

Chemical Reactions Following the IRMPD of C_2F_3Cl *

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Abstract. C_2F_3Cl is photolyzed with a TEA- CO_2 laser at 1050.44 cm^{-1} with focused fluences up to 280 J/cm^2 . The stable products in the IRMPD of C_2F_3Cl are determined for up to 10 Torr of C_2F_3Cl being photolyzed both neat and with added O_2 . C_2F_4 and trans- $C_2F_2Cl_2$ are found to occur in the greatest yield though C_3F_5Cl , $C_3F_4Cl_2$, C_4F_7Cl , and $C_2F_3Cl_3$ also appear to be primary products. When O_2 is present F_2CO , $FCICO$, and CF_2ClCOF are the exclusive products. The formation of these products are for the most part consistent with a carbene formation dissociation mechanism for C_2F_3Cl IRMPD. $C_2F_3Cl_3$ may best be explained by another mechanism competitive with carbene formation. Many products attributed to secondary photolysis mechanisms are observed for long photolysis times.

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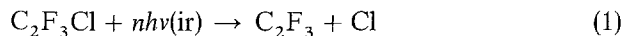
Infrared multiphoton dissociation (IRMPD) is a valuable tool in the study of the mechanisms of unimolecular dissociation and subsequent reaction. The literature on IRMPD has been recently reviewed by several authors with prejudice toward experimental results [1–3], as in the excellent tabular summary by Steinfeld and towards the theoretical treatment of the excitation and dissociation mechanisms [4–7]. There also exists several text books on the subject of laser chemistry [1, 8–10]. In addition to the works addressing the mechanisms of IRMPD, there are several studies which utilize the dissociations to other ends. IRMPD has been demonstrated to be of great potential in isotope separation and ultrapurification processes [3, 4, 9]. Other uses for IRMPD include its utility for the production of transient species for spectroscopic [11, 12], chemical reaction [13–16], and thermal [16–18] relaxation studies. In this case, the elucidation of chemical reactions prompted us to undertake the present study. In doing so, the mechanisms for the medium pressure IRMPD of C_2F_3Cl are also explored.

The study of the IRMPD of C_2F_3Cl has been of subject of moderate interest. The first reported indication that C_2F_3Cl undergoes IRMPD was given by Ambartzumian et al. [19]. In the latter study the photolysis was monitored by observing the visible luminescence given off by excited state species when 10 Torr of the sample was irradiated with a high energy TEA- CO_2 laser. The observed luminescence spectrum was found to be due to C_2 and higher carbon particles. Subsequently, this study presented no indication as to the major dissociation and reaction mechanisms. Later, Nagai et al. [20] examined the products of the medium pressure (1–10 Torr) and high pressure (> 50 Torr) IRMPD and dielectric breakdown of C_2F_3Cl . Using two lasers, they found that the dissociation could be enhanced by the use of a high intensity, off-resonance laser pulsing after a lower intensity one on-resonance with the ν_4 C–F stretching vibration of C_2F_3Cl [21]. The off-resonance laser presumably aided dissociation by interaction in Region II of the excitation, the quasicontinuum.

The final products of the IRMPD of C_2F_3Cl were also reported by Nagai et al. [20] both for neat photolysis and with added gasses used as radical scavengers. Using mass spectral and infrared absorption analysis, they reported the major products of neat IRMPD as

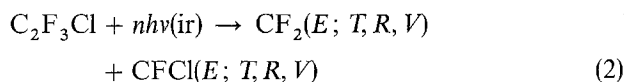
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being C_2F_4 and $trans-C_2F_2Cl_2$. The products of the photolysis with added O_2 and H_2 were also reported. Based on their findings, they postulated that the primary step in the IRMPD of C_2F_3Cl was chlorine atom loss



although no mechanisms for product formation were given. It seems likely that this dissociation mechanism was also based on the apparent low enthalpy for chlorine-atom loss which upon closer inspection is in error [22].

The first reported observation of the primary dissociation mechanism in the low-pressure (10 m Torr) IRMPD of C_2F_3Cl was given by Bialkowski et al. [11]. In this work, the IRMPD of C_2F_3Cl was used to produce $CFCl$ (\bar{X}^1A') for visible laser excited fluorescence spectroscopic studies. This study was followed by several more reports on the observation of the primary photo-products of the C_2F_3Cl and the energy content of these species [5, 22–26]. The bulk of these works were keenly summarized by King [5] with much emphasis on the overlap between the experimental results and the theoretical modellings of Stephenson et al. [24] and Stone et al. [25]. Perhaps the most significant result of these collected works is the measurement of the translational, rotational, and vibrational energy content of the primary photo-fragments;



which may lead to an understanding of the prior energy distribution of the parent species [5], and subsequently a better understanding of the dissociation mechanisms.

Presented below are the experimental results of the medium pressure (0.5–10 Torr) IRMPD of C_2F_3Cl . In these studies, the final products of the photolysis were observed and the mechanisms for photolysis and subsequent reaction were determined. These results are found to be for the most part consistent with the carbene formation photolysis mechanism observed in the low pressure studies cited above. The major products of the medium pressure IRMPD of C_2F_3Cl were found to be C_2F_4 and $trans-C_2F_2Cl_2$. However, in addition to these major products, we also observe 3 and 4 carbon species which are produced by primary reactions, in contrast to secondary photolysis mechanisms. The occurrence of the C_3 products, in particular, may be thought to confirm the carbene formation dissociation mechanism. In addition to products indicative of methylene carbene reactions, we have also

observed the formation of $C_2F_3Cl_3$ as a primary product. This is not a carbene reaction product but rather is probably formed in reactions involving atomic chlorine.

1. Experimental

The discharge section of the “home built” TEA- CO_2 laser used in these experiments was constructed out of plexiglass tubing and was fitted with Brewster angle NaCl windows. The electrodes, measuring 60 cm in length by 2.5 cm wide, were fabricated out of aluminum. These electrodes had ground edges but were not of the constant electric field design. Pre-ionization of the laser gas mixture was accomplished with the use of a series of spark plugs located perpendicular to the electrode gap and electrically coupled to the main electrode power bus via 500 nf doorknob capacitors. The energy storage capacitor was a 0.05 μ f, low inductance type, and was charged to 20 kV via a series 62 k Ω resistor. A ceramic hydrogen thyratron was used as a high-voltage switch. The gas mixture in the discharge section was; He, 17; CO_2 , 2.5; N_2 , 1.7; H_2 , 0.12, as measured by gas flow rotameters. Discharge gas was vented through about 10 m of 0.5 cm i.d. tubing and thus the pressure in the discharge section was slightly above atmospheric pressure. The laser cavity was \sim 1 m in length constructed of a 20 m radius of curvature, 90% reflecting Ge output coupler, and a 80 groove/mm original grating blazed for 9.4 μ m operation. The grating was mounted on a rotational stage so that line tuning could be easily accomplished. Determination of the laser transition was performed with a Optical Eng. model 16-A spectrum analyzer. A typical output energy for the $P(20)$ line of 9.4 μ m transition was 0.2 J/pulse as measured by a Scientech 36,0001 disk calorimeter. Because of the high-energy per pulse, the beam could be clearly seen on a carbon glass blower's paddle. The beam was square, \sim 1.3 cm on a side, and showed a concentric ring pattern in intensity profile. The temporal profile of the pulse was measured with a Rofin photon drag detector. The self mode locked pulse was comprised of an initial high intensity component of 170 ns FWHM followed by a low intensity “tail” lasting \sim 10 μ s. Over 80% of the energy was contained in the initial pulse section.

In these experiments the output from the TEA- CO_2 laser, pulsing at 2.5 Hz, was focussed into a gas cell containing the parent gas. 30 and 13 cm focal length BaF_2 lenses were used. The gas cell was of pyrex construction with NaCl windows. These windows were compression fit to the pyrex cell with Buna-N “o-ring”. Dimensions of the pyrex section of the cell are 3.0 cm i.d. by 10 cm in length. A teflon vacuum valve with Buna-N “o-ring” seals was fitted to the cell. The air

leak rate of the evacuated cell was less than 1 Torr in a 24-h period. Gas phase samples of the parent gas were introduced into the cell via a vacuum manifold. Pressures were measured with a MKS 220 BHS capacitance manometer. Silicone high-vacuum grease was used for all seals.

After focussed irradiation of the parent gas for one to several thousand pulses, the gas sample was analyzed by one of three methods. For GC/FID and GC/MS, the irradiated samples were first concentrated by cryogenic trapping in a stainless steel sampling loop maintained at 77 K. To insure that the products were completely trapped, freezeout times ran as long as 1 h. After freezeout, the sampling loop was pressurized with He and allowed to warm to room temperature. This sample was then extracted with a gas sampling syringe through a standard GC septum fitted to the sampling loop with a Swagelok "T". Product identification was performed with a HP-5985B GC/MS with library spectrum search. Product quantification was performed with a HP-7100A GC/FID. In both cases a Poropak Q column was used. Samples were run with a temperature program starting at 90 °C, ramping to 150 °C. The products were also confirmed by infrared spectrophotometry. Because of the low sensitivity of infrared spectrophotometry relative to that of GC/FID, only the major products could be observed with ir analysis.

Fluences at the focus of the photolysis arrangement can be calculated if the focussed beam waist is known. The beam waist was measured by scanning a razor blade attached to a translation stage across the focus zone while measuring the power. A focussed area of 0.0052 cm² was calculated for the 30 cm focal length lens, while the 13 cm focal length lens had a focussed area of 0.0013 cm².

The reagents used in this study were C_2F_3Cl and $C_2F_2Cl_2$ (cis-trans) both from PCR (>98%), Ar, and O_2 Matheson (>99.99%). The purity of these gasses were confirmed with GC/FID.

Results

The first step in the analysis of the stable species produced in the IRMPD of C_2F_3Cl was to identify each particular species and to characterize this species in terms of gas chromatographic retention time so that subsequent quantitative analysis could be performed. This step was easily accomplished with the use of GC/MS. A typical GC/MS analysis is shown in Fig. 1. Although there are many components to the photolyzed gas, the identification proved to be straightforward. However, in certain cases the exact isomer was not unambiguously determined. In particular, the two peaks at retention times of 13.7 and 14.6 min exhi-

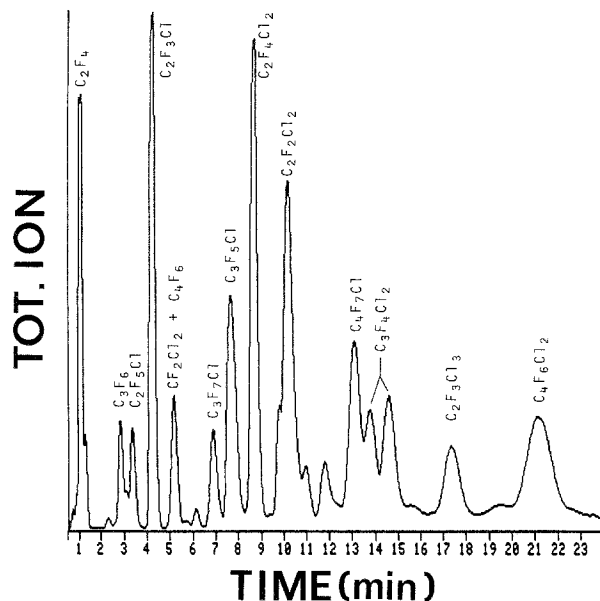


Fig. 1. Shown in this figure is the total ion output of the GC/MS analysis of the products of the IRMPD of C_2F_3Cl . The GC was performed using Poropak Q, temperature programmed for 2 min at 90 °C, then ramping at 8 °C/min to a final temperature of 150 °C. In this particular run, 5 Torr of C_2F_3Cl was photolyzed at 1055 cm⁻¹ with the fluence of 23 J/cm² to about 50% dissociation (about 3000 pulses)

bited similar ion spectra, both having an empirical formula of $C_3F_4Cl_2$. The experimental conditions for the photolysis resulting in the data of Fig. 1 were quite harsh by virtue of the fact that about 50% of the parent C_2F_3Cl has reacted. Nonetheless, data such as that of Fig. 1 were helpful in determining the mechanisms for product formation since both primary and secondary photolysis products were observed. The total ion current output, in Fig. 1 does not result in a simple quantification of the product yields. Quantification of products is more readily accomplished using FID detection since the peak area is related to concentration and carbon number [27].

The length of photolysis for these quantification experiments ranged from 100 to several thousand pulses, with a pulse energy of 0.12 ± 0.02 J/pulse. The number of product species was observed to increase with increasing number of pulses. The distributions of products determined in these experiments are shown in Table 1. For the sake of clarity only the products observed when 10% and 50% of the parent is dissociated are shown. This table is instrumental in distinguishing between primary and secondary photolysis products, the primary products being those observed at 10% dissociation. The additional products observed 50% photolysis are a result of subsequent photolysis and reaction of the primary photolysis products.

Table 1. Fractional yield of IRMPD products of C₂F₃Cl

Product ^c	Fraction of decomposition ^b	
	0.1	0.5
	Yield ^d	Yield
C ₂ F ₄	0.37	0.30
C ₂ F ₂ Cl ₂	0.28	0.12
C ₃ F ₅ Cl	0.16	0.24
C ₃ F ₄ Cl ₂	0.06	0.03
C ₄ F ₇ Cl	0.02	0.01
C ₂ F ₃ Cl ₃	0.10	0.03
C ₃ F ₆	–	0.03
C ₄ F ₆	–	0.04
C ₂ F ₄ Cl ₂	–	0.02
CF ₃ Cl	–	0.02
C ₄ F ₆ Cl ₂	Trace	0.01
C ₂ F ₅ Cl	–	Trace
CF ₂ Cl ₂	–	Trace
C ₃ F ₇ Cl	–	Trace

^a Photolysis was at 1050.44 cm⁻¹ with a maximum fluence of 23 J/cm² (focussed)

^b Fractional decomposition increased with increasing number of pulses

^c Products were identified from GC/MS

^d Yields were obtained from GC/FID using carbon number weighting

While analysis by GC/FID is ideal for the quantitation of product species it is limited by the fact that it can't distinguish certain isomers, specifically cis and trans C₂F₂Cl₂. To obtain information concerning the conformation of the C₂F₂Cl₂ produced in this experiment ir analysis was used. When 5 Torr of sample was photolyzed and subsequently analyzed, only two major products were observed; C₂F₄ and trans-C₂F₂Cl₂ [21]. Infrared spectra of a cis and trans mixture of C₂F₂Cl₂, in nearly equal proportions, were also obtained. It was found that both isomers were strong absorbers [21]. By comparison of spectra obtained from photolysis of C₂F₃Cl and those of cis-trans C₂F₂Cl₂ mixture, we estimate that if the cis isomer of C₂F₂Cl₂ were being produced in the IRMPD of C₂F₃Cl, it could not account for more than 2% of the C₂F₂Cl₂ produced. GC analysis could not confirm this fact since the two isomers are not resolved with the column used.

Since C₂F₂Cl₂ is known to dissociate under the influence of CO₂ laser radiation [16], infrared spectra of cis-trans C₂F₂Cl₂ photolyzed under identical conditions as those of C₂F₃Cl were obtained. Only the cis isomer has an absorption available to laser irradiation and it is possible that cis to trans isomerization could be taking place. However, no change in the cis-trans ratio was observed and no products were observed for this photolysis. C₂F₄ does not have an infrared active

absorption in the region of the laser and subsequent photolysis of this species is unlikely. When the parent was photolyzed for sufficient number of pulses that 25% of the parent should have dissociated, the absorptions as analyzed by ir, were still mainly due to C₂F₄ and trans-C₂F₂Cl₂. However, close inspection revealed that a weak broad absorption from about 1200 to 800 cm⁻¹. This broad absorption must be due to the other primary and secondary products of the photolysis.

The majority of products are consistent with a carbene formation mechanism, however, this mechanism cannot be used to explain the formation of C₂F₃Cl₃, C₄F₆Cl₂, or C₄F₇Cl. To determine the mechanism of the formation of these products a study of the fluence and pressure dependencies of this reaction system was undertaken. Photolysis of 5 Torr neat C₂F₃Cl were carried out at fluences ranging from 7.75 to 280 J/cm² and relative yields of C₂F₃Cl₃ and C₄F₆Cl₂ were determined for each experiment using GC/FID. The relative yield of C₂F₃Cl₃ was calculated in the following manner,

$$\text{Rel yield C}_2\text{F}_3\text{Cl}_3 = \frac{[\text{C}_2\text{F}_3\text{Cl}_3]}{[\text{C}_2\text{F}_2\text{Cl}_2] + [\text{C}_3\text{F}_4\text{Cl}_2] + [\text{C}_4\text{F}_6\text{Cl}_2] + [\text{C}_2\text{F}_3\text{Cl}_3]}$$

Products resulting from CF₂ reaction were not used in these calculations since formation of any of the aforementioned products would have no effect on C₂F₄ or C₃F₅Cl formation, as discussed below. It was observed that C₄F₆Cl₂ decreased rapidly with increasing laser fluence and in fact no C₄F₆Cl₂ was observed at fluences greater than 30 J/cm². The plot of relative yield C₂F₃Cl₃ vs. fluence is shown in Fig. 2. At fluences greater than 280 J/cm optical breakdown occurred. The ratio of products formed from carbene reactions were also found to change with laser fluence. The change in products seen as C₃F₄Cl₂ variance with fluence is shown in Fig. 3.

The relative yields of the products were also determined as a function of added argon pressure. Photolysis efficiency was observed to decrease rapidly with increasing argon pressure. C₂F₃Cl₃ formation also decreased with increasing argon pressure, and was not observed at pressures greater than 50 Torr. The percent yield C₄F₆Cl₂ vs. argon pressure is shown in Fig. 4. When fluence was varied at these pressures of argon the percent yield C₄F₆Cl₂ was observed to decrease rapidly with increasing fluence. The percent yield was calculated by comparing the amount of C₄F₆Cl₂ produced to the amount of parent remaining. In all of these experiments the parent showed less than 2% dissociation. The ratio of C₃F₄Cl₂/C₂F₂Cl₂ was observed to decrease rapidly with added argon pres-

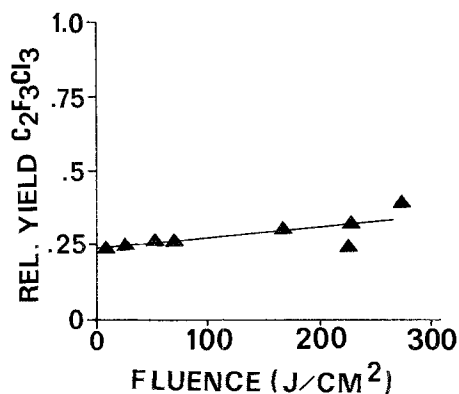


Fig. 2. A plot of the relative yield of $C_2F_3Cl_3$ as a function of CO_2 laser fluence. For all data 5.0 ± 0.2 Torr of C_2F_3Cl was photolyzed for ~ 100 pulses. At fluences below $150 J/cm^2$ a 30 cm focal length lens was used while a 13 cm lens was used to obtain the higher fluence results. The line shown is the computed least squares fit to the data

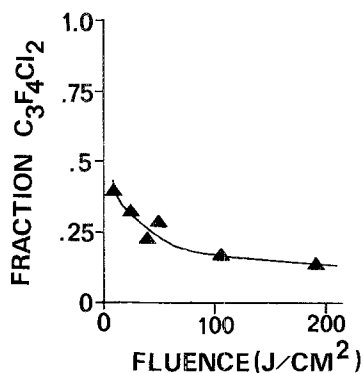


Fig. 3. Variance of the fractional yield of carbene addition products, $C_3F_4Cl_2$, with laser fluence. Same conditions as in Fig. 2

sure. The dependence of this ratio on argon pressure is shown in Fig. 5. Again the points are plotted as fraction carbene products seen as $C_3F_4Cl_2$. Experiments were also performed with added O_2 gas. The only products observed when 10 Torr of O_2 was added to 5 Torr C_2F_3Cl and photolyzed for 3600 pulses were F_2CO , $FCICO$, and CF_2ClCOF . These products were characterized by their sharp infrared absorption [29, 30]. Since no C_2F_4 or $C_2F_2Cl_2$ were observed in these experiments, it seems likely that O_2 was reacting with the primary photofragments before reaction via the mechanisms operative in the case of neat photolysis could occur.

To gain insight into the formation mechanisms of $C_2F_3Cl_3$ about 100 Torr Cl_2 was photolyzed for $19\frac{1}{2}$ h in the presence of 10 Torr C_2F_3Cl . Cl_2 is known to form atomic chlorine when photolyzed by uv radiation [39]. In this experiment a mercury pen ray was used as the light source. It should be noted that C_2F_3Cl also absorbs the mercury pen ray, and dissociation will

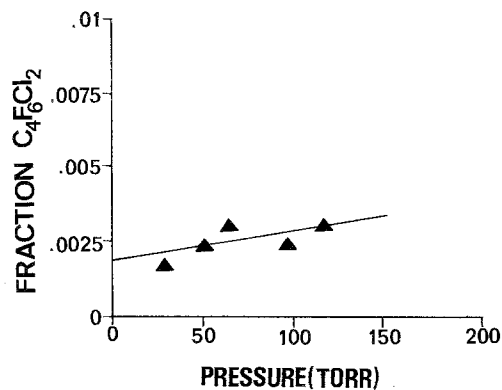


Fig. 4. A plot of fractional yield of $C_4F_6Cl_2$ vs. argon buffer gas partial pressure. All photolysis were carried out at a focussed fluence of $7.7 \pm 0.7 J/cm^2$ and with the partial pressure of C_2F_3Cl being 5.0 ± 0.2 Torr. The gas mixtures were photolyzed at $1055 cm^{-1}$ for ~ 2000 pulses using a 30 cm focal length lens. The solid line is the least squares fit to the data

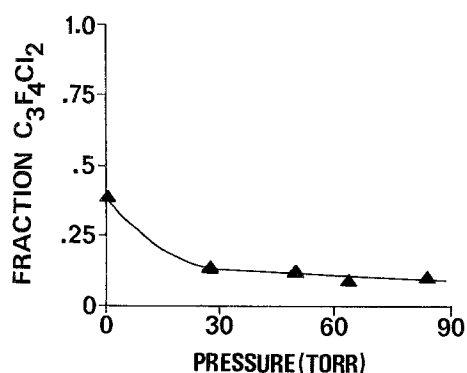


Fig. 5. A plot of the fractional yield of carbene addition products vs. argon gas pressure for 5.0 ± 0.2 Torr of C_2F_3Cl being photolyzed at $1055 cm^{-1}$ with a focussed fluence of $7.7 \pm 0.7 J/cm^2$

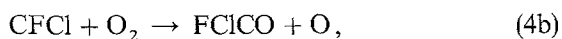
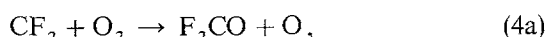
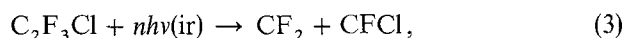
occur. The products of this reaction as determined by GC/FID were $C_2F_3Cl_3$, and to a lesser extent CF_2Cl_2 and CF_3Cl . The latter two products probably result from the reaction of CF_2 and $CFCl$ with Cl_2 , since the uv photolysis of C_2F_3Cl is known to result in the formation of these carbenes [31]. A white film, probably a polymer of C_2F_3Cl , was observed on the cell walls after photolysis.

Reactions

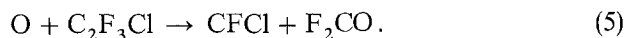
A majority of the products observed in this study are consistent with initial carbene formation. C-C bond scission, resulting in carbene formation, seems likely in view of the thermodynamics for dissociation and the direct observation of CF_2 and $CFCl$ produced in the low-pressure IRMPD of C_2F_3Cl [11, 22, 23]. The C-Cl scission requires 510 kJ/mole whereas halocarbene formation requires only 402 kJ/mole [22].

1.1. Reactions with O₂

Perhaps the greatest evidence of a carbene formation dissociation mechanism comes from the data on the uv photolysis of C₂F₃Cl with added O₂ [31]. In the latter study, direct evidence for the formation of CF₂ and CFCI was obtained by the observation of transient absorption due to these carbenes. In the presence of O₂, the uv photolysis resulted in the formation of F₂CO and FCICO. We also observed the formation of F₂CO and FCICO in the ir photolysis of C₂F₃Cl in O₂. But in addition to these products, CF₂CICOF was found in high-concentrations. It was assumed in [20] that the formation CF₂CICOF in the IRMPD case was an indication that carbene formation was not occurring. However, in the flash uv photolysis of C₂F₃Cl, a high-concentration of spacially homogeneous distributed carbenes would be formed. This is in contrast to the non-uniform distribution of species produced at the focus in the IRMPD experiments. In this case, reactions with the cold, surrounding parent gas are probable, and in fact may be held responsible for the formation of CF₂CICOF. Reactions which account for the formation of the carbonyl products in the presence of O₂ are

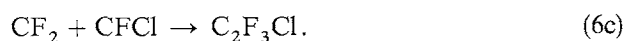


where the oxygen atom is most likely formed in the ³P state to conserve overall spin. Reactions (4a and b) are known to occur, though the activation energy of the CF₂ reaction is rather high [32]. An alternate route to carbonyl difluoride formation may be subsequent reaction of CF₂CICOF in the absence of stabilizing collisions



1.2. Dimerization

The formation of many of the products observed in the neat IRMPD can also be explained by an initial halocarbene formation mechanism. The steps resulting in C₂F₄ and trans-C₂F₂Cl₂ formation may be simple carbene recombination [33]

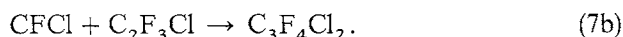
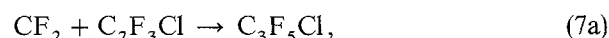


The present experiments do not yield direct evidence for (6c) but the occurrence of 6a and b) make this reaction likely. The reason for the formation of the

trans-C₂F₂Cl₂ over the cis isomer is that the C–Cl bond on the CFCI is highly polar. With the highly electronegative fluorines, the chlorine groups would be expected to be polarized positive. The electrostatic repulsion of the two chlorines would then cause the trans isomer to form preferentially. Subsequent infrared photoisomerization of cis-C₂F₂Cl₂ cannot be used to account for the occurrence of the trans isomer since photolysis of an equal mixture of cis and trans isomers did not result in any change in the isomer ratios.

1.3. Addition

Carbene reactions with olefins are known to yield three carbon products [35]. Both cyclopropanes and propenes can be formed [36]. In the present experiments, the occurring isomers of the three carbon products could not be unambiguously determined. The MS data does not lend any help in the matter since the species may isomerize at the ion source. But the C₃ products observed in this study may well be propenes since the reactions occurred at rather low pressures, i.e. energy loss collisions occur at a low rate. The reaction resulting in the formation of the observed C₃ products are



When a halocarbene, formed in the photolysis reaction of C₂F₃Cl, adds to the parent, a cyclopropane is initially formed [36]. The resulting cyclopropane would have enough energy to isomerize to a propene. Chlorine atom migration to a carbon containing only fluorine, the most electron deficient area of the molecule probably occurs [37]. In the case of C₃F₄Cl₂, this migration can lead to the production of the cis and trans isomers of the 1,3-dichlorotetrafluoropropene. In fact, two GC peaks were observed for C₃F₄Cl₂ though it was unclear whether this was due to two propene isomers or a propene and cyclopropane in the case of C₃F₅Cl only one isomer can be produced, 3-chloropentafluoropropene.

2. Other Reactions

The formation of C₂F₃Cl₃ as a primary product in the ir photolysis of C₂F₃Cl is difficult to explain by a carbene reaction mechanism. It is more likely due to a reaction of chlorine with the parent C₂F₃Cl. The uv photolysis of Cl₂ in the presence of C₂F₃Cl confirmed that C₂F₃Cl₃ was produced in the reaction of atomic chlorine with the parent. The conditions under which the uv photolysis were carried out were such that both Cl₂ and C₂F₃Cl absorbed the uv radiation. However,

the uv transition of C₂F₃Cl is dissociative and reactions between electronically excited C₂F₃Cl and molecular chlorine are unlikely. In fact, products that can be attributed to the reactions of the carbene dissociation products and Cl₂ were found in the uv photolysis. In the ir photolysis atomic chlorine may result from parent dissociation from the high energy C–Cl scission channel or might result from thermolysis of the primary carbene photoproducts. These reactions will be discussed further after assessing the degree to which thermolysis may take place. The formation of C₄F₇Cl probably occurs via a 2+2 addition mechanism of C₂F₄ with C₂F₃Cl. These 2+2 additions are known to occur in haloalkene thermolysis and in fact is the observed thermal reaction route in C₂F₃Cl pyrolysis [38]. Cyclobutane formation is thought to occur via a diradical state of one of the olefins [39], in this case where the diradical ethylene is presumably an intermediate state of



Reaction (6a). It is generally thought that the more electronegative the substituent groups on the olefin, the more stable the diradical intermediate. Since C₂F₄ and C₂F₂Cl₂ are most likely formed by similar mechanisms, one might expect to observe C₄F₅Cl₃ formation as well. But if the C₂F₂Cl₂ diradical state is short lived, the corresponding C₄F₅Cl₃ would not be observed in high-concentrations. The fact that this product was not observed in this study, then, is consistent with the theories for diradical stabilization. C₄F₆Cl₂ is formed by the same mechanism. But since there is a temperature increase in the photolysis zone, it is difficult to determine to what extent carbene association reactions can be used to account for observed yield.

3. Discussion

Although the formation of halomethylene carbenes has been shown to be the dissociation mechanism at low-pressure (10 mTorr) photolysis conditions [22], there are several factors which may influence the dissociation and product formation mechanisms when the pressure is increased. The mechanisms operative at low pressures may not be the same as those of higher pressure experiments. However, in the above discussion it was demonstrated that with the assumption of carbene formation, 90% of the products could be accounted for with known reaction mechanisms. The carbon bond scission is apparently the predominant mechanism of dissociation at these higher pressures, as well as in the low-pressure photolysis. One of the factors that might result in a different photolysis dissociation mechanism is collisions between excited

parent species prior to dissociation. These collisions may serve to randomize the energy within the excited species in the case where the energy is localized. In particular, it is not clear that the low-pressure IRMPD of C₂F₃Cl results in the formation of products with the lowest possible activation energy for formation. A lower enthalpy channel exists for C₂F₃Cl decomposition involving the 1,2 elimination of FCl



The enthalpy of the above reaction is about 88 kJ/mole lower than that of the carbon double bond scission reaction but it would be expected to have a high-activation energy in addition to the enthalpy. The fact that perfluoroacetylene was not observed as a product of these IRMPD experiments would support the thought that the channel for the above reaction lies above that of the carbon bond scission and that the channel was not passed by in the formation of the halomethylene carbenes at low-pressures. This point was not addressed in the low-pressure IRMPD studies since the low-transition strength for FCl prohibited laser excited fluorescence confirmation of the negative result [22].

In addition to randomization of energy within a molecule in the presence of collisions, randomization of energy among collision partners will also result in an effective energy distribution which is different at high-pressures vs. those at low-pressures. These randomizations come in the form of energy gain/loss collisions where one molecule gains energy and the other molecule loses energy. The effect of these collisions to change the distribution from that described by Poisson statistics, (the probability for absorption is equal to the probability for stimulating emission at low-pressures) to that described by a Maxwell-Boltzmann thermal distribution. The thermal distribution will have the same total energy, but will have a high-energy tail which can effectively cross-several dissociation channels.

It is usually difficult to estimate the number of collisions that a molecule will experience during the time required for dissociation. This estimation requires knowledge of the timescales for excitation and dissociation events. These timescales are known for the IRMPD of C₂F₃Cl [5]. In low-pressure studies it was found that the intensity of the laser controlled the dissociation rate, and the rate at which molecules dissociate is thus the rate at which they are excited to a state where the dissociation rate becomes competitive with the rate of excitation into higher energy levels in the dissociative continuum. The low-pressure C₂F₃Cl dissociation data also suggest that this rate of dissociation is proportional to the square root of photolysis laser intensity. With the low-pressure rate of CF₂ pro-

duction from C_2F_3Cl of $3 \times 10^6 s^{-1}$ at a fluence of $37 J/cm^2$, the rate of dissociation in these experiments is calculated to be $6 \times 10^6 s^{-1}$ (fluence of $150 J/cm^2$). By comparison, the collision rate at 5 Torr is $\sim 10^8 s^{-1}$.

It is also possible to assess the amount of heating that may take place in the system. The energy content of both CF_2 and $CFCI$ formed in the IRMPD of C_2F_3Cl at low-pressures is known [22]. Both products are formed with a relatively low translational energy content but with substantial energy partitioned in both rotational and vibrational degrees of freedom. Rotational energy relaxation is fast and may be equilibrated with the gas after a few gas kinetic collisions. Vibrational energy relaxation of both CF_2 and $CFCI$ is much slower and at 5 Torr, mass diffusion of vibrationally excited species out of the photolysis zone is considerable heat loss mechanism. For comparison, the diffusional half life of a species formed in the photolysis zone is about 5 ms, whereas the vibrational relaxation half life for $CFCI$ and CF_2 in 5 Torr of Ar is 0.2 and 3 ms, respectively [16, 23]. Thus vibrational relaxation occurs on a timescale which is comparable to that of diffusion. From the 40 kJ/mole of excess energy partitioned in translations and rotations of the products of low-pressure photolysis and the high-temperature heat capacity of $100 J/mole \cdot K$ for the products, the temperature jump in the photolysis zone is 400 K. Assuming complete vibrational relaxation as well, the temperature jump is about 840 K. This temperature will decrease rapidly due to the generated shock wave, mass diffusion and thermal conduction. In fact, since the heat transfer coefficient is about equal to that of mass diffusion, the temperature jump will decrease by a factor of two in about 3 ms.

Because the temperature in the photolysis zone is much higher than that of the surrounding gas, the interpretation of the mechanisms for product formation must be considered with care. The carbene addition and dimerization reactions should not be significantly perturbed by the temperature jump since these reactions are in general slow and thermal relaxation will occur on a timescale which is fast compared to these reactions. On the other hand, one possible mechanism for chlorine atom formation is thermolysis of the halomethylene carbene and C_2F_3Cl dimerization to form the observed $C_4F_6Cl_2$ is known to proceed thermally as well. However, the variation of the product yields with laser fluence and with added argon gas pressure allows one to discern between thermal and photolytic processes.

$C_2F_3Cl_3$ is most likely formed from the reaction of atomic chlorine with the parent C_2F_3Cl . Chlorine atom may be formed in two ways, photolytically from C_2F_3Cl or from the dissociation of the primary fragment, $CFCI$. It is not uncommon to observe two

dissociation mechanism in IRMPD experiments and in fact the energy of carbon chlorine bond scission is only $\cong 100$ kJ/mole greater in energy than that of the C–C bond. However, in this case we believe chlorine is formed by a thermal process. The main evidence suggesting that chlorine atom formation is not a photolytic process is found in the fluence dependence of $C_2F_3Cl_3$ formation. If Cl formation is a photolytic process the relative yield of $C_2F_3Cl_3$ should show a strong fluence dependence. As illustrated in Fig. 2, the relative yield of $C_2F_3Cl_3$ changes very little with large changes in fluence.

The most likely source of atomic chlorine formation then is a thermolytic decomposition of the “hot” $CFCI$ fragment. The vibrational temperature of $CFCI$ observed at lower pressures is about 1550 K, and this temperature does not increase significantly with increasing fluence [22]. At these temperatures the RRK unimolecular dissociation rate for $CFCI$ is $10^2 s^{-1}$, on the order of the vibrational relaxation rates calculated for this system. It is conceivable that enough $CFCI$ dissociates to account for the amount of $C_2F_3Cl_3$ observed. Cl formation from $CFCI$ also accounts for the observed mass imbalance of the products resulting from carbene reactions. If Cl is formed photolytically no mass imbalance would be observed unless the C_2F_3 fragment would undergo further dissociation to form $CF_2 + CF$. This is not likely since C_2F_3 has a lower energy dissociation channel available to it, namely



2+2 additions may occur concerted through an excited electronic state or thermally through a 4 carbon biradical intermediate. Both processes may occur in these experiments. It has been shown above that a temperature increase of up to 840 K may occur in the photolysis zone. The temperature jump, while short lived, is enough to cause thermal reaction to some extent. Excited electronic states may also be formed. The recombination of photofragments may result in electronically excited product or an inverse intersystem crossing from the ground state singlet to the first excited triplet by direct photoexcitation of the parent may occur.

C_4F_7Cl comes from the reaction of C_2F_4 with C_2F_3Cl . This reaction must involve either an electronically excited C_2F_4 or a thermal process. Any electronically excited C_2F_4 that is produced in this system must be the result of the reaction of the photofragments. C_2F_4 does not absorb the CO_2 laser radiation. It is also possible to rule out thermal processes. CF_2 dimerization reaction rates are very slow and this reaction will take place long after thermal relaxation. The addition of buffer gas to the photolysis system has been shown to cause an increase in temperature [25, 40].

However, C_4F_7Cl yield decreases very rapidly when argon is added to the system. This observation is consistent with a mechanism in which electronically excited C_2F_4 is produced in the dimerization of CF_2 . The added argon would serve to quench the excited C_2F_4 formed and thus C_4F_7Cl formation would be hindered. The fact that no change in yield of C_4F_7Cl was observed with changing fluence is also consistent with the proposed mechanism since this would also increase the temperature of the system.

$C_4F_6Cl_2$ shows the opposite behavior when argon buffer gas is added to the system. $C_4F_6Cl_2$ yield increases initially, but the yield does not change significantly with pressures of buffer gas greater than 20 Torr (Fig. 4). This eliminates the possibility of an excited electronic state being formed from the recombination Reaction (6c) since there should be a decrease in the product yield with addition of argon as observed in C_4F_7Cl .

The question then is whether the process is thermal or occurs through an excited electronic state produced by an inverse intersystem crossing. Bailey et al. [40] have shown that the addition of buffer gas to the photolysis system causes the temperature to rise initially and then decrease at higher pressures. $C_4F_6Cl_2$ exhibits similar behavior when Ar is added to the system, indicating, at first glance, a thermal process. However, at higher fluences and similar argon pressures the yield of $C_4F_6Cl_2$ decreases rapidly, and in fact little $C_4F_6Cl_2$ is observed beyond a fluence of $40 J/cm^2$ at any argon pressure. This fact suggests that $C_4F_6Cl_2$ formation is not thermal since the temperature of the system would have the opposite fluence dependence, i.e., it should increase with increasing fluence.

This observed fluence dependence can be explained by the reaction of electronically excited C_2F_3Cl formed by inverse intersystem crossing prior to dissociation. The strong fluence dependence observed would be expected in this case since the reaction yield would be dependent on the time the molecule spends in the energy states required for triplet formation. This reaction must take place at a rate competitive with the rate of pumping through the quasicontinuum. If the rate of pumping becomes significantly greater than the rate of ISC, then no $C_4F_6Cl_2$ will be observed. ISC would also show the same pressure dependence observed here, since the addition of 100 Torr or less room temperature argon would not significantly perturb the rate of pumping in the quasi-continuum [25].

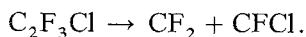
The observed changes in the ratio of $C_3F_4Cl_2/C_2F_2Cl_2$ with laser fluence and argon pressure is also interesting. CF_2 and $CFCl$ are formed in a relatively small volume of the reaction cell, the photolysis zone and subsequently diffuse throughout the cell. Initially the concentration of CF_2 and $CFCl$ near the photolysis

zone will be high so that in this area the carbene recombination reactions will predominate, then as the CF_2 and $CFCl$ diffuse away from the photolysis zone the addition reaction will predominate. Therefore the ratio of $C_3F_4Cl_2/C_2F_2Cl_2$ will be a function of 1) the reaction rates of the addition, carbene recombination rates, 2) the rate of diffusion, and the initial amount of $CFCl$ and CF_2 formed. The observed behavior then is expected since increasing argon pressure would decrease the rate of diffusion, causing the carbene recombination reactions to proceed for a longer period of time and thus decreasing the ratio of $C_3F_4Cl_2/C_2F_2Cl_2$. This behavior can be seen illustrated in Fig. 5. Increasing the fluence would increase the initial number of species formed again causing a decrease in this ratio.

Currently we are developing a quantitative model of this system in the hopes of extracting relative rate constants from product ratios.

4. Conclusion

This study shows that the dissociation mechanism in the medium pressure IRMPD of C_2F_3Cl is



Evidence is also given for the formation of Cl atom from a secondary thermal dissociation of $CFCl$ and formation of electronically excited C_2F_3Cl by intersystem crossing.

The products resulting directly from carbene formation are trans- $C_2F_2Cl_2$, C_2F_4 , $C_3F_4Cl_2$, and C_3F_6Cl . The chlorine atom in the system gives rise to $C_2F_3Cl_3$ while the excited C_2F_3Cl dimerizes to form $C_4F_6Cl_2$.

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