

[CONTRIBUTION FROM THE LABORATORIO DI CHIMICA DELLE RADIAZIONI E CHIMICA NUCLEARE DEL C.N.E.N., ISTITUTO DI CHIMICA GENERALE ED INORGANICA, UNIVERSITA DI ROMA, ROME, ITALY]

Mass Spectrometric Study of Ion-Molecule Reactions in Tetrafluoroethylene

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RECEIVED MAY 4, 1964

Ion-molecule reactions in tetrafluoroethylene have been studied up to a pressure of 0.06 torr inside the ion source of the mass spectrometer. All but two of the primary ions, *viz.*, $C_2F_4^+$ and CF_3^+ , followed the exponential decay law remarkably well, and their total cross sections of disappearance have been consequently determined. The major reactions of these primary ions lead to the formation of $C_2F_4^+$ and CF_3^+ which, together with CF^+ , show very low reactivity. The ion current due to purely secondary and higher order ions did not exceed a few per cent of the total ion current at the highest pressure attained in the present work. Most of the "product" ions have been assigned, and their cross sections of formation have been determined.

Introduction

Fluorocarbons have presented many interesting problems in chemistry both to experimentalists and to theoreticians (see, for example, the reviews in the serial publication, "Advances in Fluorine Chemistry"¹). Recently, Price and co-workers^{2,3} and Peters⁴ have demonstrated and discussed some of the interesting properties of the C-F bond both in simple and complex molecules, radicals, and ions. These properties which are reflected in the mass spectra of these compounds are also expected to influence the kinetic behavior of the fluorocarbon ions.

The mass spectra of a few fluorocarbons are now well established,⁵ and the ionization potentials and appearance potentials have been determined for a number of these compounds, their radicals, and ions.^{2,6-9} Also, although ion-molecule reactions occurring in a number of halogenated hydrocarbons have been investigated frequently,¹⁰ no such study has been carried out on fluorocarbons. It is therefore planned in the present work to study such reactions occurring in tetrafluoroethylene in the ion source of the mass spectrometer with the object of demonstrating some interesting aspects of the chemistry of fluorocarbon ions. Beside providing kinetic data in the now well-established field of ion-molecule reactions, the present investigation may further prove important in the study of the radiolysis of tetrafluoroethylene and similar compounds.

Experimental

The mass spectrometer and the procedure adopted for its operation have been described previously.¹¹ The only modification from the previously reported conditions of the ion source is that the average distance between the electron beam and the exit slit is now 0.335 cm. and the repeller field is 12.5 v. cm.⁻¹. The electron accelerating voltage is 80 v. The temperature of the ion source as recorded by a calibrated Pt-resistance thermom-

eter never increased above 160°. The pressure in the ion source has been calibrated by the previously described method¹² using the cross section of reaction of CH_2^+ primary ion from methane given by Wexler and Jesse¹³ and recently confirmed by Field, Franklin, and Munson.¹⁴ In the present work the pressure of the gas inside the ion source was varied in the range 0.004-0.06 torr.

After working the instrument with tetrafluoroethylene for several days no residual peaks or "memory effect" was observed in confirmation of the earlier observation of Mohler, Dibeler, and Reese.¹⁵ However, the lifetime of the tungsten filament was considerably shortened even though the pressure in the ion source and consequently in the surrounding of the filament was not brought to the highest values obtainable with other gases.

Attempts at appearance potentials and ionization efficiency measurements gave very erratic results which might have been caused by the rather longer-than-usual time needed for re-establishing equilibrium in the electron emission after changing the electron accelerating voltage. Other investigators¹⁶ working at high pressure have also encountered difficulties in such measurements, and in the present case the situation might have worsened because of the attack of the gas on the tungsten filament.

Tetrafluoroethylene which was prepared from 1:2 dibromotetrafluoroethane by debromination with zinc in alcohol has been kindly supplied by Dr. A. Mele of these laboratories. The sample has been purified by several bulb-to-bulb distillations and the middle fraction was collected and analyzed both gas chromatographically and mass spectrometrically and was found to be of a purity higher than 99.5%.

Results and Discussion

I. Mass Spectrum.—The mass spectrum of tetrafluoroethylene at relatively high pressure shows quite interesting features not only by the presence of secondary and higher order ions but by the relatively high abundance of $C_2F_4^+$ and CF_3^+ as compared with their values in the "zero-pressure" spectrum.

Table I records the "high-pressure," the "zero-pressure," and the "very low-pressure" mass spectra of tetrafluoroethylene. The "zero-pressure" mass spectrum, which is the spectrum of primary ions, is obtained by extrapolating to zero pressure the semilogarithmic plot of the normalized ion intensities *vs.* pressure curves. It can be seen from Table I that there is a fair agreement between the "zero-pressure" mass spectrum and the "very low-pressure" spectrum measured by Lifshitz and Long⁸ and very good agreement with the spectrum given in "Mass Spectral Data."

II. Pressure Dependence of Ion Currents. A. Primary Ions.—The variation of the primary ion

(1) "Advances in Fluorine Chemistry," M. Stacey, J. C. Tatlow, and A. G. Sharp, Ed., Butterworth and Co., London.

(2) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc. (London)*, **A268**, 459 (1960).

(3) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.*, **35**, 201 (1963).

(4) D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

(5) J. R. Majer, *Advan. Fluorine Chem.*, **2**, 55 (1961).

(6) (a) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **57**, 113 (1956); (b) R. M. Reese, V. H. Dibeler, and F. L. Mohler, *ibid.*, **57**, 367 (1956); (c) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Chem. Phys.*, **26**, 304 (1957).

(7) M. M. Bibby and G. Carter, *Trans. Faraday Soc.*, **59**, 2455 (1963).

(8) C. Lifshitz and F. A. Long, *J. Phys. Chem.*, **67**, 2463 (1963).

(9) J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(10) See, for example, the recent reviews of C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, pp. 65-115 and 163-205.

(11) A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Chem. Phys.*, **39**, 518 (1963).

(12) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, **40**, 5 (1964).

(13) S. Wexler and N. Jesse, *J. Am. Chem. Soc.*, **84**, 3425 (1962).

(14) F. H. Field, J. L. Franklin, and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).

(15) F. L. Mohler, V. H. Dibeler, and R. M. Reese, *J. Res. Natl. Bur. Std.*, **49**, 343 (1952).

(16) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **67**, 1542 (1963).

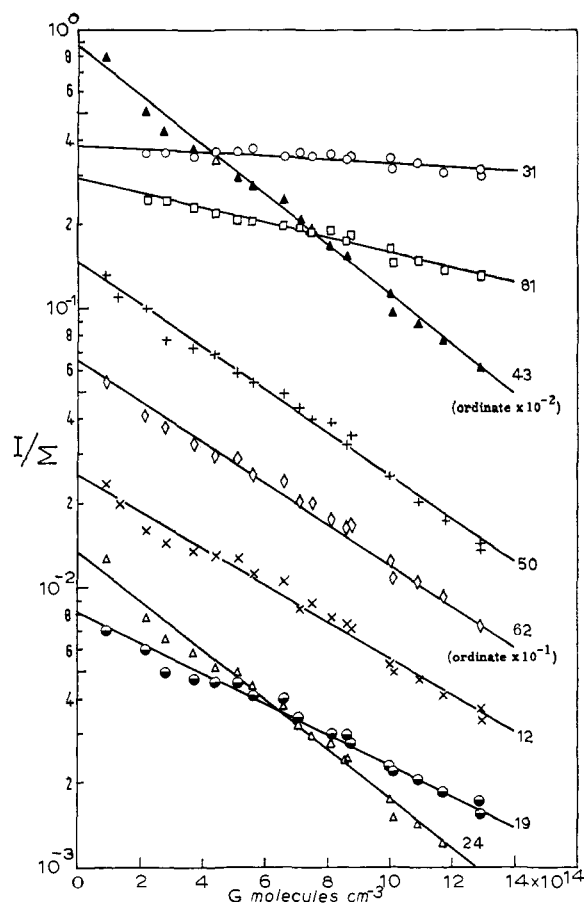


Fig. 1.—Semilogarithmic plot of normalized primary ion intensities vs. tetrafluoroethylene concentration; m/e values are indicated on the lines.

current for all the primary ions, except $C_2F_4^+$ and CF_3^+ , with the gas pressure inside the ion source has been found to follow rather well the exponential attenuation law

$$(I_p/\Sigma) = (I_p/\Sigma)^0 \exp[-\sigma_{hj}^{\tau} lG] \quad (1)$$

as illustrated in Fig. 1 where two sets of measurements, taken on different days, are reported without differentiation because of their remarkable reproducibility and the absence of any systematic deviation. In eq. 1, (I_p/Σ) is the normalized intensity of the primary ion, $(I_p/\Sigma)^0$ is the extrapolated value at zero pressure (column 4 of Table I), l is the distance between the electron beam and the exit slit of the ion source, G is the pressure of the gas inside the ion source expressed in molecules/cm³, and σ_{hj}^{τ} is the total cross section of disappearance of the primary ion.

The total cross sections of reactions of the primary ions are listed in Table II where it can be seen that they show a rather sharp division into two classes. The first is comprised of the ions $C_2F_4^+$, CF_3^+ , and CF^+ which have rather small cross sections of reaction. The second class is made up of quite reactive ions with cross sections in the range 35–60 Å². The parent-minus-one ion, $C_2F_3^+$, occupies an intermediate position between these two classes. Table II also includes the rate constants of the reactions of the primary ions calculated from the cross sections, σ^{τ} , using the equation¹⁷

$$k_{\text{exptl}} = (eEl/2m)^{1/2} \sigma^{\tau} \quad (2)$$

(17) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

TABLE I
THE MASS SPECTRUM OF TETRAFLUOROETHYLENE

m/e	Assign- ment	Normalized ion intensities, %			
		High pressure, ^a 0.06 torr	Zero pressure ^a	Low pressure— M.S.D. ^b L. and L. ^c	
12	C ⁺	0.33	2.6	2.9	..
19	F ⁺	0.15	0.8	0.55	..
24	C ₂ ⁺	0.10	1.35	0.93	..
31	CF ⁺	31.4	38.0	37.8	28.6
43	C ₂ F ⁺	0.06	0.9	0.52	..
50	CF ₂ ⁺	1.44	14.0	11.7	10.6
62	C ₂ F ₂ ⁺	0.08	0.65	0.37	0.3
69	CF ₃ ⁺	7.4	1.10	1.35	1.3
81	C ₂ F ₃ ⁺	13.0	28.0	27.6	37.3
100	C ₂ F ₄ ⁺	39.8	13.0	16.25	20.4
55	C ₃ F ⁺	0.01			
74	C ₃ F ₂ ⁺	0.01			
93	C ₃ F ₃ ⁺	0.16			
112	C ₃ F ₄ ⁺	0.05			
119	C ₂ F ₅ ⁺	0.03			
124	C ₄ F ₄ ⁺	0.01			
131	C ₃ F ₅ ⁺	6.0			
162	C ₄ F ₆ ⁺	0.2			
169	C ₃ F ₇ ⁺	0.05			
181	C ₄ F ₇ ⁺	0.02			

^a 80-v. electron beam energy and 12.5-v. cm⁻¹ repeller field.
^b "Mass Spectral Data," American Petroleum Institute Research Project 44 (70-v. electron beam energy).
^c See ref. 8 (75-v. electron beam energy).

TABLE II
TOTAL CROSS SECTIONS AND RATE CONSTANTS OF REACTIONS
OF PRIMARY IONS

Primary ion	Total cross section, 10 ⁻¹⁸ cm. ² molecule ⁻¹ , at 12.5-v. cm. ⁻¹ repeller field	Rate constant, —10 ⁻¹⁰ cm. ³ molecule ⁻¹ sec. ⁻¹ —	
		Exptl.	Theor. ^a
C ₂ F ₄ ⁺ ^b	2.4	0.34	4.2
C ₂ F ₃ ⁺	18	2.9	4.4
C ₂ F ₂ ⁺	50	9.2	4.8
C ₂ F ⁺	62	13.2	5.3
C ₂ ⁺	61	17.7	6.8
CF ₃ ⁺ ^c	4.6
CF ₂ ⁺	52	10.5	5.1
CF ⁺	4.5	1.1	6.1
F ⁺	35	11.4	7.4
C ⁺	46	19.0	8.9

^a The polarizability of C_2F_4 is calculated from bond polarizabilities (J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York, N. Y., 1954, p. 947) and a value of 4.35 Å³ is obtained. ^b The experimental cross section and rate constant quoted for $C_2F_4^+$ are those corresponding to reaction R8. ^c No figures can be given for the experimental cross section and rate constant of CF_3^+ because of its kinetic behavior in that no "product" ion was found to be formed with CF_3^+ as its precursor.

where E is the electric field strength (the repeller field) and m is the mass of the ion. It is rather interesting to compare the experimental rate constants with the calculated ones from the equation¹⁷

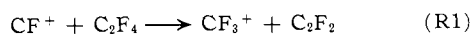
$$k_{\text{theor}} = 2\pi e(\alpha/\mu)^{1/2} \quad (3)$$

where α is the polarizability of the neutral molecule and μ is the reduced mass of the system. Thus, while the calculated rate constants all fall within the narrow range 4.2–8.9 × 10⁻¹⁰ cm.³ molecule⁻¹ sec.⁻¹, the experimentally measured ones vary within the wide range of almost zero for CF_3^+ to 19 × 10⁻¹⁰ cm.³ molecule⁻¹ sec.⁻¹ for C^+ . Furthermore, the trend observed in the reactivity of the fluorocarbon ions is not shown by the

theoretical values of the rate constants as can clearly be seen from the last two columns of Table II. It is further interesting to note here the absence of such a trend in the reactivity of the corresponding hydrocarbon ions from the analogous molecule ethylene.^{18,19}

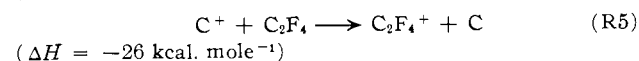
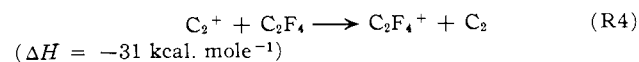
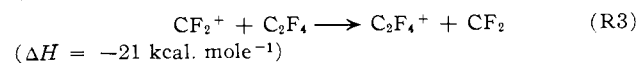
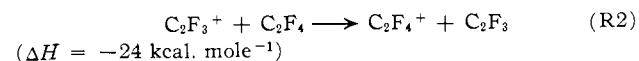
CF₃⁺ and C₂F₄⁺.—The normalized intensity *vs.* pressure curves for these two ions are shown in Fig. 2 from which it can be seen that they are also produced by other primary ions in tetrafluoroethylene. Using the "high-pressure" and the "zero-pressure" spectra given in Table I, it is possible to construct a mass balance of the ions that will help in elucidating the nature of the reactions responsible for the production of CF₃⁺ and C₂F₄⁺. The very low total intensity of the secondary and higher order ions, except *m/e* = 131, makes it possible, once the precursor of that ion is ascertained, to evaluate rather accurately the mass balance of the primary ions. As will be discussed later, there is good evidence indicating that the precursor of C₃F₅⁺ (*m/e* = 131) is C₂F₄⁺ (*m/e* = 100). Therefore, the sum Δ*I*₁₀₀ + *I*₁₃₁ should be equal to the sum of the decrease in the intensity of the ions producing C₂F₄⁺.

For CF₃⁺ the increase in its normalized intensity is found equal to the decrease in the normalized intensity of CF⁺ (*m/e* = 31), and the reaction

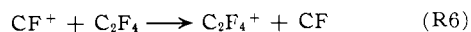


is exothermic with Δ*H* < 17 kcal. mole⁻¹.

If reaction R1 is taken to be responsible for the formation of CF₃⁺ (see later for further consideration of this point), practically all the other primary ions have to produce C₂F₄⁺. This can easily be verified by constructing the mass-balance from the data of Table I. Furthermore, all the following reactions are energetically possible.



Other ions that may produce C₂F₄⁺ are C₂F₂⁺ and C₂F⁺. In both cases the reactions are expected to be exothermic, but their total contribution to C₂F₄⁺ is rather small (~1.4%). The only major primary ion which has been left out of the above scheme is CF⁺. The reaction



is endothermic to the extent of 28 kcal. mole⁻¹, and therefore it is not expected to take place in the ion source. This may be considered as an indirect confirmation that CF⁺ is responsible for the production of CF₃⁺ as given by (R1).

B. Product ions.—The high-pressure mass spectrum of tetrafluoroethylene shows a number of product ions but their total normalized intensity, except that of C₂F₄⁺ and CF₃⁺, is only about 7% of the total ion current. The major product ion observed is at *m/e* = 131 (6% of the total ion current) which is assigned to C₃F₅⁺.

(18) F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(19) F. H. Field, *ibid.*, **83**, 1523 (1961).

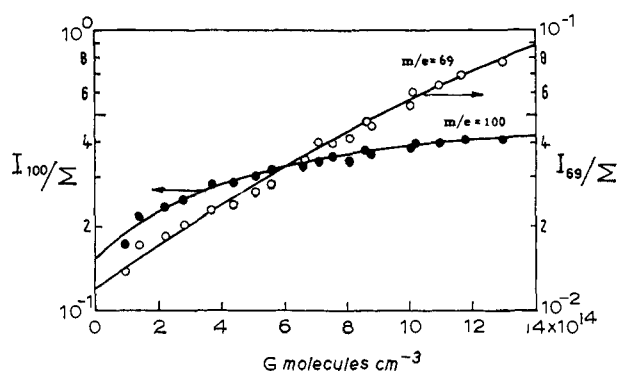


Fig. 2.—Semilogarithmic plot of normalized ion intensity *vs.* tetrafluoroethylene concentration for C₂F₄⁺ and CF₃⁺.

This leaves less than 1% of the total ion current to be shared by the other product ions. This fact has made it very difficult to carry out the usual ionization efficiency and appearance potential measurements. Coupled with this is the difficulty of carrying out such measurements at relatively high pressure as discussed in the Experimental section.

However, in order to obtain an assignment of the precursors of the observed product ions so that their kinetic order and cross sections of formation may be determined, recourse is made to the following method. The method is simply to measure the complete spectrum of tetrafluoroethylene at different electron energy values starting at the lowest energy that gives any reasonable ion current. The same measurements are then carried out at another value of the pressure inside the ion source. Then the assumption is made that for a given value of the pressure the ratio *I_s/I_p* is a constant, independent of the energy of the electron beam. This is equivalent to saying that the energetic states of the ions and hence their cross sections of reaction are not appreciably affected by the energy of the electron beam,¹¹ which assumption has been found to hold with fair accuracy in the case of ammonia²⁰ and some hydrocarbons.¹²

Furthermore, in the present studies, some insight is gained as to the nature of the primary ion producing some of the secondaries by inspecting the latter's kinetic behavior as illustrated by their normalized intensity *vs.* pressure dependence curves. For a secondary ion formed from a pure primary ion, the ion intensity *vs.* pressure curve should be curved downward at low pressure, while for a secondary ion formed from a primary ion with appreciable secondary character, such as C₂F₄⁺ and CF₃⁺, the curvature would be expected to be upward, *i.e.*, it should show some tertiary character.²⁰

Figures 3 and 4 give the normalized ion intensity *vs.* pressure curves for most of the product ions observed. From the shape of these curves and from the constancy of the *I_s/I_p* values at constant pressure, but different electron beam energies, the following parent-daughter relationship is obtained.

Parent ion	Daughter ion
C ₂ F ₄ ⁺	C ₃ F ₅ ⁺ , C ₃ F ₇ ⁺
C ₂ F ₃ ⁺	C ₂ F ₅ ⁺ , C ₃ F ₄ ⁺ , C ₄ F ₆ ⁺
C ₂ F ₂ ⁺	C ₃ F ₃ ⁺

C₃F₅⁺.—The ion intensity–pressure dependence curve (Fig. 3) for this ion shows an upward curvature with

(20) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Chem. Phys.*, **39**, 1599 (1963).

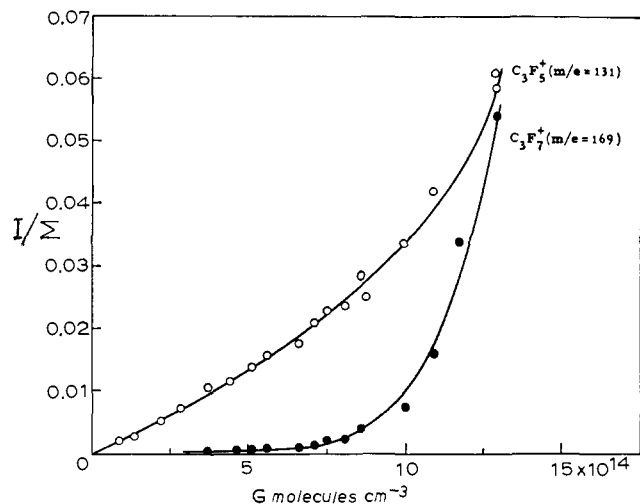
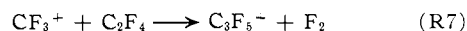


Fig. 3.—Normalized ion intensities vs. tetrafluoroethylene concentration for C_3F_5^+ and C_3F_7^+ (for the latter multiply the ordinate by 10^{-2}).

pressure indicating a complete or partial tertiary character. Since none of the pure secondary ions shows initial rate of reaction high enough to be the precursor of C_3F_5^+ , the selection of the precursor is therefore limited to a primary ion having an appreciable secondary character, *viz.*, C_2F_4^+ and CF_3^+ . The reaction

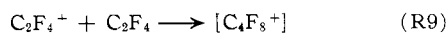


is highly endothermic ($\Delta H = 223 \text{ kcal. mole}^{-1}$) and therefore may be discarded. There remains the reaction



which is slightly exothermic ($\Delta H = -2 \text{ kcal. mole}^{-1}$). Reaction R8 is therefore considered to be responsible for the production of C_3F_5^+ with a cross section of 2.4 \AA^2 .

Following Lampe, Franklin, and Field^{18,21} in their discussion of the possible transition complex for the reaction of C_2H_4^+ in ethylene, it may be interesting to consider the similar problem in the reaction of C_2F_4^+ which may be assumed to proceed through the formation of the complex $[\text{C}_4\text{F}_8^+]$



Comparison of the secondary spectrum of $[\text{C}_4\text{F}_8^+]$ with the spectra of C_4F_8 isomers (see Table III) leaves very

TABLE III
COMPARISON OF PRIMARY MASS SPECTRA OF C_4F_8 ISOMERS WITH THE SECONDARY SPECTRUM OF $[\text{C}_4\text{F}_8^+]$ FROM ($\text{C}_2\text{F}_4^+ + \text{C}_2\text{F}_4$), BASED ON $I_{131} = 100$

Ion	Primary C_4F_8 ^a			Secondary $[\text{C}_4\text{F}_8^+]$ from $(\text{C}_2\text{F}_4^+ + \text{C}_2\text{F}_4)$
	methylpropene	1-butene	cyclobutane	
C_2F_4^+	45	5	115	
C_3F_5^+	100	100	100	100
C_4F_7^+	490	12	0.1	0.5
C_4F_8^+	125	9	0.1	...

^a Taken from "Mass Spectral Data," American Petroleum Institute Research Project 44.

little doubt that if the transition complex is assumed to be a chemically bonded molecule then its breakdown pattern is more like the spectrum of octafluorocyclobu-

(21) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, **1**, 67 (1961).

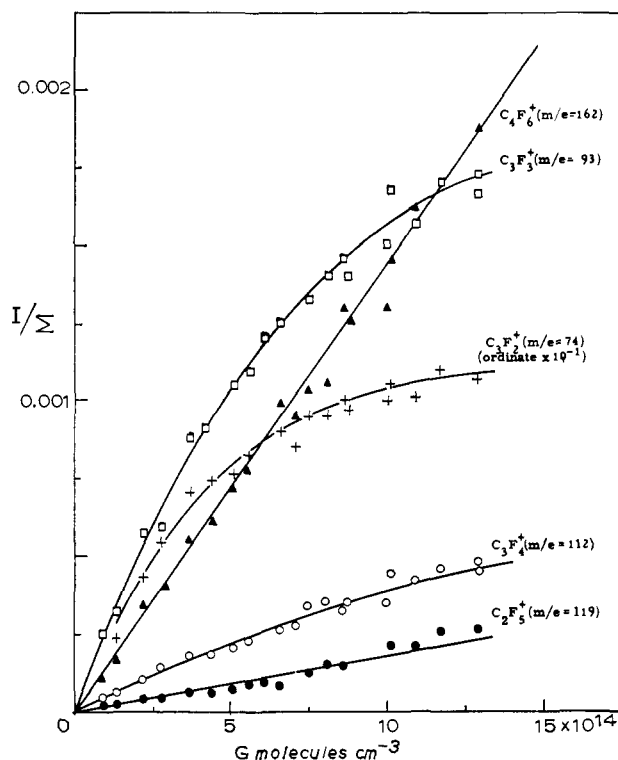
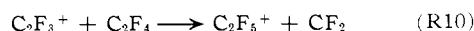


Fig. 4.—Normalized ion intensities vs. tetrafluoroethylene concentration for secondary ions.

tane than the spectra of the other two isomers. A complete thermochemical calculation cannot be carried out because of the absence of all necessary data. However if the almost complete absence of the parent peak in the mass spectrum of cyclo- C_4F_8 is taken as an indication that its ionization potential is larger than the lowest appearance potential of any of its fragment ions, *i.e.*, IP (cyclo- C_4F_8) $> 12.25 \text{ e.v.}$,⁷ then one would obtain for the heat of formation of cyclo- C_4F_8^+ a value between zero and $-70 \text{ kcal. mole}^{-1}$. This in turn will make reaction R9 either thermoneutral or endothermic. A slight endothermicity could perhaps explain the rather small cross section for the reaction of C_2F_4^+ .

C_3F_7^+ .—This is the only ion which showed rather strong dependence on pressure as can be judged from Fig. 3. In fact the normalized ion intensity of $m/e = 169$ seems to be fifth-order in pressure. Even with C_2F_4^+ or CF_3^+ as the precursors only a third-order pressure dependence is obtained. With CF_3^+ , a sticky collision subsequently stabilized will give only a fourth-order pressure dependence. Furthermore, the reaction sequence with CF_3^+ as precursor is endothermic and may be discarded. There remains C_2F_4^+ as the possible precursor of C_3F_7^+ but no reasonable mechanism could be formulated which explained its fifth-order dependence on pressure.

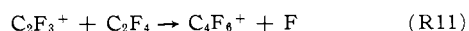
C_2F_5^+ .—In ethylene the analogous ion C_2H_5^+ is the largest secondary ion at moderate pressure¹⁸ while in tetrafluoroethylene C_2F_5^+ is only 0.03% of the total ionic current at the highest pressure used in the present work. Because of its rather low intensity (Fig. 4) it was very difficult to decide its precursor. However, the only exothermic reaction that can be formulated for the production of this ion is



with $\Delta H = -23 \text{ kcal. mole}^{-1}$. The very low yield of

$C_2F_5^+$ from tetrafluoroethylene may be due to its relative instability as demonstrated by its relatively low heat of dissociation to give $C_2F_4^+ + F$.

$C_4F_6^+$ —This ion shows an interesting linear dependence on pressure (Fig. 4) indicative of the behavior of a typical unreactive secondary ion coming from a precursor with rather low cross section of disappearance. This fact together with the remarkably good constancy of the ratio I_{162}/I_{81} at constant pressure but varying electron beam energy leads to the formulation of the following reaction for the formation of $C_4F_6^+$



which is exothermic if $\Delta H_f(C_4F_6^+) \leq 25$ kcal. mole⁻¹. Such a small heat of formation is not uncommon for large fluorocarbon ions (e.g., heats of formation of $C_2F_5^+ = 40$, $C_3F_5^+ = 46$, $C_3F_7^+ = 12$ kcal. mole⁻¹),²² and therefore reaction R11 may be taken to represent the production of $C_4F_6^+$.

C_3 Ions.—The following ions with C_3 skeleton have been observed: C_3F^+ , $C_3F_2^+$, $C_3F_3^+$, $C_3F_4^+$, besides $C_3F_5^+$ and $C_3F_7^+$ which have been discussed already. Of these, only $C_3F_3^+$ and $C_3F_4^+$ are assigned with some degree of confidence. The following reactions are considered responsible for their production.

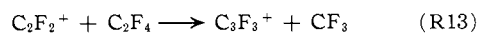
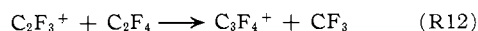


Table IV lists all the ion-molecule reactions observed in tetrafluoroethylene together with their cross sections. The majority of the secondary ions detected did

TABLE IV
CROSS SECTIONS OF ION-MOLECULE REACTIONS IN
TETRAFLUOROETHYLENE AT REPELLER FIELD OF 12.5 V. CM.⁻¹

Reaction	Cross section, 10 ⁻¹⁶ cm. ² molecule ⁻¹
$C_2F_4^+ + C_2F_4 \rightarrow C_3F_5^+ + CF_3$	2.4
$C_2F_3^+ + C_2F_4 \rightarrow C_2F_5^+ + C_2F_2$	0.01
$C_2F_3^+ + C_2F_4 \rightarrow C_3F_4^+ + CF_3$	0.05
$C_2F_3^+ + C_2F_4 \rightarrow C_4F_6^+ + F$	0.2
$C_2F_2^+ + C_2F_4 \rightarrow C_3F_3^+ + CF_3$	16

not show any decay in the pressure range studied, and in fact they show great stability as may be inferred when the ratio (I_s/I_p)-pressure dependence curves are plotted which for all the ions discussed above showed a strong upward curvature as required by the equation²⁰

(22) All the thermochemical values used in the present work are calculated from heats of formation and ionization and appearance potential data given in the literature. (See ref. 2, 3, 5-9, and 23-25.)

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$$I_s/I_p = (\sigma_{hj}/K)[1 - \exp(-KlG)] \quad (4)$$

when $K (= \sigma_{hjk}^{\tau} - \sigma_{hj}^{\tau})$ is negative. In eq. 4 σ_{hjk}^{τ} and σ_{hj}^{τ} are the total cross sections of reaction of the secondary ion and its primary ion precursor, respectively, and σ_{hj} is the cross section of the reaction, primary \rightarrow secondary. Inspection of eq. 4 shows that an upward curvature in the plot of I_s/I_p vs. pressure, G , indicates that $\sigma_{hjk}^{\tau} < \sigma_{hj}^{\tau}$. In the case where σ_{hjk}^{τ} is negligibly small eq. 4 may be simplified to give

$$(I_s/\Sigma) = (\sigma_{hj}/\sigma_h^{\tau})[(I_p/\Sigma)^0 - (I_p/\Sigma)] \quad (5)$$

For all the ions discussed above eq. 5 holds remarkably well, and thus the cross sections of formation, σ_{hj} , of these ions are calculated from the ratio $\sigma_{hj}/\sigma_h^{\tau}$.

III. Conclusions.—The general pattern of ion-molecule reactions in tetrafluoroethylene has indicated that no extensive condensation products are formed through purely consecutive ion-molecule reactions. This is in variance with the case of ethylene in which ion-molecule reactions are known to proceed to the formation of high-order condensation products.¹⁹

Among the primary ions, CF^+ , CF_3^+ , and $C_2F_4^+$ have been shown to be quite stable structurally, thermodynamically,^{2,3} and kinetically; in fact, the last two ions are formed with very large cross sections by almost all the other primary ions. Even the second-order ions, which are formed in very poor yield, themselves are very unreactive. It may therefore be surmised that the role that ion-molecule reactions may play in the radiolysis of tetrafluoroethylene is mainly through the radical products which are formed either upon neutralization of some of these stable ions or through the neutral radicals formed as partners in most of the ion-molecule reactions. Thus, for example, the neutralization of CF_3^+ and possibly other ions may lead to the formation of the radical CF_2 which is also produced as the neutral partner in some of the ion-molecule reactions. This radical which has been shown to be of remarkable stability²⁶ has been considered to be the initiator of photolytic²⁷ and radiolytic²⁸ reactions in tetrafluoroethylene.

Acknowledgments.—We sincerely wish to thank Dr. A. Mele of these laboratories for the gift of tetrafluoroethylene. We also wish to acknowledge the help of E. Luzzatti of this laboratory in the experimental work which he executed with his usual skill. G. A. W. D. wishes to thank "Consiglio Nazionale delle Ricerche" for a fellowship.

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