

PULSED CO₂ LASER PHOTOLYSIS OF CF₂Cl₂

GERARD FOLCHER* and WALTER BRAUN

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234 (U.S.A.)

(Received November 4, 1977)

Summary

The pulsed infrared laser photolysis of CF₂Cl₂ yields primarily (more than 85%) the CF₂Cl free radical and atomic chlorine. Somewhat smaller amounts (less than 15%) of CF₂ and molecular chlorine are produced in a competing primary process. Depending on experimental conditions, *e.g.* pressure and intensity, secondary processes can occur that can obscure the primary chemistry. For example, at low intensity the CF₂Cl radical can thermally dissociate to yield CF₂ plus chlorine atoms while at high intensity the CF₂Cl radical can undergo reaction with chlorine atoms to yield CF₂ and molecular chlorine. Quantitative measurements can be made of the relative importance of the primary atomic or molecular chlorine elimination channels under conditions where secondary removal of CF₂Cl is entirely eliminated. Under these conditions, the relative importance of these two channels does not depend on the intensity of the laser or on the laser wavelength.

The overall chemistry occurring in this complex system is evaluated in the absence as well as in the presence of atomic and free-radical scavengers using conventional end-product analysis techniques.

1. Introduction

The decomposition mechanism of the various five-atom halocarbon molecules is of interest for a number of reasons. The thermochemistry predicts that the atomic and molecular elimination channels are energetically very similar in some of these molecules and considerably farther apart in others. For example, for CF₂Cl₂ the activation energies for both dissociation channels



*Visiting Scientist, Summer 1977, Laser Chemistry Program, Institute for Materials Research. Permanent address: D.G.I. Centre d'Etudes Nucléaires de Saclay, B.P. 2, 91190 Gif sur Yvette, France.

are almost the same and the question of which channel has the lower activation energy cannot be simply resolved from the thermochemistry alone. These five-atom halocarbons are also very strong absorbers in the CO₂ TEA laser domain and most of them can be photodissociated with moderate strength CO₂ laser fluences, *i.e.* under mild focusing conditions. Since these molecules also contain relatively few atoms, any deviation from statistical dissociation behavior is likely to show up here. It has been proposed by Dever and Grunwald [1] that the energy required to dissociate CClF₃ and CCl₃F is localized in a single vibrational mode. However, any such postulate can only be taken seriously if the dissociation mechanism and the subsequent chemistry in these systems is very clearly established. For example, compared with the laser photodissociation of large molecules that lead to stable dissociation products [2] these halocarbon systems are very complex in that free radicals, diradicals and atoms are produced which can react in many ways and lead to a complex mixture of end products. Fortunately, much work has been done recently in connection with characterizing these reactions in both neat and scavenging experiments [3] particularly owing to the recent interest in the stratospheric halocarbon problem. The technology for unraveling the laser chemistry of these fluorochlorocarbons using conventional end product analysis techniques is, at least in principle, available.

Earlier work by Ritter and Freund on the IR photodissociation of CF₂Cl₂ has shown that the difluorocarbene diradical CF₂ is produced [4]. Additional work by Ritter has provided further evidence for the presence of CF₂ in this system [5]. In addition King and Stephenson [6] have observed the temporal behavior of CF₂ following collision-free multiphoton dissociation of CF₂Cl₂ and CF₂Br₂ indicating that some of the difluorocarbene is produced in the primary process. However, their real-time system was sensitive only to the detection of CF₂ and they could not determine the relative yields of the atomic and molecular chlorine dissociation channels.

Our primary purpose in the present investigation was to assess the relative importance of the two possible dissociation pathways (1) and (2). However, during the course of the investigation it became clear that the relative amounts of CF₂Cl and CF₂ varied considerably depending on experimental conditions, *e.g.* light intensity, partial pressure of CF₂Cl₂ and total pressure (helium or added scavenger). The results of these experiments and the explanation for this unusual behavior will be presented.

2. Experimental

The experimental arrangement is the same as that employed previously [2, 7]. Briefly, a 1 cm³ sample cell with two NaCl windows is attached to a six-port two-position sampling valve. The cell can be filled from a gas-handling system using one valve position and its contents can be injected, in entirety, into an on-line vapor phase chromatograph by switching to the

other valve position. The cell can also be isolated either from the gas-handling system or from the chromatograph. The chromatograph is equipped with a flame ionization detector. The electrometer output, measuring the flame current, is connected to an integrator as well as to a standard strip chart recorder. A Lumonics 203 TEA laser* was used either on the R24 (9.6 μm) laser line for most of the experiments or on the P34 (10.6 μm) laser line for several high intensity scavenging experiments.

Three widely varying laser intensities illuminating the gas samples were used in the present work. For the low intensity measurements the laser beam was focused using a 30 cm focal length BaF_2 lens. The reaction cell was positioned between the lens and the focal point which was about 10 cm from the exit window of the cell. In this mild-focusing configuration essentially all of the gas sample in the cell is irradiated with the same laser intensity. To achieve a higher illumination intensity the cell was positioned so that the exit window was 5 cm from the focal point. Very high intensities were achieved by focusing the laser to the center of the cell using a short focal length NaCl lens ($f = 10$ cm).

Gases used were of research grade purity. Their integrity was verified using gas chromatography. They were in most cases found to be of high purity (usually 99% plus). Gas pressures were measured using calibrated dial (Bourdon) gauges.

Column packing materials were various Poropak materials and Porocil C. Different column temperatures were often required to resolve all of the eluted compounds totally. The lowest temperature used was ice bath temperature (about 0 °C) and the highest temperature was 100 °C. Products were identified through their retention times which were determined by injecting samples of known composition. Because of the high sensitivity of the chromatographic system, the percentage decompositions of the samples could be maintained at a relatively low level; these ranged anywhere from about 1 to 10%. The number of laser pulses per single experiment usually ranged from 1 to about 100.

3. Results

3.1. Preliminary results

The CF_2Cl_2 spectrum consists of two strong absorption bands in the CO_2 laser range, one at 1100 cm^{-1} (C—F stretching mode), the other at 950 cm^{-1} (C—F rocking mode). When CF_2Cl_2 is photodissociated in either of these two bands, preliminary experiments indicate that it decomposes by

*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it necessarily imply that the material or equipment identified is necessarily the best available for the purpose.

reactions (1) and (2). End products result from the recombination of two CF_2 radicals yielding C_2F_4 and from recombination of two CF_2Cl radicals yielding $\text{C}_2\text{F}_4\text{Cl}_2$. In experiments in which the scavenger was absent, the ratio R of these two end products was used as a measure of the relative importance of the two channels (1) and (2). To substantiate this method further, supplementary experiments were performed with the compound CF_2HCl . This molecule is expected to decompose dominantly through its molecular dissociation channel $\text{CF}_2\text{HCl} \rightarrow \text{CF}_2 + \text{HCl}$, since the atomic chlorine elimination channel is considerably higher in energy. In fact, when CF_2HCl is dissociated by the R(24) ($9.6 \mu\text{m}$) CO_2 line, the only product that was found at any CF_2HCl pressure between 0.3 and 5 Torr was C_2F_4 . Adding methyl chloride as a chlorine atom scavenger did not reveal the presence of any measurable amount of atomic chlorine.

3.2. Experiments using CF_2Cl_2 neat (without additives)

The CO_2 laser illumination of CF_2Cl_2 results in the production of C_2F_4 and $\text{C}_2\text{F}_4\text{Cl}_2$ with very small amounts of a third product of higher molecular weight. Figure 1 shows the variation of the total yield *versus* the initial CF_2Cl_2 pressure. This figure shows that the yield is roughly constant at high and medium laser intensity but is somewhat more sensitive to the CF_2Cl_2 pressure at low intensities. The ratio R defined by

$$R = \frac{\text{C}_2\text{F}_4 \text{ product}}{\text{C}_2\text{F}_4\text{Cl}_2 \text{ product}} \quad (\text{I})$$

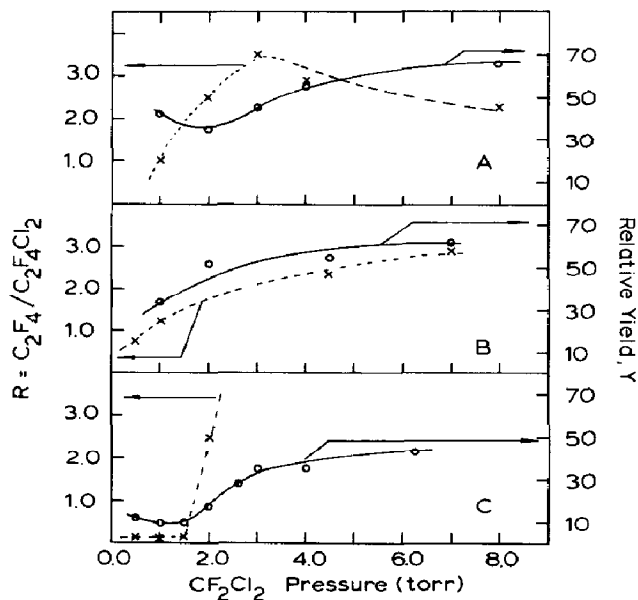


Fig. 1. Plots of relative yields and R (see eqn. (I)) as a function of CF_2Cl_2 pressure (no additives): (a) high intensity; (b) medium intensity; (c) low intensity; solid curves, total yields; broken curves, $R = \text{C}_2\text{F}_4/\text{C}_2\text{F}_4\text{Cl}_2$.

also exhibits changing behavior as the laser intensity is varied. There is a large enhancement in R at low intensity corresponding to an increase in the total product yield. The data of this figure taken by themselves do not provide sufficient information to evaluate unequivocally all of the complex chemistry occurring in this system. Additional information is obtained if buffer gas is introduced into the system.

3.3. CF_2Cl_2 + added helium

Addition of helium to the system is expected rapidly to quench excited molecules produced during the laser pulse, minimizing thermal effects following the laser pulse. Figure 2 shows the effect of adding helium to the CF_2Cl_2 on the yield and on the value of R . In all cases the yield decreases

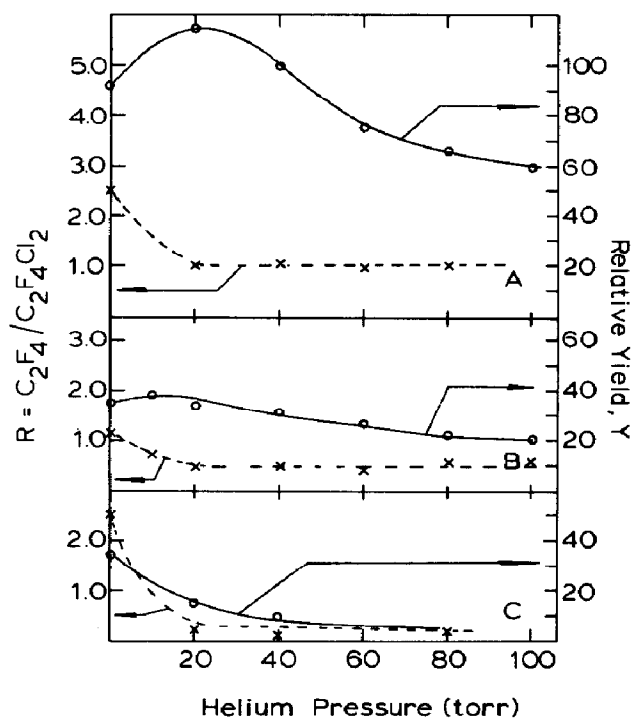


Fig. 2. Plots of yields and R as a function of helium pressure (pressure of CF_2Cl_2 , 2 Torr): (a) high intensity; (b) medium intensity; (c) low intensity; solid curves, total yields; broken curves, $R = C_2F_4/C_2F_4Cl_2$.

at high helium pressure and R reaches a limiting value. This limiting value is about 0.2 at low intensity, about 0.4 at intermediate intensity and reaches 1 at high intensity. These experiments provide evidence that there is additional CF_2 production through subsequent thermal chemistry deriving from the CF_2Cl radical. At low intensity both the yield and the ratio R are drastically reduced when helium is added. At high intensity the effect of adding helium on the reduction of the yield and on R appears to be less marked. Taken by themselves the photochemistry data with added helium provide evidence of

TABLE 1

Values of α , β and R versus laser intensity and helium pressures (no added scavenger)

	Low intensity ^a		Medium intensity ^a		High intensity ^a	
Pressure of CF ₂ Cl ₂ (Torr)	2.0		2.0		2.0	
Pressure of helium (Torr)	0	80	0	80	0	80
Yield ^b	35	1.5	34	23	93	67
ϕ^c { C ₂ F ₄	0.36	0.075	0.28	0.17	0.36	0.25
{ C ₂ F ₄ Cl ₂	0.14	0.42	0.22	0.33	0.14	0.25
$R = C_2F_4/C_2F_4Cl_2$	2.5	0.18	1.27	0.52	2.5	1.00
α^d	0.85	0.85	0.65	0.65	0.50	0.50
β^d	0.67	0.0	0.35	0.0	0.44	0.0

^a Low intensity, laser beam focused 10 cm outside cell (we assume that the entire gas volume is illuminated with the same intensity); high intensity, focal point at center of the cell; medium intensity, laser beam focused 5 cm outside of cell.

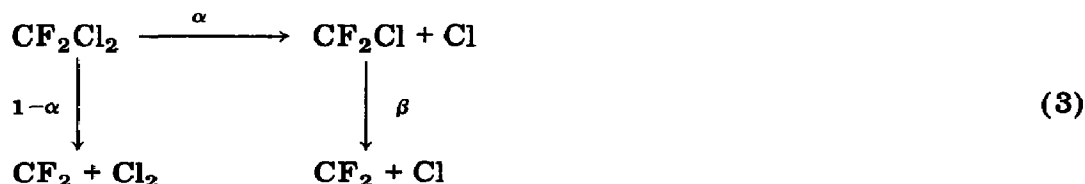
^b Total decomposition yield (percentage conversion per pulse $\times 100$).

^c Normalized yields for 1 mol CF₂Cl₂ decomposed: $2(C_2F_4 + C_2F_4Cl_2) = 1$.

^d α and β are evaluated assuming that α does not vary with helium pressure and $\beta = 0$ at 80 Torr helium.

the existence of thermal chemistry and suggest that the initial photochemical decomposition of CF₂Cl₂ produces CF₂ and CF₂Cl in relative amounts that for some reason depend on the laser intensity.

If in addition to the primary processes (1) and (2) we include provision for secondary decomposition, we can define primary and secondary effects in terms of the defined parameters α and β :



The parameter α is the branching ratio between primary atomic and molecular elimination channels and β is the fraction of secondary atomic chlorine elimination.

In terms of these parameters $(1 - \alpha + \alpha\beta)$ mol of CF₂, $\alpha(1 - \beta)$ mol CF₂Cl and $\alpha(1 + \beta)$ mol atomic chlorine are produced for 1 mol CF₂Cl₂ decomposed.

The previously defined parameter R is related to α and β by

$$R = \frac{1 - \alpha(1 - \beta)}{\alpha(1 - \beta)} = \frac{\text{CF}_2}{\text{CF}_2\text{Cl}} \quad (\text{II})$$

The values of R alone are not sufficient to describe completely the complex chemistry of this system unless $\beta = 0$. If, however, we assume that 80 Torr pressure of added helium can entirely quench all thermal processes ($\beta = 0$)

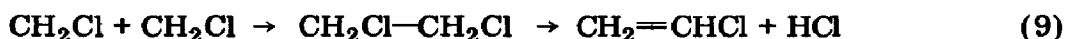
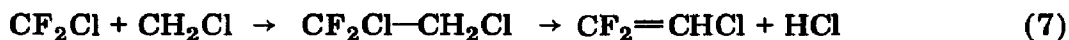
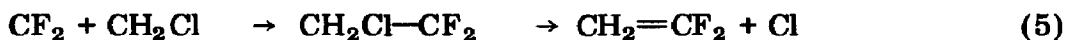
we can then calculate α values from R . These calculations are shown in Table 1 which also shows the surprising result that α varies with intensity.

Additional information must be obtained by adding a scavenger to the system. These experiments are now described.

3.4. Scavenging experiments

Evaluation of all the parameters of this system requires a detailed counting of chlorine atoms. Several scavengers are known to react rapidly with chlorine atoms [3] but these often result in side reactions which over-complicate the system.

CH_3Cl was finally selected because of its simplicity and specificity^a. The following reactions involving CH_3Cl and radicals derived therefrom can be clearly identified through products that can be readily separated using chromatography:



From measured integrated areas of the various products^b we can perform the following detailed balancing^c:

$$[\text{CF}_2] = 1 - \alpha + \alpha\beta = [\text{CF}_2=\text{CH}_2] + 2[\text{CF}_2=\text{CF}_2]$$

$$[\text{CF}_2\text{Cl}] = \alpha(1 - \beta) = [\text{CF}_2=\text{CHCl}] + [\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}] + 2[\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}]$$

$$[\text{Cl}] = [\text{CH}_2\text{Cl}] = \alpha(1 + \beta) + [\text{CH}_2=\text{CF}_2] \quad (\text{III})$$

$$= [\text{CH}_2=\text{CF}_2] + [\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}] + [\text{CF}_2=\text{CHCl}] + 2([\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}] + [\text{CHCl}=\text{CH}_2])$$

^aBoth methane and ethane were used as scavengers in the present work. Qualitatively similar results were obtained using these scavengers; however, these results are not reported here.

^bThe products $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CH}_2$ were easily separated when the column temperature was lowered. The product $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ was difficult to separate from $\text{CF}_2=\text{CHCl}$ and appeared as a small shoulder on the latter peak. Therefore in the following material balance we count the CF_2Cl only from the $\text{CF}_2=\text{CHCl}$ peak area. Only at low CH_3Cl pressures, where the $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ product is more significant, do we estimate its amount by estimating the shoulder area.

^cOther products produced in smaller amounts were also found, e.g. CF_2HCl , CH_2Cl_2 and C_2H_4 . Reactions leading to these products were not included in the following detailed balancing equations. Errors introduced by neglecting some of these products are qualitatively discussed later.

TABLE 2

Relative product yields in CH_3Cl scavenger experiments at low and high intensity (calculated values of α and β)

	Low intensity ^a					High intensity ^a							
	3.0	3.0	3.0	3.0	3.0	1.0	1.0	1.0	1.0	1.0	1.0 ^e	2.0 ^e	3.0 ^e
CF_2Cl_2 pressure (Torr)	3.0	3.0	3.0	3.0	3.0	1.0	1.0	1.0	1.0	1.0	1.0 ^e	2.0 ^e	3.0 ^e
CH_3Cl pressure (Torr)	4.0	8.0	16.0	32.0	32.0	1.0	4.0	12.0	40.0	40.0	2.0	2.0	2.0
Yield ^b	24.0	21.0	6.4	1.4	1.4	30.0	62.0	40.0	20.0	20.0	143.0	130.0	121.0
C_2F_4	0.15	0.16	0.13	0.08	0.08	0.15	0.21	0.18	0.15	0.15	0.32	0.28	0.27
$\left\{ \begin{array}{l} \text{C}_2\text{H}_2\text{F}_2 \\ \text{C}_2\text{F}_2\text{H}_2\text{Cl}_2 + \text{C}_2\text{F}_2\text{HCl} \end{array} \right.$	0.42	0.31	0.20	0.09	0.09	0.12	0.14	0.14	0.12	0.12	0.13	0.26	0.32
ϕ^c	0.29	0.36	0.55	0.76	0.76	0.58	0.44	0.49	0.58	0.58	0.23	0.18	0.14
$\left\{ \begin{array}{l} \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_3\text{Cl} \end{array} \right.$	0.65	0.55	0.45	0.40	0.40	1.06	0.98	1.15	1.06	1.06	0.36	0.61	0.41
α^d	0.84	0.80	0.89	0.90	0.90	0.40	0.70	0.82	0.82	0.82	0.30	0.40	0.35
β^d	0.66	0.50	0.41	0.33	0.33	0.23	0.37	0.39	0.29	0.29	0.16	0.54	0.60

^a Low intensity, laser beam focused 10 cm outside cell (we assume that the entire gas volume is illuminated with the same intensity); high intensity, focal point at center of the cell

^b Total decomposition yield (percentage conversion per pulse $\times 100$).

^c Normalized yields for 1 mol CF_2Cl_2 decomposed: $2\text{C}_2\text{F}_4 + \text{CF}_2\text{H}_2 + \text{C}_2\text{F}_2\text{H}_2\text{Cl}_2 + \text{C}_2\text{F}_2\text{HCl} = 1$.

^d Calculated from eqns. (III).

^e Irradiation: R(24), 9.5 μm ; all other runs: P(34), 10.6 μm .

The parameters α and β can be calculated from these equations. Typical results are presented in Table 2*. The value of R can be calculated from $[\text{CF}_2]/[\text{CF}_2\text{Cl}]$ using eqns. (III).

The values of α obtained from eqns. (III), with the added CH_3Cl , are in good agreement with those determined from the experiments performed in the absence of CH_3Cl (with added helium), both at low and at high laser intensity (compare Tables 1 and 2). The dependence of both α and R on CH_3Cl pressure is shown in Fig. 3.

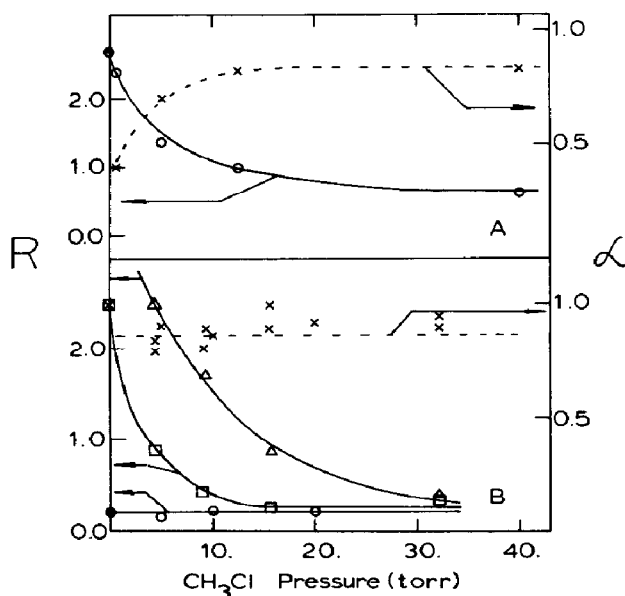


Fig. 3. Plots of $R = (2\text{C}_2\text{F}_4 + \text{CF}_2\text{H}_2)/(\text{C}_2\text{F}_2\text{Cl}_2\text{H}_2 + \text{C}_2\text{F}_2\text{HCl})$ and α (branching ratio) as a function of CH_3Cl (scavenger) pressure. (a) High intensity, 1 Torr CF_2Cl_2 ; solid curve, R ; broken curve, α . (b) Low intensity; solid curve, R ; \circ , 1 Torr CF_2Cl_2 ; \square , 2 Torr CF_2Cl_2 ; \triangle , 3 Torr CF_2Cl_2 ; broken curve, α calculated from 1 Torr, 2 Torr and 3 Torr CF_2Cl_2 runs; \otimes , values of $R = \text{C}_2\text{F}_4/\text{C}_2\text{F}_4\text{Cl}_2$ for pure CF_2Cl_2 (see Fig. 1).

At low intensity curve B shows that R is independent of added CH_3Cl at 1 Torr pressure of CF_2Cl_2 , indicative of the fact that thermal processes

*Measurement of the stabilized products $\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ required high column temperature. Both of these products are only about 10% of their respective unstabilized counterparts, $\text{CF}_2=\text{CHCl}$ and $\text{CH}_2=\text{CHCl}$. Note that the ratio of unstabilized to stabilized products is considerably higher than that found in room temperature visible and UV photolysis experiments [8]. This observation is indicative of the fact that the temperature in the laser photolysis system is considerably higher than room temperature, at least in the time interval during which the free radicals combine with one another. An analogous argument explains why there is so little $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ dimer produced in the CH_3Cl scavenger experiments.

are not important under these conditions. R maintains a constant value of 0.15 corresponding to $\alpha = 0.85$ ($\beta = 0$). If the CF_2Cl_2 pressure is increased to 2 and 3 Torr, thermal processes produce additional amounts of CF_2 as can be seen in Fig. 3(b). These thermal effects can be quenched by adding sufficient pressure of CH_3Cl as was previously observed when helium was added (Fig. 2). About 30 Torr of CH_3Cl is required in order to obtain R values close to the limiting value at 3 Torr pressure of CF_2Cl_2 . Note that with added CH_3Cl the value of α (measuring chlorine atoms produced in the primary process) remains constant throughout at about 0.80 - 0.90.

At high intensity a variation of α with added CH_3Cl pressure is observed in Fig. 3(a). At low pressure we find an α value of about 0.4 which is close to the value obtained in experiments without added CH_3Cl (with added helium). As the scavenger pressure is increased, α increases to reach its more usual value of 0.85. This result gives clear evidence that there is another decomposition mechanism occurring which produces CF_2 when there is insufficient pressure of added scavenger. This additional pathway also yields chlorine molecules. We conclude that it must be due to the reaction of Cl atoms with CF_2Cl :



At high intensity the decomposition yield at the focal point is high enough that chlorine atoms can react with CF_2Cl radicals rather than be scavenged by CH_3Cl (at low CH_3Cl pressure). However, if the $\text{CH}_3\text{Cl}/\text{CF}_2\text{Cl}_2$ ratio exceeds 10/1 the chlorine atom reaction with CF_2Cl radicals can be entirely eliminated. Under these conditions the primary channels can be correctly assessed.

The wavelength was varied during the course of these high intensity scavenging experiments from 1077 cm^{-1} to 929 cm^{-1} for two reasons. Methyl chloride absorbs some radiation at 1077 cm^{-1} and a measurable amount of its decomposition can be observed when the CH_3Cl pressure is greater than 10 Torr (as evaluated by C_2H_6 formation). However, CH_3Cl is transparent at 929 cm^{-1} and does not decompose even at pressures greater than 60 Torr. Therefore at the laser wavelength of 929 cm^{-1} , high pressures of CH_3Cl can be added to assure complete chlorine atom removal. It was also of further interest to see whether the branching ratio of the two primary decomposition channels was the same at the two different wavelengths. We do in fact observe the same branching ratio at these two wavelengths and also observe similar thermal effects.

4. Discussion

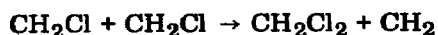
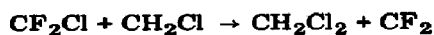
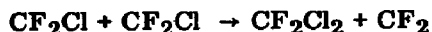
Results of all of these experiments lead us to a consistent picture of the laser-induced decomposition of CF_2Cl_2 . The primary channel leading to the elimination of atomic chlorine and CF_2Cl occurs to the extent of about 85% or greater and the primary channel producing molecular chlorine and CF_2

comprises no more than 15%*. Secondary processes can occur which complicate the picture. For example, the C—Cl bond in the CF_2Cl radical is considerably weaker than the C—Cl bond in the parent CF_2Cl_2 . This labile radical is therefore very temperature sensitive and can decompose in the high temperature regime following the laser pulse. Also, the secondary reaction of chlorine atoms with the CF_2Cl radical is apparently temperature sensitive. This reaction can lead to the disappearance of CF_2Cl and to the formation of additional CF_2 and molecular chlorine. Interestingly these two competing secondary processes depend differently on experimental conditions.

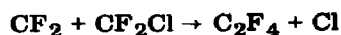
At low intensity the thermal decomposition of CF_2Cl is the dominating complicating secondary process. At high intensity the secondary reaction of chlorine atoms with the CF_2Cl radical is dominant. We know from previous work that high substrate pressures and low laser intensities favor thermal over photochemical processes [9, 10]. Since both of these complicating secondary processes are assumed to be thermal in nature, why do they not both dominate at low laser intensity? The thermal dissociation $\text{CF}_2\text{Cl} \rightarrow \text{CF}_2 + \text{Cl}$ is a unimolecular process and the rate at which it occurs should be dependent only on the concentration of CF_2Cl . The reaction of chlorine atoms with CF_2Cl is a bimolecular process and depends on the concentration of both Cl and CF_2Cl . At high intensity this bimolecular reaction can proceed at a rate which is fast compared with relaxation processes, while at low intensity the bimolecular collision rate can be slow compared with rates of relaxation and temperature collapse by fluid-mechanical mechanisms. At the highest intensity the time between a collision of a chlorine atom and a CF_2Cl radical can be as short as 100 ns while at the lowest intensity the time between collisions can be of the order of 100 μs **.

Our experiments also reveal that the addition of quenching gas (helium or CH_3Cl) has considerably more effect on the quenching of the reaction of $\text{Cl} + \text{CF}_2\text{Cl}$. This observation is not difficult to rationalize if we consider the likely case that the activation energy for the unimolecular dissociation

*Reactions (1) - (9) and corresponding material balance eqns. (III) result in excellent material balances; however, we should point out that we have entirely neglected all disproportionation reactions, *e.g.*



as well as the reaction



We cannot properly assess these reactions at this time, but since all of them occur to a small extent and result in the production of or the counting of additional CF_2 we can only be absolutely certain that no more than 15% CF_2 is produced in the primary process; the actual amount produced may be somewhat less than this.

**In previous work [9] we measured the duration of the thermal pulse to be about 100 - 200 μs under mild focusing conditions using a piezoelectric transducer. This device measures the time of collapse of the thermal pulse due to fluid-mechanical mechanisms.

of CF_2Cl is considerably higher than the activation energy for the secondary reaction of $\text{Cl} + \text{CF}_2\text{Cl}^*$.

This rationale for the substrate pressure and intensity behavior of the two competing secondary thermal processes can also explain in more detail the experimental trends shown in Figs. 1 and 2. Figure 1(c), low laser intensity, shows that the value of R is approximately constant at low CF_2Cl_2 pressure but increases dramatically at high pressure and apparently does not reach a limiting value. This behavior is consistent with the thermal decomposition of CF_2Cl to yield CF_2 and atomic chlorine. This process becomes more important as the substrate (CF_2Cl_2) pressure is increased. At higher intensity the thermal decomposition of CF_2Cl becomes less important but the value of R increases because of the reaction $\text{Cl} + \text{CF}_2\text{Cl}$. The value of R appears to reach a limiting value of about 3.0 at moderate (Fig. 1(b)) and high (Fig. 1(a)) intensities.

This limiting value is achieved more rapidly at the highest intensity and derives from the relative rates of $\text{Cl} + \text{CF}_2\text{Cl}$ versus $\text{CF}_2\text{Cl} + \text{CF}_2\text{Cl}$. The ratio of 3.0 is somewhat larger than the statistical value since additional chlorine atoms are produced from the thermal dissociation of CF_2Cl and chlorine atoms do not recombine at these low pressures. Since R apparently does not monotonically increase but reaches a finite value at the higher intensities, this suggests that the thermal decomposition $\text{CF}_2\text{Cl} \rightarrow \text{CF}_2 + \text{Cl}$ is less important under these conditions. This trend was also demonstrated in the CH_3Cl scavenging experiments. The yields at the highest intensities (Fig. 1(a), (b)) do not show any significantly different behavior. However, there is a somewhat larger increase in the yield at low intensity as the CF_2Cl_2 pressure is increased. This may be evidence for additional thermal decomposition of CF_2Cl through a chain initiating process:



The effect of added helium on the value of R at low intensity (Fig. 2(c)) is more pronounced than at high intensity simply because of the strong quenching effect on the secondary decomposition of CF_2Cl which is the dominant process at low laser intensity. At the higher intensities (Fig. 2(a), (b)) there is some quenching effect, presumably also a quenching of the thermal decomposition of CF_2Cl ; however, a limiting value of R is reached at helium pressures above 20 Torr. This limiting value is higher at higher intensity because helium has less effect on the quenching of the reaction $\text{Cl} + \text{CF}_2\text{Cl}$. The effect of added helium on the overall yields is less marked.

*Throughout this discussion, by thermal processes we mean processes that can occur following the laser pulse. We cannot, however, determine the extent to which the system is equilibrated while these secondary thermal processes occur. The time domain for the various equilibration processes is discussed in more detail in refs. 9 and 10. In the present work it is likely that, since the unimolecular dissociation of CF_2Cl has a high activation energy, the time scale over which its dissociation occurs can in many cases be considerably shorter than the time scale during which the reaction $\text{Cl} + \text{CF}_2\text{Cl}$ takes place.

The maximum, which is most evident at high intensity, is probably due to a pressure-broadening effect on the absorption process, initially increasing the yield. This effect has been seen in other systems [11].

Fortunately, experiments with added CH_3Cl scavenger provide us with clear evidence that thermal secondary processes can be completely eliminated. For example, the same limiting value of R is achieved at high intensity and high CH_3Cl pressure as at low intensity with low added CH_3Cl pressure (see Fig. 3). These experiments also show that the primary dissociation channels (1) and (2) occur to the same extent independent of the laser intensity and wavelength. These findings are consistent with our present knowledge that the energy required to dissociate a molecule in an intense IR laser field is randomly distributed in all of the internal (vibrational) degrees of freedom of the dissociating molecule.

This discussion leads us now to the initially posed question of which dissociation channel, (1) or (2), requires the lower activation energy. Figure 4 displays schematically the one-dimensional reaction coordinate for the two CF_2Cl_2 dissociation channels.

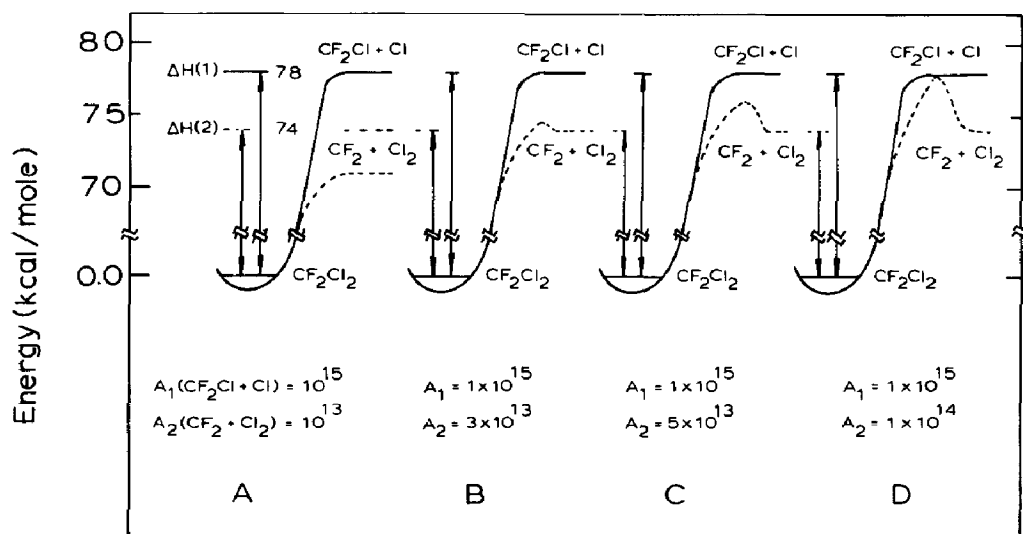


Fig. 4. Activation energy diagram for both CF_2Cl_2 decomposition channels (calculated assuming a vibrational temperature of 1500 K). A_1 and A_2 are the pre-exponential factors for atomic and molecular chlorine elimination respectively. Solid curves, atomic elimination; broken curves, molecular elimination.

These curves were calculated assuming a vibrational temperature of 1500 K during the laser pulse. This temperature was arrived at by assuming a pre-exponential factor of 10^{15} for the atomic elimination channel and an estimated activation energy of 78 kcal mol^{-1} . The dissociation time was assumed to be of the order of 200 ns, the laser pulse duration. This value for the pre-exponential and a temperature of about 1500 K predicts approximately several tenths of a per cent dissociation per laser pulse which is what

we measure in our low intensity uniform-illumination experiments. Curve A predicts zero activation energy for the reverse reaction $\text{CF}_2 + \text{Cl}_2$ and falls below the dissociation enthalpy for molecular chlorine elimination which is clearly not possible. Curves B, C and D are all possible and predict ever increasing activation energies for the reverse process $\text{CF}_2 + \text{Cl}_2$ but require progressively higher values for the pre-exponential factor A_2 . The pre-exponential factors in curves C and D are in reasonable agreement with the measured [12] pre-exponential factor $A_2 = 10^{13.84} = 6.9 \times 10^{13}$ for the dissociation of CF_2HCl to yield CF_2 plus the molecule HCl.

Acknowledgments

The authors gratefully acknowledge the many helpful suggestions and expert advice given them by P. Ausloos. The authors wish to thank J. Stephenson and D. King for suggesting this problem and making available results of concurrent real-time measurements on this CF_2Cl_2 system. Very helpful discussions and encouragement by T. Coyle and Wing Tsang are also gratefully acknowledged. The work was supported in part by the Energy Research and Development Administration under contract EA-77-A-01-6010.

References

- 1 D. F. Dever and E. Grunwald, *J. Am. Chem. Soc.*, **98** (1976) 5055.
- 2 W. Braun and W. Tsang, *Chem. Phys. Lett.*, **44** (1976) 354.
- 3 See the following references and references contained therein.
R. E. Rebbert and P. J. Ausloos, *J. Photochem.*, **4** (1975) 419.
R. E. Rebbert and P. J. Ausloos, *J. Photochem.*, **6** (1976 - 77) 265.
R. E. Rebbert, S. G. Lias and P. Ausloos, *J. Photochem.*, **8** (1978) 17.
S. Hautecloque and A. Bernas, *J. Photochem.*, **7** (1977) 73.
- 4 J. J. Ritter and S. M. Freund, *Chem. Commun.*, (1976) 811.
- 5 J. J. Ritter, *J. Am. Chem. Soc.*, submitted for publication.
- 6 D. S. King and J. C. Stephenson, *Chem. Phys. Lett.*, in the press.
- 7 A. E. Ledford, Jr., and W. Braun, *Rev. Sci. Instrum.*, **48** (1977) 537.
- 8 P. Ausloos and R. E. Rebbert, personal communication, 1977.
- 9 D. Gutman, W. Braun and W. Tsang, *J. Chem. Phys.*, **67** (1977) 4291.
- 10 W. C. Danen, W. Munslow and D. W. Setser, *J. Am. Chem. Soc.*, **99** (1977) 6961.
- 11 N. C. Peterson, R. G. Manning and W. Braun, *J. Res. Nat. Bur. Stand.*, in the press.
- 12 J. W. Edwards and P. A. Small, *Nature (London)*, **202** (1964) 1329.