

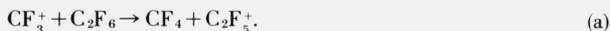
Reactions of Fluorocarbon Ions in C₂F₆. Implications for the Radiolysis*

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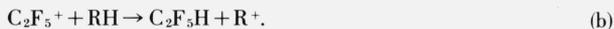
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Reactions of the fragment ions formed in the photoionization of C₂F₆, Xe-C₂F₆, and Kr-C₂F₆ mixtures have been investigated in the NBS photoionization mass spectrometer using both helium (21.2 eV) and neon (16.66–16.84 eV) resonance radiation. Contrary to previously held views, it is shown that CF₃⁺ ions having no internal excitation energy undergo the F⁻ transfer reaction:



A rate constant of $4 \pm 1 \times 10^{-11} \text{ cm}^3/\text{molecule} \cdot \text{s}$ is determined for reaction (a) at pressures below 10^{-2} torr. On the basis of the collision rate for these reactants, it can be estimated that, on the average, each CF₃⁺ ion undergoes 16 unreactive collisions before undergoing reaction (a). Therefore, from the facts that (1) in pure C₂F₆, all CF₃⁺ ions undergo reaction (a) at high pressures, and (2) CF₃⁺ ions formed by charge transfer from Xe⁺ ions with a maximum of 8.4 kJ/mol (2 kcal/mol) excess energy undergo reaction (a), one must conclude that reaction (a) is either thermoneutral or exothermic for ground state CF₃⁺ ions. Therefore, the earlier estimate for $\Delta H_f(\text{C}_2\text{F}_5^+)$ of $\sim 33 \text{ kJ/mol}$ (8 kcal/mol) must be revised downward: $\Delta H_f(\text{C}_2\text{F}_5^+) \leq 3.8 \text{ kJ/mol}$ (0.9 kcal/mol).

The C₂F₅⁺ ion is unreactive towards C₂F₆, but does react with alkanes through the H⁻ transfer reaction:



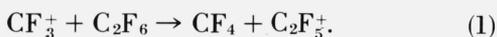
It is suggested that the CF₄ observed in previous gas and liquid phase radiolysis studies of C₂F₆-O₂ mixtures can be entirely ascribed to reaction (a). Small concentrations of impurities or accumulated products will react with the C₂F₅⁺ ions under normal low dose rate radiolysis conditions.

Key words: Fluorocarbons; heats of formation; ion-molecule reactions; mass spectrometry; photoionization; rate constants.

1. Introduction

The direct and the rare gas-sensitized radiolysis of gaseous and liquid C₂F₆ has been investigated extensively [1].¹ In addition, several mass spectrometric studies have dealt with the reactions of the perfluorinated ions (mainly CF₃⁺ and C₂F₅⁺) formed in C₂F₆ by electron impact [2].

The main reaction channel of the CF₃⁺ ion with C₂F₆ is as follows:



From the generally accepted heats of formation of these species [3-4] (for C₂F₅⁺ only an estimated heat

of formation was available), it was calculated that reaction (1) was endothermic by at least 29 kJ/mol (7 kcal/mol) [2]. On this basis, the observation of reaction (1) in the ion source of the mass spectrometer has been explained as the reaction of an internally excited CF₃⁺ ion. Since this seemed to indicate that the dissociation of the C₂F₆⁺ ion resulted in the formation of excited CF₃⁺ fragment ions:



the charge exchange reactions of the CF₃⁺ ion formed in reaction (2) were investigated in a tandem mass spectrometer [2b]. In these experiments, CF₃⁺ ions having an average kinetic energy of 0.3 eV², were

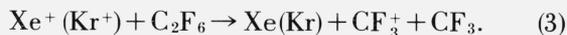
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¹ Figures in brackets indicate the literature references at the end of this paper.

² 1 eV = 96.485 kJ · mol⁻¹.

reacted with a variety of compounds having ionization potentials above and below the reported value for CF_3 (9.17 eV) [3]. The results suggested that some fraction of the CF_3^+ ions had as much as 2.9 eV internal energy under the conditions of these experiments, since charge exchange was found to occur with C_2H_4 (I.P. = 10.5 eV), C_3H_8 (I.P. = 11.1 eV), and C_2H_6 (I.P. = 11.5 eV) [5]. However, these same charge transfer reactions were not detected in experiments carried out in an ion cyclotron resonance instrument (icr) [2c], and it was concluded that the internally excited CF_3^+ ions initially produced in reaction (2) had sufficient time to relax during the long time scale of the icr experiment (10^{-3} s between collisions).

The present study was undertaken with the intention of examining the effect of varying internal energy on the reactions of the CF_3^+ ion, and to see if reaction (1) can also occur for ground state CF_3^+ ions. The CF_3^+ ions were produced by photoionization of C_2F_6 using neon (16.66–16.84 eV) and helium (21.2 eV) resonance radiation, and by the charge exchange reaction between C_2F_6 and Xe^+ and Kr^+ ions:



The reactions of the CF_3^+ ions formed in these ways were examined in the NBS high pressure photoionization mass spectrometer [5], at a temperature of 300 K. Under these conditions, the ions have no excess kinetic energy.

2. Experimental Procedure

All experiments were carried out on the NBS high pressure photoionization mass spectrometer, which has been described in detail previously [5]. The instrument was equipped with the enclosed neon and helium resonance light sources, which deliver photons of 16.66–16.84 eV and 21.2 eV, respectively.

Meaningful experiments could not be carried out at pressures above about 0.5 torr in C_2F_6 , because of the appearance of product ions due to reaction with impurities, as well as to a general deterioration of the performance of the quadrupole mass analyzer apparently because of adsorption of C_2F_6 on the detector surface. During the early stages of this study, it was found that the mass spectrum obtained from the photoionization of C_2F_6 at pressures above approximately 0.1 torr exhibited a number of product ions such as CF_2Cl^+ and $\text{C}_2\text{F}_3\text{Cl}^+$, which were obviously produced in reactions of CF_3^+ and C_2F_5^+ with chlorinated impurities present in the sample (mainly CF_3Cl). CF_3Cl has also been reported as an impurity in C_2F_6 in several radiolysis investigations [1]. The effects due to this impurity were reduced when the C_2F_6 was subjected to gas chromatographic purification, but remaining traces prevented quantitative results from being obtained at C_2F_6 pressures above about 0.5 torr. However, for all of the experiments reported here, the total

contribution from impurity ions never exceeded 2 percent of the composite mass spectrum.

3. Results and Discussion

3.1. Photoionization of Pure C_2F_6

When C_2F_6 was irradiated with 21.2 eV photons, the major primary ions observed at low pressures ($< 10^{-4}$ torr) were CF_3^+ (58.5%) and C_2F_5^+ (36.8%). Other ions observed were CF^+ , 3.8 percent, and CF_2^+ , 0.9 percent. Figure 1 shows the variations in the intensities of the CF_3^+ , C_2F_5^+ , and CF^+ ions as the pressure of C_2F_6 in the reaction chamber of the mass spectrometer was increased. These results show that reaction (1) does occur under these conditions. That is, the intensity of the CF_3^+ ion shows a decrease with increasing C_2F_6 pressure, and the ionic product of the reaction between CF_3^+ and C_2F_6 must be C_2F_5^+ since no other ions show an increase in intensity in this pressure range. From the data obtained at low pressures ($< 10^{-2}$ torr), an average rate coefficient of $4 \pm 1 \times 10^{-11}$ cm³/molecule-second can be estimated for reaction (1). Within experimental error, the same rate coefficient for this reaction is obtained in experiments in which ionization of C_2F_6 is effected by 16.66–16.84 eV photons; (in that case, only CF_3^+ , 39% and C_2F_5^+ , 61%, ions are observed in the system at the "zero" pressure limit). It is important to note that this estimate of the rate coefficient for reaction (1) is based on a slope of a decay curve for CF_3^+ which represents the reaction of only 5 percent of these ions. Nevertheless, this value agrees within the

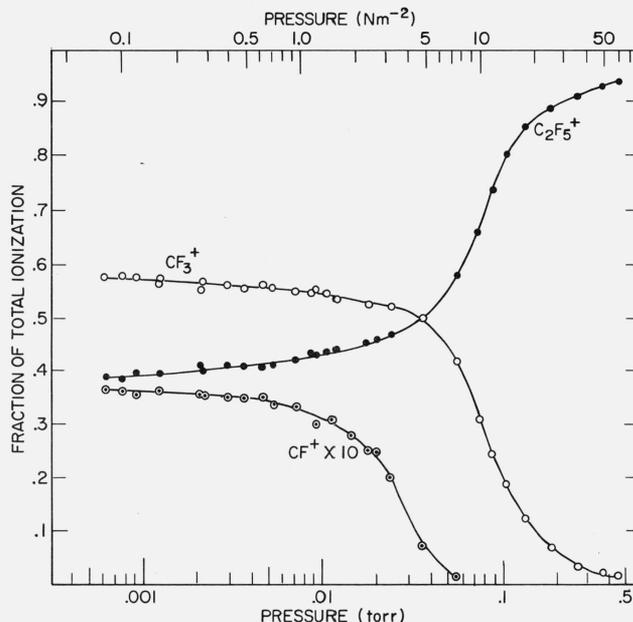


FIGURE 1. Photoionization of C_2F_6 at 58.4 nm (21.2 eV).

Fractional intensities of CF^+ , CF_3^+ , and C_2F_5^+ as a function of pressure.

experimental limits with the value of 3.4×10^{-11} cm³/molecule-second reported earlier [2b].

Because the residence time of the ions in the mass spectrometer is not precisely known at pressures above 10^{-2} torr, reliable rate coefficient estimates can not be obtained from the data taken in the higher pressure ranges. These results are, however, of interest, since they show that at pressures around 0.5 torr, essentially all of the CF₃⁺ ions have reacted to form C₂F₅⁺ (the fact that the ion currents shown in the figure do not add up to 100 percent in the high pressure region is to be explained by the impurity effects described in the Experimental Section). This observation is in general agreement with the results obtained by Marcotte and Tiernan [2b] in a time-of-flight mass spectrometer, which showed that at a pressure of ~0.4 torr, about 50 percent of the CF₃⁺ ions had reacted with C₂F₆. Since the observed rate constant for reaction (1) is about 4×10^{-11} cm³/molecule-second, and the rate constant for collisions between such fluorocarbon ions and C₂F₆ is on the order of 7×10^{-10} cm³/molecule-second [6-7], a CF₃⁺ ion undergoes ~16 unreactive collisions with C₂F₆ on the average before reacting. This means that if only CF₃⁺ ions having excess internal energy could undergo reaction (1), one would expect to observe a decrease in the rate of reaction (1) as collisional deactivation becomes more important at higher pressures. The fact that all CF₃⁺ ions eventually react in our system is inconsistent with this interpretation.

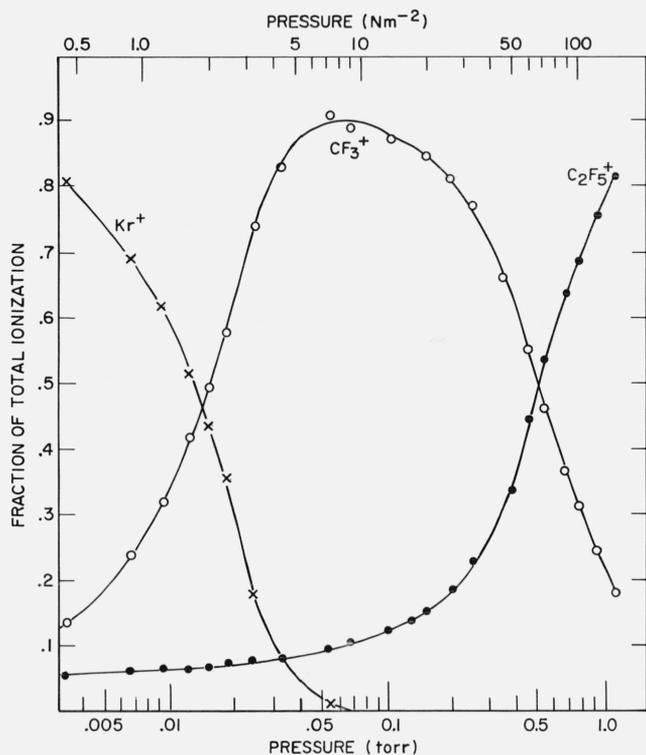


FIGURE 2. Photoionization of Kr-C₂F₆ (1:0.08) mixture at 74.4-73.6 nm (16.67-16.84 eV).

Fractional intensities of Kr⁺, CF₃⁺, and C₂F₅⁺ as a function of pressure.

The results given in Figure 1 also confirm the observation made previously [2] that the C₂F₅⁺ ions produced either as primary fragments or as reaction products do not react further with C₂F₆.

The results obtained in the 21.2 eV photoionization experiments also lead to estimates of the values of the rate coefficients for the reactions of the CF⁺ and CF₂⁺ ions with C₂F₆ of $1.9 \pm 0.4 \times 10^{-10}$ cm³/molecule-second and $1.45 \pm 0.30 \times 10^{-9}$ cm³/molecule-second, respectively.

3.2. Photoionization of C₂F₆-Rare Gas Mixtures

Figures 2 and 3 show the results of experiments in which krypton or xenon was irradiated with 16.66-16.84 eV photons in the presence of small amounts (8.2 %) of added C₂F₆. In such experiments, most of the initial ionization is effected in the rare gas, which, upon collision with C₂F₆ molecules, transfers charge (if charge transfer is exothermic) according to reaction (3). The energies available from the recombination energies of the rare gas ions are 14.0 and 14.7 eV in the case of Kr⁺, and 12.13 or 13.44 eV in the case of Xe⁺ [5]. Therefore, charge transfer from these ions to C₂F₆ should not result in the formation of C₂F₅⁺ fragment ions since there is insufficient energy available (the observed appearance potential of C₂F₅⁺ from C₂F₆ is about 15.4 eV) [7]. Actually, in the case of Kr⁺ ions,

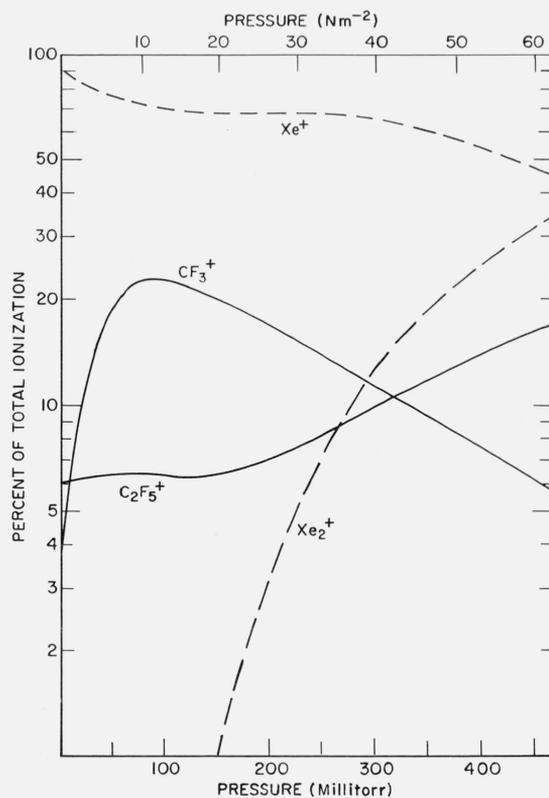


FIGURE 3. Photoionization of Xe-C₂F₆ (1:0.08) mixture at 74.4-73.6 nm (16.67-16.84 eV).

Fractional intensities of Xe⁺, Xe₂⁺, CF₃⁺ and C₂F₅⁺ as a function of pressure.

reported charge transfer spectra of C_2F_6 confirm that process (3) accounts for 93–98 percent of the $Kr^+ \cdot C_2F_6$ reactive encounters. In the case of xenon ions, only those ions produced in the $^2P_{1/2}$ state (13.44 eV) have sufficient energy to undergo reaction (3), while the ground state $^2P_{3/2}$ Xe^+ ions (12.13 eV) will be unreactive with C_2F_6 .

The results presented in figure 2 show that the intensity of the Kr^+ ion diminishes as that of CF_3^+ increases because of the occurrence of reaction (3) as the pressure is increased in the $Kr \cdot C_2F_6$ mixture. At pressures above 0.05 torr, reaction of the CF_3^+ ion to form $C_2F_5^+$ is observed. At the low pressure limit, where charge exchange does not occur to any appreciable extent, some $C_2F_5^+$ is produced by direct photoionization of C_2F_6 .

More interesting conclusions can be derived from the results given in figure 3 which shows the data obtained in the xenon- C_2F_6 mixture irradiated with 16.67–16.84 eV photons in the photoionization mass spectrometer. Here the $Xe^+(^2P_{1/2})$ ions (apparently about 30% of the Xe^+ ions formed under these conditions) undergo reaction (3) to produce CF_3^+ ions in C_2F_6 . The interesting point here is that if one accepts a heat of formation of CF_3^+ of 414 kJ/mol (99.1 kcal/mol) [3], then the CF_3^+ ions formed in reaction (3) involving $Xe^+(^2P_{1/2})$ and C_2F_6 can only have a *maximum* of 8.4 kJ/mol (2 kcal/mol) excitation energy. Even so, these CF_3^+ ions undergo reaction (1) to form $C_2F_5^+$ product ions (fig. 3). Since it is to be expected that an endothermic reaction would proceed at a rate which would not be observable under these experimental conditions, we are forced to conclude that if the overall sequence (reaction (3) followed by reaction (1)):



is thermoneutral, then the heat of formation of $C_2F_5^+$ can not be greater than 12 kJ/mol (2.9 kcal/mol). If we accept, as is probably the case, that the CF_3^+ ions have no internal energy at the time of reaction (1), a value for $\Delta H_f(C_2F_5^+)$ of 4 kJ/mol (0.9 kcal/mol) is obtained. Thus we must conclude that the value of 34 kJ/mol (8.1 kcal/mol) calculated earlier [1b] for $\Delta H_f(C_2F_5^+)$ is too high, and reaction (1) has therefore erroneously been assumed to be an endothermic reaction.

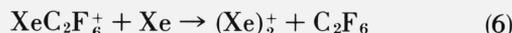
Figure 3 also shows that there is a slight increase in the yield of $C_2F_5^+$ at pressures below about 0.1 torr, where reaction (1) can not be important. It is likely that this observation is an experimental artifact caused by slight changes in the composition of the xenon- C_2F_6 mixture due to fractionation at the automatic leak assembly. However, the possibility can not be excluded that a reaction occurs between $Xe^+(^2P_{1/2})$ and C_2F_6 to form $C_2F_5^+$:



Accepting an estimate of the Xe-F bond strength of

134 ± 17 kJ/mol (32 ± 4 kcal/mol) [8], one obtains an estimate for $\Delta H_f(XeF)$ of -54 ± 17 kJ/mol (-13 ± 4 kcal/mol) and on this basis, reaction (5) may be slightly exothermic. In this connection, it should be pointed out that when Marcotte and Tiernan [2b] impacted Xe^+ ions onto C_2F_6 in a tandem mass spectrometer, they observed $C_2F_5^+$ as the major product ion (79%) even though, as discussed above, charge transfer from Xe^+ ions to yield this fragment is strongly endothermic. This unusual result could perhaps be explained by the occurrence of a reaction such as (5), which might be favored for ions which are translationally heated. On the other hand, it should be mentioned that in experiments carried out in this laboratory in an icr instrument, there was no evidence for the production of $C_2F_5^+$ ions through a reaction of Xe^+ with C_2F_6 .

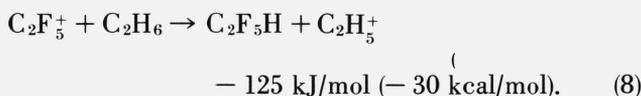
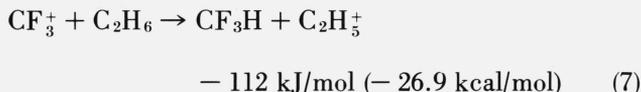
A final point to be mentioned in connection with the results given in figure 3 is the formation of Xe_2^+ as a product ion in a pressure region in which this ion would not be observed in pure xenon. This can be explained by the occurrence of a switching reaction involving the $XeC_2F_6^+$ association ion and xenon atoms:



Apparently the $XeC_2F_6^+$ is not detected in our experiments due to the fact that the dissociative lifetime of $XeC_2F_6^+$ is much shorter than the total ion transit time in our instrument.

3.3. Photoionization of C_2F_6 -Alkane Mixtures

In view of the fact that the photoionization curves of $C_2F_5^+$ and CF_3^+ indicate that these species probably do contain excess energy when formed by fragmentation of $C_2F_6^+$ [7], and because these species have been reported, under certain conditions [2b] to undergo charge transfer with molecules such as ethane and propane, with which charge transfer involving ground state ions would be endothermic, it was considered worthwhile to add ethane to C_2F_6 irradiated with 16.66–16.84 eV photons. The results of such experiments, in which C_2F_6 containing 5 percent ethane was irradiated at various pressures with 16.66–16.84 eV photons are given in figure 4. It is seen that there is no evidence for charge transfer reactions from CF_3^+ or $C_2F_5^+$ to C_2H_6 . However, both these fluorinated ions undergo exothermic hydride transfer reactions with ethane:

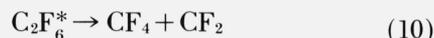


Small amounts of $C_2H_4^+$ and $C_2H_6^+$ are observed, and can be attributed to direct photoionization of the

3.4. Implications for Radiolysis

In the 70 eV mass spectrum, CF_3^+ and C_2F_5^+ account for 48 percent and 25.5 percent of the cations, respectively. The parent ion is absent, as is the case for many halocarbons. Since the parent ion apparently has a short lifetime, and it may therefore be anticipated that fragmentation will still be important at the pressures encountered in radiolysis experiments. However, the relative abundances of the various fragment ions can not be predicted with certainty, since these will depend on the density of the system. It can, however, be surmised that the major ion in the mass spectrum, CF_3^+ , will be present in the gas phase radiolysis of C_2F_6 and possibly even in the liquid phase radiolysis.

In some of the experiments performed during the course of this study in the photoionization mass spectrometer, up to 10 percent oxygen was added to C_2F_6 and no interactions between O_2 and the fluorocarbon ions were observed. Thus, it is of interest that radiolysis experiments carried out on C_2F_6 in the presence of 1 mol percent oxygen, at a pressure of two atmospheres [1a], show the formation of CF_4 as a product with a G value of 1.3 [$M/N_+ = 0.46$ since $W(\text{C}_2\text{F}_6) = 35.8$ eV. (table 1)] In the same study [1a], the yields of C_3F_8 and C_4F_{10} are reduced to zero when oxygen is added, indicating that the fluorocarbon radicals are effectively scavenged by oxygen. Therefore, reaction of CF_3 can not contribute to the formation of CF_4 in the presence of oxygen. These results indicate that the formation of CF_4 in this experiment can be attributed to reaction (1), and therefore, that ionization of C_2F_6 at a pressure of two atmospheres leads to the formation of CF_3^+ fragment ions with an ion pair yield of approximately 0.46. It may also be mentioned that an alternate channel for formation of CF_4 which has been mentioned, namely the decomposition of excited C_2F_6



can be excluded since the formation of this product is inhibited by the addition of bromine to the system [1g]. There is no reason to expect that small concentrations of bromine would have any effect on the primary decomposition of an electronically excited molecule.

Similar conclusions can be reached in the radiolysis of C_2F_6 in the liquid phase [1d] (table 1). That is, the addition of 10 percent oxygen inhibits the formation of C_3F_8 and C_4F_{10} , but CF_4 is formed in the presence of

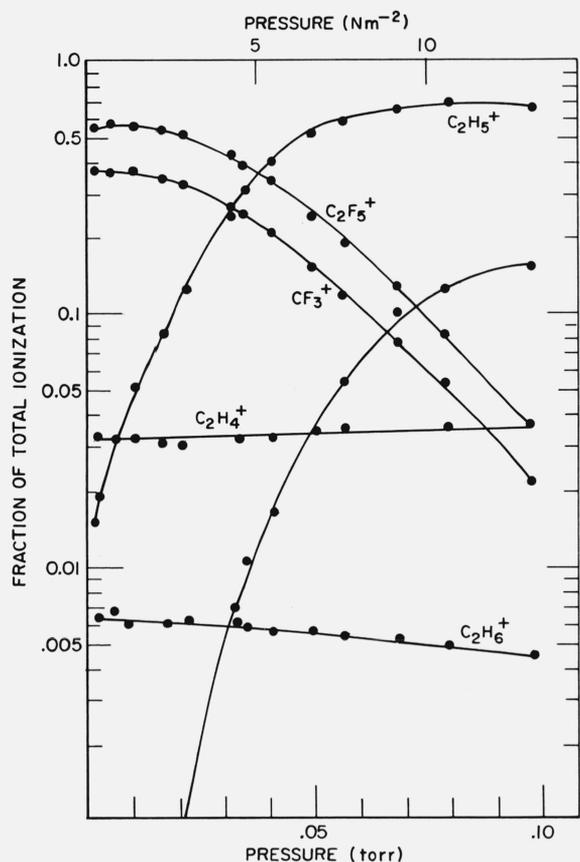
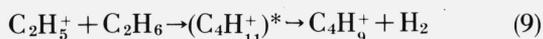


FIGURE 4. Photoionization of C_2F_6 - C_2H_6 (1:0.05) mixture at 74.4–73.6 nm (16.67–16.84 eV).

Fractional intensities of C_2H_4^+ , C_2H_5^+ , C_2H_6^+ , C_4H_9^+ , CF_3^+ , and C_2F_5^+ as a function of pressure.

ethane additive. At pressures above about 0.03 torr, the C_4H_9^+ product ion is formed through the occurrence of the well-known reaction sequence:



Addition of higher alkanes, C_3H_8 (I.P. 11.1 eV) and n - C_4H_{10} (I.P. 10.6 eV) indicates that in these cases H^- transfer to CF_3^+ and C_2F_5^+ is also the only reaction mode. It should be noted that because we are dealing here with dilute C_2F_6 -alkane mixtures the CF_3^+ and C_2F_5^+ ions will probably be collisionally deactivated at the time of reaction with the alkane molecule.

TABLE 1. Product yields per 100 eV (G) in C_2F_6 Radiolysis

| Conditions | $G(\text{CF}_4)$ | $G(\text{C}_3\text{F}_8)$ | $G(n\text{-C}_4\text{F}_{10})$ | Other | Reference |
|---|------------------|---------------------------|--------------------------------|---|----------------|
| Gas. 2 atm (200 kNm^{-2})..... | 2.5 | 0.45 | 0.20 | | [1a]. |
| Gas. 2 atm (200 kNm^{-2}) + 1% O_2 | 1.3 | 0.0 | 0.0 | | [1a]. |
| Gas. (7–500 kNm^{-2}) + Br_2 | undetectable | 0.0 | 0.0 | $G(\text{CF}_3\text{Br}) = 2.70 \pm 0.3$ $G(\text{C}_2\text{F}_5\text{Br}) = 3.00 \pm 0.3$ | [1g]. [1g]. |
| Liquid..... | 1.72 | 0.87 | 0.45 | | [1d]. |
| Liquid + ~10% O_2 | 0.97 | 0.0 | 0.0 | | [1d]. |

oxygen with a G value of approximately unity. Thus, as in the gas phase, evidence points to the formation of CF_4 through reaction (1). We can tentatively conclude, therefore, that ionic fragmentation to form CF_3^+ does occur in the liquid phase radiolysis of C_2F_6 .

As pointed out earlier in the discussion, reaction (1) is a slow reaction. This means that if any other reactive compound is present in the system—as an impurity, an additive, or as an accumulated product—the CF_3^+ ions may be intercepted by the foreign compound before reacting with C_2F_6 . Consequently, one would expect the yield of CF_4 to be sensitively affected by the presence of foreign compounds in the system. The reduction of the yield of CF_4 in the radiolysis of C_2F_6 when bromine is added illustrates this point [1g]. The results presented in that study showed that a small concentration of CF_3Cl impurity affected the ion-molecule kinetics of the system strongly, especially with respect to the fate of the unreactive C_2F_5^+ ion.

We do not at present have any information concerning the ionic reactions which occur when bromine, chlorine, or HCl are added to C_2F_6 , as they were in a recent radiolysis study [1g]. It is of interest, however, that in that study CF_3Cl was found as a product in the radiolysis of C_2F_6 - HCl mixtures, while CF_3 radicals are known to react with HCl to give CF_3H , exclusively [9]. As pointed out by the authors of that study, this may be considered as evidence of a contribution from ionic processes.

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