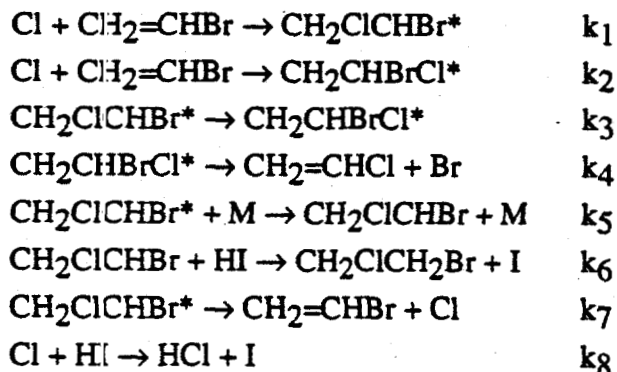
$k_8/(k_1+k_2)=0.68$, $k_2=0.1k_1$, $k_3/k_7=0.67$, $k_7=k_5[M]$ at 900 torr (From ref. 3)

## MECHANISM B

$$Cl + CH_2=CHBr \rightarrow CH_2ClCHBr^* \qquad k_1$$
$$Cl + CH_2=CHBr \rightarrow CH_2CHBrCl^* \qquad k_2$$
$$CH_2ClCHBr^* \rightarrow CH_2=CHBr + Cl \qquad k_7$$
$$CH_2CHBrCl^* \rightarrow CH_2=CHCl + Br \qquad k_4$$
$$CH_2ClCHBr^* + M \rightarrow CH_2ClCHBr + M \qquad k_5$$
$$CH_2ClCHBr + HI \rightarrow CH_2ClCH_2Br + I \qquad k_6$$
$$CH_2CHBrCl^* + M \rightarrow CH_2CHBrCl + M \qquad k_9$$
$$CH_2CHBrCl \rightarrow CH_2BrCHCl \qquad k_{10}$$
$$CH_2BrCHCl + HI \rightarrow CH_2BrCH_2Cl + I \qquad k_{11}$$
$$Cl + HI \rightarrow HCl + I \qquad k_8$$

$k_8/(k_1+k_2)=0.62$, $k_2=0.96k_1$, $k_7=k_5[M]$ at 650 torr, $k_4=k_9[M]$ at 1850 torr (From ref. 3)

$k_8/(k_1+k_2)=0.56$, $k_2=0.71k_1$, $k_7=k_5[M]$ at 1390 torr, $k_4=k_9[M]$ at 2420 torr (From this work)

The mass spectrometer used for data collection was a standard HP 5970 MSD. It was set to acquire in the scan mode over three time intervals. The first from 0 to 6 minutes ran from m/e=33 to m/e=190. After this the unreacted $COCl_2$ and $CH_2=CHBr$ eluted, so to protect the detector from the high signal the acquisition was shifted up to m/e=250-800. At 20 minutes the scan was returned to m/e=33-190. After 50 minutes the detector was shut down and the system reset for the next run.

A typical chromatogram using $D_2S$ as the radical scavenger is shown in Figure 1. $CH_2=CHCl$, was seen at 4.34 minutes. Its identity was confirmed by retention time as well as mass spectroscopic analysis. Figure 2 shows the spectra of a standard with that of the reaction product. The stabilization products were seen in a group at 44.0 minutes. This was a co-elution of two kinds of 1,2-Br,Cl-ethane: $CH_2ClCHDBr$ from reaction (6') and $CH_2BrCHDCl$ from reaction (11'). In addition, this group included $CH_2ClCH_2Br$. The $D_2S$ used in this experiment

$$CH_2ClCHBr + D_2S \rightarrow CH_2ClCHDBr \qquad (6')$$
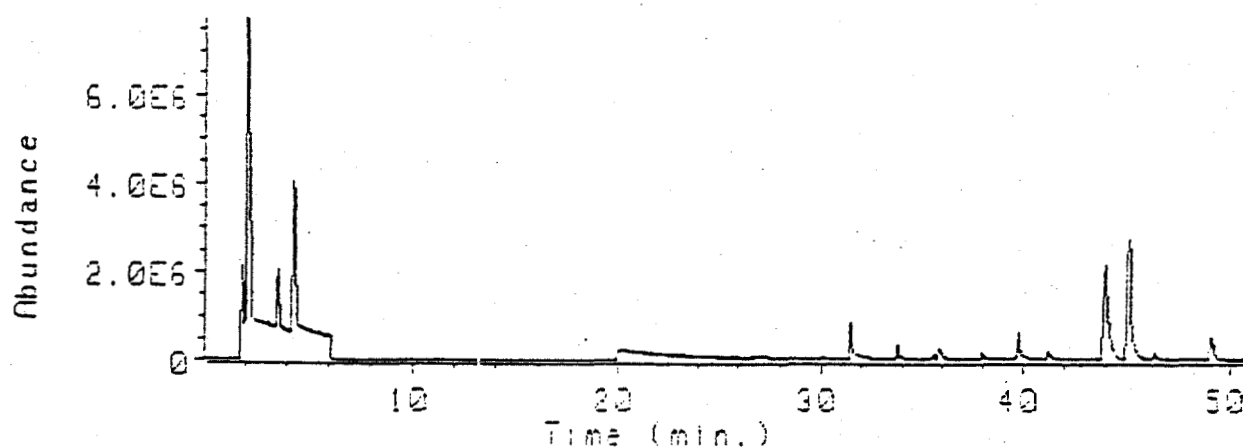$$CH_2BrCHCl + D_2S \rightarrow CH_2BrCHDCl \qquad (11')$$
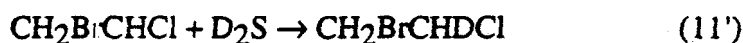
had a specified isotopic purity of >97%, however, it appears that HDS was being formed in the reaction vessel and vacuum line by an isotopic exchange reaction of $D_2S$ on the glass surfaces. The observed $CH_2ClCH_2Br$ presumably resulted from reaction of the bromochloroethyl radicals with HDS. The group peak was confirmed to have the same retention time as the $CH_2ClCH_2Br$ standard, and the mass spectra were consistent with a mixture of the three products.

Figure 3 shows the mass spectra averaged over the elution of the three stabilization products, included is the spectra of a non-deuterated standard. A preliminary analysis of these spectra confirms the presence of the three stabilization products. The region m/e=142-147 shows a change in response that demonstrating the presence of both deuterated and non-deuterated products. Peaks at 142, 144 and 146 are primarily the non-deuterated parent molecule with isotope pattern of $[^{35}Cl^{79}Br]$, $[^{37}Cl^{79}Br + {}^{35}Cl^{81}Br]$ and $[^{37}Cl^{81}Br]$. The peaks at 143, 145 and 147 show the same pattern, but for the deuterated parent molecule. The region m/e=49-52 shows both $CH_2Cl$ and $CHDCl$ fragments in the product. Roughly examined, 49 and 51 are composed of $CH_2{}^{35}Cl$ and $CH_2{}^{37}Cl$, with 50 and 52 being $CHD^{35}Cl$ and $CHD^{37}Cl$. Some deuteration on the $CH_2Br$ fragment can be seen from 93 to 96. As with the chlorinated side of the molecule; $CH_2{}^{79}Br$ and $CH_2{}^{81}Br$ are at 93 and 95, and $CHD^{79}Br$ and $CHD^{81}Br$ are at 94 and 96. The presence of the deuterated product $CH_2BrCHDCl$ shows the 1,2-bromine migration in reaction (10) is important in describing the mechanism. Because the presence on the same carbon atom of Cl and D is not explained by mechanism A, this result lends strong qualitative support to mechanism B, i.e. weak, not strong, anti-Markownikoff preference by Cl for the CH2 end.

Determining the amount of chlorine produced in this system was not possible. $COCl_2$ dissociates to produce two atomic chlorines and one molecule of CO. The CO can usually be

Figure 1. Typical Chromatographic Run.



| TIME(MIN) | COMPOUND |
|---|---|
| 1.86* | $CO_2$ |
| 2.06* | $D_2S$, HDS |
| 3.55 | $SO_2$ |
| 4.34* | $CH_2CHCl$ |
| 6.00 to 20.00* | $COCl_2$, $CH_2CHBr$ (ion-multiplier off) |
| 31.48 | $CH_2BrCl$ |
| 33.71 | $C_2H_2BrCl$ |
| 35.44 | $CH_2ClCHDCl$, $CH_2ClCH_2Cl$ |
| 35.81 | $CH_3CHBrCl$ (and deuterated form) |
| 38.04 | $C_2H_2Br_2$ |
| 39.76 | $C_2H_2BrCl$ |
| 41.19 | $CH_2Br_2$ |
| 43.99* | $CH_2BrCHDCl$, $CHDBrCH_2Cl$, $CH_2BrCH_2Cl$ |
| 45.09 | $C_2H_3DBr_2$, $C_2H_4Br_2$ |
| 46.30 | $C_2H_2Cl_2O$ |
| 49.21 | $C_2H_2Br_2$ |

*Confirmed with standards (all other assignments made by mass spectra alone)
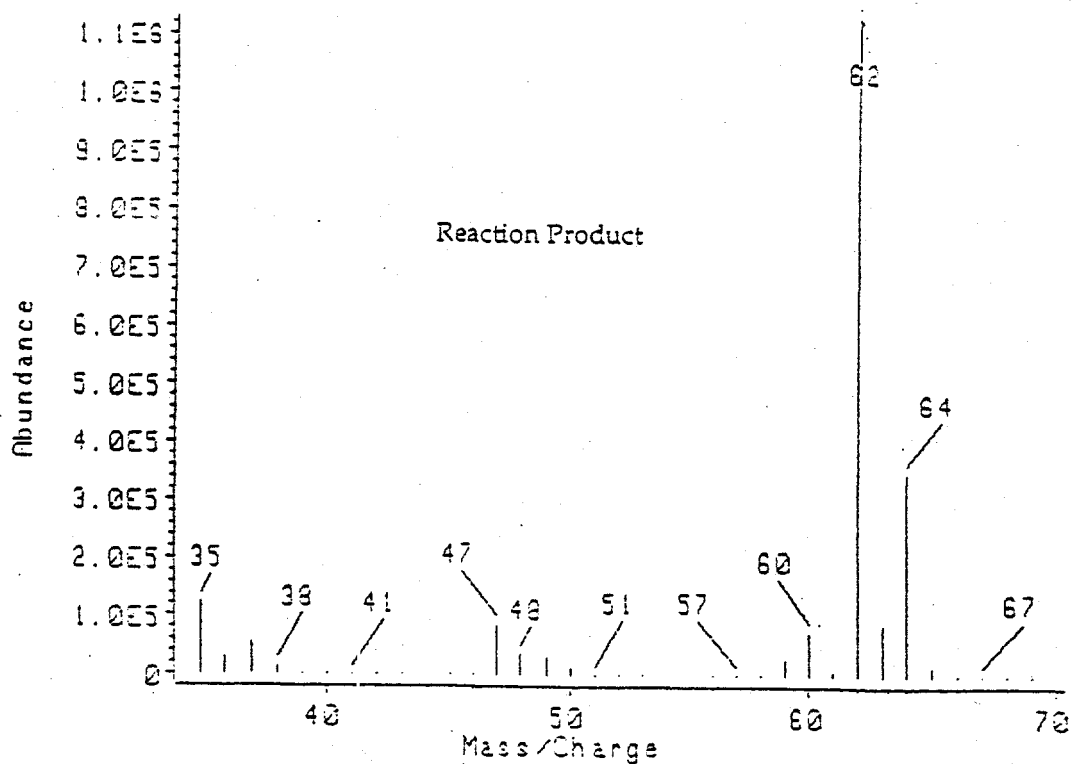
Figure 2. CH2=CHCl, Reaction Product and Standard.

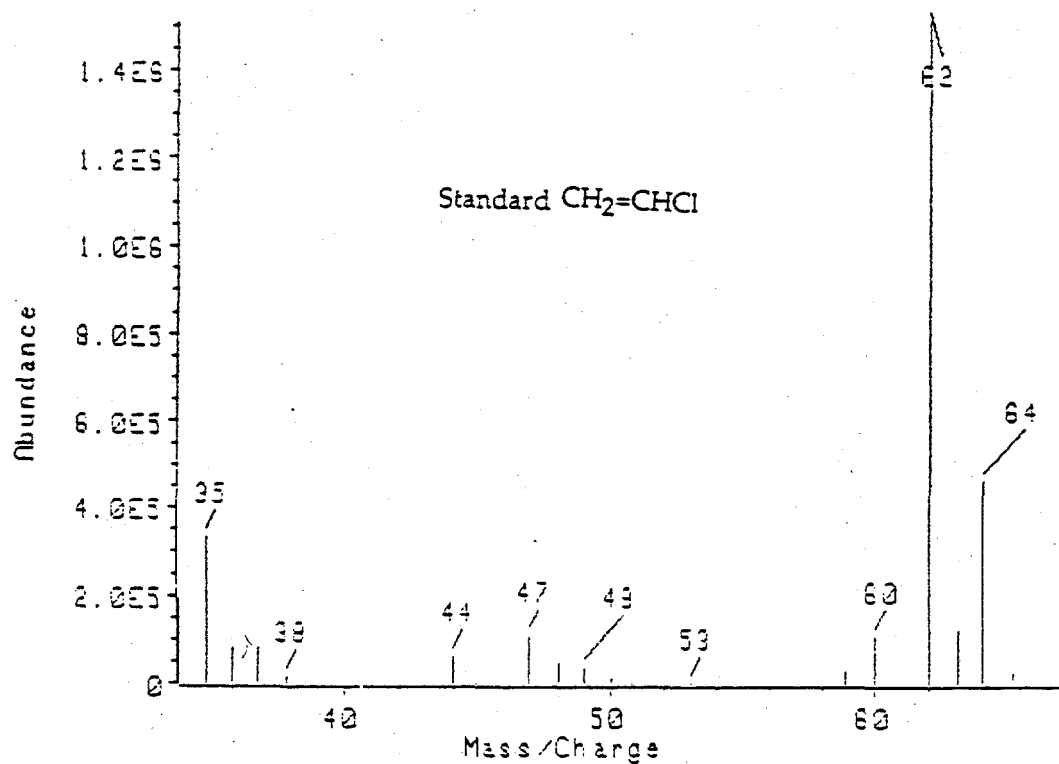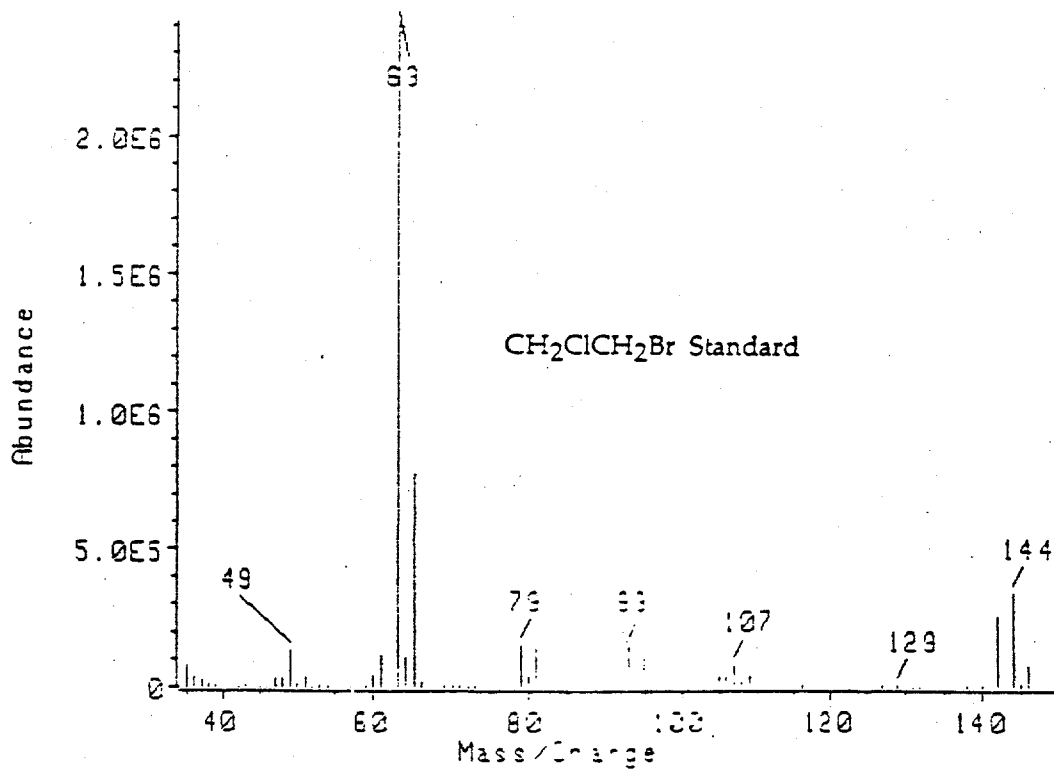Figure 3. Average Mass Spectra of Stabilization Products with non-
Deuterated Standard.



Stabilization Products

CH2ClCH2Br Standard
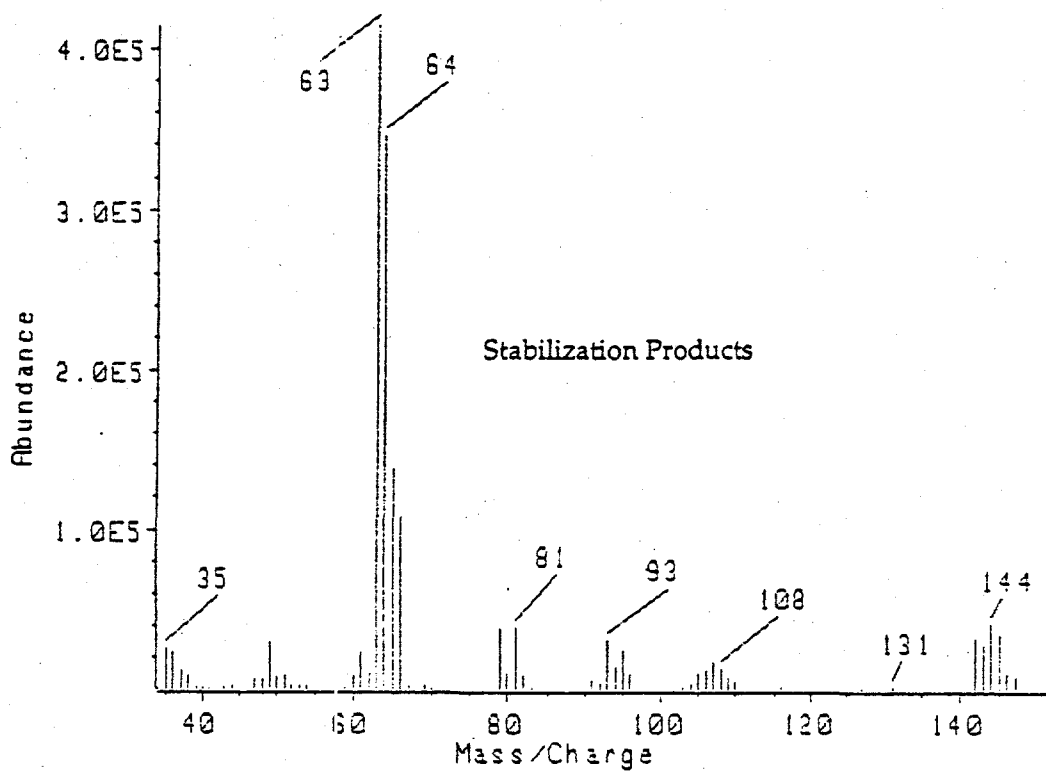
quantified to determine the overall chlorine yield. This value is then used to carry out a material balance. However, in this system, $N_2$ was used as a bath gas. Both $N_2$ and CO have the same molecular weight and could not be separated using the gas chromatographic techniques employed in this work, so the attempt at a material balance was abandoned.

In the absence of this material balance and therefore quantitative yield data, a plot was constructed with the relative yields of the decomposition product, $Y_D$, divided by that of the three stabilization product, $Y_S$, versus the reciprocal pressure. According to the reactions in mechanism B the ratio $Y_D/Y_S$ can be expressed by the following equation;

$$\frac{Y_D}{Y_S} = \frac{1}{[M]} \frac{k_4[CH_2CHBrCl^*]}{(k_7[CH_2CHBrCl^*] + k_5[CH_2ClCHBr^*])}$$

Table 2. Sample Data.

| Sample | Pressure (torr) $D_2S$ | $CH_2=CHBr$ | $N_2$ | $Y_D/Y_S$ |
|---|---|---|---|---|
| 1 | 0.91 | 0.91 | 533 | 1.90 |
| 2 | 0.91 | 0.91 | 561 | 2.56 |
| 3 | 0.91 | 0.91 | 599 | 1.77 |
| 4 | 0.91 | 0.91 | 793 | 1.57 |
| 5 | 0.91 | 0.91 | 1033 | 1.49 |
| 6 | 0.91 | 0.91 | 1133 | 1.47 |
| 7 | 0.91 | 0.91 | 1161 | 1.25 |
| 8 | 0.91 | 0.91 | 1528 | 1.24 |
| 9 | 0.91 | 0.91 | 1548 | 1.02 |
| 10 | 0.91 | 0.91 | 1602 | 0.913 |
| 11 | 0.91 | 0.91 | 1664 | 0.929 |
| 12 | 0.91 | 0.91 | 1671 | 1.13 |
| 13 | 0.91 | 0.91 | 1710 | 1.05 |
| 14 | 0.91 | 0.91 | 1741 | 1.10 |
| Sample | $D_2S$ | $CH_2=CHBr$ | $N_2$ | $Y_D/Y_S$ |
| 1 | 0.45 | 0.45 | 588 | 2.45 |
| 2 | 0.45 | 0.45 | 1702 | 1.31 |
| 3 | 0.45 | 0.45 | 781 | 2.04 |
| 4 | 0.45 | 0.45 | 1339 | 1.71 |
| 5 | 0.45 | 0.45 | 1327 | 1.86 |
| 6 | 0.45 | 0.45 | 1346 | 1.76 |
| 7 | 0.45 | 0.45 | 1180 | 1.77 |
| 8 | 1.8 | 1.8 | 1153 | 1.39 |
| 9 | 0.15 | 0.15 | 1146 | 2.52 |

Here [M] is the concentration of the bath gas, pressure. A plot of $Y_D/Y_S$ versus 1/pressure should therefore be linear with an intercept of zero.

The strongest peak in the mass spectra of $CH_2=CHCl$ was at m/e=62. Therefore, this fragment was used to observe the change in relative yield with pressure. For the deuterated stabilization products, mass 64 was the strongest, so it was used. The fully protonated stabilization product was observed using the strong peak at 63. All three stabilization products were assumed to fragment in the same way, so that the total yield of the stabilization products was the sum of 63 and 64. Using standards of $CH_2=CHCl$ and $CH_2ClCH_2Br$, a relative response factor was calculated. The initial pressures of reactants, $Y_D/Y_S$ values and reciprocal pressures are listed in Table 2. Figure 4 shows the plot described above for the $D_2S$ runs. The slope for the data obtained from the experiments of Iyer and Rowland with $CClF_3$ as the bath gas was 795 (23); this work with $N_2$ as the bath gas gave a value of 894 (114). The 13% difference is within the error of this analysis.

The intercept for the data from this work was 0.52 (.12), not the expected value of zero. This is the result of the low scavenging efficiency of $D_2S$. In work with $CF_2=CFBr$, described in section II of this report, the stabilized $CF_2ClCFBr$ radical reacted very slowly with $H_2S$ and a fraction of the radicals was lost through reactions with the wall. Therefore, runs were made with $H_2S$ in order to test for this wall effect. $H_2S$ was chosen over $D_2S$ to simplify the data analysis. The results obtained from these experiments are plotted in Figure 5. The line was plotted with samples prepared with the pressure of $H_2S$ equal to $CH_2=CHBr$ at 0.45 torr, and 0.91 torr of $COCl_2$. The duplicate samples at a reciprocal pressure of $7.3 \times 10^{-4}$ torr$^{-1}$ showed good reproducibility. The slope for this line was 812 (162), in good agreement with the $D_2S$ work; but the intercept, 1.07 (.17) was significantly higher. Since the $D_2S$ run were made with 0.91 torr each of $D_2S$ and $CH_2=CHBr$ instead of the 0.45 used here, this would support wall reactions, with a greater fractional loss to the wall in the $H_2S$ experiments.

To specifically test for wall reactions, three samples were then run at a reciprocal pressure of $8.6 \times 10^{-4}$, varying amounts of $H_2S$ and $CH_2=CHBr$, while keeping their ratio at one. This changed the wall to reagent ratio, while leaving the internal competition fixed. With pressures of $H_2S$ and $CH_2=CHBr$ equal to 1.8 torr the $Y_D/Y_S$ ratio dropped resulting from more efficient scavenging competition with the wall. When the pressures were dropped to 0.15 torr the ratio increased as a greater fraction of the stabilized radical was lost to the wall. The data obtained in this work have been analyzed with the assumption that the same fractional loss to the wall occurs for both $CH_2ClCHBr$ and $CH_2BrCHCl$ radicals.

Because the three stabilization products had very similar retention times, their elutions overlapped and in the ion chromatogram shown in Figure 1 they appear as one large peak. Therefore, determination of their individual yields required a detailed examination of the mass

spectra over this time period. The deuterated products eluted first. Half-way through the peak the deuterated products could no longer be detected and only the fully protonated product was still eluting. This was fortunate, because initial study of the peak showed a small amount of 1,2-dibromoethene at the end of the stabilization elution time. To remove this overlapping product from the analysis only the first half of the peak was used.

A standard of $CH_2ClCH_2Br$ was run, and an average mass spectra was generated by integrating the mass fragments over the scans made during the first half of the peak. The same was done for the second half of the peak. A comparison of the two showed no significant difference, as can be seen in Table 3. Using the first spectra, each m/e peak of the spectra was broken down to determine the ion fragments contributing to it and their individual contribution. This assignment was successfully carried out for all areas of the spectra except that between 46 to 57. Doubly charged ions were found in this region at the half integral points of 46.5 and 47.5. Doubly charged ion fragments at the integral values were very likely the cause of difficulty in making ion assignments in this small range.

The assignments made in the range 91 to 95 were used to determine the ratio of $CHDBrCH_2Cl$, $CH_2BrCHDCl$ and $CH_2BrCH_2Cl$. In the calculation, the fragment at m/e=91 contains only the fragment $C^{79}Br$. Because it contains no hydrogens, its intensity should not change as deuterium is added to the molecule. The change in intensity of the other peaks in the range of 92 to 96 relative to 91 can then be used to determine the amount of deuterium substituted on the brominated carbon.

The next step in the calculation was to remove the interference of radical scavenging by HDS, which resulted in the product $CH_2BrCH_2Cl$. A correction factor for this interference was obtained by taking the ratio of peaks with m/e=63 and 64. These m/e values represent the fragments $C_2H_4{}^{35}Cl$ and $C_2H_3D^{35}Cl$. By calculating the peak intensity ratio 63/(63+64) for each sample, the percent of hydrogen scavenging in the stabilization product is determined, H. The total yield of stabilization product can now be divided by percents into the three products. $CH_2BrCH_2Cl$=H, $CHDBrCH_2Cl$=D and $CH_2BrCHDCl$=100 -(H + D).

A program was created in QBASIC to model the system using the qualitative reactions in mechanism B. The yield data obtained by Iyer and Rowland for the $^{38}$Cl experiments was then installed for the purpose of optimizing rate constants to generate a best fit. The following equation was calculated in determining the fit, and minimized to get the best fit;

$$\sum (A_{exp} - A_{mod})^\wedge 2 + (B_{exp} - B_{mod})^\wedge 2$$

Where A is $CH_2=CH^{38}Cl$, B is $CH_2{}^{38}ClCH_2Br$, *exp* is the experimentally observed value and *mod* is the model value. The program started from a set of randomly selected rate constants and calculated the sum value. Then it varied those rates to determine the sum values for the surrounding sets. Finding the lowest neighbor, the program moved there, repeating the process until it reached a minima and was stuck. At that point it was restarted with a new set of random values. After 20 runs, only one global minima was found. This is better than the value of $19.47 \times 10^{-3}$ calculated using the rate constants determined by Iyer and Rowland. Both rate constant sets are listed in Table 1 under mechanism B.

The results of this work has shown the presence of the 1,2-bromine migration postulated in mechanism B and, therefore, lends strong support for the chlorine atom addition to both the carbon atoms of $CH_2=CHBr$ at very similar rates-as proposed in this mechanism.

$^{38}$Cl

# References

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## II.    Chlorine Atom Reactions with $CF_2=CFBr$

Various aspects of the addition of thermal chlorine atoms to $CF_2=CFBr$ are of interest for comparison with those observed for $CH_2=CHBr$. These aspects include the intramolecular selectivity for the addition, the unimolecular decay characteristics of the two possible adduct radicals, $CF_2ClCFBr^*$ and $CF_2CFBrCl^*$, the existence of any 1,2 Br atom shift in $CF_2CFBrCl$, and the rate constant for the addition reaction. From a study over the pressure range 10-300 torr Brarda and Starrico reported that $CF_2=CFCl$, $CF_2ClCFCl_2$, $CF_2ClCFBrCl$, and $CF_2BrCFBrCl$ are formed as products in the 436 nm photolysis of $Cl_2 + CF_2=CFBr +$ both gas ($C_2Cl_2F_4$ or $c\text{-}C_4F_8$ or He) mixtures [1]. They proposed that the product, $CF_2=CFCl$ is formed by two separate routes:
(1) by a pressure independent "substitution" of Br in $CF_2=CFBr$ by Cl and
(2) the formation of a vibrationally excited radical $C_2F_3BrCl^*$, the decomposition of which led to the formation of $CF_2=CFCl$ as in reactions (a) and (b).

$$Cl + CF_2=CFBr \rightarrow (C_2F_3BrCl)^* \qquad \text{(a)}$$
$$CF_2CFBrCl^* \rightarrow CF_2=CFCl + Br \qquad \text{(b)}$$
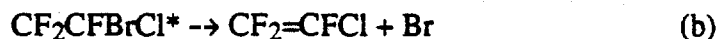
Collisional stabilization of $C_2F_3BrCl^*$ radicals as in (c) followed by reaction (d) with $Cl_2$ was proposed as the route for the formation of the observed product $CF_2ClCFBrCl$.

$$CF_2ClCFBr^* + M \rightarrow CF_2ClCFBr + M \qquad \text{(c)}$$
$$CF_2ClCFBr + Cl_2 \rightarrow CF_2ClCFBrCl + Cl \qquad \text{(d)}$$

No explanation was given by the authors as to why, for the same excited radical, the structure $CF_2CFBrCl^*$ was assigned for the decomposition path (b), while the isomeric structure $CF_2ClCFBr^*$ was used for the stabilizaition path (c). While the loss of Br proposed in reaction (b) would be expected to be rapid for the $CF_2CFBrCl^*$ radical, the most likely decomposition path for the $CF_2ClCFBr^*$ radical is by C-Cl bond scission to form $CF_2=CFBr + Cl$. Brarda and Starrico reported a lifetime of $\sim 10^{-7}$ sec for the excited $C_2F_3BrCl^*$ radical. This lifetime is quite long for the Br atom loss in (b) in comparison to the lifetime of $\sim 10^{-10}$ sec we had reported for the analogous $CH_2CHBrCl^*$ radicals from $Cl + CH_2=CHBr$ reaction.[2] The much longer lifetime reported by Brarda and Starrico appears to be more consistent with a Cl atom loss from $CF_2ClCFBr^*$, a step not included in their proposed mechanism. If the lifetime of $CF_2CFBrCl^*$ radical is $\leq 10^{-10}$ sec, no significant stabilization of these radicals would have occurred in the pressure range of 10-300 torr used in their study. Furthermore, even if collisional stabilization of $CF_2CFBrCl^*$ radicals occurred, the reaction of

the stabilized radicals with $Cl_2$ would have resulted in the formation of $CF_2ClCFBrCl$, which is identical to the product from reaction (d). Hence, no information on the intramolecular selectivity of Cl atom addition to the olefin is obtained.

Our experiments on the addition of thermal chlorine atoms to $CF_2=CFBr$ has involved two separate sets of experiments: (a) the use of Cl atoms from the photolysis of $COCl_2$ and (b) the use of radioactive $^{38}Cl$ atoms produced by (n,γ) reaction in $CClF_3$. $N_2$ was used as the bath gas in these experiments and $H_2S$ as the radical scavenger. The photolysis experiments with product identification by GC-MS, focussed on establishing the reaction mechanism, particularly on examining the existence of any 1,2 Br atom migration in $CF_2CFBrCl$, while the $^{38}Cl$ experiments were carried out with emphasis on product yield measurements. With $H_2S$ as the radical scavenger, collisional stabilization of $CF_2ClCFBr^*$ radicals followed by reaction with $H_2S$ would produce $CF_2ClCHFBr$. If $CF_2CFBr^*Cl$ radicals were collisionally stabilized and then reacted with $H_2S$, the expected end-product is $CHF_2CFBrCl$. If 1,2 Br atom migration in $CF_2CFBrCl$ produces $CF_2BrCFCl$, subsequent reaction of the isomerized radical with $H_2S$ would lead to the formation of $CF_2BrCHFCl$. These three isomeric compounds, $CF_2ClCHFBr$, $CHF_2CFBrCl$, and $CF_2BrCHFCl$ can be distinguished by GC-MS making use of the unique mass spectra of each isomer. The expected decompositon product, $CF_2=CFCl$ following Cl atom addition to the CFBr end can readily be separated and measured by GC-MS in the photolysis experiments and by radio gas chromatography in the $^{38}Cl$ experiments.

The photolysis were carried out in a 165 cc quartz cell. The component gases $COCl_2$, $CF_2=CFBr$, $H_2S$ and $N_2$ were added to the photolysis cell by standard techniques using a grease-free, Hg-free vacuum line. In order to minimize the photolysis of $CF_2=CFBr$, low concentration of $CF_2=CFBr$ and short irradiation times were used. A typical photolysis mixture contained 0.15 torr $CF_2=CFBr$, 1.2 torr of $H_2S$ and 2.3 torr of $COCl_2$. Sufficient $N_2$ as a bath gas, was added to bring the final sample pressures between 600 and 3000 torr. The samples were irradiated for one minute with 253.7 nm radiation from a low pressure Hg-lamp. After the irradiation, the contents of the photolysis cell were passed through a trap held at 77K and $N_2$ was pumped out. The fraction collected in the trap was analyzed by GC-MS using a capillary column (J & W Scientifc DB-624, 30 meters with 1.8 μm film thickness) for the separation. The temperature program and data acquisition were optimized for this experiment. The column oven was set to hold at the starting temperature of 40°C for 10 minutes and then warmed at a rate of 10°C/minute to 150°C. The mass spectrometer was operated in the scan mode with a range of m/e = 33 to 250.

A typical chromatogram is shown in Figure 1. The product $CF_2=CFCl$ was seen at 2.79 minutes. This was confirmed by retention time as well as mass spectroscopic analysis. In the figure, it is shown using an ion scan of m/e=100-250 to separate it from $H_2S$, with which it co-elutes. The stabilization product was seen at 19.50 minutes, and was identified by mass spectrometry (Figure 2) to be $CF_2ClCHBr$. The peak at 19.5' did not show the presence of any detectable levels of the two

Figure 1. GC/MS Chromatogram
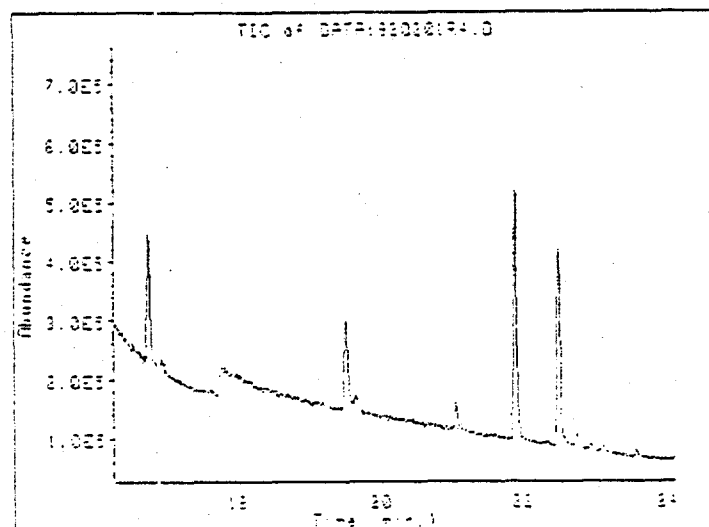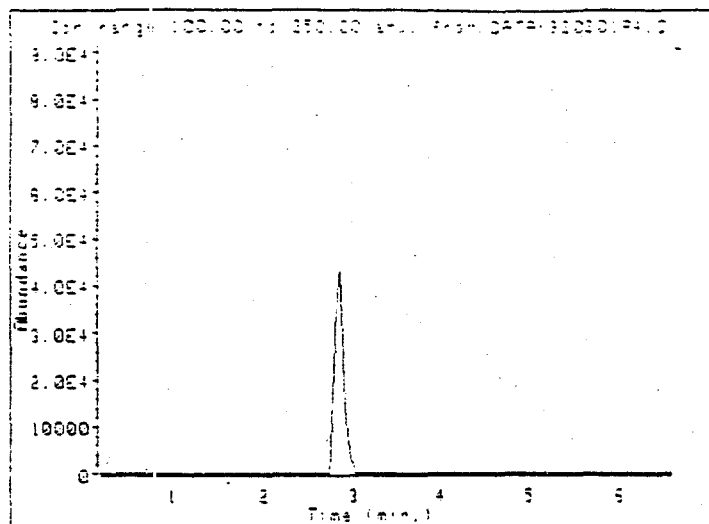


| Time (min) | Component |
|---|---|
| 2.8 | $CF_2=CFCl$ |
| 16.7 | $CS_2$ |
| 19.4 | $CF_2ClCHFBr$ |
| 19.6 | $\overset{S}{CF_2CFBr}$ |
| 21.1 | $CHFBr_2$ |
| 21.9 | $CF_2BrCHFBr$ |
| 22.5 | $\overset{NH}{CF_2CFBr}$ |

**Figure 2.** Mass Spectra of Stabilization Product ($CF_2ClCHFBr$).
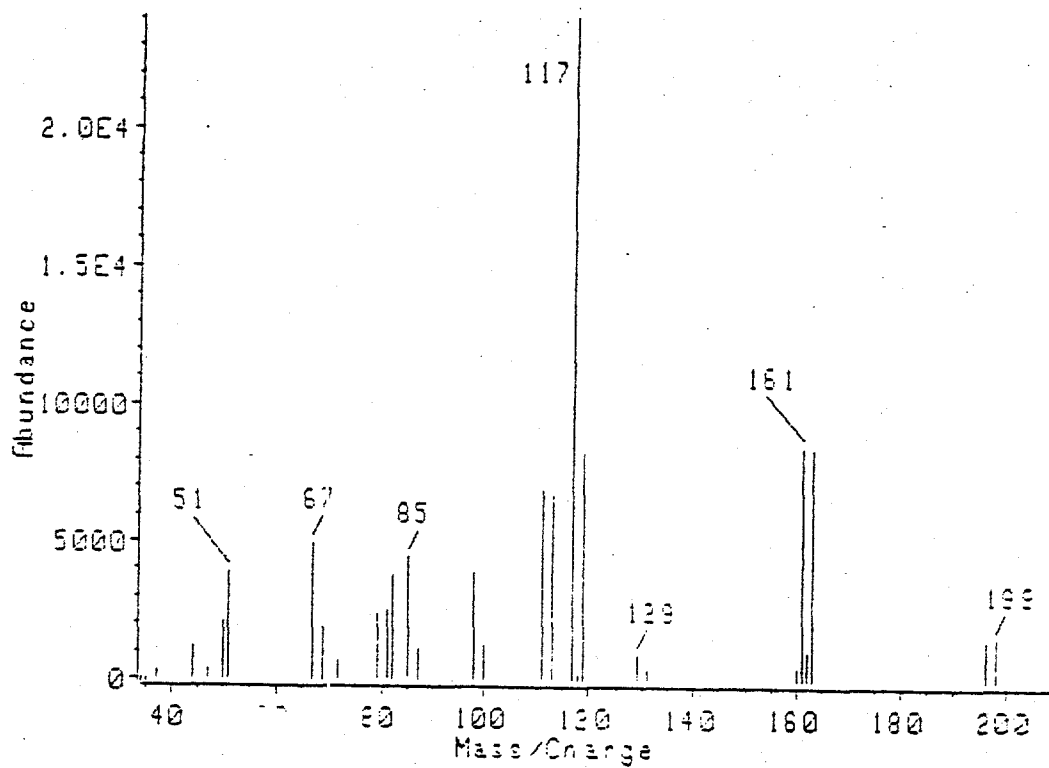
isomeric compounds, $CHF_2FBrCl$ and $CF_2BrCHFCl$. The mass spectra of commercially available $CF_2BrCHFCl$ (Peninsular Chem Research) is shown in Figure 3. $CHF_2CFBrCl$ was present as an impurity in this compound, and the mass spectra of this isomer is also shown in Figure 3. These two compounds had retention times similar to the stabilization product, but different mass spectra, as can be seen in Figure 3.

This suggested that the stabilization product was mainly $CF_2ClCHFBr$ with the possible pressence of small amounts of the other two products. To eliminate this possibility, one of the samples was spiked with the standards before photolysis. A chromatogram of the products showed a large peak containing the three compounds. The mass spectra showed the three isomeric compounds had slightly different retention times (as indicated in Figure 4), even if at these levels they could not be resolved. Figure 4 shows the three spectra of the component peaks from this run. Thus, in spite of the coelution of the three isomers as one peak, spectral analysis of the segments of the peak can be used to establish the presence or absence of all three isomers. The peak from the photolysis mixtures showed the presence of only $CF_2ClCHFBr$. If the other two products were formed in the reaction system their yields were less than 1% of the $CF_2ClCHFBr$ yield.

Having eliminated $CF_2BrCHFCl$ and $CHF_2CFBrCl$ as major products in the reaction, the mechanism can be qualitatively defined. This mechanism is given in Figure 5.

The stabilization by collision of $CF_2CFBrCl^*$ as in (8) and subsequent reaction (9) with $H_2S$ are not included in this mechanism as $CHF_2CFBrCl$ was not observed as a product.

$$CF_2CFBrCl^* + M \rightarrow CF_2CFBrCl + M \qquad (8)$$
$$CF_2CFBrCl + H_2S \rightarrow CHF_2CFBrCl + HS \qquad (9)$$

If the $CF_2CFBrCl$ isomerized to $CF_2BrCFCl$ by a 1,2 Br atom shift (analogous to the isomerization proposed for $CH_2CHBrCl$[2]), the reaction of the isomerized radical with $H_2S$

$$CF_2CFBrCl \rightarrow CF_2BrCFCl \qquad (10)$$
$$CF_2BrCFCl + H_2S \rightarrow CF_2BrCHFCl \qquad (11)$$
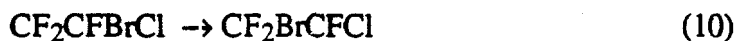
should produce $CF_2BrCHFCl$. This compound was also not detected as a product. The absence of any collisional stabilization of $CF_2CFBrCl^*$ radicals even up to pressures of 3000 torr would imply that the Br atom loss in (6) occurs much faster than the collision frequency at these pressures i.e. $k_6 \gg 10^{10}$ sec$^{-1}$. In Brarda and Staricco's experiments[1], $CF_2BrCFCl$ radicals, if formed, would have reacted with $Cl_2$ to form $CF_2BrCFCl_2$. They reported that this compound was not seen as a product, which is consistent with our observations of the lack of stabilization of $CF_2CFBrCl^*$ radicals and the absence of any product from a 1,2 Br atom shift.

Figure 3. Mass Spectra of $CHF_2BrCHFCl$ and $CHF_2CFBrCl$ Standards.
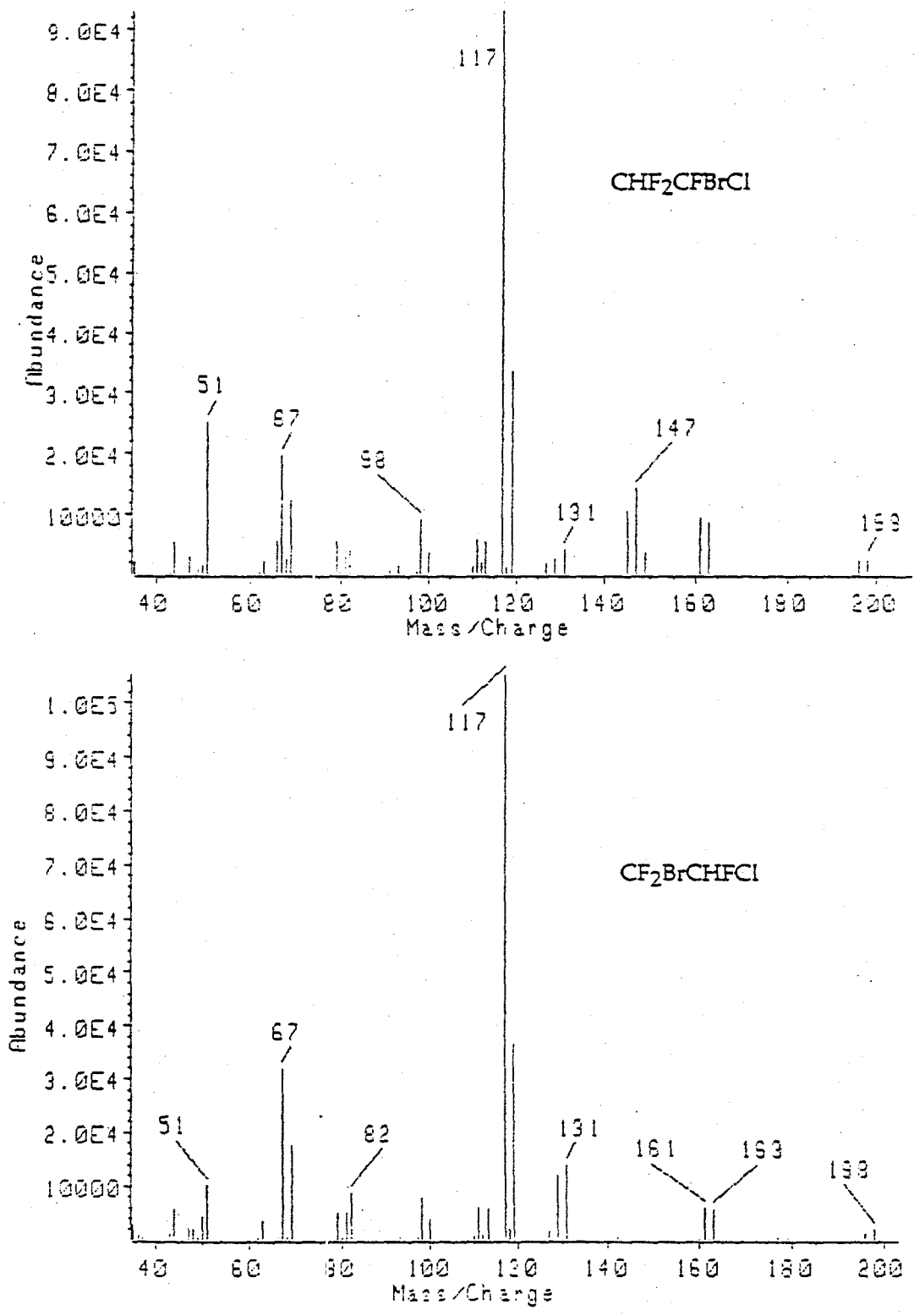
**Figure 4.** $C_2HF_3BrCl$ Compounds in Spiked Reaction Mixture. Different Retention Times Are Shown.

t=19.39 min. $CHF_2CFBrCl$

Abundance — Mass/Charge

1.0E5 — 117
5.0E4 — 51, 67, 98, 147, 161, 198, 199

t=19.47 min. $CF_2ClCHFBr$

Abundance — Mass/Charge

3.0E5, 2.0E5, 1.0E5 — 117
51, 67, 93, 129, 161, 199, 199

t=19.53 min. $CF_2BrCHFCl$

Abundance — Mass/Charge

5.0E5, 4.0E5, 3.0E5, 2.0E5, 1.0E5 — 117
51, 67, 93, 129, 161, 199, 199
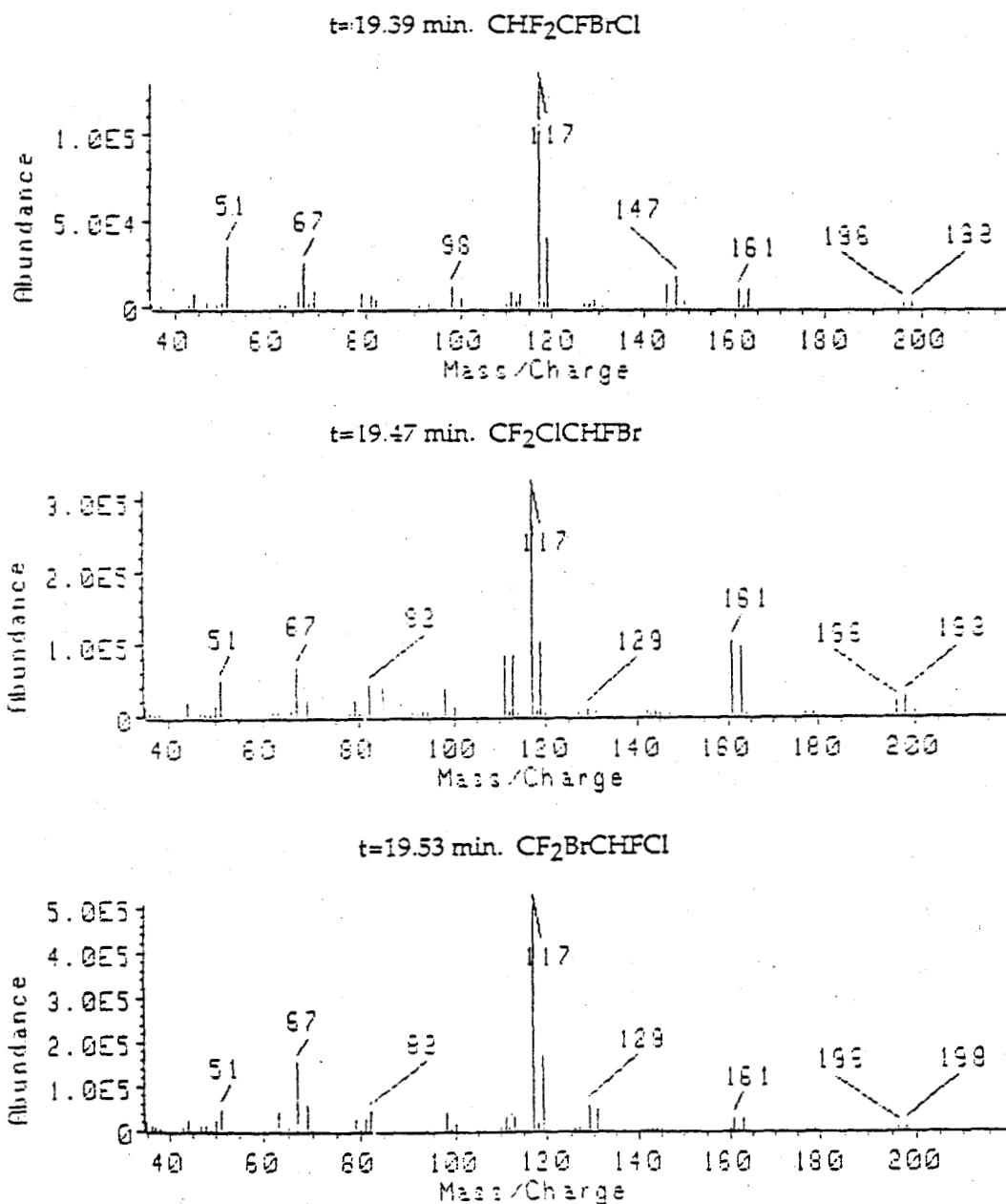
Figure 5. Qualitative Mechanism for $CF_2=CFBr$ System.

$$Cl + CF_2=CFBr \rightarrow CF_2CFBrCl^* \qquad k_1$$

$$Cl + CF_2=CFBr \rightarrow CF_2ClCFBr^* \qquad k_2$$

$$CF_2ClCFBr^* \rightarrow CF_2=CFBr + Cl \qquad k_3$$

$$CF_2ClCFBr^* + M \rightarrow CF_2ClCFBr + M \qquad k_4$$

$$CF_2ClCFBr + H_2S \rightarrow CF_2ClCHFBr + HS \qquad k_5$$

$$CF_2CFBrCl^* \rightarrow CF_2=CFCl + Br \qquad k_6$$

$$Cl + H_2S \rightarrow HCl + HS \qquad k_7$$
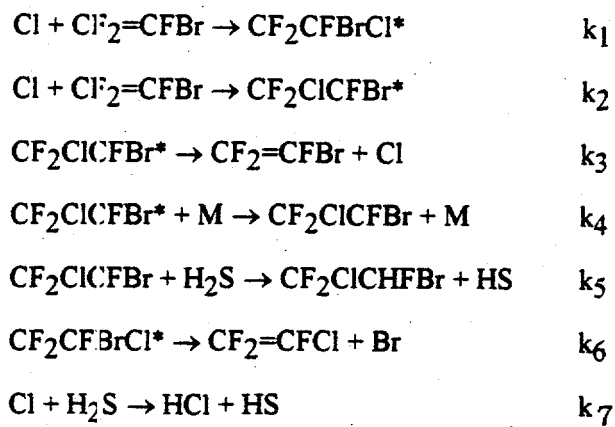
The $^{38}Cl$ experiments with $CF_2=CFBr$ were carried out for the quantitative measurement of product yields. $CClF_3$ was used as the target compound for the $^{37}Cl(n,\gamma)$ $^{38}Cl$ reaction.[3] $N_2$ was used as the bath gas in these experiments also in order to keep the system comparable to that used in the photolysis experiments. Argon was used as an internal neutron flux monitor through the $^{40}Ar$ $(n,\gamma)$ $^{41}Ar$ reaction for the determination of total $^{38}Cl$ production in each sample. The mixtures consisting of $CClF_3$, $CF_2=CFBr$, $H_2S$, Ar and $N_2$ were sealed in 20 cc ampoules made from Pyrex 7740 glass. The experiments were carried out at total sample pressures of 1050, 2200, and 3000 torr with varying pressures of $H_2S$ and $CF_2=CFBr$. The pressures of $CClF_3$ and Ar were maintained at 100 torr and 5 torr respectively for all the samples. Sufficient $N_2$ was added to bring the sample to the desired total pressure. The samples were irradiated for 2 minutes at a reactor power level of 10 kW in the rotating specimen rack of the UCI Triga Mark I nuclear reactor. The irradiated samples were analyzed by radio gas chromatography[4,5], using a gas flow sandwich-type proportional counter for the radioactivity measurements. The chromatographic separation employed two packed columns in series, one run isothermally and the other manually switched between two water baths at two different tempertures. The first column was a 10-ft diisodecylphthalate column operated at 43°C. All compounds of interest with the exception of $CF_2^{38}ClCHFBr$ eluted quickly from this column onto the second. The second column, a 24-ft propylene carbonate on alumina (PCA) was kept initially at 0° in an ice bath. This column allowed the separation of $^{41}Ar$ from $C^{38}ClF_3$. Following the elution of the $^{41}Ar$ peak, the second coumn was transferred from the ice bath to a water bath at 23°C and $CF_2=CF^{38}Cl$ was eluted from the column combination. The second column was then removed from the combination and $CF_2^{38}ClCHFBr$ was eluted from the first column and passed directly to the detectors. A typical chromatogram is shown in Figure 6.

The absolute yields of the two observed products, $CF_2=CF^{38}Cl$ and $CF_2^{38}ClCHFBr$ formed from thermal $^{38}Cl$ reactions with $CF_2=CFBr$ in these samples are listed in Table I. The errors listed for the yields represent only the statistical uncertainties ($1\sigma$) in the proportional counter measurements. The reciprocal of the sum of the measured yields of $CF_2=CF^{38}Cl$ and $CF_2^{38}ClCHFBr$ (after allowing for 5% loss of $^{38}Cl$ through energetic reaction with $CClF_3$[3]) are plotted against $[H_2S]/[CF_2=CFBr]$ ratios in Figures 7-9 for the three pressures, 1050, 2200, and 3000 torr. The straight line plots obtained in these figures are consistent with a kinetic competition for thermal $^{38}Cl$ atoms between $H_2S$ and $CF_2=CFBr$. If significant fraction of $CF_2^{38}ClCFBr^*$ radicals decompose by $^{38}Cl$ loss (reaction 3) at these pressures, an increase in the slopes for these plots would be expected as the sample pressure is decreased because of an increasing fractional loss of the recycling $^{38}Cl$ through reaction (7) with $H_2S$. However, the measured slopes for these plots are not significantly different, suggesting that $k_3$ is much smaller than the collisional frequencies at these pressures. If all the thermal $^{38}Cl$ atoms (95% of total $^{38}Cl$ production) formed in these samples divided among the three products, $CF_2=CF^{38}Cl$, $CF_2^{38}ClCHFBr$, and $H^{38}Cl$ (from reaction7), the intercepts expected for the

Figure 6.   Radio-Gas Chromatographic Run.

## Proportional Counter



Y-axis: Counts/10 sec
X-axis: Retention Time (min.)

Peaks labeled: $^{41}Ar$; $CF3^{80,80m}Br$; $CF2=CF^{38}Cl$; $CF2^{38}ClCHFBr$

## Thermal Conductivity Detector



X-axis: Retention Time (min.)

Labels: Air from Crusher; 5.552 $N_2 + H_2S$; 17.542 $CF_3Cl$; Column Two Isolated; Column Two Purged; 183.631 $CF_2=CFBr$; START; STOP
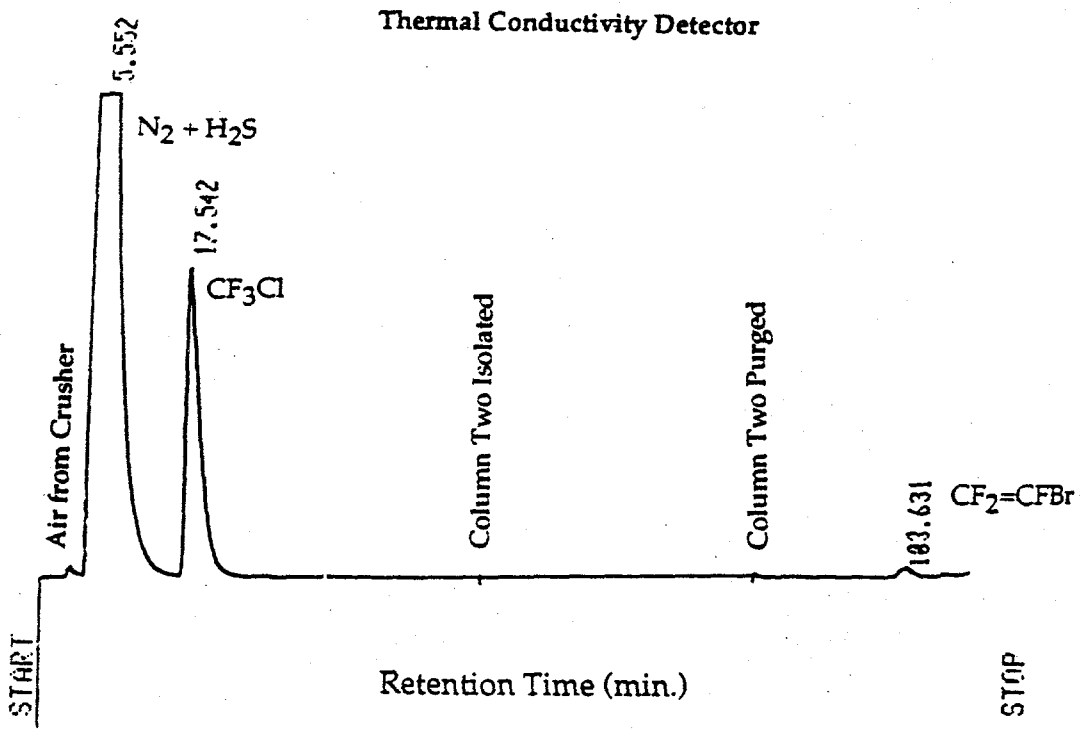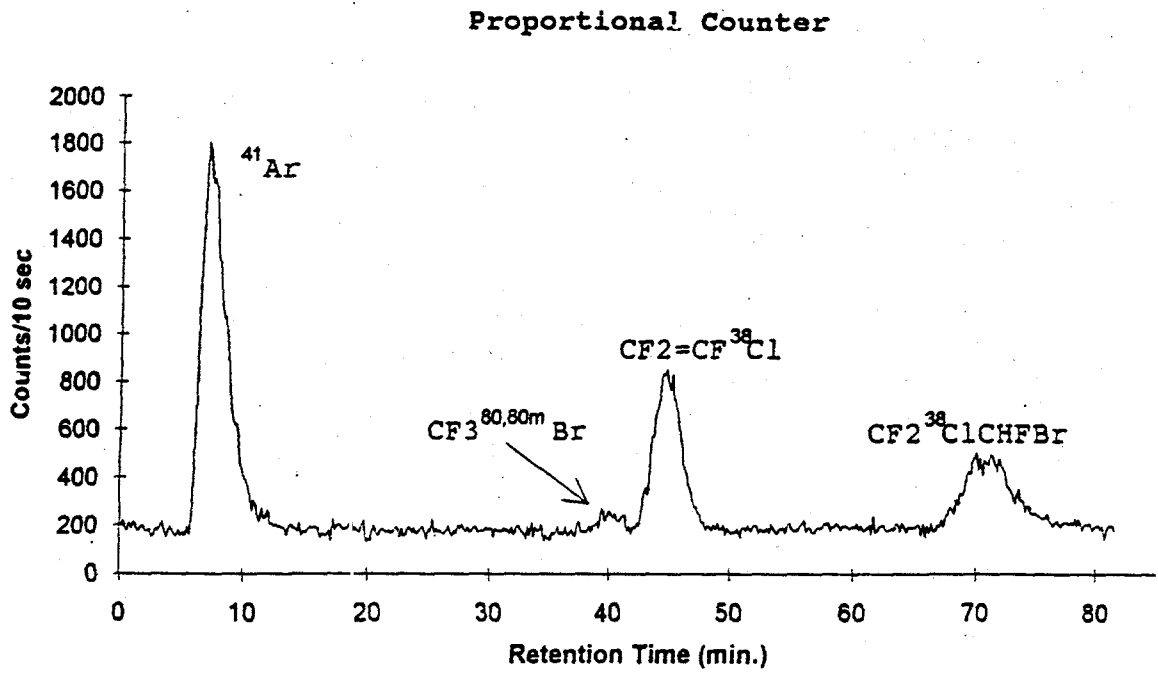
Table 1. $^{38}Cl$ Samples: Initial Conditions and Product Yields.

| Sample | Pressure (torr) | | | Product Yields (percent) | |
| --- | --- | --- | --- | --- | --- |
| | $N_2$ | $H_2S$ | $CF_2=CFBr$ | $CF_2=CF^{38}Cl$ | $CF_2^{38}ClCHFBr$ |
| 1 | 901 | 0.00 | 10.0 | 30.80 (±0.256) | 0.00 |
| 2 | 921 | 5.02 | 5.45 | 12.96 (±0.30) | 4.965 (±0.489) |
| 3 | 921 | 5.00 | 10.0 | 17.28 (±0.24) | 18.11 (±0.36) |
| 4 | 975 | 10.0 | 5.00 | 7.060 (±0.106) | 8.997 (±0.379) |
| 5 | 937 | 10.0 | 10.0 | 6.867 (±0.178) | 14.99 (±0.33) |
| 6 | 921 | 20.0 | 10.0 | 6.924 (±0.228) | 10.41 (±0.46) |
| 7 | 921 | 30.0 | 10.0 | 5.091 (±0.106) | 7.068 (±0.204) |
| 8 | 975 | 30.2 | 5.02 | 2.730 (±0.150) | 3.060 (±0.39) |
| 9 | 917 | 50.0 | 10.0 | 3.464 (±0.098) | 5.962 (±0.193) |
| 10 | 1320 | 0.00 | 10.0 | 30.37 (±0.262) | 0.00 |
| 11 | 2067 | 0.00 | 9.99 | 29.13 (±0.46) | 0.00 |
| 12 | 2117 | 0.99 | 10.0 | 25.61 (±0.24) | 12.63 (±0.24) |
| 13 | 2117 | 2.00 | 10.0 | 22.01 (±0.20) | 14.53 (±0.22) |
| 14 | 2063 | 5.00 | 10.0 | 15.47 (±0.23) | 16.31 (±0.32) |
| 15 | 2109 | 5.00 | 5.00 | 11.44 (±0.14) | 16.51 (±0.23) |
| 16 | 2063 | 7.98 | 7.98 | 9.886 (±.0212) | 11.25 (±0.38) |
| 17 | 2040 | 9.99 | 9.99 | 10.45 (±0.19) | 15.93 (±0.34) |
| 18 | 2071 | 16.0 | 7.98 | 6.696 (±0.177) | 8.849 (±0.382) |
| 19 | 2113 | 20.0 | 0.00 | 0.00 | 0.00 |
| 20 | 2074 | 20.0 | 20.0 | 11.10 (±0.15) | 18.06 (±0.13) |
| 21 | 2082 | 20.0 | 10.0 | 6.924 (±0.108) | 10.24 (±0.21) |
| 22 | 2028 | 20.0 | 5.00 | 3.966 (±0.158) | 4.737 (±0.337) |
| 23 | 2047 | 20.0 | 10.0 | 6.896 (±0.222) | 8.255 (±0.444) |
| 24 | 2086 | 20.0 | 10.0 | 6.982 (±0.112) | 10.57 (±0.20) |
| 25 | 2101 | 30.0 | 10.0 | 4.451 (±0.138) | 8.463 (±0.319) |
| 26 | 2008 | 30.0 | 5.00 | 2.939 (±0.178) | 4.325 (±0.352) |
| 27 | 2078 | 30.0 | 15.0 | 6.802 (±0.11) | 11.25 (±0.20) |
| 28 | 1362 | 32.0 | 7.98 | 3.522 (±0.202) | 2.634 (±0.354) |
| 29 | 2125 | 4.00 | 2.00 | 6.409 (±0.104) | 6.778 (±0.161) |
| 30 | 2055 | 40.0 | 40.0 | 11.60 (±0.15) | 21.85 (±0.31) |
| 31 | 2047 | 40.0 | 40.0 | 11.80 (±0.14) | 20.22 (±0.27) |
| 32 | 2040 | 40.0 | 40.0 | 11.16 (±0.14) | 20.86 (±0.29) |
| 33** | 2163 | 40.0 | 40.0 | 0.00 | 0.00 |
| 34 | 2790 | 0.00 | 10.0 | 28.69 (±0.444) | 0.00 |
| 35 | 2740 | 5.00 | 10.0 | 15.35 (±0.309) | 21.59 (±0.548) |
| 36 | 2798 | 10.0 | 10.0 | 11.13 (±0.142) | 17.72 (±0.28) |
| 37 | 2759 | 10.0 | 10.0 | 10.68 (±0.19) | Lost* |
| 38 | 2806 | 15.0 | 10.0 | 8.303 (±0.122) | 13.56 (±0.23) |
| 39 | 2748 | 20.0 | 10.0 | 7.966 (±0.13) | 11.61 (±0.35) |
| 40 | 2783 | 25.0 | 10.0 | 5.367 (±0.106) | 9.670 (±0.239) |
| 41 | 2763 | 30.0 | 10.0 | 4.649 (±0.142) | 8.058 (±0.309) |

*Product lost due to rubber seal leak in chromatograph.
**All samples contained 100 torr $CF_3Cl$ and 5 torr Ar, except 33 which had no $CF_3Cl$

Figure 7. 0.95/Total Yield vs [H2S]/[CF2=CFBr] for 1050 torr samples with [CF2=CFBr]=10
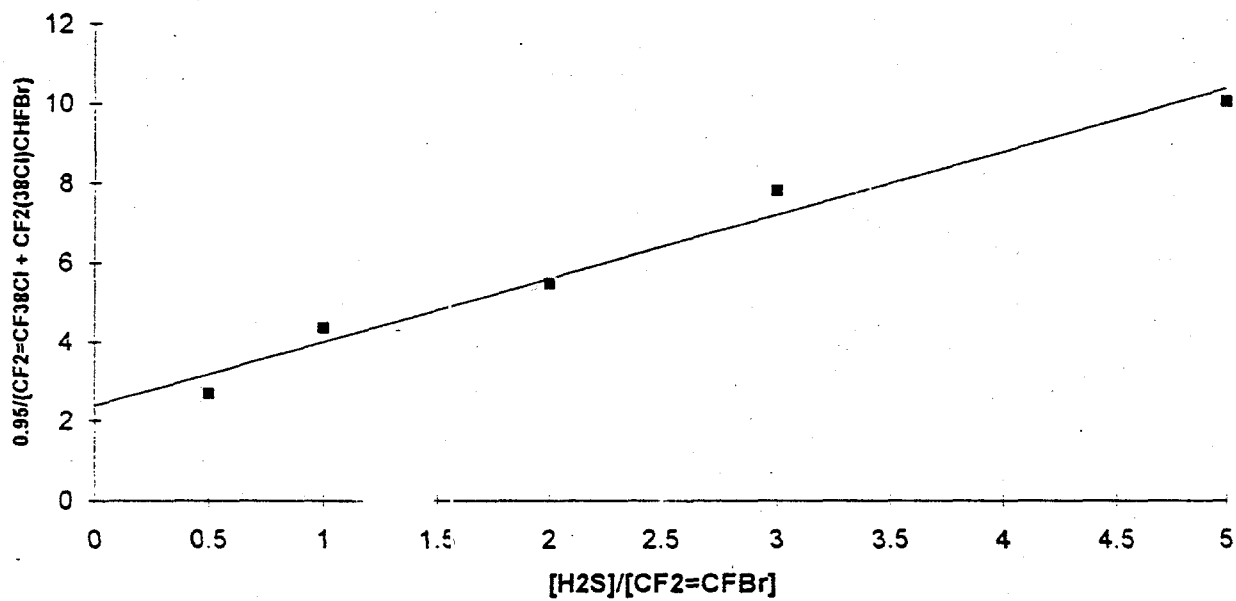
Figure 8. 0.95/Total Yield vs [H2S]/[CF2=CFBr] for 2200 torr samples with [CF2=CFBr]=10 torr
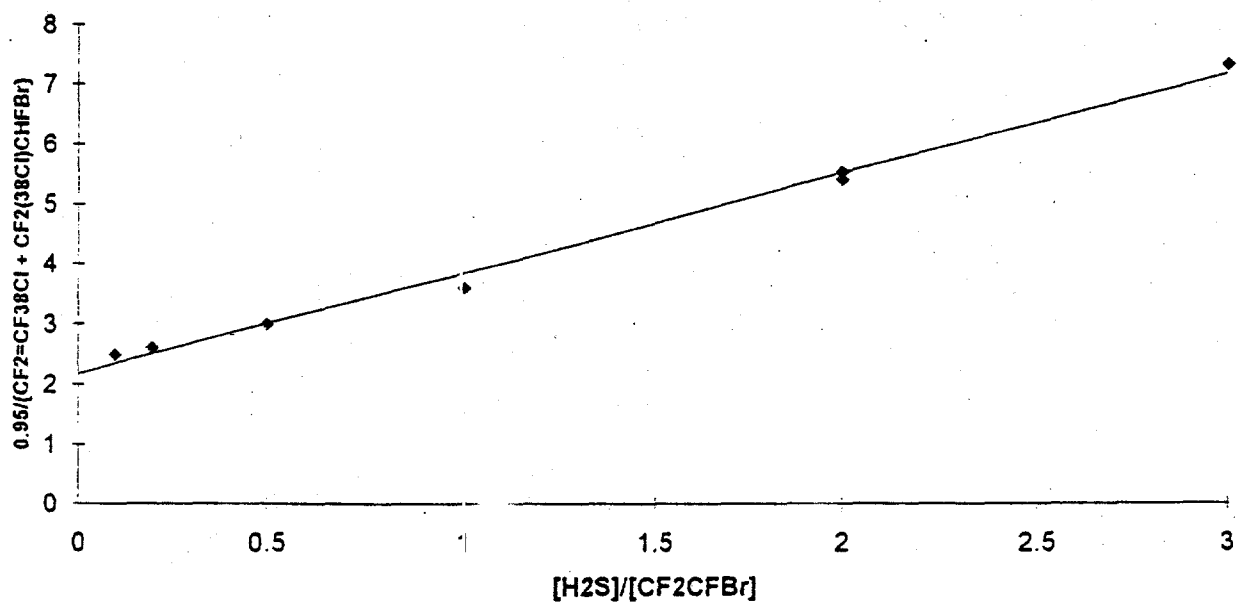
Figure 9. 0.95/Total Yield vs [H2S]/[CF2=CFBr] for 3000 torr Samples with [CF2=CFBr]=10 torr
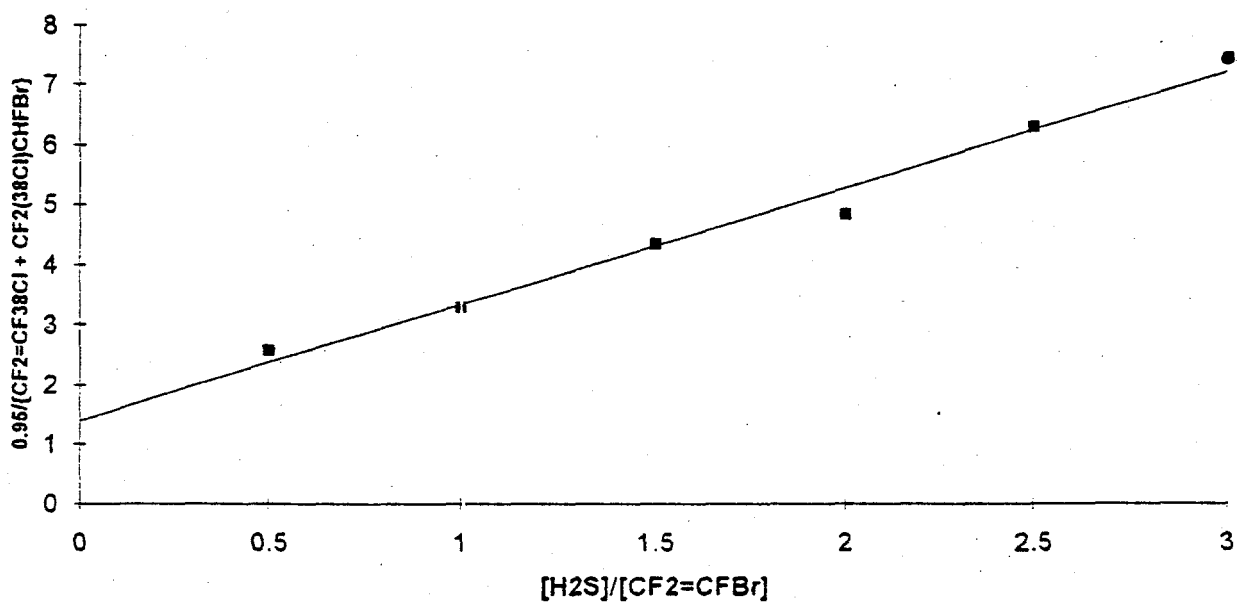
plots in Figures 7-9 is 1.0. However, it can be seen from these figures that the experimental data are not consistent with this expectation. A possible explanation for the intercepts of > 1.0 observed in these plots is that reaction (5) of $CF_2{}^{38}ClCFBr$ with $H_2S$ is not sufficiently rapid in these samples to quantitatively scavenge these radicals. It is likely that a fraction of these radicals is lost through reaction (12) with $CF_2=CFBr$ and/or through reaction (13) with the walls of the sample bulb.

$$CF_2{}^{38}ClCFBr + CF_2=CFBr \rightarrow C_4F_6Br^{38}Cl^* \qquad (12)$$

$$CF_2{}^{38}ClCFBr + Wall \rightarrow Product\ loss \qquad (13)$$
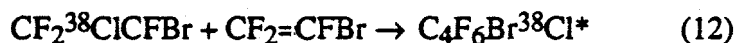
In order to test if such loss processes are occurring in these samples, several runs were made at fixed $[H_2S]/[CF_2=CFBr]$ ratios of 1 or 2, but with varying absolute concentrations of the two reactants. A decrease in the yield of $CF_2{}^{38}ClCHFBr$ was observed in these runs at either ratios, as the absolute concentration of $H_2S$ was decreased as shown in figures 10 and 11. This observation is consistent with the existence of loss processes for $CF_2ClCFBr$ other than reaction (12) with $CF_2=CFBr$. If this reaction (12) were the main loss process competing with the scavenging reaction (5) by $H_2S$, no change in the yield of $CF_2{}^{38}ClCHFBr$ would be expected for a fixed $[H_2S]/[CF_2=CFBr]$ ratio which was held constant at either 1 or 2 for these runs. It appears that radical reaction (13) with the wall is the loss process in these samples.

The yield data obtained from the $^{38}Cl$ experiments have been fitted with a kinetic model shown in Figure 5 with reaction (13) included as an additional step in the mechanism. A program in QBASIC was used to optimize the rate constants to generate a best fit to the experimental data. The least squares minimization technique used for the optimization generated two minima and the rate constant values corresponding to these minima are listed below:

Fit 1: $k_3=k_4[M]$ at 180 torr, $k_7/(k_1=k_2)=1.92$

$k_2=2.26k_1$, and $k_1=4.10k_{13}$

Fit 2: $k_3=k_4[M]$ at 682 torr, $k_7/(k_1+k_2)=1.67$

$k_2=2.77k_1$, and $k_5=4.00k_{13}$

The $p_{1/2}$ value of 682 torr (pressure at which $k_3=k_4[M]$) obtained in Fit 2 is inconsistent with the lack of change in the slopes observed for the plots of Figures 7-9. This observation requires that the value of $p_{1/2}$ for $CF_2{}^{38}ClCFBr^*$ radicals is << the pressures used in these experiments. Fit 1 which gives a value of 180 torr for $p_{1/2}$ is therefore, chosen as the preferred fit to the data. The model fits to the data showing competition between scavenging of $CF_2ClCFBr$ by $H_2S$ vs. loss process (possibly through wall reactions) for Fit 1 are shown in Figures 10 and 11.

The value of $k_7/(k_1+k_2)=1.92$ obtained for this fit indicates a rate constant of $5.4 \times 10^{-11}$ $cm^3 molecule^{-1} sec^{-1}$ at T=296K for Cl atom addition to $CF_2=CFBr$ based on the value of $k_7=10.5 \times 10^{-11} cm^3 molecule^{-1} sec^{-1}$.[6] This rate constant for $CF_2=CFBr$ is about a factor of 4 lower

Figure 10. CF2(38Cl)CHFBr Yield vs [H2S] for 2200 torr samples with
[H2S]/[CF2=CFBr]=1
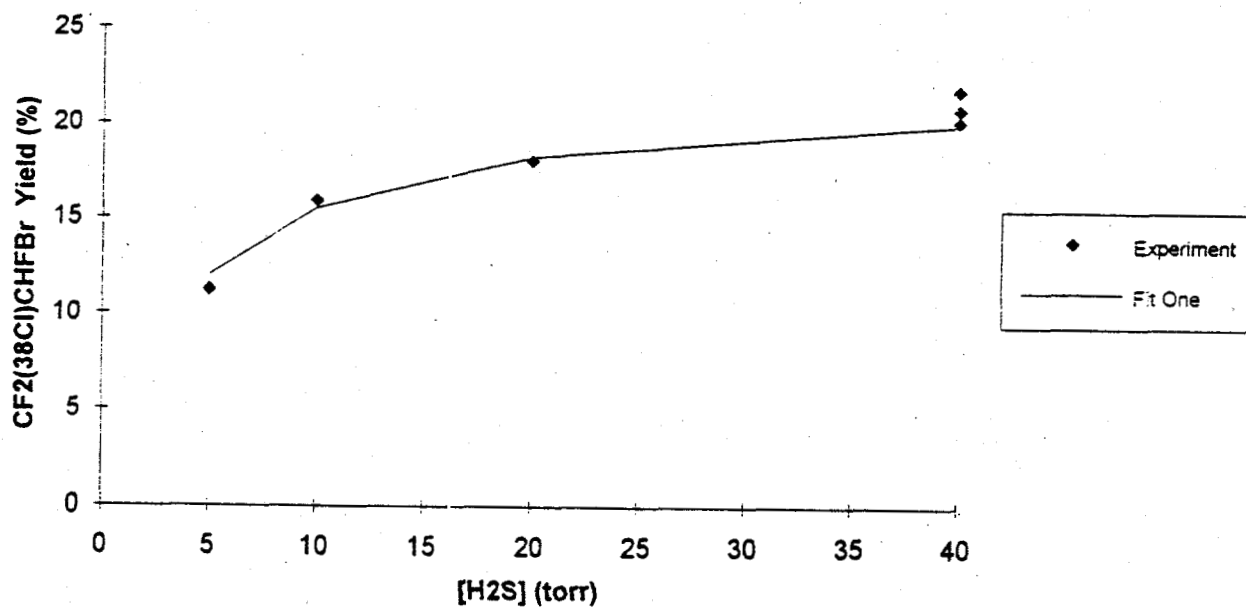
Figure 11. CF2(38Cl)CHFBr Yield vs [H2S] for 2200 torr samples with [H2S]/[CF2=CFBr]=2
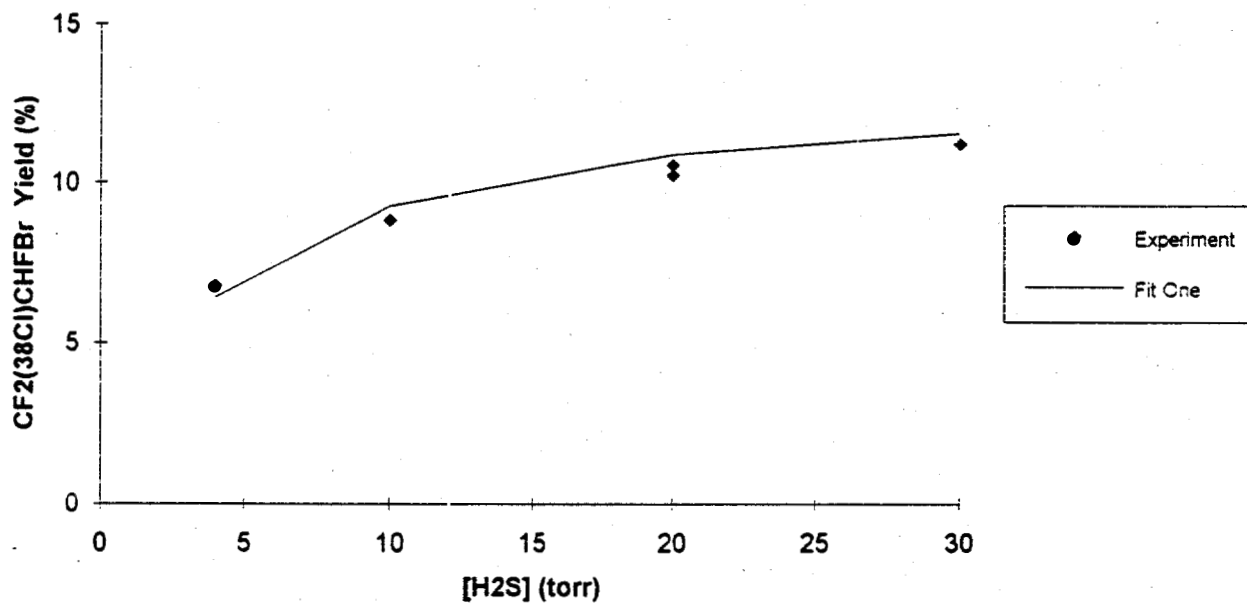
than that for $CH_2=CHBr^2$, consistent with an expected deactivation of the $\pi$-bond towards chlorine atom addition of the fluorine substituents in $CF_2=CFBr$. The kinetic model (Fit 1) to the data indicates a preference by a factor of 2.3 favoring Cl atom addition to the $CF_2$ over the CFBr end of the molecule.

Experiments carried out in the range from 1000-3000 torr (without the addition of $H_2S$ so as to increase the yield and hence the statistical accuracy of $CF_2=CF^{38}Cl$ measurements) showed only a small increase in the yield of $CF_2=CF^{38}Cl$ with decreasing pressure as shown in Figure 12. This observed increase can be accounted for by an increase in the fraction of $^{38}Cl$ release from reaction (3) with decreasing pressure, and the recycling of these $^{38}Cl$ atoms through reactions (1) and (2). Thus, as assumed in the kinetic model, the decomposition of $CF_2CFBrCl^*$ radicals is too rapid for any collisional stabilization of these radicals in the pressure range used in these experiments. The pressures of $CClF_3$ used in these experiments have been kept at 100 torr in order to use $N_2$ as the bath gas for comparison of the results with the photolysis runs. The accuracy of the yield measurements for $CF_2=CF^{38}Cl$ can be improved by carrying out further experiments using $CClF_3$ as the bath gas also i.e. with no $N_2$ added to the samples. Measurements covering the pressure ranges 100-4000 torr can conveniently be made in such samples. Further experiments with the more efficient radical scavenger HI in place of $H_2S$ are also planned for improving the determination of the yields of $CF_2^{38}ClCHFBr$ without incurring product losses as encountered with the use of $H_2S$ in the present experiments. Additional confirmation as to whether or not any collisional stabilization of $CF_2CFBr^{38}Cl^*$ radicals can be achieved will also be sought in those experiments.

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## III. GAS PHASE THERMAL $^{38}$CL REACTIONS WITH $(CH_2=CH)_N M$ (M= SN, SI, N=4; M=SB, N=3; M=HG, N=2)

The addition of thermal $^{38}$Cl to $C_1$ and $C_2$ of $V_{n-1}MCH=CH_2$ (in which $V=CH_2=CH-$ )would lead to the production of the two vibrationally excited radicals, $V_{n-1}MCHCH_2{}^{38}Cl^*$ (I) and $V_{n-1}MCH^{38}ClCH_2^*$ (II) respectively as in reactions (1) and (2).

$$V_{n-1}MCH=CH_2 + {}^{38}Cl \rightarrow V_{n-1}MCHCH_2{}^{38}Cl^* \qquad (1)$$

$$V_{n-1}MCH=CH_2 + {}^{38}Cl \rightarrow V_{n-1}MCH^{38}ClCH_2^* \qquad (2)$$
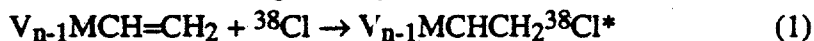
The excited radical I may undergo decomposition by loss of $^{38}$Cl as in (3) unless stabilized by collision with the bath gas, M' as in (4), but has no other energetically available reaction pathway.

$$V_{n-1}MCHCH_2{}^{38}Cl^* \rightarrow V_{n-1}MCH=CH2 + {}^{38}Cl \qquad (3)$$

$$V_{n-1}MCHCH_2{}^{38}Cl^* + M' \rightarrow V_{n-1}MCHCH_2{}^{38}Cl + M' \qquad (4)$$

A weak M-C bond (e.g. M=Hg, Sn, Sb) might be expected to facilitate the decomposition of radical II by M-C bond scission, as is (5)

$$V_{n-1}MCH^{38}ClCH_2^* \rightarrow V_{n-1}M + CH_2=CH^{38}Cl \qquad (5)$$
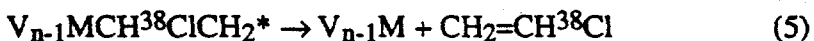
to form $CH_2=CH^{38}Cl$ as a product. The stabilization by collision of radical II could occur as in (6).

$$V_{n-1}MCH^{38}ClCH_2 + M' \rightarrow V_{n-1}MCH^{38}ClCH_2 + M' \qquad (6)$$
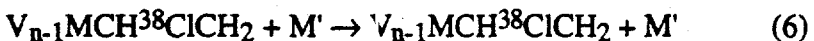
If competition between reactions (5) and (6) occur in the pressure range of the experiment, the yield of $CH_2=CH^{38}Cl$ can be expected to increase as the sample pressure is decreased. If $k_5 >> k_6 [M]$, the yield of $CH_2=CH^{38}Cl$ would be independent of pressure, if no additional pressure-dependent routes contribute to its formation. The competition between the decomposition reaction (3) and collisional stabilization (4) for radical I, if occurring, would lead to an increasing fraction of $^{38}$Cl released from (3) as the pressure is decreased. These $^{38}$Cl atoms are then available for recycling through reactions (1) and (2) until they eventually form either $CH_2=CH^{38}Cl$ or one of the collisionally stabilized radicals in (4) or (6). In this case, a contribution towards an increasing $CH_2=CH^{38}Cl$ yield with decreasing pressure from this recycling $^{38}$Cl reactions would be expected.

With $(CH_2=CH)_4Sn$ as the reactant and $CClF_3$ as the bath gas (M), thermal $^{38}$Cl reactions resulted in the formation of $CH_2=CH^{38}Cl$ in high yields ranging from 66±2% at 4300 torr to 91±4% at 130 torr total pressure.[1] The $CH_2=CH^{38}Cl$ yield data observed in this system were consistent with this reaction mechanism with $k_5>>k_6[M]$, such that no collisional stabilization of radical II (M=Sn) occurred in these samples, and the increase in the $CH_2=CH^{38}Cl$ yield with decreasing pressure resulted from recycling of the $^{38}$Cl yield from (3) through the same competitive addition processes of

(1) versus (2). The best fits to the yield data indicated a pressure for half-stabilization ($k_3=k_4[M]$) of $650\pm150$ torr in $CClF_3$ for the $V_3SnCHCH_2^{38}Cl^*$ radical. Previous studies of $^{38}Cl$ addition to $CH_2=CH_2$ and $CH_3CH=CH_2$ have shown half-stabilization pressures of $800\pm120$ torr for $CH_2CH_2^{38}Cl^*$ and $150\pm50$ torr for $CH_3CHCH_2^{38}Cl^*$ for chlorine atom loss versus collisional stabilization in $CClF_3$.[2,3] The rate constants for the subsequent loss of chlorine following thermal addition are anticipated from RRKM theory to be dependent upon the number of vibrational degrees of freedom over which the energy can be distributed: 15 for $CH_2CH_2^{38}Cl$, 24 for $CH_3CHCH_2^{38}Cl$, and 60 for $(CH_2=CH)_3SnCHCH_2^{38}Cl$. A half-stabilization pressure for $^{38}Cl$ addition to $V_3SnCH=CH_2$ almost equal to that from $CH_2=CH_2$ and greater than that from $CH_3CH=CH_2$ implies that the number of available vibrational degrees of freedom for distribution of the excitation energy in $(CH_2=CH)_3SnCHCH_2^{38}Cl^*$ is much smaller than the maximum total of 60 in the radical. The most probable explanation for this near-equivalence between $CH_2CH_2^{38}Cl^*$ and $V_3SnCHCH_2^{38}Cl^*$ in rates of excited radical decomposition is the nonparticipation of the three other vinyl groups in the energy equilibration process, i.e. "heavy-atom blocking" of energy transfer through the Sn-C bond from the ligand in which reaction occurred to the other three substituent groups. This "heavy-atom blocking" of energy transfer resulting in non-RRKM behavior has previously been hypothesized for the addition of thermal $^{18}F$ atoms to tetrallyltin, $(CH_2=CHCH_2)_4Sn_4$ and tetrallylgermaniun, $(CH_2=CHCH_2)_4Ge_5$ with the release of $CH_2=CH^{18}F$ from the excited $A_3MCH_2CH^{18}FCH_2^*$ radicals ($A=CH_2=CHCH_2-$; M=Sn or Ge). Slow energy transmission through such bonding has been supported by simplified theoretical calculations.[6]

Experiments with $(CH_2=CH)_4Si$, $(CH_2=CH)_3Sb$, and $(CH_2=CH)_2Hg$ as the substrates for thermal $^{38}Cl$ reaction have been carried out to examine whether of analogous non-RRKM behavior from heavy central atom blocking of internal energy redistribution following chlorine atom addition occurs with these substrates. The results of these studies are discussed below.

(a)    (CH_2=CH)_4Si

The reactor neutron irradiation of sample mixtures containing $CClF_3$, $(CH_2=CH)_4Si$ and Ar and subsequent analysis by radio gas chromatography showed no detectable yields of $CH_2=CH^{38}Cl$. These experiments have been carried out at total pressures of 4000, 2000 and 100 torr. Based on the total $^{38}Cl$ production in these samples and the detection limit for $CH_2=CH^{38}Cl$ in the radio gas chromatogram, the upper limits for its yield have been estimated to be 0.1% at 4000 torr, 0.3% at 1000 torr, and 2% at 100 torr. The absence of a significant yield of $CH_2=CH^{38}Cl$ even at pressures as low as 100 torr suggests that $k_5 << k_6[M']$. A slower decomposition rate for reaction (5) involving M-C bond scission with M=Si compared to that with M=Sn is consistent with the much greater strength of the Si-C bond relative to the Sn-C bond. Direct confirmation of $^{38}Cl$ additions (1) and (2) with $V_3Si CH=CH_2$ followed by collisional stabilization reactions (4) and (6) to form the two radicals, $V_3SiCHCH_2^{38}Cl$ and $V_3SiCH^{38}ClCH_2$ can be accomplished by our standard method of

including a radical scavenger such as HI or $H_2S$ in the samples and measuring the $^{38}Cl$-products by radio gas chromatography. However, in the present set of experiments we have not made such direct confirmation, but have instead determined the reactivity of $V_4Si$ towards thermal Cl atom reactions indirectly through competitive runs in mixtures with $CH_2=CHBr$. These competitive runs have been carried out at total sample pressures of 120, 500 and 4000 torr and the yields of $CH_2=CH^{38}Cl$ from reaction of $^{38}Cl$ with $CH_2=CHBr$[7] as in (7) have been measured at various ratios of

$$^{38}Cl + CH_2=CHBr \rightarrow (C_2H_3Br^{38}Cl)^* \rightarrow CH=CH^{38}Cl + Br \qquad (7)$$

$[V_4Si]/[CH_2=CHBr]$. The reciprocal yields of $CH_2=CH^{38}Cl$ determined at the three pressures were plotted against $[V_4Si]/[CH_2=CHBr]$ ratios, and gave good linear plots. The slope of the linear plot obtained at each pressure is a measure of the effective rate constant ($k^{eff}$) for chlorine atom removal by $V_4Si$ relative to the effective rate constant ($k_7$) for $CH_2=CH^{38}Cl$ formation at that pressure. In order to place these relative rate constants on an absolute basis, competitive runs of $CH_2=CHBr$ with $C_2H_6$ have also been made at these three pressures. The rate constant for chlorine atom reaction (8) with $C_2H_6$ is well established as $5.7 \times 10^{-11}$ $cm^3$

$$^{38}Cl + C_2H_6 \rightarrow H^{38}Cl + C_2H_5 \qquad (8)$$

molecule$^{-1}$sec$^{-1}$ at the 295K temperature of our experiments.[8] The slopes for plots of the $[C_2H_6]/[CH_2=CHBr]$ competitive run data represent the rate constant ratios, $(k_8/k_7)$ at the three experimental pressures. The ratio of the slope obtained at a given pressure from $[V_4Si]/[CH_2=CHBr]$ data to that from $[C_2H_6]/[CH_2=CHBr]$ at the same pressure, therefore, gives the ratio $(k^{eff}/k_8)$. The measured slopes for these plots and the values of these relative rate constants are listed in Table 1.

Table 1. Results of $V_4Si$/VBr and $C_2H_6$/VBr Competitive Runs for Reactions with Thermal $^{38}Cl$ Atoms

| Total Pressure (Torr) | Measured Slopes | | $(k^{eff}/k_8)$ | $10^{10} \times k^{eff}$ |
| | $V_4Si$/VBr data | $C_2H_6$/VBr data | | |
| | $(k^{eff}/k_7)$ | $(k_8/k_7)$ | | $(cm^3 molecule^{-1}s^{-1})$ |
| 4000 | 18.4 ± 0.9 | 1.24 ± 0.07 | 14.8 ± 1.1 | 8.4 ± 0.6 |
| 500 | 8.65 ± 0.45 | 0.62 ± 0.05 | 14.0 ± 1.3 | 8.0 ± 0.7 |
| 120 | 6.21 ± 0.85 | 0.41 ± 0.07 | 15.1 ± 3.3 | 8.6 ± 1.9 |

The values of $k^{eff}/k_8$ obtained for the three pressures 4000, 500, and torr are identical within the error limits of these measurements suggesting that the efficiency of $V_4Si$ for competition with $C_2H_6$ for thermal chlorine atom reactions is unchanged over this pressure range. If significant recycling of $^{38}Cl$ through the decomposition reaction (3) were occurring, a diminished efficiency for $^{38}Cl$ removal
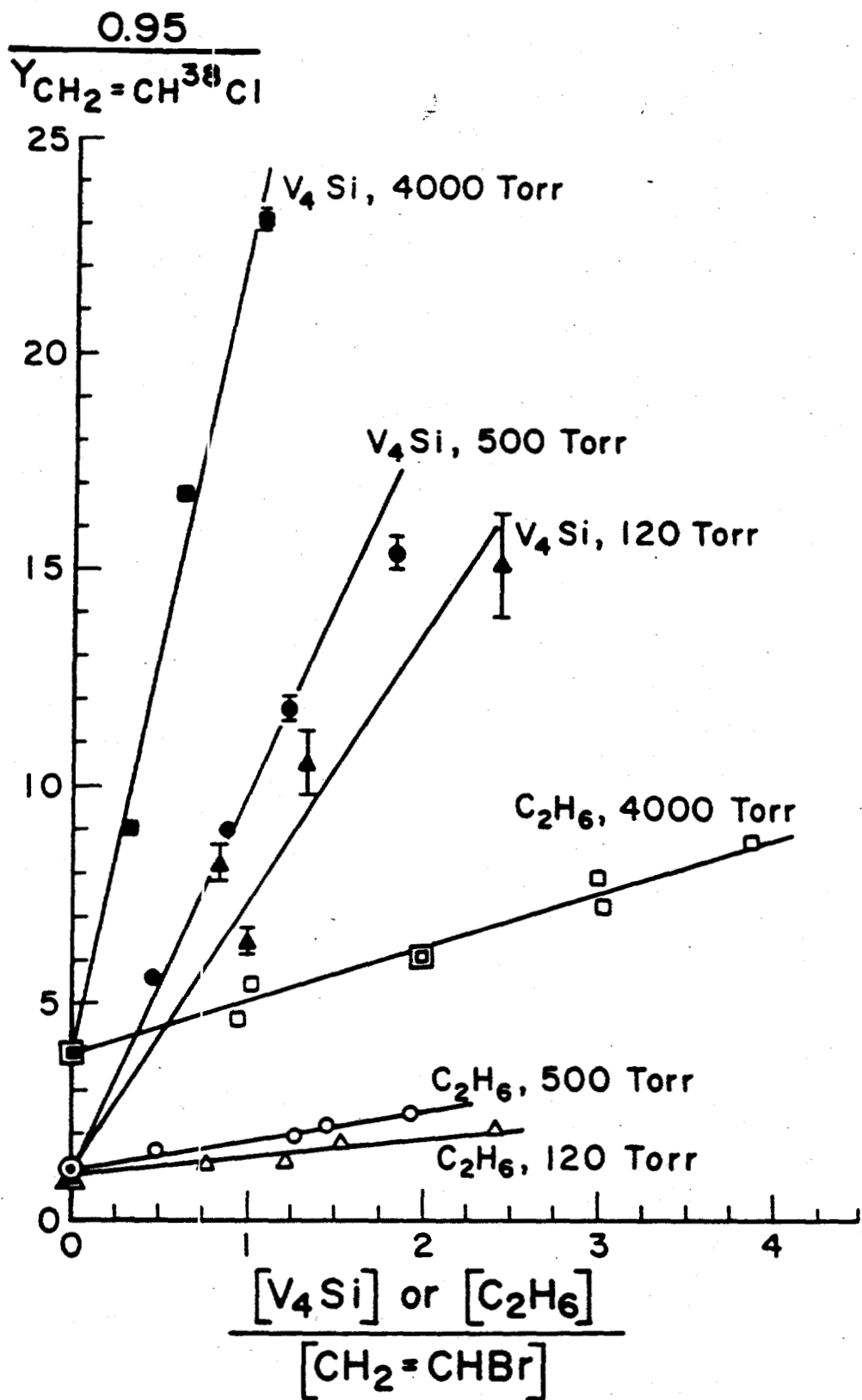
Figure 1. Reciprocal yields of $CH_2=CH^{38}Cl$ from thermal $^{38}Cl$ plus $CH_2=CHBr$ vs. $[C_2H_6]/[CH_2=CHBr]$ ratio in competitive experiments at various total pressures.

by $V_4Si$ would be expected as the pressure is decreased in these competitive runs. These experimental data indicate a pressure less than 100 torr for half-stabilization ($k_3=k_4[M']$) of $V_3SiCHCH_2{}^{38}Cl^*$ radicals and suggest no "blocking effect" of energy distribution by the Si atom in this radical. This observation of RRKM behavior with Si vs. non-RRKM behavior with Sn as the central atom is consistent with the hypothesis of the mass of the central atom as a factor in the "blocking effect" proposed for the Group IV organometallic compounds.[1,4,5] Experiments with $(CH_2=CH)_4Ge$ and $(CH_2=CH)_4Pb$ as the substrates for thermal $^{38}Cl$ reactions would be useful for further confirmation of this hypothesis.

The lack of a pressure effect on the $k^{eff}$ values obtained implies that both the decomposition reaction (3) and (5) are not significant in the 120-4000 torr pressure range of these experiments and therefore, $k^{eff}=k_1+k_2$. The radioactivity measurements in the experiments at 4000 torr have greater statistical accuracy and the conditions $k_3 \ll k_4[M']$ and $k_5 \ll k_6[M']$ are most satisfied at this highest pressure used for the experiments. The measured value of $k^{eff}$ at this pressure then gives a value of $(8.4 \pm 0.6) \times 10^{-10} cm^3$ molecule$^{-1}$sec$^{-1}$ for $(k_1+k_2)$. When the uncertainty factor of 1.1 is the reference rate constant for $C_2H_6{}^8$ is included, the absolute rate constant, $(k_1+k_2)$ for the addition of chlorine atom to $(CH_2=CH)_4Si$ at 295K is $(8.4 \pm 1.0) \times 10^{-10} cm^3$molecule$^{-1}$sec$^{-1}$.

(b)     (CH₂=CH)₃Sb

$CH_2=CH^{38}Cl$ was observed in high yields ($68 \pm 2\%$) from the reaction of thermal $^{38}Cl$ atoms with $(CH_2=CH)_3Sb$. The experiments carried out over a pressure range of 50-4000 torr showed no change in the $CH_2=CH^{38}Cl$ yield with pressure as shown in Figure 2. This observation suggests that $k_5 \gg k_6[M']$. A pressure-independent direct homolytic substitution as in (9) can also account for the lack of pressure dependence of the $CH_2=CH^{38}Cl$ yields. Such a mechanism is indistinguishable in our experiments from the formation of $CH_2=CH^{38}Cl$ through the addition reaction (2) followed by the rapid decomposition in (5). However, the yield of $CH_2=CH^{38}Cl$ from (9) might be small relative to that from the addition-decomposition mechanism, based on the general observation of only low yields of $R^{38}Cl$ from $^{38}Cl$ reactions with $R_4M$ except in the case of M=Pb, as discussed in Section V of this report. For example, with $(CH_3)_4Sn$ as the substrate only 0.5% of the $^{38}Cl$ atoms reacted to form $CH_3{}^{38}Cl$. Similar experiments with $R_3Sb$ (R=$CH_3$, $C_2H_5$) would be useful to examine the yields of $R^{38}Cl$ from "direct" substitution at the Sb-C bond.

Competitive runs of $V_3Sb$ with $C_2H_6$ have been carried out at total sample pressures of 4000 torr and 110 torr. Plots of the reciprocal yields measured for $CH_2=CH^{38}Cl$ v. $[C_2H_6]/[V_3Sb]$ ratios at these two pressures are shown in Figures 3 and 4. At p=4000 torr, the linear plot obtained gave an intercept of $1.42 \pm 0.06$ and a slope of $0.086 \pm 0.006$. The intercept and slope for the p=110 torr data were $1.43 \pm 0.03$ and $0.074 \pm 0.006$ respectively. The lack of an increase in the yield of $CH_2=CH^{38}Cl$ with decreasing pressure, and the observation of identical slopes and intercepts for the plots in figures (3) and (4) suggest that in the pressure range 110-4000 torr, $k_5 \gg k_6[M']$ and
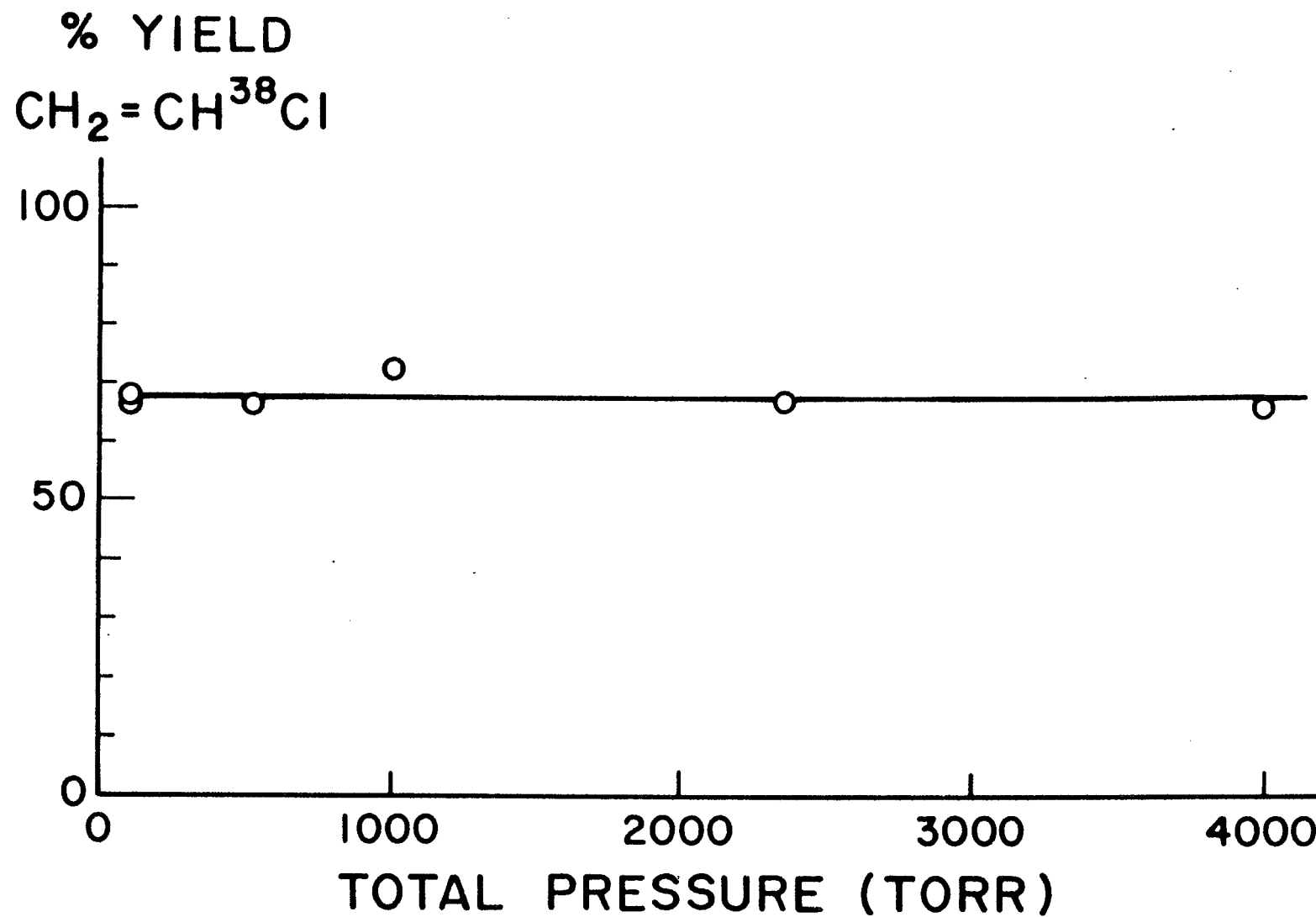
Figure 2. Percentage yields of $CH_2=CH^{38}Cl$ from thermal $^{38}Cl$ reactions with $(CH_2=CH)_3Sb$ vs. total pressure in neutron-irradiated mixtures of $CClF_3$, $(CH_2=CH)_3Sb$, and Ar.
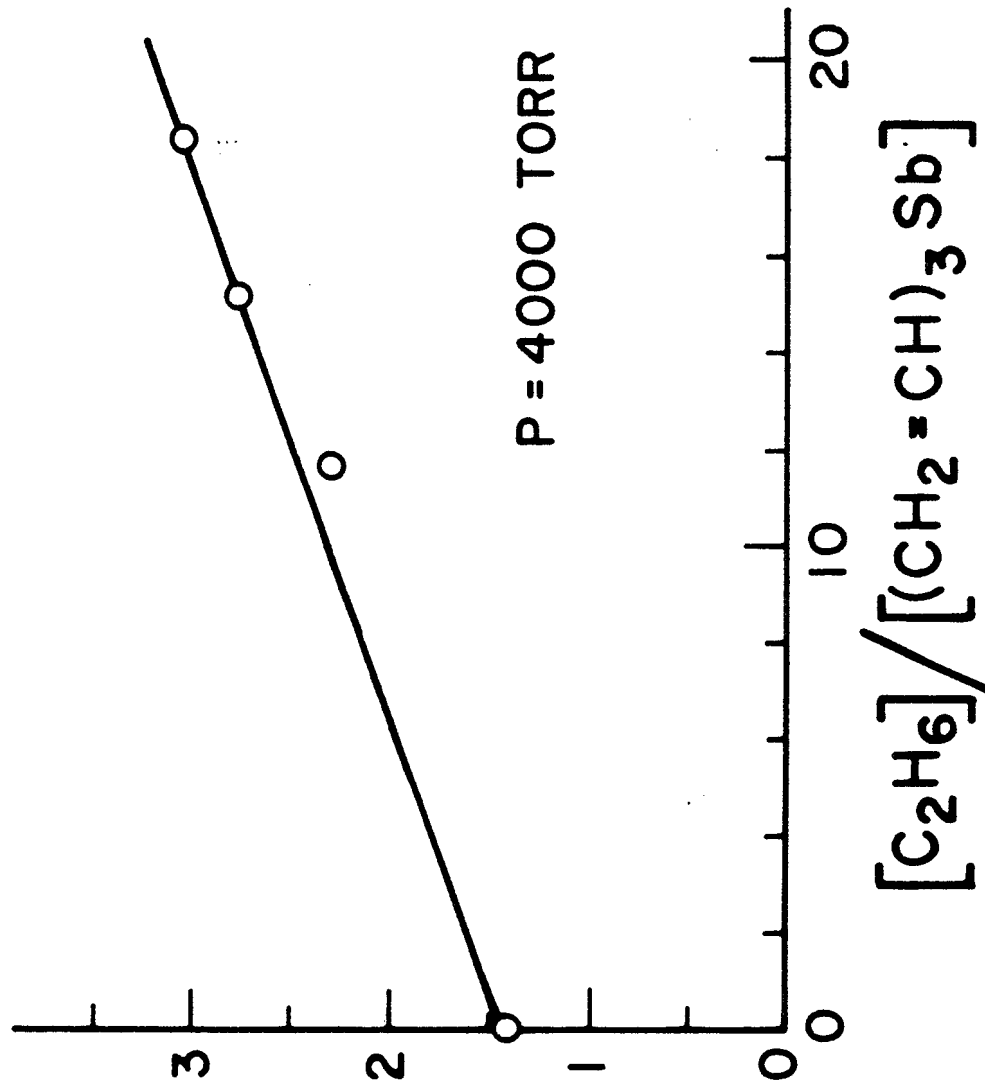
Figure 3. Reciprocal yields of $CH_2=CH^{38}Cl$ from thermal $^{38}Cl$ plus $(CH_2=CH)_3Sb$ vs. $[C_2H_6]/[(CH_2=CH)_3Sb]$ ratio in competitive experiments at a total pressure of 4000 torr in $CClF_3$.
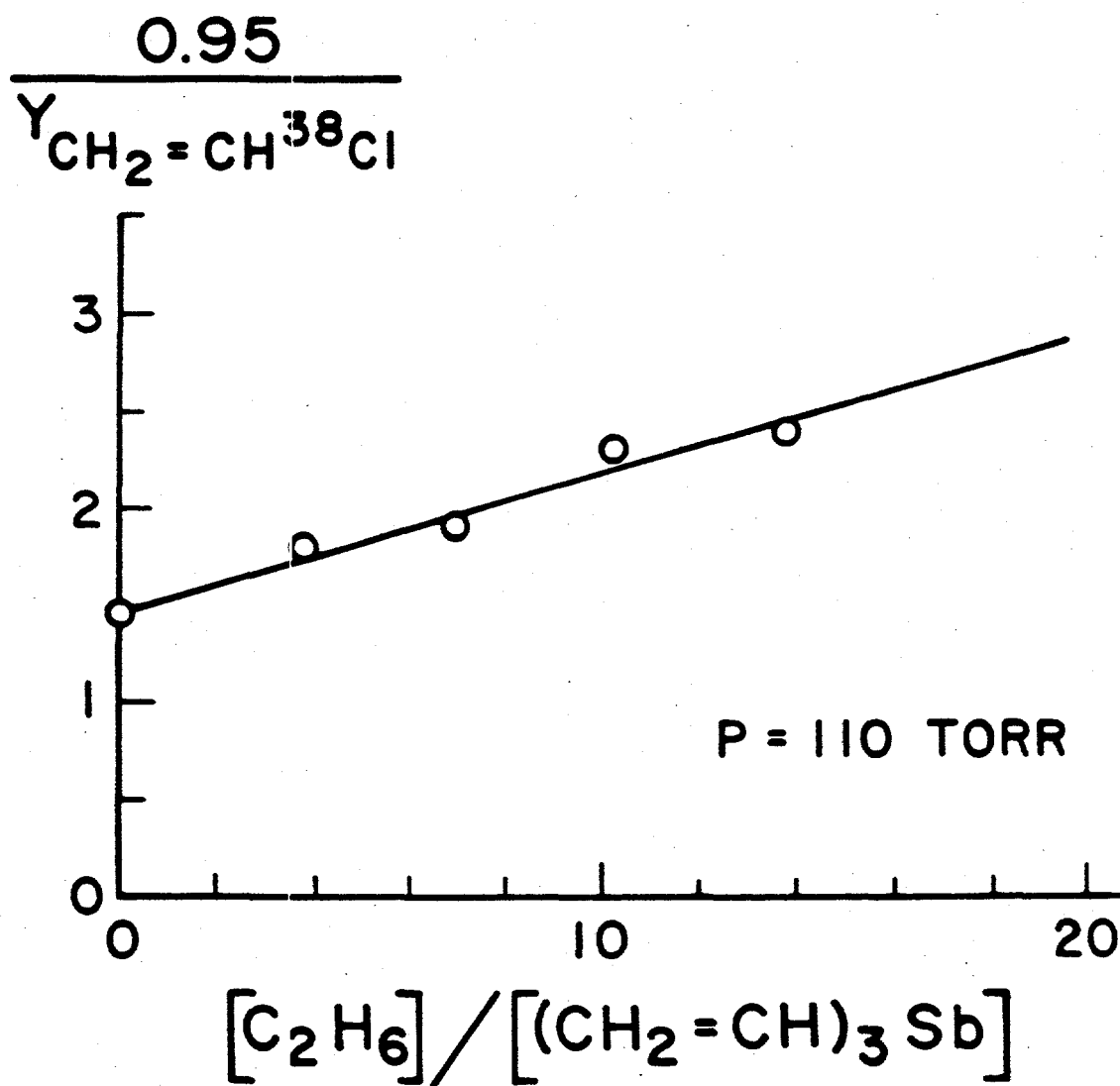
Figure 4. Reciprocal yields of $CH_2CH^{38}Cl$ from thermal $^{38}Cl$ plus $(CH_2=CH)_3Sb$ vs. $[C_2H_6]/[(CH_2=CH)_3Sb]$ ratio in competitive experiments at a total pressure of 110 torr in $CClF_3$.

$k_3 \ll k_4[M']$. If significant fraction of the $V_2SbCHCH_2{}^{38}Cl^*$ radicals were decomposing by $^{38}Cl$ loss (3). An increase in the yield of $CH_2=CH^{38}Cl$ with decreasing pressure as well as a lower intercept for the p=110 torr data in figure 4 would have been expected, as observed in the case of $(CH_2=CH)_4Sn$.[1] The observation that $k_3 \ll k_4[M']$ even at p=110 torr suggests that there is no evidence from these experiments for a non-RRKM behavior in the decomposition of $V_2SbCHCH_2{}^{38}Cl^*$. This sharp difference in the ability of Sn in $V_3SnCHCH^{38}Cl^*$ to "block" internal energy transfer vs the inability of Sb for a similar effect in $V_2SbCHCH_2{}^{38}Cl^*$, despite the similar masses of these two metal atoms, suggests that the mass of the heavy atom alone is insufficient to explain the proposed non-RRKM behavior. Perhaps differences arising from the geometry of these molecules -- tetrahedral with Sn in the center of the tetrahedron in $V_4Sn$, vs. pyramidal with Sb at the apex of the pyramid in $V_3Sb$ might also have a role in the ability of the heavy atom in blocking the energy transfer.

The addition of $^{38}Cl$ to $V_3Sb$ as in (10) to form an intermediate radical $V_3Sb^{38}Cl^*$ might be

$$^{38}Cl + V_3Sb \rightarrow V_3Sb^{38}Cl^* \qquad\qquad (10)$$

a possible reaction for thermal $^{38}Cl$ atoms in this system. A pressure dependent reverse decomposition of this radical releasing the $^{38}Cl$ can be excluded from the reaction mechanism as no pressure dependence is observed for the $CH_2=CH^{38}Cl$ yields. The subsequent fate of the $V_3SbCl^*$ radicals, if formed, is undetermined from the present experiments. With the conclusions made above that $k_5 \gg k_6[M']$ and $k_3 \ll k_4[M']$, the measured slope of $0.086 \pm 0.006$ in Figure 3 represents the rate constant ration $(k_8/k_2)$. Using the value of $k_8=5.7 \times 10^{-11} cm^3 molecule^{-1}s^{-1}$, $k_2$ is determined as $(6.6 \pm 0.5) \times 10^{-10} cm^3 molecule^{-1}s^{-1}$. As the measured yield of $CH_2=CH^{38}Cl$ is $(68 \pm 2)\%$, the overall rate constant, $(k_1 + k_2 + k_9 + k_{10})$ for thermal chlorine atom reactions with $V_3Sb$ (corresponding to reaction with $95 \pm 5\%$ of $^{38}Cl$ produced) is estimated as $(9.2\ 0.9) \times 10^{-10} cm^3 molecule^{-1}s^{-1}$.

(c) $(CH_2=CH)_2Hg$

The observations with $(CH_2=CH)_2Hg$ as the substrate for thermal $^{38}Cl$ reactions parallel those with $V_3Sb$. The observed yields of $CH_2=CH^{38}Cl$ were high $(65 \pm 4\%)$ and showed no variation with total pressures from 100 to 4000 torr (Figure 5). Competitive runs with $C_2H_6$ at total pressures of 120 torr and 4000 torr and plots (Figure 6) of the reciprocal yields of $CH_2=CH^{38}Cl$ against $[C_2H_6]/[V_2Hg]$ ratios showed no significant change in the slopes and intercepts with pressure. At 120 torr, the slope and intercept for this plot were determined to be $0.090 \pm 0.005$ and $1.51 \pm 0.03$ respectively. The values for the slope and intercept for the 4000 torr data were $0.093 \pm 0.003$ and $1.36 \pm 0.16$ respectively. These observations lead to the conclusion that for $V_2Hg$ also $k_3 \ll k_4[M']$ and $k_5 \gg k_6[M']$. as in the case of $V_2SbCHCH_2{}^{38}Cl^*$, no non-RRKM behavior is indicated by these experiments for $VHgCHCH_2{}^{38}Cl^*$. The difference in RRKM vs. non-RRKM behavior for M=Sb, Hg vs. M=Sn has not been definitely identified in mechanistic terms.

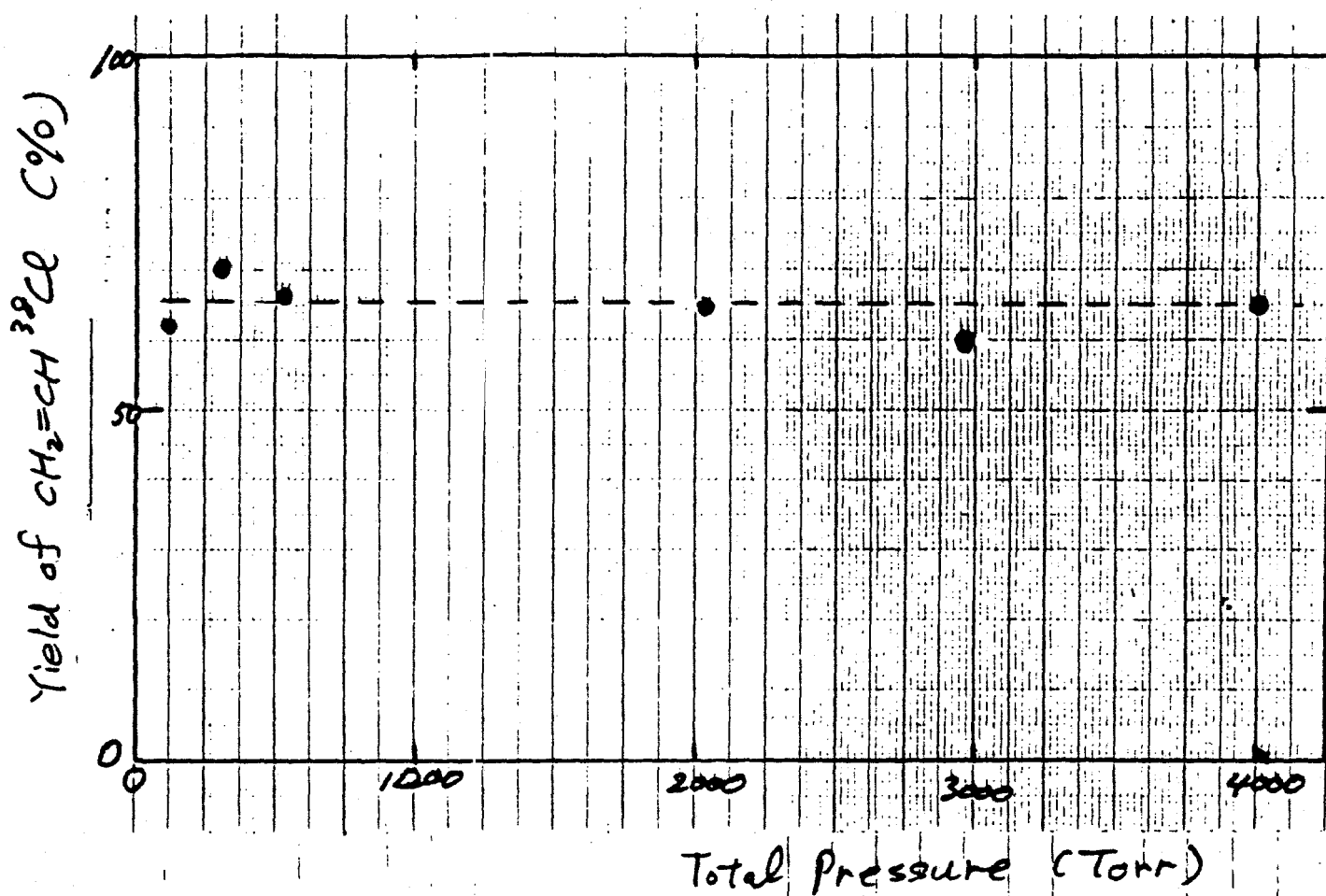Figure 5. Percentage yields of $CH_2=CH^{38}Cl$ from thermal $^{38}Cl$ reactions with $(CH_2=CH)_2Hg$ vs. total pressure in neutron-irradiated mixtures of $CClF_3$, $(CH_2=CH)_2Hg$, and Ar.
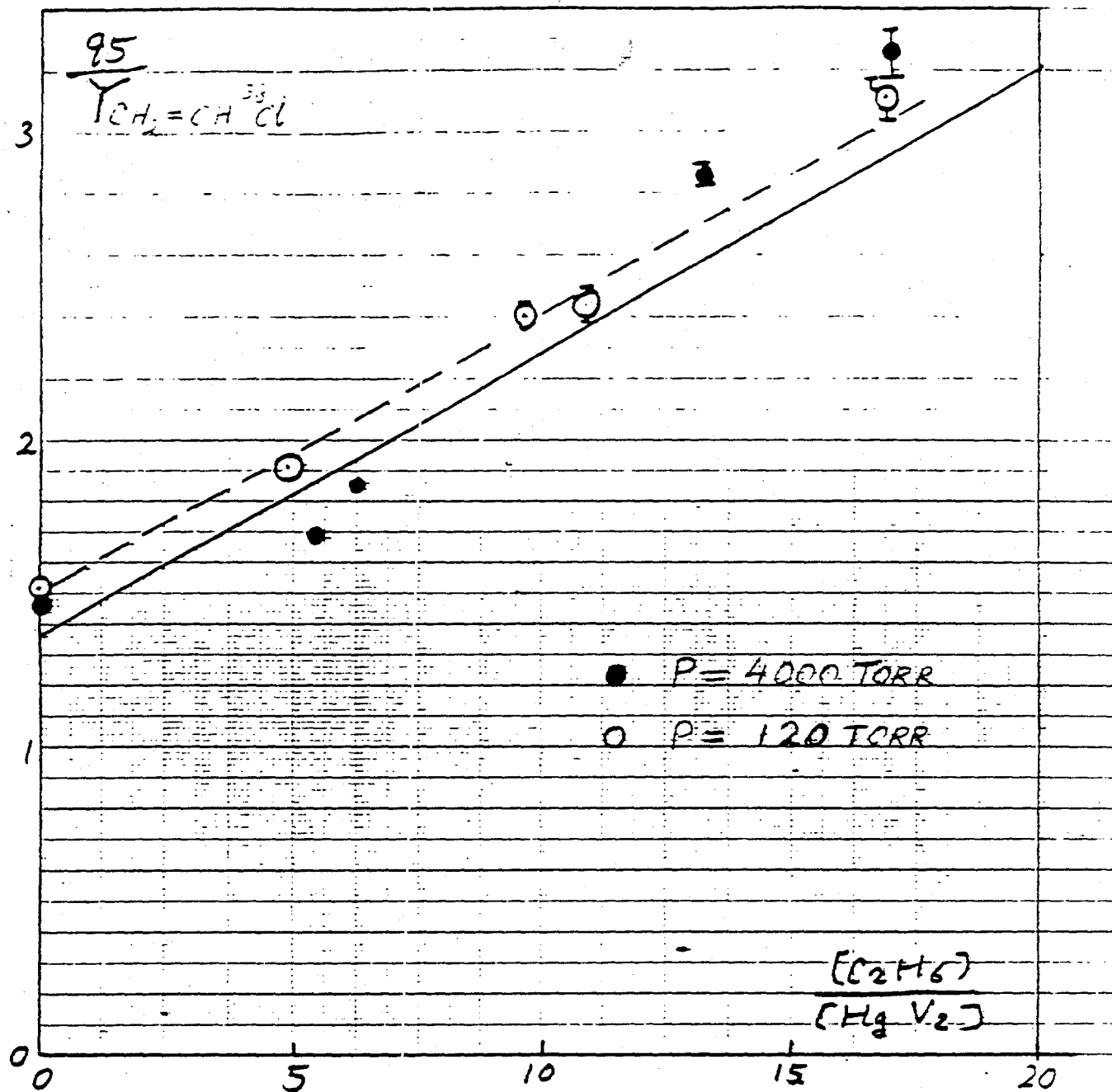
Figure 6. Reciprocal yields of $CH_2=CH^{38}Cl$ from thermal $^{38}Cl$ plus $(CH_2=CH)_2Hg$ vs. $[C_2H_6]/(CH_2=CH)_2Hg]$ ratio in competitive experiments at total pressures of 4000 torr (●), and 120 torr (O).

The competitive run data with $C_2H_6$ yields a relative rate constant, $(k_8/k_2)$ of $0.093 \pm 0.003$ at $P=4000$ torr. As $k_8 = 5.7 \times 10^{-11} cm^3 molecule^{-1}s^{-1}$, the value of $k_2$ is determined as $(6.1 \pm 0.2) \times 10^{-10} cm^3 molecule^{-1}s^{-1}$. The observed yield of $CH_2=CH^{38}Cl$, interpreted to be resulting from reaction (2) followed by the rapid decomposition (5) for M=Hg has been determined to be $65 \pm 4\%$. The overall rate constant for thermal $^{38}Cl$ reaction with $V_2Hg$ is; therefore, estimated as $(8.9 \pm 0.8) \times 10^{-10} cm^3 molecule^{-1}s^{-1}$. In addition to the addition channels (1) and (2) this overall rate constant might include other possible reactions of $^{38}Cl$ with $V_2Hg$ such as the direct substitutions at the Hg-C bond to form either $CH_2=CH^{38}Cl$ or $VHg^{38}Cl$ as in (11) and (12).

$$^{38}Cl + VHgCH=CH_2 \rightarrow VHg + CH_2=CH^{38}Cl \qquad (11)$$

$$^{38}Cl + VHgCH=CH_2 \rightarrow VHg^{38}Cl + CH_2=CH \qquad (12)$$
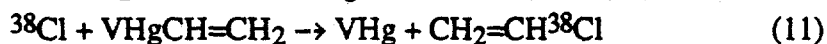
The formation of $CH=CG^{38}Cl$ with no pressure dependence by reaction (11) is experimentally indistinguishable from its formation through reaction (2) followed by rapid decomposition (5). The yield of $CH_2=CH^{38}Cl$ from such a direct substitution reaction (11) may be relatively small, based on the observation of less than 1% yield of $CH_3{}^{38}Cl$ from $^{38}Cl$ reaction with $(CH_3)_2Hg$.[9] Whether or not reaction (12) is significant has not been determined from the present experiments.

The overall rate constants measured for thermal chlorine atom reactions with $V_nM$ (M=Sn, Si, n=4; M=Sb, n=3; and M=Hg, n=2) and the rate constants for reaction per $CH_2=CH$-group obtained by dividing the total rate constant by n for each of these substrates are listed in Table 2.

Table 2. Rate constants for Thermal Chlorine Atom Reactions (T=295K)

| Substrate | Overall Rate Constant $(cm^3 molecule^{-1}s^{-1})$ | Rate Constant per $CH=CH$-group $(cm^3 molecule^{-1}s^{-1})$ |
|---|---|---|
| $(CH_2=CH)_4Sn$ | $6.9 \times 10^{-10}$ [a] | $1.7 \times 10^{-10}$ |
| $(CH_2=CH)_4Si$ | $8.4 \times 10^{-10}$ | $2.1 \times 10^{-10}$ |
| $(CH_2=CH)_3Sb$ | $9.2 \times 10^{-10}$ | $3.1 \times 10^{-10}$ |
| $(CH_2=CH)_2Hg$ | $8.9 \times 10^{-10}$ | $4.5 \times 10^{-10}$ |

a. Reference 1.

Earlier studies of chlorine atom addition to $CH_2=CH_2$, $CH_3CH=CH_2$, and $CH_2=CHX$ (X=F, Cl, Br) substrates have demonstrated rate constants for each of $(1.5-2.0) \times 10^{-10} cm^3 molecule^{-1}s^{-1}$.[1-3,10-12] The rate constants per $CH_2=CH$-group for $V_4Sn$ and $V_4Si$ also fall in this range, consistent with the conclusion that in these cases, the measured rate constants represent the sum of the rate constants for the two addition channels (1) and (2). All these addition reactions are quite rapid,

occurring almost on every collision. The higher values of the rate constants on a per $CH_2$=CH-group basis observed in the case of $V_3Sb$ and $V_2Hg$ might be an indication that the overall rates measured in these cases include additional reaction channels for chlorine atoms besides reactions (1) and (2), as discussed earlier.

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## IV. GAS PHASE REACTIONS OF THERMAL CHLORINE ATOMS WITH $(CH_3)_4$ M (M=C, Si, Ge, Sn, Pb)

The formation of $CH_3^{38}Cl$ as one of the products in substantial yields from the reaction of thermal $^{38}Cl$ atoms with $(CH_3)_4Pb$ has been reported previously.[1] The $CH_3^{38}Cl$ yield data in those experiments showed no pressure dependence over 500-5000 torr pressure range indicating that the mechanism for $CH_3^{38}Cl$ formation did not involve any intermediate with lifetimes $> 10^{-10}$ sec. The formation of $CH_3^{38}Cl$ was therefore concluded to be the result of a direct bimolecular substitution at the Pb-C bond. Similar direct substitution processes yielding $R^{18}F$ have been observed earlier in thermal $^{18}F$ reactions with various organo-tin compounds $(R_4Sn)$.[2]

The occurrence of reaction (1) has now been examined for the entire Group IV tetramethyls

$$^{38}Cl + (CH_3)_4M \rightarrow CH_3^{38}Cl + (CH_3)_3M \qquad (1)$$

using $^{38}Cl$ atoms produced by $(n,\gamma)$ reaction in $CClF_3$ and moderated to thermal energies in samples containing an excess ($>95\%$) of $CClF_3$ as the moderator.[3] With $(CH_3)_4Pb$ as the substrate, $(22\pm1)\%$ of the $^{38}Cl$ atoms have been observed as $CH_3^{38}Cl$ over the total sample pressure range of 500-4000 torr. As expected, the addition of an competitor $(C_2H_6)$ for thermal $^{38}Cl$ atoms in the sample mixtures decreases the yield of $CH_3^{38}Cl$ with increasing $[C_2H_6]/[(CH_3)_4Pb]$ ratios, as shown in Figure 1. The lack of any pressure dependence on the $CH_3^{38}Cl$ yield data can be seen in these competitive runs also by the single straight line fitting the data obtained for total sample pressures from 500 to 4000 torr. The slope of the straight line plot obtained in Figure 1 is equal to the ratio of the rate constant for chlorine atom reaction (2) with $C_2H_6$ to that for reaction (1) with $(CH_3)_4Pb$. The measured slope for the plot in

$$^{38}Cl + C_2H_6 \rightarrow H^{38}Cl + C_2H_5 \qquad (2)$$

Figure 1 is $0.59\pm0.03$, and using the recommended[4] rate constant of $5.7 \times 10^{-11} cm^3 molecule^{-1}sec^{-1}$ for the hydrogen abstraction reaction (2), the rate constant for reaction (1) with $(CH_3)_4Pb$ is determined to be $(9.66 \pm 0.49) \times 10^{-11} cm^3 molecule^{-1}sec^{-1}$. When the uncertainty factor of 1.1 for the reference rate constant $k_2$[4] is included, the value of $k_1$ is $(9.7 \pm 1.4) \times 10^{-11} cm^3 molecule^{-1}sec^{-1}$ for M=Pb.

With $(CH_3)_4Sn$ as the reacting molecule, a small yield $(0.5\%)$ of $CH_3^{38}Cl$ was observed, again independent of total sample pressures from 500 to 400 torr. The experiments carried out with $(CH_3)_4Ge$, $(CH_3)_4Si$, and $(CH_3)_4C$ showed no detectable yields $(\pm0.1\%)$ of $CH_3^{38}Cl$. The overall rate constant for chlorine atom reaction with $(CH_3)_4Sn$ has been determined from competitive experiments with $CH_2=CHBr$ (discussed later in this section) to be $(2.66 \pm 0.31) \times 10^{-10} cm^3 molecule^{-1}sec^{-1}$. With 95% of $^{38}Cl$ atoms available for thermal reactions with $(CH_4)_4Sn$ to be $(1.37\pm0.19) \times 10^{-12} cm^3 molecules^{-1}sec^{-1}$.

The trend observed in the values of $k_1$ for the Group IV tetramethyls can be seen to depend markedly on the strengths of the $(CH_3)_4M$-$CH_3$ bonds. The dissociation energies for these bonds in
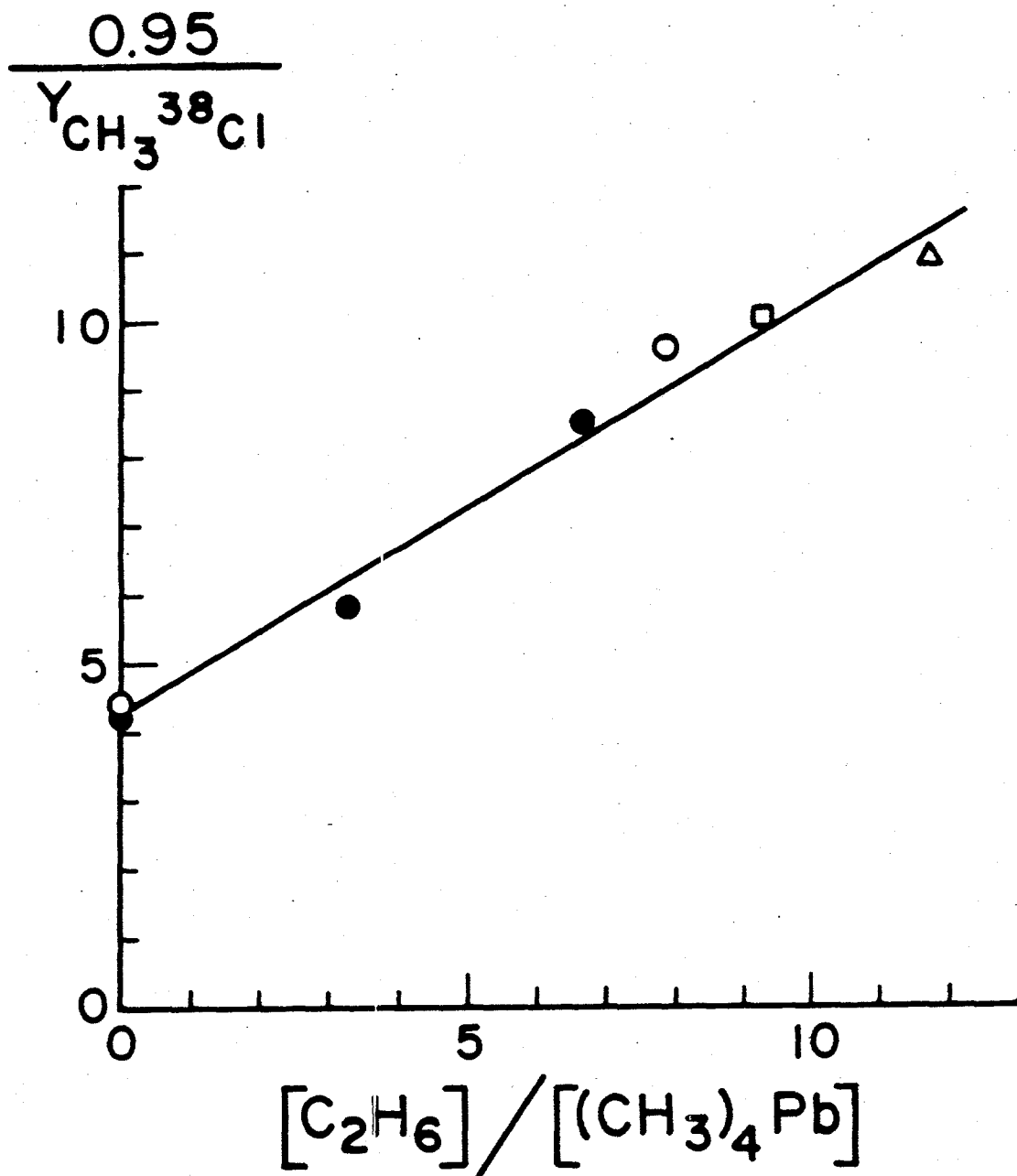
Figure 1. Reciprocal yields of $CH_3{}^{38}Cl$ from thermal $^{38}Cl$ plus $(CH_3)_4Pb$ vs. $[C_2H_6]/[(CH_3)_4Pb]$ ratio in competitive experiments. total pressures (in torr): 500, 0; 1500, □ ; 3000, △ ; 4000, ●.
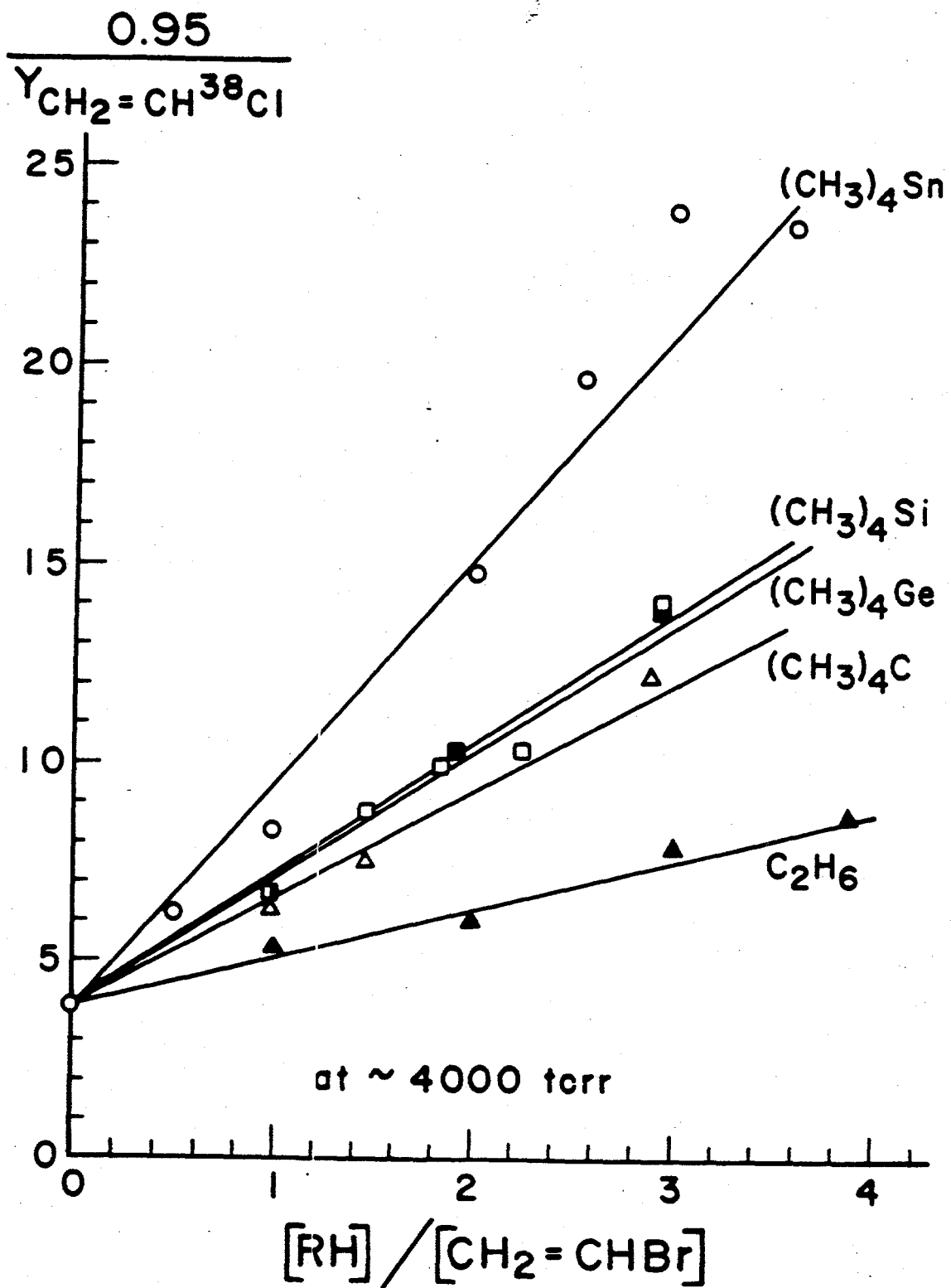
Figure 2. Reciprocal yields of $CH_2=CH^{38}Cl$ from thermal $^{38}Cl$ plus $CH_2=CHBr$ vs. [RH]/[$CH_2=CHBr$] ratio in competitive experiments at a total pressure of 4000 torr in $CClF_3$. RH: $(CH_3)_4Sn$, O; $(CH_3)_4Si$, □; $(CH_3)_4Ge$, ■; $(CH_3)_4C$, △; $C_2H_6$, ▲.

Table I.

Rate Constant for Chlorine Atom Reactions with $(CH_3)_4M$

| S | Measured Slope | $k_S/K_3$ | $k_S \times 10^{10}$ $(cm^3molecule^{-1}sec^{-1})$ [a] |
|---|---|---|---|
| $(CH_3)_4C$ | $2.72 \pm 0.22$ | $2.22 \pm 0.28$ | $1.27 \pm 0.16$ |
| $(CH_3)_4Si$ | $3.29 \pm 0.26$ | $2.70 \pm 0.34$ | $1.54 \pm 0.19$ |
| $(CH_3)_4Ge$ | $3.20 \pm 0.18$ | $2.62 \pm 0.30$ | $1.49 \pm 0.17$ |
| $(CH_3)_4Sn$ | $5.69 \pm 0.34$ | $4.66 \pm 0.54$ | $2.66 \pm 0.31$ |
| $(CH_3)_4Pb$ | | | $4.17 \pm 0.36$ [b] |
| $C_2H_6$ | $1.22 \pm 0.12$ | 1.00 (Reference) | 0.57 (ref. 4) |

a. The uncertainties are $1\sigma$ of these measurements, and do not include the uncertainty factor of 1.1 in the rate constant for $C_2H_6$[4].

b. Using data from $(CH_3)_4Pb/C_2H_6$[4].

The total reactivities of the tetramethyls of C, Si, and Ge towards thermal chlorine atoms can be seen to be about the same while the observed reactivites of $(CH_3)_4Sn$ and $(CH_3)_4Pb$ relative to that of $(CH_3)_4C$ are higher by factors of 2 and 3 respectively. The abstraction of H from $(CH_3)_4M$ as in (5) is believed to be the predominant thermal $^{38}Cl$ reaction for these compounds, although the

$$^{38}Cl + (CH_3)_3MCH_3 \rightarrow (CH_3)_3MCH_2 + H^{38}Cl \qquad (5)$$
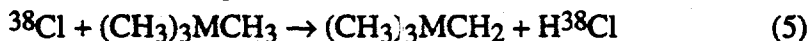
product $H^{38}Cl$ is not measured in our standard radio gas chromatographic technique[3]. The substitution of a $CH_3$ group in $(CH_3)_4M$ by chlorine an atom as in (6) is endothermic (6 kcal/mole) for M=C and is exothermic for M=Si, Ge, Sn and Pb.[5] The endothermic reaction (6) is not expected

$$^{38}Cl + (CH_3)_3MCH_3 \rightarrow (CH_3)_3M^{38}Cl + CH_3 \qquad (6)$$
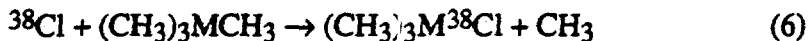
to occur in our experiments carried out at 296K, and the only reaction of importance for thermal $^{38}Cl$ reaction with $(CH_3)_4C$ is, therefore, the H-abstraction reaction (5). The measured values of $k_S$ for $(CH_3)_4C$, $(CH_3)_4Si$, and $(CH_3)_4Ge$ are the same within the error limits (Table I.). Hence, it is reasonable to conclude that for these three tetramethyls $k_5 >> (k_1 + k_6)$ and therefore, $k_S = k_5$. For $(CH_3)_4Sn$, $k_1 = (1.37 \pm 0.19) \times 10^{-12} cm^3 molecule^{-1} sec^{-1}$, and by difference $(k_5 + k_8) = (k_S - k_1) = (2.65 \pm 0.31) \times 10^{-10} cm^3 molecule^{-1} sec^{-1}$. Similarly, for $(CH_3)_4Pb$ $k_1 = (9.66 \pm 0.49) \times 10^{-11} cm^3 molecule^{-1} sec^{-1}$, and $(k_5 + k_S)$ is estimated as $(k_S - k_1) = (3.20 \pm 0.36) \times 10^{-10} cm^3 molecule^{-1} sec^{-1}$. If we can assume that for these two tetramethyls also $k_6 << k_5$, the values of $(k_S - k_1)$ would represent the rate constants $(k_5)$ for H-abstraction from these molecules. The rate constant values thus obtained for the H-abstraction reaction from the various tetramethyls are compared in Table II.

**Table II.**
**Absolute Reaction Rate Constants for Abstraction of Hydrogen from $M(CH_3)_4$ Substrates.**

| $M(CH_3)_4$ | $k_5 (cm^3 molecule^{-1} sec^{-1})^a$ |
|---|---|
| $C(CH_3)_4$ | $(1.27 \pm 0.16) \times 10^{-10}$ |
| $Si(CH_3)_4$ | $(1.54 \pm 0.19) \times 10^{-10}$ |
| $Ge(CH_3)_4$ | $(1.49 \pm 0.17) \times 10^{-10}$ |
| $Sn(CH_3)_4$ | $(2.65 \pm 0.31) \times 10^{-10}$ |
| $Pb(CH_3)_4$ | $(3.20 \pm 0.36) \times 10^{-10}$ |
| $C_2H_6$ | $(5.7 \times 10^{-11})$ (Standard) |

a. For M=Sn and Pb the values $k_5$ are based on the assumption that $k_5 >> k_6$.

The abstraction rate constants with $(CH_3)_4C$, $(CH_3)_4Si$ and $(CH_3)_4Ge$ are all within 2.3 to 2.7 times as rapid as with $C_2H_6$, which is itself a very rapid reaction. These molecules each have twice as many H atoms as $C_2H_6$, and the availability of each of the 12 individual C-H bonds is therefore about 15% to 35% greater per C-H bond in these three $(CH_3)_4M$ molecules than for the six C-H bonds in $C_2H_6$. However, hydrogen abstraction from the 12 C-H bonds in $(CH_3)_4Sn$ and $(CH_3)_4Pb$ are, respectively, 2.3 and 2.8 times easier per C-H bond than from $C_2H_6$. In contrast to the observations of steadily weakening C-M bond strengths with increasing atomic weight of M, the C-H bond strengths are quite similar and actually strengthen perceptibly in the sequence C, Si, Ge, Sn, Pb.[6] The explanation for increasing yield of $H^{38}Cl$ with heavier central atoms is not clear, but may be related to an energetically or sterically easier relaxation process for the residual $(CH_3)_3PbCH_2$ than for $(CH_3)_3SiCH_2$ radical because of longer C-M bonds (2.29 Å for Pb-C versus 1.87 Å for Si-C and 1.54 Å for C-C). Energetically easier pathways and consequent higher yields were postulated earlier for abstraction reactions from $CH_4$, $CHF_3$, etc. by energetic tritium atoms when the residual radical structure from the transition state of the abstraction reaction is more nearly like the fully relaxed radical structure.[7]

The abstraction of H from $(CH_3)_4M$ (M=C,Si, Ge, Sn) by $CF_3$, $CD_3$, and $CH_3$ radicals have been reported to show a reactivity sequence Si>Sn>Ge>C with silicon having approximately twice the reactivity of carbon. This observed sequence in reactivity was reported to follow the Allred-Rochow electronegativity values of the central atom and also qualitatively correlate with the proton chemical shifts. These abstraction reactions are extremely slow compared to those with Cl atoms,

e.g. H abstraction from $(CH_3)_4Sn$ at 298K by $CF_3$ radicals is slower by a factor of 108 as compared to Cl. The very fast reactions with Cl atoms show no obvious difference in reactivity for C, Si, and Ge and the observed sequence from our data is $Pb>Sn>Ge\sim Si\sim C$. The observed increase in reactivity for $(CH_3)_4Sn$ relative to $(CH_3)_4C$ is a factor of 2. A similar incrase by a factor of 2 has been reported for $CF_3$ reactions with these two compounds.

An exchange reaction as in (7) has been reported to occur for the reactions of $CF_3$ radicals with $(CH_3)_4Sn$. At 423K the relative rate for this exchange versus H abstraction has been reported to

$$CF_3 + (CH_3)_3SnCH_3 \rightarrow (CH_3)_3SnCF_3 + CH_3. \qquad (7)$$
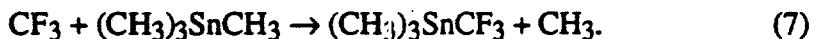
be 0.11. Whether or not a similar substitution reaction occurs for Cl atom reaction with $(CH_3)_4Sn$ and $(CH_3)_3Pb$ has not been established from our experiments. The radio gas chromatographic procedures used in these experiments have been confined to the measurements of products such as $CH_3{}^{38}Cl$ and $CH_2=CH^{38}Cl$ which are readily eluted from the 30-ft dimethylsulfolane column used for the product separation. No search for products with long retention times (>2 hours) has been made in these analyses. The procedure can readily be modified to elute other volatile products such as $(CH_3)_3C^{38}Cl$ and $(CH_3)_3Si^{38}Cl$ if formed in these experiments. However, these products are not expected to be formed from thermal $^{38}Cl$ reaction with the corresponding tetramethyls. With increasing exothermicity of the Cl-for $CH_3$ substitution reactions in $(CH_3)_4M$ with M=Ge, Sn and Pb, the possibility exists for the formation of $(CH_3)_3M^{38}Cl$, and further experimentation is needed to examine if such substitutions do occur. The analysis of such products may require the use of gas chromatographic columns and conditions not commonly used in our routine experiments. Attempts made earlier to search for similar products in the reactions of thermal $^{18}F$ atoms with selected organotin compounds failed to show the elution of any $R_3Sn^{18}F$ products.[8]

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## V. HYDROGEN ABSTRACTION REACTIONS BY THERMAL CHLORINE ATOMS WITH HFCs, HCFCs, AND HALOMETHANES

Concern about the role of man-made chlorinated and brominated compounds has prompted interest in the atmospheric sink reactions for other compounds in addition to the fully-halogenated CFCs (e.g. $CCl_2F_2$, $CCl_3F$, $CCl_2FCClF_2$), halons (e.g. $CBrF_3$, $CBrClF_2$, $CBrF_2CBrF_2$), and carbon tetrachloride, ($CCl_4$). The prime atmospheric removal process in the troposphere for compounds with C-H bonds is usually reaction with hydroxyl radicals, as in reaction (1). However, the major removal process in the stratosphere for molecules such as ethane is believed to be reaction with chlorine atoms,[1] as in reaction (2). The major factor in determining whether Cl reactions are

$$RH + HO \rightarrow H_2O + R \qquad (1)$$

$$C_2H_6 + Cl \rightarrow HCl + C_2H_5 \qquad (2)$$

important sinks for such hydrogen-containing species as ethane is the relative magnitude of the reaction rate constants for attack by Cl versus attack by HO. The rate constant ratio $k_{Cl}/k_{HO}$ is known to be ~200 for $C_2H_6$ at 298K and ~700 at 220K[2] (the approximate temperature of the lower stratosphere). The proposed use of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) as refrigerants and blowing agents has brought new interest in their rate constants for reaction with HO and Cl radicals. The atmospheric chemistry of $CH_3Br$ has also received renewed attention in the past year because of the potentially very effective role played by atomic bromine in polar stratospheric ozone depletion. Although the reaction rates of HO with $CH_3Br$ and with HFCs and HCFCs are well-known, few data are available for their reaction rate constants with Cl. The primary known sources of tropospheric $CH_3Br$ are its use as a fumigant by the agricultural industry, production by marine algae and release during biomass burning. Two non-chlorinated substances, HFC-134a ($CH_2FCF_3$) and HFC-152a ($CH_3CHF_2$), have been proposed to replace CFC-12 (refrigerant), while HCFC-123 ($CHCl_2CF_3$) is an alternative for CFC-11 (blowing agent) and CFC-113 (cleaning agent).

Thermalized $^{38}Cl$ atoms formed from the neutron irradiation[3] of chlorotrifluoromethane ($CClF_3$) were used to determine the relative rate constants for hydrogen abstraction by Cl for HCFC-123, HCFC-124 ($CHClFCF_3$), HFC-134a and HFC-152a and other haloalkanes in the gas phase at 298K versus a common competitor, bromotrifluoroethylene. The decomposition product of the competitor reaction, $CF_2=CF^{38}Cl$, formed following $^{38}Cl$ addition to $CF_2=CFBr$ as in (3), can readily be measured by radiogas chromatography. The reactants, RH and

$$^{38}Cl + CF_2=CFBr \rightarrow (C_2F_3Br^{38}Cl)^* \rightarrow CF_2=CF^{38}Cl + Br \qquad (3)$$

CF2=CFBr, were present as minor components in mixtures with an excess (>0.90) of CClF3 at a total pressure of 4000 torr. About 10 torr of argon was also added to serve as an internal thermal neutron flux monitor through the $^{40}Ar$ (n,γ) $^{41}Ar$ nuclear reaction. The component gases were added to 20-ml cylindrical ampules made of Pyrex 1720 glass using standard vacuum line techniques. The sealed sample bulb was placed inside a TRIGA tube and irradiated in the rotating specimen rack of the UCI TRIGA Mark I nuclear reactor. Short irradiation times of 1 minute and a low reactor power level of 10kW were used to avoid complications from radiolysis. The irradiated samples were analyzed by radio-gas chromatography[4-7] using two chromatographic columns in series: 50-ft propylene carbonate on alumina (PCA) and 25-ft PCA[a] at 23°C for the separation of volatile radioactive products and a gas flow "sandwich" type proportional counter for radioactivity measurements.

In samples containing CF2=CFBr as the only reactant for thermal $^{38}Cl$ atoms, the yield of CF2=CF$^{38}$Cl has been measured to be 26.6 ± 1.0% at a total sample pressure of 4000 torr and T = 298K. When a competitor RH for reaction with thermal $^{38}Cl$ atoms (reaction (4)) is also present in the sample mixture, the relative rate constant for the two competitor reactions (3) and (4) is

$$^{38}Cl + RH \rightarrow R + H^{38}Cl \qquad (4)$$

determined through measurement of the diminished yields of CF2=CF$^{38}$Cl as the [RH]/[CF2=CFBr] ratio is increased.

The reciprocal yields of CF2=CF$^{38}$Cl, with allowance for a 5% loss of total $^{38}Cl$ through hot reactions,[3,4] are plotted against [RH]/[CF2=CFBr] ratios in Figures 1a through 1f for reactions at room temperature. These lines provide slopes whose ratios give the ratios of the respective rate constants ($\frac{k(RH)}{k(CH_4)} = \frac{slope\ (RH)}{slope\ (CH_4)}$). The reaction of Cl with CH4, with a well-known rate constant, was chosen as the basis for the conversion of the measured relative rate constants onto an absolute scale.

The experiments with methane, methyl fluoride, and methyl bromide as the competing reactant were carried out at two temperatures: 298K and 343K.[8] The high temperature samples were heated by immersion in boiling water for approximately 15 minutes and the temperature of the samples were kept constant while in the reactor by the use of a double-TRIGA tube filled with hot water at 343 ± 4K.

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[a] With one exception: For samples containing CH₃Cl as a reactant, a dimethylsulfolane (DMS) column was used in series with the PCA column. CH₃Cl and any CH₃$^{38}$Cl formed were retained in the DMS column while CF₂=CF$^{38}$Cl was allowed to elute from the column combination.

The measured slopes for the various [RH]/[CF$_2$=CFBr] competitive runs at 298K and the absolute rate constants using the recommended value[2] of $(1.0 \pm 0.1) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for RH = CH$_4$ are listed in Table 1. The rate constant values reported in the literature for these compounds are also listed for comparison. The reliability of the rate constant data obtained in this study is checked by comparing the ratio of the measured slope for CH$_3$Cl to that of CH$_4$ with the ratio of rate constants determined for these two compounds by other techniques. The value of $5.4 \pm 0.8$ obtained for the ratio of these slopes is in agreement within the uncertainty limits with the ratio of $4.9 \pm 1.1$ for the respective rate constants at 298K recommended[2] for these two compounds. The measured value for the rate constant of CH$_3$F plus Cl and of CH$_3$Br plus Cl at room temperature in this study are lower than the current literature values. For CH$_3$F, the value of $(2.2 \pm 0.3) \times 10^{-13}$ cm$^3$ molecule$^{-1}$sec$^{-1}$ obtained in this study is about 40% lower than the value reported by Manning and Kurylo[9] using the FPRF technique, which has the lowest quoted error limits of the three other reported measurements. For CH$_3$Br, the rate constant of $(2.3 \pm 0.3) \times 10^{-13}$cm$^3$molecule$^{-1}$sec$^{-1}$ from our measurements is about 60% lower than the value reported by Tschnikow-Roux et. al.[11]The measured rate constants of the HFCs and HCFCs studied compare with their current literature values as follows: While reactions of HFC-134a and HCFC-123 were found to be faster than their current literature values, the rate constant for HFC-152a obtained in this work does not support as high a rate constant for this molecule as has been reported (the path for H abstraction from C$_2$ being negligibly small), and the rate constants for HCFC-124 agree within uncertainty limits. While the three other measurements reported for HFC-152a show very good agreement, the rate constant determined for this compound in our study is lower by a factor of ~4.

The ratios of $k_{Cl}/k_{HO}$ have also been calculated (see Table 2). Atmospheric modeling suggests that reaction with Cl can become important as an atmospheric sink only when [Cl] x $k_{Cl}$ is much larger than [HO] x $k_{HO}$. Because [Cl]/[HO] $\approx$ 0.01 in the stratosphere,[1] $k_{Cl}$ must be at least 100 times greater than $k_{HO}$ for a given compound in order for the Cl sink to be of major importance. For each of the compounds studied, the results of this study as well as those reported in the literature for these compounds show that Cl reactions are a relatively minor sink in the stratosphere compared to HO.

Table 3 lists the rate constants for CH$_3$F and CH$_3$Br at a temperature of 343K. The ratio of the slope measured for CH$_4$/CF$_2$=CFBr competitive runs at 343K to that at T=298K is in good agreement with the temperature dependence recommended[2] for the Cl + CH$_4$ rate constant, suggesting a negligible temperature dependence for the olefinic addition reaction (3). For CH$_3$F, the rate constant obtained in this work is in good agreement with the value recommended by DeMore et. al.[2] The value obtained for CH$_3$Br at T=343K is about a factor of 5 lower than the value reported in the literature,[2] which suggests that further work would be very useful.

Previous studies using CH$_2$=CHBr as the common competitor with different RH substrates for $^{38}$Cl reaction have shown that plots of reciprocal yields of CH$_2$=CH$^{38}$Cl versus [RH]/[CH$_2$=CHBr] ratios yield straight lines whose slopes could be used for rate constant determination for the various RH compounds.[6,7,15] The olefin CH$_2$=CHBr as well as the various RH compounds (C$_2$H$_4$, C$_2$H$_6$, PH$_3$, HI, H$_2$S, and (CH$_3$)$_4$M and selected (CH$_2$=CH)$_4$M with M = C, Si, Ge, Sn, Pb) used in those competitive runs all react very rapidly with Cl atoms and sufficient data points were obtained by carrying out the experiments with [RH]/[CH$_2$=CHBr] ratios $\leq$ 5 and a high moderator (CClF$_3$) mole fraction of >0.97. In contrast RH compounds involved in the present experiments all react with chlorine atoms at much slower rates, with rate constants slower by $\geq$ 2 factors of 10 than the RH compounds of the previous studies. In competition with a reactive olefin such as CH$_2$=CHBr, these RH compounds are inert within experimental precision until the amounts of RH exceed the mole fractions for which the assumption of collisional thermalization of $^{38}$Cl is acceptable,

The choice of CF$_2$=CFBr in place of CH$_2$=CHBr as the common competitor was made with the hope that the fluorine substituents in the former would deactivate the $\pi$-bond towards thermal Cl atom addition and hence might be expected to serve as a weaker competitor than CH$_2$=CHBr for Cl atoms in the present experiments. Separate competitor runs of CF$_2$=CFBr and CH$_2$=CHBr with RH = C$_2$H$_6$ have shown that at a total pressure of 4000 torr in CClF$_3$ and T = 298K, the formation of CF$_2$=CF$^{38}$Cl from $^{38}$Cl reaction with the former is about 3 times slower than that for CH$_2$=CH$^{38}$Cl formation from the latter of only a factor of three. This diminution in reactivity does not really meet the need for a less reactive olefinic competitor. Nevertheless with CF$_2$=CFBr as the common competitor in the present series of experiments ratios of [RH]/[CF$_2$=CFBr] up to 800 were necessary to observe sufficient diminution in the yields of CF$_2$=CF$^{38}$Cl as shown the plots shown in Figures 1a through 2c. The mole fraction of CClF$_3$ has been maintained > 0.90. The use of such high concentrations of RH raises the concern as to whether or not non-thermal $^{38}$Cl reactions might be involved. Tests for the truly thermal nature of the rate constants by this technique will be carried out by determination of the temperature dependence of the rate constants for selected RH compounds (e. g. CH$_4$ and CH$_3$Cl) whose temperature dependent rate constants have been reported from other studies.

It can be seen in Figure 1 that the data points obtained for T = 298K show slight upward curvature as the [RH]/[CF$_2$=CFBr] ratio is increased. However, no such curvature is observed for the data at T = 343K, as can be seen from the plots shown in Figures 2a through 2c. Experiments are still under way to determine the cause of the curvature observed at room temperature.

**Table 1: Measured Slopes and Rate Constants, T=298K[a]**

| Competing Reagent | | Measured Slope | This Work $k_{Cl} \times 10^{13}$ $cm^3 \, molec^{-1} \, sec^{-1}$ | Literature $k_{Cl} \times 10^{13}$ $cm^3 \, molec^{-1} \, sec^{-1}$ |
|---|---|---|---|---|
| CH4 | | 0.0298 ± 0.0021 | | 1.0 ± 0.1[b] |
| CH3F | | 0.0665 ± 0.0040 | 2.2 ± 0.3 | |
| | | | | 3.60 ± 0.10[c] |
| | | | | 3.40 ± 0.35[d] |
| | | | | 4.21 ± 1.27[e] |
| CH3Cl | | 0.1610 ± 0.0127 | 5.4 ± 0.8 | |
| | | | | 4.9 ± 1.0[b] |
| CH3Br | | 0.0692 ± 0.0059 | 2.3 ± 0.3 | |
| | | | | 5.53 ± 1.7[f] |
| CH2FCF3 | (HFC-134a) | 0.0041 ± 0.0003 | 0.14 ± 0.02 | |
| | | | | 0.016 ± 0.002[d] |
| | | | | 0.014 ± 0.09[g] |
| CHCl2CF3 | (HCFC-123) | 0.0184 ± 0.0040 | 0.62 ± 0.12 | |
| | | | | 0.14 ± 0.02[d] |
| | | | | 0.122 ± 0.018[g] |
| CH3CHF2 | (HFC-152a) | 0.0164 ± 0.0013 | 0.55 ± 0.08 | |
| | | | | 2.40 ± 0.25[d] |
| | | | | 2.39 ± 0.07[g] |
| | | | | 2.64 ± 0.24[h] |
| CHClFCF3 | (HCFC-124) | 0.0019 ± 0.0003 | 0.062 ± 0.012 | |
| | | | | 0.027 ± 0.03[d] |
| | | | | 0.027 ± 0.058[b] |

[a] all reported errors 1σ,
[b] DeMore et al, (ref. 2) evaluation,
[c] Manning and Kurylo (ref. 9) using FPRF technique
[d] Tuazon et al. (ref. 10), using competitive photochlorination (CP) technique, and using an uncertainty in k(CH4) of ±20%
[e] Tschuikow-Roux et al.(ref. 11) using CP technique
[f] Tschuikow-Roux et al. (ref. 12) using CP technique
[g] Wallington and Hurley (ref. 13),
[h] Yano et al. (ref. 14) using CP technique

**Table 2: Rate Constants with HO and $k_{Cl}/k_{HO}$ at T=298K[a,b]**

| Competing Reagent | $k_{HO}(298) \times 10^{14}$, $cm^3$ $molec^{-1}$ $sec^{-1}$ | at T=298K: $k_{Cl}/k_{HO}$ |
|---|---|---|
| $CH_4$ | $0.65 \pm 0.07$ | $15 \pm 2$ |
| $CH_3F$ | $1.8 \pm 0.4$ | $12 \pm 3$ |
| $CH_3Cl$ | $4.4 \pm 0.9$ | $11 \pm 3$ |
| $CH_3Br$ | $3.0 \pm 0.3$ | $8 \pm 1$ |
| $CH_2FCF_3$ | $0.48 \pm 0.14$ | $3 \pm 1$ |
| $CHCl_2CF_3$ | $1.2 \pm 0.6$ | $5 \pm 3$ |
| $CH_3CHF_2$ | $3.7 \pm 0.7$ | $1.5 \pm 0.4$ |
| $CHClFCF_3$ | $2.7 \pm 0.5$ | $0.23 \pm 0.07$ |

[a]all reported errors $1\sigma$,
[b]All k(298) with HO DeMore *et al* (ref. 2) evaluation,
[c] all $k_{Cl}/k_{HO}$ ratios calculated with values from Tables 1 (this work) and from DeMore *et al* (ref. 2) evaluation


**Table 3: Measured Slopes and Rate Constants, T=343K[a]**

| Competing Reagent | Measured Slope | This Work $k_{Cl}(343) \times 10^{13}$ $cm^3$ $molec^{-1}$ $sec^{-1}$ | Reference 2 $k_{Cl}(343) \times 10^{13}$ $cm^3$ $molec^{-1}$ $sec^{-1}$ |
|---|---|---|---|
| $CH_4$ | $0.050 \pm 0.004$ | $1.68 \pm 0.24$ | |
| $CH_4$ | | | $1.86 \pm 0.37$ |
| $CH_3F$ | $0.122 \pm 0.002$ | $5.04 \pm 2.40$ | |
| $CH_3F$ | | | $5.09 \pm 4.42$ |
| $CH_3Br$ | $0.057 \pm 0.002$ | $1.90 \pm 0.24$ | |
| $CH_3Br$ | | | $9.42 \pm 3.30$ |

[a] all reported errors $1\sigma$

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# VI. HALF-STABILIZATION PRESSURE OF CHLORINE ATOMS PLUS ETHYLENE IN A NITROGEN BATH

Recent atmospheric measurements made by the Rowland group during the Airborne Arctic Stratospheric Experiment (AASE-II)[1] revealed readily detectable concentrations of ethylene under conditions for which most alkanes other than $CH_4$ and $C_2H_6$ are below the detection limit of about 2 parts in $10^{12}$. In the atmosphere, ethylene can undergo an exothermic addition reaction with either hydroxyl radicals or chlorine atoms, forming a vibrationally excited $HOC_2H_4*$ or $C_2H_4Cl*$ radical. These radicals will undergo reverse decomposition to the reactants unless stabilized by collision, and have no exothermic reaction paths. Reactions (1), (2), and (3) represent these

$$Cl + C_2H_4 \rightarrow C_2H_4Cl* \qquad (1)$$

$$C_2H_4Cl* + M \rightarrow C_2H_4Cl \qquad (2)$$

$$C_2H_4Cl* \rightarrow Cl + C_2H_4 \qquad (3)$$

reactions for chlorine atom addition to ethylene. In the troposphere, the dominant removal process for ethane and ethylene is by reaction with HO. Under these conditions in the remote troposphere are controlled by the inverse ratio of their respective rate constants with HO, $k_{C_2H_4}/k_{C_2H_6}$ with values $\geq 30$. The observed $[C_2H_6]/[C_2H_4]$ ratio in source regions can be in the 1 to 5 range but the remote tropospheric ratio falls quickly as expected from the higher reactivity of $C_2H_4$. However, in the stratosphere, recent atmospheric measurements made by the Rowland group revealed a $[C_2H_6]/[C_2H_4]$ ratio as high as 2 rather than 30. This observation of high $C_2H_4$ concentrations raises the interesting question of the sources and removal processes for $C_2H_4$ at these high altitudes, and the postulate has been made that the attack of HO or Cl on $C_2H_6$ can leave $C_2H_4$ as an insitu product. The study of Cl atom addition to $C_2H_4$ using air as the bath gas for collisional stabilization of the $C_2H_4Cl*$ radicals is of interest in understanding the role of Cl atoms as a sink for $C_2H_4$.

Previous work by Lee and Rowland has shown that the half-stabilization pressure, i.e. the pressure at which $k_3 = k_2[M]$, is $800 \pm 120$ torr in $CClF_3$ at 298K.[1] In our experiments using radioactive $^{38}Cl$, the $C_2H_4{}^{38}Cl$ radicals formed through reactions (1) and (2) are measured as $C_2H_5{}^{38}Cl$ following reaction with a radical scavenger such as HI or $H_2S$, reaction (4). The use of air as a bath gas in such

$$C_2H_4{}^{38}Cl + H_2S \rightarrow C_2H_5{}^{38}Cl \qquad (4)$$

experiments will cause interference with the measurements because of the reaction of $C_2H_4{}^{38}Cl$ with $O_2$. Hence, in the present set of experiments, we have resorted to the use of $N_2$ only as the bath gas in sample mixtures with $C_2H_4 + H_2S + CClF_3 + Ar$. It has been shown that the stabilization efficiencies of $O_2$ and $N_2$ are indistinguishable within experimental uncertainties ($\pm 10\%$).[3]
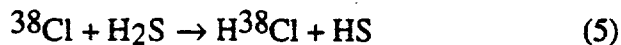
Radioactive $^{38}Cl$ and $^{41}Ar$ were produced as described in an earlier section, but with an irradiation time of 2 minutes rather than 1 minute to enhance the $^{38}Cl$ yield. The experiments were carried out at various ratios of $\dfrac{[H_2S]}{[C_2H_4]}$ a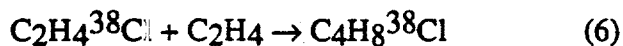t three pressures: 1000, 2000, and 3000 torr. The reaction intermediate, $C_2H_4{}^{38}Cl^*$ reacted with $H_2S$ following collisional stabilization, and the resulting radioactive product, $C_2H_5{}^{38}Cl$, was analyzed by radiogas chromatography using two chromatographic columns in series: 15-ft dimethylsulfolane (DMS) and 50-ft propylene carbonate on alumina (PCA). The radioactive molecules were again passed from the chromatographic columns into a gas flow "sandwich" type gas proportional counter for radioassay.

Plots of $\dfrac{0.95}{\text{Yield }(C_2H_5{}^{38}Cl)}$ versus $\dfrac{[H_2S]}{[C_2H_4]}$ ratios are shown in Figure 1 for the three pressures used for the measurements. Reaction (5) with $H_2S$ competes against $C_2H_4$ for reactions with $^{38}Cl$ atoms in these samples. If all the thermal $^{38}Cl$ atoms formed in these

$$^{38}Cl + H_2S \rightarrow H^{38}Cl + HS \qquad (5)$$

samples react by (1) and (2) to form $C_2H_4{}^{38}Cl$ or with $H_2S$ (reaction (5)) to form $H^{38}Cl$, and if the $C_2H_4{}^{38}Cl$ radicals are scavenged by $H_2S$ (reaction (4), a common intercept of 1.0 is expected for such a plot for all these pressures at $[H_2S]/[C_2H_4] = 0$. Previous experiments with HI as a radical scavenger and $CClF_3$ as the bath gas have shown results consistent with these arguments.[2] However, the data obtained in the present experiments show intercepts considerably greater than 1, as can be seen in Figure 1, indicating significant losses of $^{38}Cl$-products. An explanation for the "missing" $^{38}Cl$ fraction is that $H_2S$ dos not efficiently scavenge all the $C_2H_4{}^{38}Cl$ radicals formed. A fraction of these radicals are probably lost through reaction with $C_2H_4$ as in (6). If the

$$C_2H_4{}^{38}Cl + C_2H_4 \rightarrow C_4H_8{}^{38}Cl \qquad (6)$$

$C_4H_8{}^{38}Cl$ radicals are then scavenged by $H_2S$ to form $C_4H_9{}^{38}Cl$, the rather long retention times of such compounds on the DMS column used would have precluded their detection in the present experiments. The formation of such compounds can be tested using an appropriate g. c. column (e. g.

silicone oil) with shorter retention times for such products. The $C_2H_4^{38}Cl$ radicals in the present experiments might also be lost through reactions with the walls of the sample bulb and through reactions with other radicals formed in the system. Further experiments with higher $H_2S$ concentrations are currently being carried out to examine if the $C_2H_4^{38}Cl$ radicals can be scavenged quantitatively. If $C_2H_4^{38}Cl$ radicals are assumed to be partly removed through reaction (6) with $C_2H_4$ in competition with reaction (4) with $H_2S$, the expression (7) can be derived for the reciprocal yields of $C_2H_5^{38}Cl$ in these samples, where $A(p) = 1 + ( 1 + \dfrac{P_{1/2}}{P} ) \dfrac{k_5 k_6}{k_1 k_4}$.

$$\frac{0.95}{\text{Yield } (C_2H_5^{38}Cl)} = A(p) + \frac{k_5}{k_1} ( 1 + \frac{P_{1/2}}{P} ) \frac{[H_2S]}{[C_2H_4]} \qquad (7)$$

The reciprocal yield $\dfrac{0.95}{\text{Yield } (C_2H_5^{38}Cl)}$ is then directly proportional to $\dfrac{[H_2S]}{[C_2H_4]}$ which will give a slope

of $\dfrac{k_5}{k_1} ( 1 + \dfrac{P_{1/2}}{P} )$ when plotted against each other. When plotting at more than one pressure,

simultaneous equations of the slopes will yield a half-stabilization pressure for the reaction system. The straight lines obtained in Figure 1 are consistent with the existence of a kinetic competition between $C_2H_4$ and $H_2S$ for reaction with $^{38}Cl$ atoms. The increase in the value of the slope observed with decreasing pressure (Table 1) is also consistent with an increase in the fraction of $^{38}Cl$ released from reaction (3) with decreasing pressure; these $^{38}Cl$ atoms are then available for successive competitive reactions between $H_2S$ and $C_2H_4$ until they are finally bound as $H^{38}Cl$ or $C_2H_4^{38}Cl$. From the measured slopes at the three pressures, the half-stabilization pressure for $C_2H_4Cl*$ in $N_2$ is estimated as $2100 \pm 300$ torr at 298K. Such a high value for the $p_{1/2}$ implies negligible stabilization of $C_2H_4^{38}Cl*$ radicals at the stratospheric pressures of $p_{1/2} < 75$ torr, and hence poor efficiency for chlorine atom reactions as a removal process for $C_2H_4$. Further experiments using higher concentrations of $H_2S$ are being carried out for understanding the loss mechanism for $C_2H_4^{38}Cl$ radicals in the present runs. Experiments at temperatures relevant to the stratosphere will also be carried out.

**Table 1: Slopes of Plots at Each Pressure**

| Pressure (torr) | Slope | 1 s | R |
|---|---|---|---|
| 1034 | 3.746 | 0.761 | 0.895 |
| 2009 | 2.552 | 0.499 | 0.875 |
| 2996 | 2.109 | 0.384 | 0.867 |

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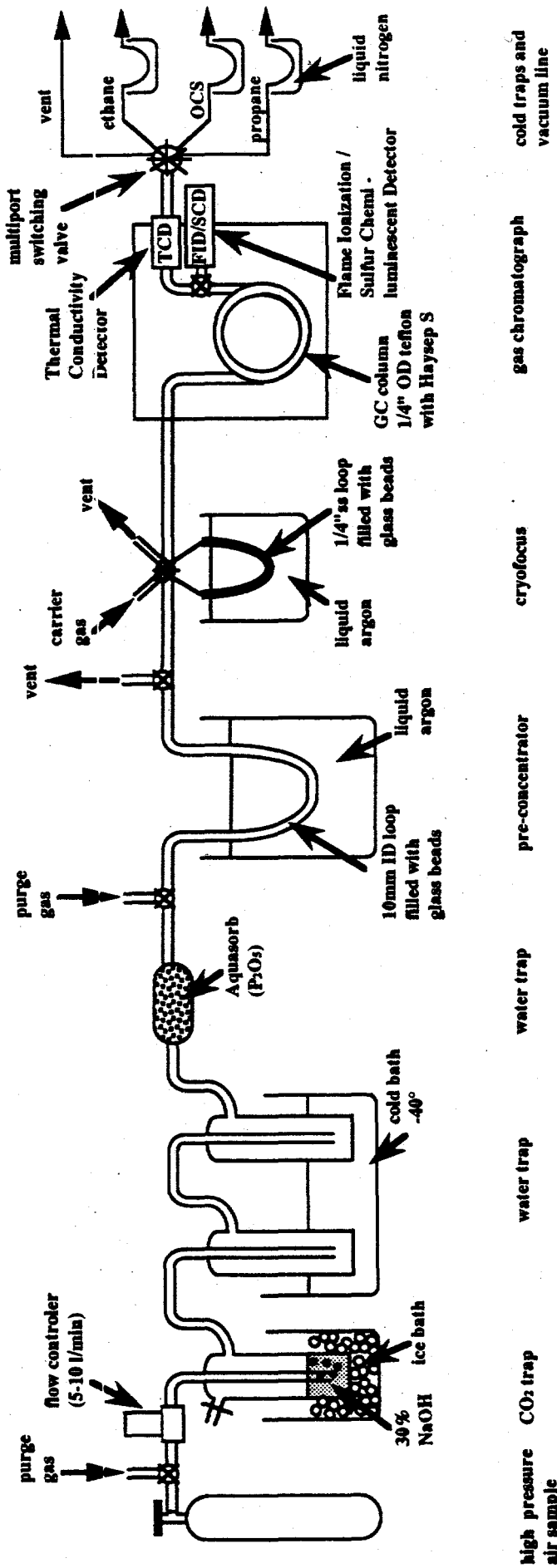
# VII. $^{14}$C CONTENT OF ATMOSPHERIC OCS, $C_2H_6$ AND $C_3H_8$

The previous proposal included an outline of an experiment whereby enough of the trace atmospheric gases OCS, ethane, and propane could be collected to allow the determination of their $^{14}$C content. An estimate of the proportion of their sources that are anthropogenic as opposed to natural could then be made, based on the plausible assumption that the "natural" sources would be biological in origin and therefore possesing the $^{14}$C content of modern biological species.

The initial experimental setup is described in Figure 1. First, the samples are collected in high pressure aluminum cylinders deactivated with a Spectraseal or Aculife treatment. The first cylinders that have been purchased with the Spectraseal treatment appear to have some contamination problems which need to be investigated more thoroughly. Since OCS has a fairly constant background concentration of approximately 500 pptv, the accumulation of even 20μg of carbon requires that all the OCS has to be collected from at least 10 such cylinders, each with a capacity of approximately 7.5 m$^3$. The background concentrations of ethane and propane vary a great deal more with latitude and season so would require between 2 and 8 cylinders to be collected per sample. The air is pressurized employing a Rix air compressor which appears to be free of contamination. This type of compressor has a built in centrifugal water separator so supplies sufficiently dry air that OCS does not appear to hydrolyze during storage in the cylinders, even without the use of a chemical desiccant.

Collection of clean background air requires a steady clean sector wind for the many hours required to fill all the cylinders. This could possibly be achieved by "piggy backing" on a short sea cruise designed for another experiment. The sample could be collected through a tube placed at the bow of the ship as it headed into the wind.

One of the major challenges of this experiment is to strip the samples of atmospheric $CO_2$, which is present in air at a concentration approximately $10^6$ times greater than OCS, without at the same time removing more than a very small fraction of the OCS. Relatively high concentrations of $CO_2$ will tend to clog the cryogenic preconcentrator trap, but more importantly will interfere with the necessary separation of OCS from all other carbon containing compounds. This aspect would not be of so much concern if a GC column material could be found that eluted OCS before $CO_2$, unlike all the established sulfur/hydrocarbon separative column materials investigated so far. Use of these columns without an efficient $CO_2$ trap would mean that OCS will be a tiny peak eluting in the $CO_2$ tail.

purge gas

flow controler (5-10 l/min)

30% NaOH

ice bath

cold bath -40°

Aquasorb (P₂O₅)

purge gas

10mm ID loop filled with glass beads

liquid argon

vent

carrier gas

vent

1/4"ss loop filled with glass beads

liquid argon

Thermal Conductivity Detector

TCD

FID/SCD

Flame Ionization / Sulfur Chemi - luminescent Detector

GC column 1/4" OD teflon with Haysep S

multiport switching valve

vent

ethane

OCS

propane

liquid nitrogen

high pressure air sample

water trap

water trap

CO₂ trap

pre-concentrator

cryofocus

gas chromatograph

cold traps and vacuum line

Figure 1.

Various methods of removing $CO_2$ from the air have been considered. They include bubbling the air through 30% NaOH which is being tested. This bubbling method exploits the difference in the solubility of the two gases $CO_2$ and OCS at high pH. Over the high pH range, where the solubility of $CO_2$ rises because of its equilibration with carbonates, values for carbonyl sulfide are invariant and correspond to the low pH Henry's Law constant value of approximately 2. Therefore, at pH 10, the difference in solubility of the two gases is a factor of nearly $10^5$ (Elliott et al., 1987). At such high pH values hydrolysis of OCS occurs rapidly, however, significant loss of OCS can be avoided by bubbling the air through the NaOH solution at a fast enough flow rate. In fact, bubbling a 10 ppm mixture of OCS in He at 5 l min.$^{-1}$ through a 6 cm column of 30% NaOH resulted in the loss of less than 2% OCS. It should then be possible to separate the remaining $CO_2$ by using a long chromatographic column.

The most inconvenient aspect of $CO_2$ removal by the bubbling method described above is the fact that it adds of a great deal of moisture during this step which will in turn tend to clog the preconcentrator trap. Passage through solid NaOH (drierite) was tried but efficiently removed both $CO_2$ and OCS. Thus, if the bubbler method is to be employed the moisture has to be removed by a combination of large cold traps and a chemical desiccant. The chemical desiccant $P_2O_5$ on a support (e.g., Sicapent) has been proved to be compatible with low concentrations of OCS.
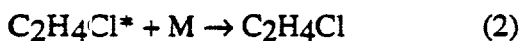
An alternative for removing $CO_2$, and one which has not yet been tested, exploits the two facts, first, that $CO_2$, unlike OCS, sublimes at atmospheric pressures, and second, that OCS is at a much lower partial pressure in air than $CO_2$. Thus, even though OCS has a higher boiling point than $CO_2$ (-50°C compared to -78°C) a large cold trap held at about -120°C would collect solid $CO_2$ while the partial pressure of OCS would remain low enough that no OCS was trapped. This cryogenic method, while having the advantage of not introducing moisture into the system, may not be able to reduce the $CO_2$ by the necessary amount to allow a successful GC separation of the two components.

The separated COS and hydrocarbon fractions are then collected as they elute from the column employing an electrically activated multiport switching valve to direct the components into separate liquid nitrogen cooled traps.

The OCS and hydrocarbons then have to be converted to $CO_2$ then graphite so that their ^{14}C content can be determined by the Accelerating Mass Spectrometer at Lawrence Livermore National Laboratories.
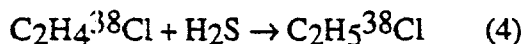
## VI. HALF-STABILIZATION PRESSURE OF CHLORINE ATOMS PLUS ETHYLENE IN A NITROGEN BATH

Recent atmospheric measurements made by the Rowland group during the Airborne Arctic Stratospheric Experiment (AASE-II)[1] revealed readily detectable concentrations of ethylene under conditions for which most alkanes other than $CH_4$ and $C_2H_6$ are below the detection limit of about 2 parts in $10^{12}$. In the atmosphere, ethylene can undergo an exothermic addition reaction with either hydroxyl radicals or chlorine atoms, forming a vibrationally excited $HOC_2H_4^*$ or $C_2H_4Cl^*$ radical. These radicals will undergo reverse decomposition to the reactants unless stabilized by collision, and have no exothermic reaction paths. Reactions (1), (2), and (3) represent these

$$Cl + C_2H_4 \rightarrow C_2H_4Cl^* \qquad (1)$$

$$C_2H_4Cl^* + M \rightarrow C_2H_4Cl \qquad (2)$$

$$C_2H_4Cl^* \rightarrow Cl + C_2H_4 \qquad (3)$$

reactions for chlorine atom addition to ethylene. In the troposphere, the dominant removal process for ethane and ethylene is by reaction with HO. Under these conditions in the remote troposphere are controlled by the inverse ratio of their respective rate constants with HO, $k_{C_2H_4}/k_{C_2H_6}$ with values $\geq 30$. The observed $[C_2H_6]/[C_2H_4]$ ratio in source regions can be in the 1 to 5 range but the remote tropospheric ratio falls quickly as expected from the higher reactivity of $C_2H_4$. However, in the stratosphere, recent atmospheric measurements made by the Rowland group revealed a $[C_2H_6]/[C_2H_4]$ ratio as high as 2 rather than 30. This observation of high $C_2H_4$ concentrations raises the interesting question of the sources and removal processes for $C_2H_4$ at these high altitudes, and the postulate has been made that the attack of HO or Cl on $C_2H_6$ can leave $C_2H_4$ as an insitu product. The study of Cl atom addition to $C_2H_4$ using air as the bath gas for collisional stabilization of the $C_2H_4Cl^*$ radicals is of interest in understanding the role of Cl atoms as a sink for $C_2H_4$.

Previous work by Lee and Rowland has shown that the half-stabilization pressure, i.e. the pressure at which $k_3 = k_2[M]$, is $800 \pm 120$ torr in $CClF_3$ at 298K.[1] In our experiments using radioactive $^{38}Cl$, the $C_2H_4{}^{38}Cl$ radicals formed through reactions (1) and (2) are measured as $C_2H_5{}^{38}Cl$ following reaction with a radical scavenger such as HI or $H_2S$, reaction (4). The use of air as a bath gas in such

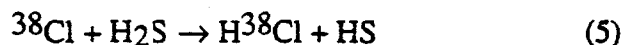$$C_2H_4{}^{38}Cl + H_2S \rightarrow C_2H_5{}^{38}Cl \qquad (4)$$

experiments will cause interference with the measurements because of the reaction of $C_2H_4{}^{38}Cl$ with $O_2$. Hence, in the present set of experiments, we have resorted to the use of $N_2$ only as the bath gas in sample mixtures with $C_2H_4 + H_2S + CClF_3 + Ar$. It has been shown that the stabilization efficiencies of $O_2$ and $N_2$ are indistinguishable within experimental uncertainties ($\pm 10\%$).[3]

Radioactive $^{38}Cl$ and $^{41}Ar$ were produced as described in an earlier section, but with an irradiation time of 2 minutes rather than 1 minute to enhance the $^{38}Cl$ yield. The experiments were carried out at various ratios of $\dfrac{[H_2S]}{[C_2H_4]}$ a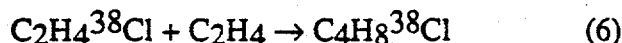t three pressures: 1000, 2000, and 3000 torr. The reaction intermediate, $C_2H_4{}^{38}Cl^*$ reacted with $H_2S$ following collisional stabilization, and the resulting radioactive product, $C_2H_5{}^{38}Cl$, was analyzed by radiogas chromatography using two chromatographic columns in series: 15-ft dimethylsulfolane (DMS) and 50-ft propylene carbonate on alumina (PCA). The radioactive molecules were again passed from the chromatographic columns into a gas flow "sandwich" type gas proportional counter for radioassay.

Plots of $\dfrac{0.95}{\text{Yield } (C_2H_5{}^{38}Cl)}$ versus $\dfrac{[H_2S]}{[C_2H_4]}$ ratios are shown in Figure 1 for the three pressures used for the measurements. Reaction (5) with $H_2S$ competes against $C_2H_4$ for reactions with $^{38}Cl$ atoms in these samples. If all the thermal $^{38}Cl$ atoms formed in these

$$^{38}Cl + H_2S \rightarrow H^{38}Cl + HS \qquad (5)$$

samples react by (1) and (2) to form $C_2H_4{}^{38}Cl$ or with $H_2S$ (reaction (5)) to form $H^{38}Cl$, and if the $C_2H_4{}^{38}Cl$ radicals are scavenged by $H_2S$ (reaction (4), a common intercept of 1.0 is expected for such a plot for all these pressures at $[H_2S]/[C_2H_4] = 0$. Previous experiments with HI as a radical scavenger and $CClF_3$ as the bath gas have shown results consistent with these arguments.[2] However, the data obtained in the present experiments show intercepts considerably greater than 1, as can be seen in Figure 1, indicating significant losses of $^{38}Cl$-products. An explanation for the "missing" $^{38}Cl$ fraction is that $H_2S$ dos not efficiently scavenge all the $C_2H_4{}^{38}Cl$ radicals formed. A fraction of these radicals are probably lost through reaction with $C_2H_4$ as in (6). If the

$$C_2H_4{}^{38}Cl + C_2H_4 \rightarrow C_4H_8{}^{38}Cl \qquad (6)$$

$C_4H_8{}^{38}Cl$ radicals are then scavenged by $H_2S$ to form $C_4H_9{}^{38}Cl$, the rather long retention times of such compounds on the DMS column used would have precluded their detection in the present experiments. The formation of such compounds can be tested using an appropriate g. c. column (e. g.

silicone oil) with shorter retention times for such products. The $C_2H_4{}^{38}Cl$ radicals in the present experiments might also be lost through reactions with the walls of the sample bulb and through reactions with other radicals formed in the system. Further experiments with higher $H_2S$ concentrations are currently being carried out to examine if the $C_2H_4{}^{38}Cl$ radicals can be scavenged quantitatively. If $C_2H_4{}^{38}Cl$ radicals are assumed to be partly removed through reaction (6) with $C_2H_4$ in competition with reaction (4) with $H_2S$, the expression (7) can be derived for the reciprocal yields of $C_2H_5{}^{38}Cl$ in these samples, where $A(p) = 1 + (1 + \dfrac{P_{1/2}}{P})\dfrac{k_5 k_6}{k_1 k_4}$.

$$\frac{0.95}{\text{Yield }(C_2H_5{}^{38}Cl)} = A(p) + \frac{k_5}{k_1}(1 + \frac{P_{1/2}}{P})\frac{[H_2S]}{[C_2H_4]} \qquad (7)$$

The reciprocal yield $\dfrac{0.95}{\text{Yield }(C_2H_5{}^{38}Cl)}$ is then directly proportional to $\dfrac{[H_2S]}{[C_2H_4]}$ which will give a slope

of $\dfrac{k_5}{k_1}(1 + \dfrac{P_{1/2}}{P})$ when plotted against each other. When plotting at more than one pressure, simultaneous equations of the slopes will yield a half-stabilization pressure for the reaction system. The straight lines obtained in Figure 1 are consistent with the existence of a kinetic competition between $C_2H_4$ and $H_2S$ for reaction with $^{38}Cl$ atoms. The increase in the value of the slope observed with decreasing pressure (Table 1) is also consistent with an increase in the fraction of $^{38}Cl$ released from reaction (3) with decreasing pressure; these $^{38}Cl$ atoms are then available for successive competitive reactions between $H_2S$ and $C_2H_4$ until they are finally bound as $H^{38}Cl$ or $C_2H_4{}^{38}Cl$. From the measured slopes at the three pressures, the half-stabilization pressure for $C_2H_4Cl^*$ in $N_2$ is estimated as $2100 \pm 300$ torr at 298K. Such a high value for the $p_{1/2}$ implies negligible stabilization of $C_2H_4{}^{38}Cl^*$ radicals at the stratospheric pressures of $p_{1/2} < 75$ torr, and hence poor efficiency for chlorine atom reactions as a removal process for $C_2H_4$. Further experiments using higher concentrations of $H_2S$ are being carried out for understanding the loss mechanism for $C_2H_4{}^{38}Cl$ radicals in the present runs. Experiments at temperatures relevant to the stratosphere will also be carried out.

**Table 1: Slopes of Plots at Each Pressure**

| Pressure (torr) | Slope | 1 s | R |
|---|---|---|---|
| 1034 | 3.746 | 0.761 | 0.895 |
| 2009 | 2.552 | 0.499 | 0.875 |
| 2996 | 2.109 | 0.384 | 0.867 |

**References**

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3.  Wallington, T. J., Andino, J. M., Lorkovic, I. M., Kaiser, E. W., and Marston, G., "Pressure Dependence of the Reaction of Chlorine Atoms with Ethene and Acetylene in Air at 295K", *J. Phys. Chem.*, **94**, 3644-3648, 1990.