Gas Phase Ion Chemistry and Photochemistry of Ions Generated from Perfluoropropylene. Photodissociation of the Perfluoroallyl Cation

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Abstract: The mass spectrometry, gas phase ion chemistry, and photochemistry of positive ions generated from perfluoropropylene are reported. Fragmentation mechanisms are formulated with the use of breakdown diagrams and metastable ion information. Trapped ion icr studies conducted with the major ions CF_3^+, $C_2F_4^+$, $C_3F_5^+$, and $C_3F_6^+$ demonstrate that CF_3^+ alone reacts by fluoride transfer to generate $C_3F_5^+$. The ions $C_2F_4^+$, $C_3F_5^+$, and $C_3F_6^+$ are unreactive with perfluoropropylene neutrals, making it possible to examine their photochemistry while trapped for periods up to three seconds and irradiated with a mercury–xenon arc lamp. Only the $C_3F_5^+$ ion, which is assumed to be the perfluoroallyl cation, is observed to dissociate upon photoexcitation, yielding CF_3^+ and C_2F_2. Interestingly, this decomposition pathway also corresponds to the most intense metastable peak observed in the ion kinetic energy spectrum. The CF_3^+ produced photochemically reacts to regenerate $C_3F_5^+$, leading to a photostationary state, which is analyzed in terms of the photodissociation and bimolecular reaction kinetics. The excitation function for photodissociation of $C_3F_5^+$ obtained using a monochromator set for a bandpass of 75 Å exhibits an onset at 295 ± 10 nm and λ_{max} 270 nm at which wavelength a photodissociation cross section of $\sigma(\lambda_{max}) \cong 0.2$ Å^2 is estimated. These results are compared to theoretical calculations of excitation energies for allyl cations and to absorption spectra measured for allyl cations in solution. Possible reasons for the failure to observe photodissociation of the parent ion are discussed.

I on cyclotron resonance spectroscopy[2] (icr) is ideally suited for studying photochemical processes involving ionic species in the gas phase. The particular advantage of the technique involves the ability to trap ions for long periods of time in a well-defined spatial region.[3,4] By delaying the time between ion formation and ion sampling it has proven possible to monitor the temporal behavior of ion concentrations for periods approaching several minutes. The major application of trapped ion icr techniques in our laboratory has been to studies involving bimolecular encounters between ions and neutrals in the gas phase.[4-8] More recently, these techniques have been applied to study unimolecular processes, including those resulting from interaction of photons with ions in the gas phase. Studies of photodetachment of electrons from negative ions by Brauman and coworkers have yielded electron affinities and related thermochemical data important in describing the intrinsic acidity of organic and inorganic molecules.[9-13] Dunbar and coworkers have demonstrated the application of icr techniques to study an even wider range of photochemical processes involving gaseous ions, including photodissociation[14-18] and photoinduced reactions.[19]

Compared to studies in condensed phases, dramatic differences are expected in examining the photochemistry of ions in gases. The major changes expected are related to the lack of collisional dissipation of energy afforded in solution (nonradiative decay). In the gas phase nonradiative decay processes are expected to involve unimolecular decomposition if the internal excitation exceeds dissociation thresholds.[14-18] Alternatively, photon absorption by an ionic species may lead to specific modification of its reactivity in subsequent collisions with neutral gas molecules.[19] Excitation functions obtained by varying photon wavelength while observing either photodecomposition or modified reactivity thus provide information relating to specific absorption characteristics of ions. Direct monitoring of photon absorption in the gas phase necessitates observation of ions in concentrations that are difficult to produce and maintain.[20-23]

Published accounts of photodissociation processes using icr techniques have thus far been limited to studies involving radical cations.[14-18] Photodissociation of the parent ion of methyl chloride with polarized light yields methyl cations with an angular distribution characteristic of the symmetry of the excited state.[14,15] The

(1) Camille and Henry Dreyfus Teacher-Scholar, 1971–1976.
(2) For a general discussion of ion cyclotron resonance spectroscopy, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, 22, 527 (1971).
(3) R. T. McIver Jr., *Rev. Sci. Instrum.*, 41, 555 (1970).
(4) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, 43, 509 (1972).
(5) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 94, 8934 (1972).
(6) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 96, 1269 (1974).
(7) R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, *Inorg. Chem.*, 13, 1511 (1974).
(8) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, 94, 4728 (1972).
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(10) K. C. Smyth, R. T. McIver, Jr., and J. I. Brauman, *J. Chem. Phys.*, 54, 2758 (1971).
(11) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, 56, 1132 (1972).
(12) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, 56, 4620 (1972).
(13) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, 56, 5993 (1972).

(14) R. C. Dunbar, *J. Amer. Chem. Soc.*, 93, 4354 (1971).
(15) R. C. Dunbar and J. M. Kramer, *J. Chem. Phys.*, 58, 1266 (1973).
(16) J. M. Kramer and R. C. Dunbar, *J. Chem. Phys.*, 59, 3092 (1973).
(17) R. C. Dunbar and E. Fu, *J. Amer. Chem. Soc.*, 95, 2716 (1973).
(18) R. C. Dunbar, *J. Amer. Chem. Soc.*, 95, 6191 (1973).
(19) J. M. Kramer and R. C. Dunbar, *J. Amer. Chem. Soc.*, 94, 4346 (1972).
(20) R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.*, 35, 2237 (1961).
(21) R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.*, 37, 2278 (1962).
(22) R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, 38, 1540 (1963).
(23) G. Herzberg, *Quart. Rev., Chem. Soc.*, 25, 201 (1971).

interpretation of excitation functions for such photo-decomposition processes is facilitated by the availability of photoelectron spectra which detail many of the excited states of radical cations. The complementary nature of the information obtained in both experiments is strongly reflected in studies of unsaturated hydrocarbons.[16-18] Dunbar has shown that photodissociation thresholds are determined by a combination of factors, including thermochemical changes associated with the fragmentation processes and absorption characteristics of the reactant ion.[14-18] Differing absorption characteristics make it possible to identify structural isomers with photodissociation data. Dunbar and coworkers have clearly demonstrated this interesting application of photodissociation data in the case of butene cations,[16] $C_7H_8^+$ cations,[17] and various alkylbenzene cations.[18]

The ion trapping technique employed by Dunbar and coworkers involves continuous ion formation and sampling from an ion distribution where the mean lifetime is in excess of several seconds. Sampled ion concentrations represent, however, a distribution of ion irradiation times and, in the event that bimolecular reactions are an important consideration, a distribution of reaction times. Recently we reported the development in our lab of a versatile trapped ion cell[4] which has been extensively employed to investigate the kinetics and equilibria of ion–molecule reactions.[4-8] We report in this paper the application of controlled ion trapping to the study of photodissociation processes involving gaseous ions and demonstrate the advantages inherent in being able to effectively monitor bimolecular processes which occur in conjunction with unimolecular photodecomposition reactions. As part of our continuing studies of properties and reactions of fluorocarbons,[5,6,24] we chose to examine the gas phase photochemistry of ions derived from perfluoropropylene. This choice was based on our observation that several ions of photochemical interest, including the parent ion and the perfluoroallyl cation, are unreactive with the parent neutral in this system. To detail our observations we report the results of other investigations including mass spectrometry, gas phase ion chemistry, photoelectron spectroscopy, and ion thermochemical studies, which corroborate the photochemical results.

Experimental Section

Experimental techniques associated with icr spectroscopy have been previously described in detail.[2,4-6,25-27] A modified Varian V-5900 spectrometer equipped with a specially designed flat cell, similar to that described by McMahon and Beauchamp,[4] was employed for these studies. The trapped ion cell was positioned with the source region adjacent to an optical port[28] near the edge of the magnetic field pole piece in order to maximize overlap of the focused light source with the ion spatial distribution. The plate at the end of the source region was replaced with an 84% open mesh screen to admit light from a Hanovia 2.5 kW mercury–xenon arc lamp. Circuitry developed for use in conjunction with the trapped ion cell permits ion residence times in the source region to be varied continuously.[29] Photodissociation processes were ascertained by

(24) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Pratt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972).

(25) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

(26) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **42**, 1632 (1971).

(27) B. S. Freiser, T. B. McMahon, and J. L. Beauchamp, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 249 (1973).

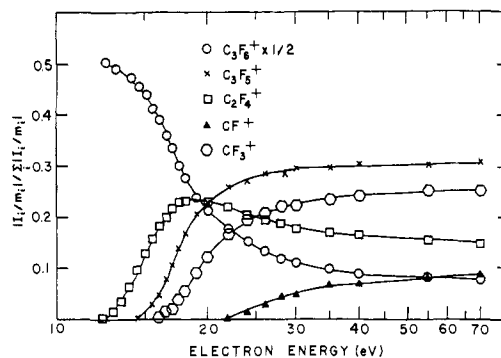(28) Varian 1-in. sapphire viewing port (Model No. 954-5035).

Figure 1. Variation of ion abundance with electron energy for perfluoropropylene.

noting ion intensities in the presence and absence of radiation and substantiated using icr double resonance and ion ejection techniques.[2,4-6,25,27] Low-pass Corning glass filters were used to determine photodissociation thresholds. Excitation functions were obtained using dispersed light from a Bausch and Lomb 0.25-m monochromator equipped with a 2700 groove/mm grating blazed at 2500 Å which covered the wavelength region 2000-4000 Å with a 32 Å/mm dispersion. Dispersed light intensities were measured with a calibrated Epply thermopile.

Perfluoropropylene was obtained from Peninsular Chemresearch and used as supplied except for freeze–pump–thaw cycles used to remove noncondensable gases. Mass spectrometry showed no detectable impurities.

Results

Mass Spectrometry of Perfluoropropylene. The mass spectrum of perfluoropropylene at 70-eV electron energy is listed in Table I. The data in Table I are taken

Table I. 70-eV Mass Spectrum of Perfluoropropylene

m/e	Species	Relative abundance[a]
31	CF^+	0.085
50	CF_2^+	0.010
69	CF_3^+	0.252
81	$C_2F_3^+$	0.032
93	$C_3F_3^+$	0.012
100	$C_2F_4^+$	0.149
131	$C_3F_5^+$	0.311
150	$C_3F_6^+$	0.158

[a] Measured from mass corrected icr single resonance intensities at 5×10^{-7} Torr. Reported as a fraction of total ion abundance.

from an icr single resonance spectrum recorded at 5×10^{-7} Torr, where bimolecular reactions are avoided. The breakdown diagram in Figure 1 illustrates the variation with electron energy of the abundances of the major ions. From these data it is apparent that the lowest energy fragmentation process involves loss of CF_2 from the parent ion.[30] At higher energies direct bond cleavage competes, leading to the formation of $C_3F_5^+$ as an abundant ion.

The ion kinetic energy (IKE) spectrum[31] of perfluoro-

(29) T. B. McMahon, Ph.D. Thesis, 1973, California Institute of Technology, Pasadena, Calif.

(30) This is a common process in molecules possessing the CF_3 functional group. See, for instance, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 441.

(31) Recorded on a Du Pont Model 492B double focussing high resolution mass spectrometer. For details relating to the interpretation of IKE spectra, see K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davies, Ed., United Trade Press, London, 1967, p 105, and references cited therein.
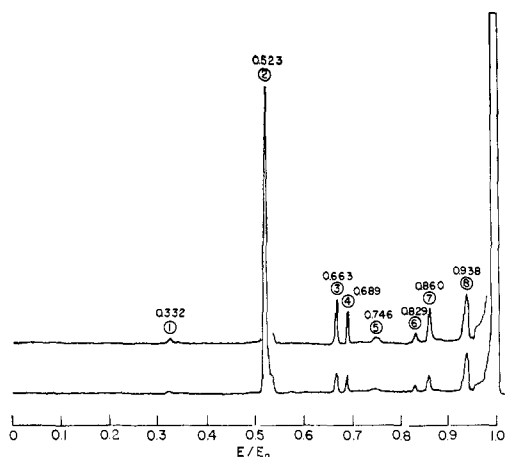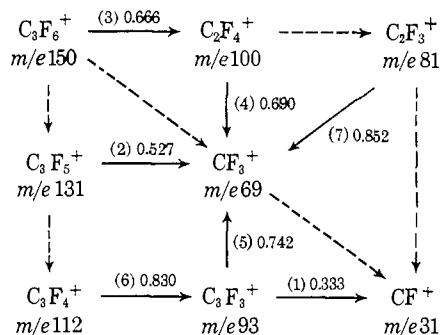
Figure 2. Ion kinetic energy spectrum of perfluoropropylene at 70 eV: E is the energy of ions transmitted by the electrostatic analyzer and E_0 is the energy of the main beam. The ratio E/E_0 is equal to the ratio of the fragment ion mass to the precursor ion mass. The spectrum is obtained by sweeping the electrostatic analyzer voltage. The upper scan is at an increased sensitivity.

Figure 3. Temporal variation of ion abundance in perfluoropropylene at 1.67×10^{-6} Torr. The electron beam was pulsed on for 10 msec at 25 eV.

propylene (Figure 2) reveals several metastable transitions which are useful in assessing fragmentation mechanisms. The peaks designated 1–7 and by the experimental ratio $E/E_0 =$ (mass of daughter ion)/(mass of parent ion) each correspond to at least one metastable transition, the most intense being m/e 131 → m/e 69 ($E/E_0 = 0.523$). Examination of the mass of the daughter ion for each of the peaks in the metastable spectrum confirms the assignments shown in Scheme I. Peak number 8 at $E/E_0 = 0.938$ corresponds to no possible process in C_3F_6 and is attributed to reflection of the main beam as has been noted by others in IKE spectra.[32] The dashed arrows in Scheme I indicate probable decompositions which do not exhibit metastable peaks.

Scheme I

Gas Phase Ion Chemistry of Perfluoropropylene. Before examining unimolecular and bimolecular processes associated with photoexcitation of ions produced from perfluoropropylene it is first necessary to delineate the bimolecular processes which occur in the absence of irradiation. The major ions present at 25 eV (Figure 1) include CF_3^+ (m/e 69), $C_2F_4^+$ (m/e 100), $C_3F_5^+$ (m/e 131), and $C_3F_6^+$ (m/e 150). The initial relative abundances can be assessed from Figure 3, which illustrates the temporal behavior of ion concentrations at 1.7×10^{-6} Torr determined in a trapped ion icr experiment.

(32) See, for example, J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 479 (1970).

From the data in Figure 3 it is evident that the fluoride transfer reaction 1 occurs and this process is confirmed

$$CF_3^+ + C_3F_6 \longrightarrow C_3F_5^+ + CF_4 \qquad (1)$$
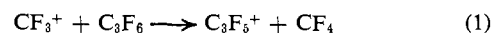
by ion cyclotron double resonance. From the disappearance of CF_3^+ a reaction rate constant $k = 5 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} is calculated for reaction 1. The ions $C_2F_4^+$ and $C_3F_6^+$ as well as $C_3F_5^+$ remain unreactive with the parent neutral. At higher electron energies the variety of minor fragment ions produced (including CF^+) react predominantly by fluoride transfer to yield $C_3F_5^+$.

Photochemistry of Ions Derived from Perfluoropropylene. An overall assessment of the photochemical processes resulting from irradiation of ions in perfluoropropylene was obtained by recording mass spectra at appropriate delay times after ion formation under otherwise identical conditions with and without irradiation from the mercury–xenon arc lamp filtered in the ir and cut off below 220 nm by a Corning low pass glass filter. Observed differences in ion abundance due to irradiation are illustrated in Figure 4. From these data it is apparent that photochemical processes do not affect the concentrations of $C_2F_4^+$ and $C_3F_6^+$ and that CF_3^+ and $C_3F_5^+$ are involved in the photochemical process 2. It

$$C_3F_5^+ \xrightarrow{h\nu} CF_3^+ + C_2F_2 \qquad (2)$$
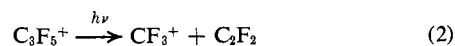
would normally be expected that the extent of photodissociation would increase with time. That this is *not* observed in Figure 4, which indicates a fairly constant extent of photodissociation after ∼500 msec, can be attributed to the bimolecular reaction 1 regenerating the ion $C_3F_5^+$ from CF_3^+. Thus a photostationary state is reached in which the overall reaction 3 involves $C_3F_5^+$ and CF_3^+ as ionic intermediates in the photochemical conversion of C_3F_6 to CF_4 and C_2F_2.

$$C_3F_6 \xrightarrow{h\nu} CF_4 + C_2F_2 \qquad (3)$$
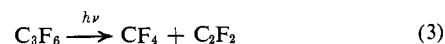
The data in Figures 5a and 5b confirm these results. Figure 5a indicates a continuous recording of the variation in abundance of $C_3F_5^+$ with time, with and without irradiation. Figure 5b presents similar data for CF_3^+.
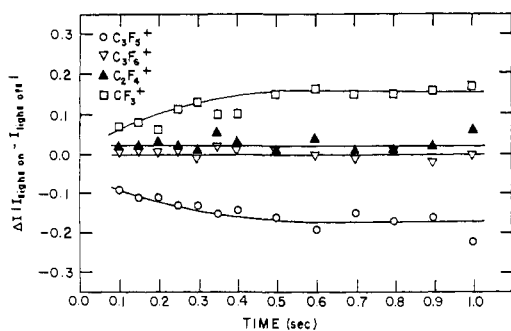
Figure 4. Observed differences in ion abundance at 70 eV and 2.5×10^{-7} Torr due to irradiation with full lamp output filtered in the ir and cut off below 220 nm by a Corning low-pass glass filter.

These data illustrate the ability of trapped ion icr experiments to store ions for extended periods of time with only minimal losses.

The data in Figures 5a and 5b indicate that a photostationary state is reached after ~2 sec. The photostationary state can be analyzed more fully in terms of a steady state solution to eq 4 describing the time de-

$$d[C_3F_5^+]/dt = nk_r[CF_3^+] - k_p[C_3F_5^+] \qquad (4)$$

pendence of the $C_3F_5^+$ ion concentration, where n is the number density of perfluoropropylene neutrals, k_r is the reaction rate constant for process 1, and k_p is the photodissociation rate. A steady state solution gives expression 5 for the photodissociation rate in terms of the

$$k_p = nk_r[CF_3^+]_{ss}/[C_3F_5^+]_{ss} \qquad (5)$$

steady state ion concentrations. Using equation 5 and the data in Figure 5, a photodissociation rate $k_p = 0.31$ sec^{-1} is obtained. This may be directly measured in a rather straightforward experiment. Continuous ejection of CF_3^+ in a time short compared to the time between collisions prevents the regeneration of $C_3F_5^+$ in reaction 1 and thus this species decays continuously as it is photodissociated. The observed exponential yields a value of $k_p = 0.29$ sec^{-1}, in good agreement with the value determined from steady state ion concentrations.

Corning low pass filters yielded an approximate threshold for the photodissociation process 2 of 300 ± 20 nm. A complete excitation function, representing the variation of the photodissociation cross section with photon energy, was obtained using a high intensity monochromator with a bandwidth of 75 Å. Identical excitation functions were observed for the appearance of CF_3^+ and the disappearance of $C_3F_5^+$ under steady state conditions. Optimum signal to noise was obtained, however, by monitoring the decrease in $C_3F_5^+$ signal observed upon irradiation, with continuous ejection of CF_3^+. These data are shown in Figure 6. There is no correlation between the excitation function in Figure 6 and the variation in lamp intensity with wavelength.

The photodissociation rate constant is related to the photon flux $\varphi(\lambda)$ and the photodissociation cross section or excitation function $\sigma(\lambda)$ by eq 6 where $f(\lambda)$ is a nor-

$$k_p = \int_0^\infty f(\lambda')\varphi(\lambda')\sigma(\lambda')d\lambda' \qquad (6)$$

malized photon distribution function.[14] For the purpose of this work, if we assume that the bandwidth of the
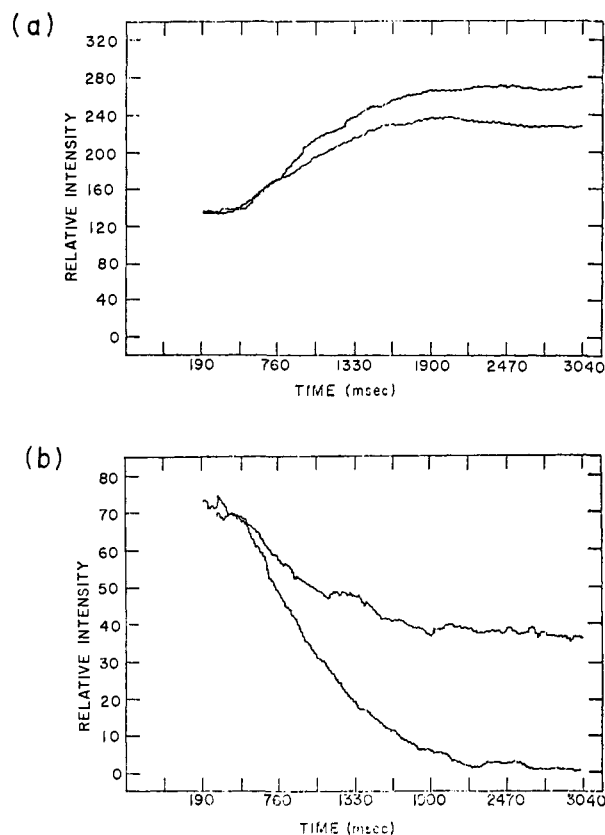
Figure 5. Variation of signal intensity with time at 70 eV and 1.0×10^{-7} Torr for (a) $C_3F_5^+$ and (b) CF_3^+ with and without irradiation at 270 nm using output of monochromator set for 100-Å bandwidth. Scales are proportional to true ion abundances such that "a" and "b" may be directly compared.
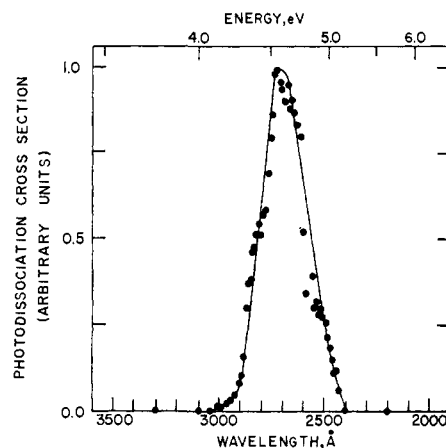
Figure 6. Excitation function for the photodecomposition of $C_3F_5^+$ to CF_3^+ and C_2F_2. Data obtained with monochromator set for 75-Å bandwidth. No decomposition was observed above 300 nm. The shortest wavelength examined was 220 nm.

monochromator is narrow compared to the wavelength region over which the excitation function varies appreciably (equivalent to assuming monochromatic photons), we may rewrite eq 6 in the approximate form of eq 7, which may be used with measured photon fluxes to

$$k_p = \varphi(\lambda)\sigma(\lambda) \qquad (7)$$

estimate the photodissociation cross section. Since the overlap of the focused photon beam with the ion spatial distribution is not well characterized, we can obtain only

an order of magnitude estimate of the maximum cross section, the value arrived at being $\sigma(270 \text{ nm}) \cong 0.2$ Å^2.[33]

Discussion

Thermochemistry. Very little reliable data are available for heats of formation of fluorinated ions and in many instances for heats of formation of fluorinated neutrals. The best available data for ions and neutrals pertinent to this study are summarized in Table II.

Table II. Heats of Formation of Fluorinated Ions and Neutrals[a]

Neutrals	ΔH_f	Ref	Ions	ΔH_f	Ref
F	18.7	b	CF^+	274	g
CF	61	c	CF_3^+	99.3	b
CF_2	-39.0	b	$C_2F_4^+$	85.2	h
CF_3	-112.2	b	$CF_2CFCF_2^+$	32	i
CF_4	-223.0	b	$CF_2CFCF_3^+$	-14.0	j
C_2F_2	$+5(?)$	d			
C_2F_3	-46	e			
C_2F_4	-157.4	f			
CF_2CFCF_3	-258.9	e			

[a] All data in kcal/mol at 298°K. [b] Reference 6. [c] Reference 36, [d] See discussion in text. [e] Reference 35. [f] J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968). [g] Calculated using IP(CF) = 9.23 eV [T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, **51**, 3531 (1969)] and $\Delta H_f(CF) = 61$ kcal/mol (ref 36). [h] Calculated using IP(C_2F_4) = 10.52 eV (ref 53). [i] Estimated (± 10 kcal/mol) from F^- transfer reactions in mixtures of CF_2CFCF_3 with other fluorinated hydrocarbons (see ref 6 for a description of the methodology employed). [j] Calculated using IP(CF_2CFCF_3) = 10.62 eV (this work).

Discrepancies in the available data are made evident by considering the species C_2F_2 which is presumed to be the neutral product in reaction 2. Studies of species present in a high temperature MnF_3–graphite reactor led Ehlert[34] to report $\Delta H_f(C_2F_2) = -45 \pm 6$ kcal/mol, within range of the value -51 kcal/mol suggested by Bryant.[35] These data contrast markedly with the estimate 5 ± 5 kcal/mol quoted in the most recent JANAF tabulation and considered to be a lower limit.[36] Using methods which in many instances give good agreement with known heats of formation, Dewar and Lo calculate $\Delta H_f(C_2F_2) = 10$ kcal/mol.[37] We have rather arbitrarily adopted the JANAF value, the only basis for our choice being that the threshold calculated for reaction 2 is likely to be an upper limit. Interestingly, the lower value leads to the overall reaction 3 being 15 kcal/mol exothermic and the elimination reaction 2 being only slightly endothermic.

Thermochemical changes associated with unimolecular and bimolecular reactions involving ions derived from perfluoropropylene are summarized in Table III. The elimination of CF_2 is predicted to be the lowest energy process for decomposition of the parent ion, consistent with our observations (Figure 1). The data in Figure 1 suggest that the threshold for loss of F should be somewhat higher than calculated and further suggest that the major source of CF_3^+ may be from sequential

(33) This compares to the value of 0.08 Å^2 estimated by Dunbar for the photodissociation of CH_3Cl^+ to CH_3^+ and Cl (ref 14).

(34) T. C. Ehlert, *J. Phys. Chem.*, **73**, 949 (1969).

(35) W. M. D. Bryant, *J. Polym. Sci.*, **56**, 277 (1962).

(36) JANAF Thermochemical Tables, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, No. 37 (1971).

(37) M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5296 (1972).

Table III. Thermochemical Changes Associated with Reactions Involving Perfluoropropylene

Process	ΔH, kcal/mol[a]
$CF_2{=}CFCF_3^+ \longrightarrow CF_2{=}CFCF_2^+ + F$	65
$\longrightarrow CF_3^+ + C_2F_3$	67
$\longrightarrow CF_2{=}CF_2^+ + CF_2$	60
$CF_2{=}CFCF_2^+ \rightarrow CF_3^+ + C_2F_2$	72
$CF_2{=}CF_2^+ \rightarrow CF_3^+ + CF$	72
$CF_2{=}CFCF_3 \rightarrow CF_4 + C_2F_2$	41
$CF^+ + CF_2{=}CFCF_3 \rightarrow CF_2{=}CFCF_2^+ + CF_2$	-22
$CF_3^+ + CF_2{=}CFCF_3 \rightarrow CF_2{=}CFCF_2^+ + CF_4$	-31

[a] Calculated with data summarized in Table II.

decompositions involving $CF_2{=}CFCF_2^+$ as an intermediate.

The threshold for photodissociation of $C_3F_5^+$ occurs at 295 ± 10 nm corresponding to a minimum internal excitation of 97 ± 3 kcal/mol. This is above the 72 kcal/mol threshold estimated *as an upper limit* for reaction 2 and suggests that the threshold is spectroscopically rather than thermodynamically controlled.

Photochemistry of $C_3F_5^+$. In all of the above considerations it has been assumed that the structural isomer I is appropriate for $C_3F_5^+$. In the absence of ex-

perimental data or theoretical calculations relating to their stability,[38] it is difficult to rule out the remaining isomers II–V as plausible structures for $C_3F_5^+$. Calculations on the related $C_3H_5^+$ isomers indicate that I is the most stable form, with II, III, IV, and V being less stable by 17, 32, 39, and 43 kcal/mol, respectively.[39] Since the effects of fluorine substituents on ion stability are large[5,6,40] compared to these differences, it is not possible to infer the relative stabilities of I–V from the results for $C_3H_5^+$. Structural isomers I, II, and III are directly accessible in fragmentation of the parent ion and in the bimolecular reaction 1. The structural isomers III and V are mechanistically convenient structures to explain the decomposition process 2.

We feel that the best evidence for the structure of $C_3F_5^+$ is obtained by comparing the excitation function in Figure 6 to the results of theoretical calculations on allyl cation excitation energies and previously reported absorption spectra of allyl cations in solution.

While allyl and 2-methylallyl cations have been observed in strongly acidic media by nmr,[41,42] attempts

(38) Semiempirical INDO calculations relating to structure and bonding in perfluoroallyl cation I are presented by Kispert, *et al.*, *J. Amer. Chem. Soc.*, **94**, 5979 (1972). However, they do not consider structural isomers II–V.

(39) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(40) J. .., Beauchamp, D. P. Ridge, T. B. McMahon, and J. Y. Park, unpublished studies of fluorine substituent effects on carbonium ion stabilities using the methodology discussed in ref 5 and 6.

(41) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 4442 (1966).

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at observing their uv absorption spectra have been unsuccessful to date due to complications introduced by the formation of strongly absorbing condensation products. However, 1,1,3,3-tetramethylallyl cation is reported to show an absorption with λ_{max} 305 nm (4.1 eV) in H_2SO_4.[42,43] Olah also reports that with increasing substitution of alkyl groups on these ions the position of maximum absorption progressively shifts to longer wavelengths.[42] The implication then is that the lowest singlet excitation energy of the allylic cation would occur with λ_{max} corresponding to energies greater than 4.1 eV.

Recent theoretical calculations of allyl cation excitation energies show the lowest excited $\pi \rightarrow \pi^*$ triplet ($^3B_2$) and singlet ($^1B_2$) at 3.0 and 5.8 eV above the ground state, respectively.[44] These calculations assumed a frozen σ core. Relaxation of the σ core generally lowers singlet excitation energies by $\sim$0.5 eV.[45] Confusing this issue are the configuration interaction calculations of Peyerimhoff and Buenker, which give explicit consideration to the σ core and arrive at the conclusion that the lowest excited singlet excitation is $\sigma \rightarrow \pi^*$ in nature and not $\pi \rightarrow \pi^*$.[46] Excitation energies calculated by Peyerimhoff and Buenker are significantly higher than those reported by Levin, Goddard, and Huestis.[44] The only spin allowed $\sigma \rightarrow \pi^*$ excitation lying below the $\pi \rightarrow \pi^*$ $^1B_2$ state in the calculations of Peyerimhoff and Buenker has $^1A_2$ symmetry and is thus symmetry forbidden.

Dunbar[19] has recently reported that photoexcitation of allyl cations in the gas phase leads to a modification of their reactivity, the observed process being as indicated in reaction 8. The threshold observed for this

$$C_3H_5^+ + C_2H_4 \xrightarrow{h\nu} C_3H_7^+ + C_2H_2 \qquad (8)$$
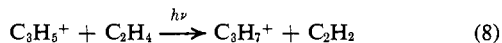
process at λ 520 nm (2.38 eV) is quoted as evidence for what appears to be an unusually low-lying excited state of the allyl cation.

Our results shown in Figure 6 for the excitation function are generally consistent with the absorption spectra of allylic cations in solution, the observed λ_{max} 270 nm (4.57 eV) falling within a typical range. The extinction coefficient ϵ_{max} 2×10^3 is comparable to ϵ_{max} observed for allylic cations in solution and is large enough to suggest an allowed dipole transition consistent with the prediction of Levin, Goddard, and Huestis for the lowest π to π^* excitation. It is unlikely that the lowest singlet excitation in the absorption spectra of structural isomers II-V would occur at these relatively long wavelengths with moderate extinction coefficients. Reconciliation of our results with Dunbar's evidence for a low-lying state of $C_3H_5^+$ would require an electronically excited state of $C_3F_5^+$ which lies below dissociation thresholds and thus is not observed in the present experiments.

In summary it is envisioned that the photodissociation process involves a $\pi \rightarrow \pi^*$ excitation, followed by rotation of the CF_2 group about the C-C bond and 1,2-elimination of CF_3^+ across the C-C bond of the C_2F_2.

(43) N. C. Deno, J. M. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Amer. Chem. Soc.*, **85**, 2998 (1963).

(44) G. Levin, W. A. Goddard III, and D. L. Huestis, *Chem. Phys.*, **4**, 409 (1974).

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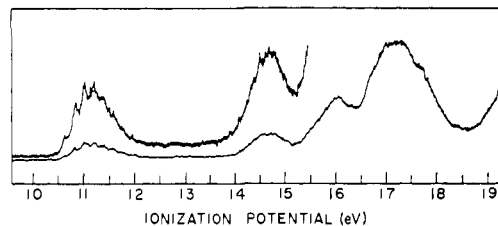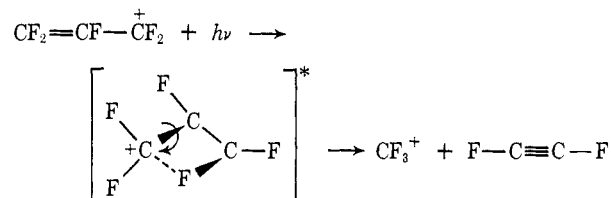(46) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).

Figure 7. Photoelectron spectrum of perfluoropropylene taken with HeI radiation. The energy scale is correct to ±0.04 eV.

neutral product.[47] This process is depicted in Scheme II. The proposed intermediate is similar to structural

Scheme II

isomers III and V. It is not clear whether the decomposition occurs in the electronically excited state or in a highly excited ground state following radiationless conversion of electronic to vibrational excitation. The latter is normally assumed to occur in mass spectral fragmentation processes.[48]

Failure to Observe Photodissociation of $C_3F_6^+$. It was originally anticipated that photoexcitation of the parent ion would lead to the two processes 9 and 10,

$$CF_2{=}CF{-}CF_3^+ \xrightarrow{h\nu} \begin{cases} C_2F_4^+ + CF_2 & (9) \\ CF_2{=}CF{-}CF_2^+ + F & (10) \end{cases}$$
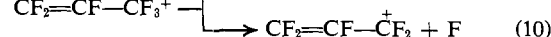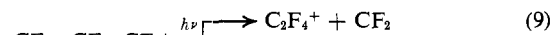
neither of which were observed except as electron impact induced fragmentation processes.[49] Information relating to excited electronic states of the parent ion may be obtained from the He(I) photoelectron spectrum in Figure 7.[50]

To our knowledge, the photoelectron spectrum of perfluoropropylene has not previously been reported or discussed in the literature. The effects of fluorine substitution evident in comparing the spectra of propylene[51,52] and perfluoropropylene are similar to those reported for related systems by Brundle, et al.,[53] namely both the π and σ ionizations occur at higher energies in

(47) The barrier to CF_2 rotation in the excited state is probably considerably less than for the ground state. Ground state barriers to rotation are calculated to be 38.4 kcal/mol for $C_3F_5^+$ (ref 38) and 34.8 kcal/mol for $C_3H_5^+$ (ref 39). If internal conversion resulted in the formation of a vibrationally excited ground state, the internal excitation of the ion would greatly exceed the barrier to internal rotation.

(48) M. Vestal in "Fundamental Processes in Radiation Chemistry," P. J. Ausloos, Ed., Interscience, New York, N. Y., 1968, Chapter 2.

(49) A reaction analogous to process 9 has been observed in the photodissociation of $C_6H_5CF_3^+$: B. S. Freiser and J. L. Beauchamp, unpublished results. Process 10 would be analogous to loss of H from $CH_2{=}CHCH_3^+$ as reported by J. M. Kramer and R. C. Dunbar in ref 16.

(50) The photoelectron spectrum in Figure 7 was recorded with HeI radiation on a spectrometer of standard design (127° electrostatic analyzer) built in the Caltech instrument shop.

(51) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

(52) U. Weidner and A. Schweig, *J. Organometal. Chem.*, **39**, 261 (1972).

(53) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972).

the perfluorinated compound. The first (π bonding), second (C-C bonding), and third bands occur with adiabatic (vertical) ionization potentials of 9.69 (9.9), 11.76 (12.3), and 12.8 (13.2) eV in propylene. In perfluoropropylene the three lowest bands are observed at 10.62 (11.1), 13.77 (14.7), and 15.1 (16.0) eV. The lowest excitations (those falling within the range of our light source) from the ground state of the ion to the states revealed by photoelectron spectroscopy would have thresholds at 3.15 (394 nm) and 4.5 eV (276 nm). The calculated thresholds for the two processes 9 and 10 are 2.60 and 2.82 eV, respectively. Excitation of either state should thus produce an ion with sufficient internal excitation to observe both decomposition processes. There is no requirement that this occurs, however, and in fact is not observed. Several explanations may be offered for this behavior: (1) the cross section for photon absorption is low (even with the uncertainties in assignment of the states for the parent ion, in analogy with propylene[16] at least one of the two energetically accessible transitions is likely to be symmetry allowed); (2) the excited state may fluoresce before unimolecular decomposition occurs; or (3) internal conversion may result in cross over to a bound long-lived state which could subsequently fluoresce or phosphoresce. We conservatively estimate that with the full lamp output it is possible to detect a photodissociation process with a maximum cross section greater than 0.001 Å^2, and this represents an upper limit on the cross section for photodissociation of the parent ion. It is of interest to note that beyond triatomics, the only polyatomic ion for which fluorescence has been observed and reported is the parent ion of perfluorobenzene.[54] Benzene itself is not observed to fluoresce. Fluorescent deactivation generally requires a species with a lifetime of 10^{-8} sec. Observation of well-defined vibrational structures in a photoelectron band would indicate a lifetime in excess

of 10^{-12} sec. The evidence for vibrational structure in the lowest excited states of $C_3F_6^+$ is minimal at best. While it would be of interest to search for fluorescence from $C_3F_6^+$, the first explanation offered for failure to observe photodissociation of the parent ion is more likely.

Finally, it is of interest to note that the most abundant metastable peak in the ion kinetic energy spectrum corresponds to the only ion photodecomposition process observed in this study. Comparison of photodissociation and metastable results to date show that this observation is perhaps not unexpected. For example, the the photodissociations observed for the parent cations of propylene,[16] toluene,[17] ethylbenzene,[18] p-xylene,[18] trifluorotoluene,[49] and nitrous oxide[14] all show prominent metastables related to the same decomposition processes.[55-61] These observations suggest that factors which might relate intense metastables to photodissociation processes warrant further investigation. In particular, an examination of the relationship between collisional activation[57] (where electronic excitation of the reactant ion in high energy collisions is inferred) to the decomposition of ions in photochemically excited ionic states would be of considerable interest.

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