Experimental Section

All preparations were carried out under nitrogen, and the benzene used was dried over sodium and calcium hydride. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Nuclear magnetic resonance spectra were obtained on Varian A-60, T-60, and modified HA-60 spectrometers as saturated solutions in $CDCl_3$. Infrared spectra were obtained as Nujol mulls on a Perkin–Elmer Model 700 or a Beckman IR 8 spectrometer. Melting points were obtained on a Fischer-Johns apparatus and are uncorrected. The complexes $(P(C_6H_5)_3)_2Pt(H)Cl$, $(P(C_6H_5)_3)$-$Pt(H)CN$, and $(P(C_6H_5)_3)_2Pt(H)NCS$ (ν_{CN} 2100, ν_{CS} 872 cm^{-1}) were prepared as described in the literature. The protonic acids used were commercial samples and used without purification except for HCN which was prepared from KCN and H_2SO_4. $(P(C_6H_5)_3)_4Pt$[25] was prepared by the hydrazine reduction method, and $(P(C_6H_5)_3)_2Pt(C_2H_4)$[26] was prepared by the reduction of the oxygen compound with $NaBH_4$. Potassium tetrachloroplatinite was obtained from Engelhard Industries, Inc. The yields of the complexes were essentially quantitative.

Hydridothioacetatobis(triphenylphosphine)platinum(II).—To a filtered solution of $(P(C_6H_5)_3)_4Pt$ in benzene was added thioacetic acid when immediate decolorization of the yellow solution occurred. The solvent was removed at room temperature and ether was added to give a colorless precipitate which was recrystallized from a benzene–hexane mixture to give the pure *complex* which was dried *in vacuo;* mp 122° dec. *Anal.* Calcd for $C_{38}H_{34}OP_2PtS$: C, 57.4; H, 4.31; S, 4.03. Found: C, 57.1; H, 4.04; S, 4.25. $\nu_{C=O}$ 1625 cm^{-1}, ν_{Pt-H} 2140 cm^{-1}, τ_{CH_3} 8.40, $J_{Pt-CH_3} = 6$ Hz, τ_{Pt-H} 19.8, $J_{Pt-H} = 998$ Hz.

Hydridothiobenzoatobis(triphenylphosphine)platinum(II).—To a filtered solution of $(P(C_6H_5)_3)_4Pt$ in benzene was added thiobenzoic acid dropwise until the yellow color of the solution disappeared. The solvent was removed and C_2H_5OH added to give the pure *complex* which was dried *in vacuo;* mp 160° dec. *Anal.* Calcd for $C_{43}H_{36}OP_2PtS$: C, 60.2; H, 4.23. Found: C, 60.0; H, 4.09. $\nu_{C=O}$ 1595 cm^{-1}, ν_{Pt-H} 2125 cm^{-1}. This complex is too insoluble to obtain a high-field nmr spectrum.

Hydridobromobis(triphenylphosphine)platinum(II).—Through a solution of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ in benzene was bubbled HBr. The solvent was removed and ether was added to obtain the crude product. Recrystallization from a benzene–ether mixture gave the pure complex which was dried *in vacuo*. *Anal.* Calcd for $C_{36}H_{31}BrP_2Pt$: C, 54.0; H, 3.88; Br, 10.0. Found: C, 53.9; H, 3.71; Br, 10.2. ν_{Pt-H} 2215 cm^{-1}, τ_{Pt-H} 26.4.

Bis(thioacetato)bis(triphenylphosphine)platinum(II).—To a solution of $(P(C_6H_5)_3)_2Pt$(butyne-2) or $(P(C_6H_5)_3)_2Pt(C_6H_5C\equiv CC_6H_5)$ in benzene was added thioacetic acid and the mixture was stirred. After 1 hr the colorless precipitate was filtered, washed well with solvent, and dried *in vacuo*. *Anal.* Calcd for $C_{40}H_{36}O_2P_2PtS_2$: C, 55.2; H, 4.17; S, 7.37. Found: C, 55.3; H, 4.12; S, 8.29. $\nu_{C=O}$ 1630 cm^{-1}. The ^1H nmr spectrum in CF_3COOH shows a phenyl resonance at τ 2.92 (5) and a methyl resonance at τ 8.92 (1), the area ratio confirming the stoichiometry.

Bromochloroallenylcarbonylbis(triphenylphosphine)rhodium(III).—To a solution of $(P(C_6H_5)_3)_2Rh(CO)Cl$ in CH_2Cl_2 was added excess propargyl bromide, and the solution was allowed to stand for several hours. The solvent was removed and C_2H_5OH was added to give a dark yellow precipitate. The product was recrystallized from CH_2Cl_2–C_2H_5OH to give mustard yellow crystals of the *complex* which were dried *in vacuo*; mp 180°. *Anal.* Calcd for $C_{40}H_{33}BrClO_2P_2Rh$: C, 59.3; H, 4.1; halogen, 14.25. Found: C, 58.0; H, 3.8; halogen, 14.67. $\nu_{C=C=C}$ 1920 cm^{-1}, $\nu_{C=O}$ 2080 cm^{-1}, $\tau_{=CH_2}$ 6.1, $\tau_{=CH}$ 8.2.

Hydrido-2-mercaptobenzothiazolatobis(triphenylphosphine)platinum(II).—To a filtered solution of $(P(C_6H_5)_3)_4Pt$ in benzene was added 2-mercaptobenzothiazole. The solution became pale yellow and the solvent was reduced to low volume on a rotary evaporator. Addition of C_2H_5OH gave a yellow crystalline *complex* which was dried *in vacuo;* mp 147° dec. *Anal.* Calcd for $C_{43}H_{36}NP_2PtS_2$: C, 58.2; H, 4.09. Found: C, 58.2; H, 3.80. ν_{Pt-H} 2170 cm^{-1}. This complex is rather unstable, decomposing slowly in solution in the absence of excess ligand.

Acknowledgments.—We wish to thank Dr. J. A. Magnuson for assistance with the high-field nmr spectra and Dr. K. Thomas for many helpful discussions. This investigation was supported in part by funds provided by the Graduate School Research Fund and by Cities Service Oil Co., Cranbury, N. J.

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Reactions of Gaseous Inorganic Negative Ions. II. SF_6^- and Nonmetal Fluorides[1,2]

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Received June 12, 1970

The reactions of negative ions produced *via* electron capture in SF_6 at low electron energies with nonmetal fluorides have been studied. It is observed that the radical ion SF_6^- reacts with nonmetal fluorides AF_n (AF_n = BF_3, SiF_4, PF_5, PF_3) *via* fluoride ion transfer. Rate constants and reaction cross sections are presented and discussed.

Introduction

Gas-phase ion–molecule reactions have been known since the beginning of mass spectrometry[3] but only in the past decade have these processes been the subject of intensive study. Investigations of ion–molecule reactions have in general been directed toward positive ion systems, and outside the area of atmospheric studies little emphasis has been placed on studies of the reactions of gaseous negative ions in simple inorganic systems. Since it is likely that negative ions may be important constituents in gaseous discharges,[4] in flames,[5]

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[1] Presented in part at the 21st Southeastern Regional Meeting, American Chemical Society, Richmond, Va., Nov 1969.

[2] This study is a portion of a dissertation to be presented by T. C. Rhyne to the Graduate School of Virginia Polytechnic Institute in partial fulfillment of the requirements for the degree Doctor of Philosophy.

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in radiation chemistry,[6] and in other inorganic reactions, an investigation of the reactions of negative ions in inorganic chemistry is significant.

Studies of the formation of secondary negative ions in the gas phase may aid in attempts to describe the bonding and structural properties of negative ions. Since inorganic molecules composed of different elements and elements in different oxidation states may have dissimilar molecular geometries, examination of ion–molecule reactions in inorganic chemistry is particularly suitable for elucidating the importance of factors such as molecular structure, formal oxidation state, bond orders, and electronegativity in describing ionic reactions in the gas phase. Studies have been initiated in this area to provide information regarding the reactions which occur in the gas phase and the importance of the factors indicated above in influencing the rate constants and reaction cross sections for inorganic chemical systems.

Sulfur hexafluoride (SF_6) is known to have a high electron capture cross section for thermal electrons at 0.08 eV.[7] Although SF_6 is in general inert chemically, condensed-phase reactions of SF_6 with sodium in diphenylethylene glycol–dimethyl ether solutions,[8] with ammoniated electrons,[9] and with hydrated electrons[10] have been reported. The initial formation of the SF_6^- ion is postulated as an important step in these reactions, with the process then proceeding *via* a fluoride ion transfer mechanism leading to formation of the SF_5 radical. Thus it seems reasonable that SF_6^-, which is a radical ion, might react with simple inorganic molecules in the gas phase where single collision events can occur.

Recently[11] a preliminary report of gas-phase reactions of negative ions produced from SF_6 by electron capture at low electron energies was presented. The reaction of the primary ion (SF_6^-) with neutral nonmetal fluorides by fluoride ion transfer was described. In this paper a detailed discussion of these studies is presented.

Experimental Section

The compounds used in this study were purchased from commercial sources. Unless mass spectrometric analysis indicated the presence of impurities, the compounds were used without further purification. When necessary, purification was accomplished by repeated trap-to-trap vacuum distillation.

The mass spectrometer was a Hitachi Perkin-Elmer RMU-7 double-focusing instrument described previously.[11,12] It was interfaced with a Digital Equipment Corp. PDP-8/I computer. The MADCAP IV data acquisition program[13] was utilized for time averaging the ion signal and for obtaining the ionization efficiency curves directly from the mass spectrometer. Graphical data were output from the computer to a Hewlett-Packard X-Y recorder (Model 2D-2AM).

The ion source and pumping systems were modified to permit high-pressure investigations. The ion source was constructed of stainless steel with an electron path length of 15 mm. The electrons, produced from a rhenium filament, enter and leave the ionization chamber through slits 4.0 × 0.25 mm and are collimated by an external permanent magnet. The ion exit slit, positioned 1.5 mm from the plane of the electron beam and 4.0 mm from the repeller electrode, has the dimensions 8.0 × 0.25 mm and is covered with 80–90% transmittance stainless steel mesh to reduce field penetration into the ionization chamber. The ion source may be operated at temperatures from 55 to 300°. Temperature was measured using a thermocouple attached directly to the ionization chamber. In these studies the temperature was maintained at approximately 100° for all measurements of ionization efficiency curves and rate studies.

Pressure in the ionization chamber was measured with a Model 144 MKS Baratron capacitance manometer which operates in the region of 10^{-5}–1 Torr. The Baratron pressure head was connected to one side of the ionization chamber by about 10 mm of a 6-mm diameter stainless steel cone attached to a Kovar metal-to-glass tubing section. The glass tubing passes out of the ion source pump housing envelope through a Cajon Ultra-Torr O-Ring fitting. A second Kovar metal-to-glass tube is attached to 0.5-in. copper tubing which was welded to the pressure head coupling. The total length of tubing from the ion source to the pressure head is about 1 ft.

Gases were introduced into the mass spectrometer from a dual reservoir system whose total volume was about 6 l. Gases were delivered through two identical leaks into a common line connected to the mass spectrometer. Gas flow was controlled by stainless steel fine metering valves, and the partial pressure of each gas was measured using the Baratron gauge. The ion chamber pressure was maintained at 0.1–10 μ to reduce electron beam scattering and to maintain a well-collimated electron beam. The ion source housing envelope pressure was maintained at about 10^{-6}–10^{-5} Torr. Pressure in the analyzer tube was always less than 2.0×10^{-6} Torr, as measured with an ionization gauge attached to the analyzer tube.

To extend the lifetime of the source and to reduce the probability of secondary electron formation on exposed metal surfaces, the source surfaces and the repeller electrode were coated with a thin layer of colloidal carbon (Dag Dispersion No. 154). During the experiments no effects due to thermal decomposition of the compounds were detected, nor was there any evidence of deposits on the surfaces of the ion source due to reaction and/or decomposition.

Ion currents were measured using a Faraday cup collector or the electron multiplier calibrated for negative ions using the Faraday cup. The ion current ratios used in calculating the reaction cross sections and rate constants were evaluated by measuring the ion intensity at the electron energy corresponding to the maximum in the electron capture ionization efficiency curve for the primary ion.

The variation of electron energy was accomplished as described earlier[11,12] with points on the electron capture ionization efficiency curves taken at 0.05-V intervals. As before[12] precautions were taken to ensure that the thermal energy distribution on the electron beam was not distorted in shape and was as narrow as possible yet permitting adequate negative ion current to be detected. To maintain a distribution width at half-height of the order of 0.3–0.6 eV the filament current was nominally 2.8–3.2 A, and the electron trap current less than 1 μA. The trap potential was maintained at 5.0 V relative to the ionization chamber.

The reaction cross sections and rate coustants were evaluated for the reactions studied as outlined by other workers.[14,15] The reaction cross section, Q_R, is defined according to Stevenson and Schissler[15]

$$Q_R = \frac{i_s}{i_p}\left(\frac{1}{nd}\right) \qquad (1)$$

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where Q_R is the reaction cross section, i_s is the secondary ion current, i_p is the primary ion current, n is the number of molecules per cubic centimeter, and d is the ion path length in the ion chamber. The experimentally measured parameters are the ion current ratio and the pressure used to calculate n; d is known from the ion source geometry.

The specific rate constant is evaluated from the expression

$$k = \frac{i_s}{i_s + i_p}\left(\frac{1}{nt}\right) \qquad (2)$$

where t is the average ion residence time of the primary ion. The residence time is calculated according to the expression

$$t = \left(\frac{2dm_i}{eE}\right)^{1/2} \qquad (3)$$

where m_i is the mass of the primary ion, e the electronic charge, and E the repeller field strength. At repeller fields used in this study the thermal and kinetic energies are negligible.

In initial experiments the ion–molecule reactions

$$Ar^+ + H_2 \longrightarrow ArH^+ + H \qquad (4)$$

$$CD_4^+ + CD_4 \longrightarrow CD_5^+ + CD_3 \qquad (5)$$

$$O^- + N_2O \longrightarrow NO^- + NO \qquad (6)$$

were studied to evaluate the ion source focusing conditions and performance of the mass spectrometer for high-pressure studies. Comparison of the results obtained in this study and earlier investigations[15] are presented in Table I for reaction 4. The variation of reaction cross sections with field strength for reaction 4 is presented graphically in Figure 1. For reaction 5 the rate constant and reaction cross section at 10-V/cm field strength measured in this study, 7.12×10^{-10} cm^3/molecule sec and 58×10^{-16} cm^2/molecule, respectively, compare favorably with the values determined in earlier reports.[14] For reaction 6, the rate constant, 3.14×10^{-11} cm^3/molecule sec, compares favorably with that reported previously[16] at the same field strength.

TABLE I

REACTION CROSS SECTION FOR THE ION–MOLECULE REACTION $Ar^+ + H_2 \rightarrow ArH^+ + H$

Stevenson and Schissler[15] (377°K)

$(dE)^{-1/2}$, $V^{-1/2}$	1.701	1.200	0.849	0.600
Q_R, Å^2/molecule	248	179	133	97

This Work (378°K)

$(dE)^{-1/2}$, $V^{-1/2}$	2.00	1.41	1.16	1.00	0.894	0.707
Q_R, Å^2/molecule	291	205	178	155	139	115

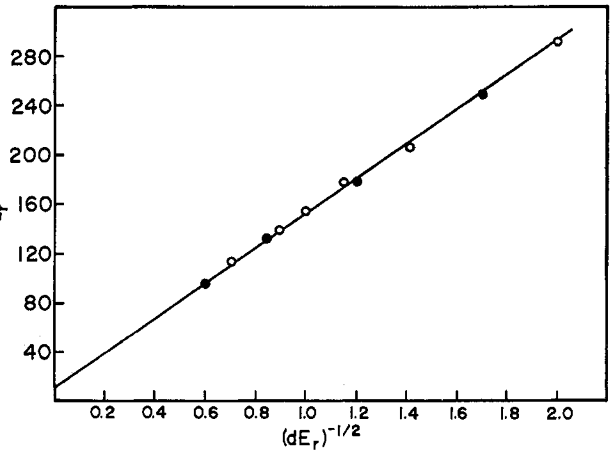

Figure 1.—Reaction cross section (Å^2/molecule) as a function of $(dE)^{-1/2}$ ($V^{-1/2}$) for the reaction $Ar^+ + H_2 \rightarrow ArH^+ + H$: O, this study; ●, Stevenson and Schissler.[15]

Results and Discussion

Ion–Molecule Reactions.—In gaseous mixtures of SF_6 and nonmetal fluorides AF_n (AF_n = BF_3, SiF_4, PF_5, PF_3,), at low electron energies and high pressure in the mass spectrometer, ions of the type AF_{n+1}^- are observed. Since these ions are not present at low electron energies in the low-pressure (10^{-7} Torr) mass spectra of nonmetal fluoride–SF_6 mixtures, it appears that these ions are formed *via* ion–molecule reactions.

The most abundant negative ions formed from SF_6 are SF_6^- and SF_5^- [7] which have maxima in the electron capture ionization efficiency curves at 0.08 and 0.16 eV, respectively. The fluoride ion has also been detected at near 0 eV, with the abundance of F^- about 0.01 that of SF_6^-.[17] Since the abundance of the secondary ion in SF_6–AF_n mixtures is about 0.01 that of SF_6^-, it is unlikely that F^- is the primary reactant ion. In the mass spectrum of the nonmetal fluorides, F^- is formed at electron energies above zero and cannot contribute to the ion–molecule reactions observed at low electron energies.

Although the secondary ions BF_4^- and SiF_5^- have been observed[18] in the mass spectra of BF_3 and SiF_4, respectively, at higher electron energies (>10 eV), ions of sufficient abundance were not detected at near-zero electron energies to account for the formation of secondary ions when either PF_5, PF_3, SiF_4, or BF_3 only was introduced into the mass spectrometer. Reactions of the type

$$AF_n^- + AF_n \longrightarrow AF_{n+1}^- + AF_{n-1} \qquad (7)$$

$$AF_n^- + SF_6 \longrightarrow AF_{n+1}^- + SF_5 \qquad (8)$$

where AF_n^- represents a parent or fragment nonmetal–fluorine negative ion, are thus excluded. It is suggested that the AF_{n+1}^- ions arise *via* reactions of negative ions formed from SF_6 with the nonmetal fluoride.

The secondary ions PF_6^-, PF_4^-, SiF_5^-, and BF_4^- appear in the energy region where the SF_6^- and SF_5^- ions from SF_6 are abundant. Ion–molecule reactions which may explain the occurrence of the secondary ions are (using SiF_4 as the example)

$$SF_6^- + SiF_4 \xrightarrow{k_1} SiF_5^- + SF_5 \qquad (9)$$

$$SF_5^- + SiF_4 \xrightarrow{k_1} SiF_5^- + SF_4 \qquad (10)$$

$$SF_6^- + SiF_4 + M \xrightarrow{k_2} SiF_5^- + SF_5 + M \qquad (11)$$

$$SF_5^- + SiF_4 + M \xrightarrow{k_2} SiF_5^- + SF_4 + M \qquad (12)$$

Reactions 9 and 10 are bimolecular processes involving the formation of the secondary ion and neutral SF_5 or SF_4, respectively, while reactions 11 and 12 involve collisional stabilization of the secondary negative ion. Expressions 13 and 14 represent the pressure dependence of the ion current ratio, $i_s/(i_s + i_p)$, for first- and sec-

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ond-order dependence, respectively, where (AF_n) is the

$$\frac{i_s}{i_s + i_p} = k_1t(AF_n) \qquad (13)$$

$$\frac{i_s}{i_s + i_p} = k_2t(AF_n)(M) \qquad (14)$$

density of the nonmetal fluoride and (M) is the density of a bath molecule, either SF_6 or AF_n, which is involved in collisional stabilization. If it is assumed that SF_6 and AF_n are equally efficient as bath molecules, a plot of the ion current ratio *vs.* AF_n pressure at constant SF_6 pressure should lead to an idenitfication of the order of the reaction. A typical presentation of ion current ratio *vs.* AF_n pressure is given in Figure 2 for an SiF_4–SF_6 mixture at constant SF_6 pressure. The observed pressure variation is in agreement with the prediction of eq 13 confirming that the process observed is a simple bimolecular reaction. Similar results were obtained for the other nonmetal fluoride systems, PF_5, PF_3, and BF_3.

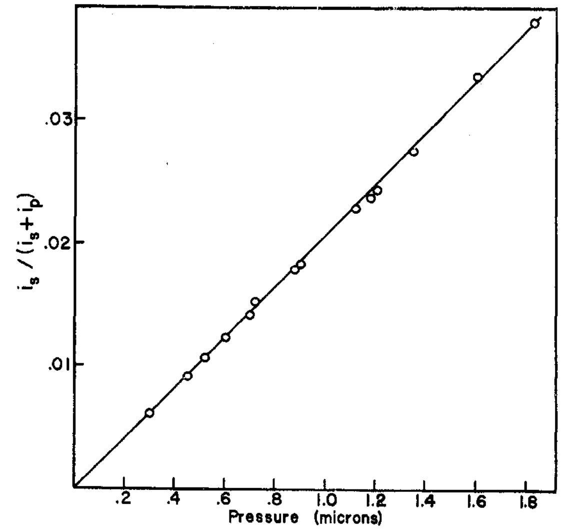

Figure 2.—Ion current ratio as a function of SiF_4 pressure for the reaction $SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$.

The primary reactant ion, SF_6^- or SF_5^-, is identified by comparison of the electron capture ionization efficiency curves for SF_6^- and SF_5^- with that for the secondary ion AF_{n+1}^-. Coincidence of the ionization efficiency curves for primary and secondary ions identifies the primary ion unless kinetic energy in the primary ion is necessary. It has been shown[11] that the primary ion is SF_6^- in the reactions producing PF_6^- and PF_4^-. Similar results were obtained for the formation of BF_4^- and SiF_5^-. The comparison of the electron capture curves supports reaction 9 as the process leading to the formation of the AF_{n+1}^- ions at low electron energies where the general reaction

$$SF_6^- + AF_n \longrightarrow AF_{n+1}^- + SF_5 \qquad (15)$$

summarizes the fluoride ion transfer process with SF_6^- as the primary ion.

Reaction Cross Sections and Rate Constants.—Since the primary reactant ion is a "temporary negative ion"[19] which undergoes autodetachment, the measured SF_6^- ion current must be corrected to give the SF_6^- ion current at the ion source exit slit. Two reactions, in addition to the ion–molecule reaction, result in destruction of SF_6^-: autodetachment

$$SF_6^- \longrightarrow SF_6 + e^- \qquad (16)$$

and collisional detachment

$$SF_6^- + M \longrightarrow SF_6 + M + e^- \qquad (17)$$

The autodetachment lifetime for SF_6^- has been reported to be 26,[19] 10,[20] and 500[21] μsec. These differences in lifetime probably arise from different source temperatures and electron energies.[22] The value determined by Compton, *et al.*,[19] was used for the correction because SF_6^- is formed under experimental conditions similar to those in this study. The SF_6^- ion flight time between acceleration and collection is of the order of 20 μsec in our instrument. The correction factor is established from the known[19] autodetachment lifetime of SF_6^-, the ion flight path length in the analyzer tube, and the magnitude of the ion accelerating voltage. The correction factors are 2.087 and 2.465 for accelerating voltages of 3.75 and 2.5 kV, respectively. The reaction cross section where the SF_6^- ion current has been corrected for autodetachment should exhibit no dependence on accelerating voltage. Reaction cross sections for BF_4^- formation are presented in Table II at two accelerating voltages for a series of repeller potentials. It is observed that consistent reaction cross sections are obtained at the accelerating voltages studied and that the measured cross section is independent of accelerating voltage. It appears that the correction factor applied to the measured SF_6^- ion current is reasonable.

TABLE II

REACTION CROSS SECTIONS FOR THE REACTION

$$SF_6^- + BF_3 \longrightarrow BF_4^- + SF_5$$

AS A FUNCTION OF ACCELERATING VOLTAGE

	Reaction cross section, Å²/molecule	
	Accelerating voltage	
Repeller voltage, V	3.75 kV	2.50 kV
2.0	74.5	73.9
2.5	56.4	57.3
3.0	54.4	56.7
3.5	46.0	46.9
4.0	47.5	51.2

Collisional detachment of SF_6^- with a bath molecule M (where M may be SF_6 or the nonmetal fluoride) is probably not a significant pathway for destruction of SF_6^-. The rate of collisional detachment for SF_6^- by Xe has been measured[23] to be 2×10^{-15} cm³/sec. Since it is likely that the rate of collisional detachment for SF_6^- by SF_6 or AF_n would not differ significantly from that by Xe, it is assumed that the loss of SF_6^- by col-

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(19) R. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 4634 (1966).

(20) D. Edelson, J. E. Griffiths, and K. B. McAfee, *ibid.*, **37**, 917 (1962).

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(23) J. B. Hasted and S. Beg, *Brit. J. Appl. Phys.*, **16**, 1779 (1965).

lisional detachment is small compared to the loss of SF_6^- *via* autodetachment or the ion–molecule reaction. In addition, it is observed that in SF_6 alone the SF_6^- ion current is first order in pressure. This suggests that SF_6^- is not lost by reaction 17 in the case in which $M = SF_6$. Similar behavior would be expected for the nonmetal fluorides considered here for reaction 17. Thus it has been assumed in the calculation that SF_6^- was lost only *via* the ion–molecule reaction and autodetachment and not through collisional detachment or other processes. Since the secondary ions correspond to stable ions (*i.e.*, completed electron structures and no odd electron ions), it has been considered that the secondary ion lifetime is long compared to its flight time. Thus the experimentally measured secondary ion current without correction was used in all calculations.

The reaction cross sections and rate constants for the reactions forming AF_{n+1}^- ions are given in Tables III and IV, respectively. The cross sections vary as a function of ion energy for these reactions, but it is not possible to distinguish between E^{-1} or $E^{-1/2}$ dependence.

TABLE III

REACTION CROSS SECTIONS FOR THE FORMATION OF SECONDARY IONS AS A FUNCTION OF REPELLER VOLTAGE

Repeller voltage, V	Cross section, Å²/molecule			
	BF_4^-	SiF_5^-	PF_6^-	PF_4^-
1.5	73.6	68.8	34.4	3.88
2.0	73.9	56.5	31.9	2.88
2.5	57.3	52.1	28.5	2.60
3.0	56.7	50.1	25.7	1.89
3.5	46.9	47.2	24.9	1.68
4.0	51.2	48.8	23.3	1.59

TABLE IV

REACTION RATE CONSTANTS FOR THE FORMATION OF SECONDARY IONS AS A FUNCTION OF REPELLER VOLTAGE

Repeller voltage, V	Rate constant × 10^{10}, cm³/molecule sec			
	BF_4^-	SiF_5^-	PF_6^-	PF_4^-
1.5	3.17	2.97	1.48	0.167
2.0	3.68	2.81	1.59	0.143
2.5	3.19	2.90	1.59	0.145
3.0	3.45	3.06	1.57	0.116
3.5	3.09	3.11	1.64	0.111
4.0	3.60	3.44	1.64	0.112

Schaefer and Henis[24] have proposed an electron density rearrangement model for qualitatively predicting the magnitude of the reaction cross sections for low-energy ion–molecule reactions. This model is restricted to systems which are exothermic and in which the reactants have a relative kinetic energy of less than about 1 eV and are not vibrationally excited. This allows use of a two-state approximation for describing the course of the reaction, and the process of predicting the relative magnitude of the reaction cross section is reduced to a determination of the change in electron density around the reaction centers.

The general negative ion–molecule reaction

$$A^- + BC \longrightarrow AB^- + C \qquad (18)$$

is considered in terms of the relative electronegativities at the reaction centers A and B. If the electronegativity of A is larger than that of B, then little change in electron density will be necessary around center B upon proceeding to the AB^- ion since the electronegative A moiety will command a larger share of the electron density in the product ion. However, if the electronegativity of B is much larger than that of A, then formation of the product ion will require a net shift of electron density to B at or near the time of reaction. The authors[24] thus predict that for the situation requiring little effective rearrangement of electron density the reaction will be enhanced and a large reaction cross section ($Q > 1$ Å²/molecule) will probably be observed. Likewise, if the relative values of the electronegativities of A and B are such that extensive rearrangement occurs, then a small cross section is expected for the reaction. Although this treatment[24] has thus far been restricted to reaction centers consisting of carbon, nitrogen, and oxygen, the extension of these concepts to the SF_6^-–AF_n system appears reasonable.

Application of the criteria of Schaefer and Henis[24] to the fluoride ion transfer reactions results in the prediction of large reaction cross sections for each of the reactions reported. The electronegativities for atoms of interest in these reactions follow:[25] fluorine, 4.0; phosphorus, 2.2; boron, 2.0; silicon, 1.9. Since the electronegativity of fluorine is much larger than that of either of the atoms occupying the reaction center of the neutral species, little shift of electron density to that reaction center should be required upon transfer of a fluoride ion to the neutral species to form the secondary ion. Calculations of electronic distributions in the molecules SF_6 and PF_5 tend to support this prediction.

Santry and Segal[26] have pointed out that the electronic distribution in SF_6 involves a net shift of electron density to the fluorine atoms. These authors propose that the electronic distribution in PF_5 is quite similar to that in SF_6, with electron density on the fluorine atoms being significant due to inefficient back-donation of π electrons to the phosphorus. Similar electronic distributions may be expected with the boron and silicon fluorides. Mitchell[27] has suggested that the unpaired electron in SF_6^- may lie in a molecular orbital having a large contribution from the sulfur atomic orbitals, thus maintaining significant electron density on the fluorine atoms. Since both the reactant ion and the neutral species are likely characterized by a high electron density on the fluorine atoms, little shift of electron density away from the fluorine is necessitated by transfer of a fluoride ion to the neutral molecule and the prediction of a high reaction cross section for this process is deemed reasonable. Although the results reported here are in general agreement with predictions based on the description of Schaefer and Henis,[24] it is noted that gross structural properties may be quite important for these processes.

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Both PF_5 and PF_3 are predicted to have large reaction cross sections, but the large differences in the measured values show that the description is not complete. The octahedral[28] PF_6^- ion is well known[29] in condensed phases, whereas PF_4^- is apparently not readily formed[29] in solution. Structural stability attained in the reaction product seems to enhance the reaction, an observation which is supported by the large cross sections observed for the formation of BF_4^- (tetrahedral structure)[28] and SiF_5^- (trigonal-bipyramidal structure).[28] Although the electron density rearrangement description of ion–molecule reactions provides useful qualitative predictions of the magnitude of reaction cross sections, in some cases the inherent instability of a product ion (*e.g.*, PF_4^-) may present a barrier which precludes the success of predictions based on the simple two-state approximation. Additional experiments are in progress to sort out the effect of structural stability on reaction cross sections.

Thermodynamic Calculations.—The fluoride ion transfer reactions studied here can provide thermodynamic information about the species since some of the ions have been detected in condensed phases. The reactions studied are exothermic as evidenced by the decrease in reaction cross section with increasing primary ion energy (*i.e.*, repeller potential). Since ion–molecule reactions for low ion energies are usually exothermic,[14] an upper limit to the heat of formation of the negative ions can be established assuming the ions are formed with negligible kinetic energy according to reaction 15. Kinetic energies have not been measured in this study so the calculated ionic heats of formation represent upper limits. SF_6^- is formed at 0.08 eV;[7] thus $\Delta H_f(SF_6(g)) = \Delta H_f(SF_6^-(g)) = -289$ kcal/mol (see Table V). The heat of formation of $SF_5(g)$ can be estimated from the reaction $SF_6 + e^- \rightarrow F^- + SF_5$. Curran[17] has reported the formation of F^- at near 0 eV, where the total kinetic energy was 0.23 eV. The value of $D(SF_5\text{–}F)$ is evaluated from the expression $AP(F^-) + EA(F) \leq D(SF_5\text{–}F) + KE_{total}$. Using the reported appearance potential, total kinetic energy, and the electron affinity of fluorine (3.45 eV),[30] $\Delta H_f(SF_5(g)) = -234$ kcal/mol. Combining the values for $\Delta H_f(SF_6^-(g))$, $\Delta H_f(SF_5(g))$, and $\Delta H_f(AF_n(g))$ given in Table V, the values for ΔH_f of the AF_{n+1}^- ions were calculated and are given in Table V.

TABLE V

HEATS OF FORMATION OF GASEOUS NEUTRAL SPECIES AND GASEOUS IONS

M(g)	ΔH_f, kcal/mol	M(g)	ΔH_f, kcal/mol	M(g)	ΔH_f, kcal/mol
SF_4	-185.2^a	SiF_4	-385.98^a	SF_5^-	-304^b
SF_6	-289^a	BF_3	-271.75^a	PF_4^-	-275^b
PF_3	-219.6^a	F	18.88^a	PF_6^-	-436^b
PF_5	-381.4^a	SF_5	-234^b	SiF_5^-	-441^b
		SF_6^-	-289^b	BF_4^-	-327^b

[a] D. D. Wagman, W. H. Evans, V. P. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-3** (1968). [b] See text.

Other investigators have evaluated ionic heats of formation from lattice energy calculations[31,32] and from ion–molecule reactions.[18] A value of $\Delta H_f(BF_4^-(g))$ has been estimated to be -407 kcal/mol[31,32] and $\Delta H_f(SiF_5^-(g))$ is calculated to be $\leqslant -583$ kcal/mol.[18] These results compare with the present values of ΔH_f for $BF_4^-(g)$ and $SiF_5^-(g)$, -327 and -441 kcal/mol, respectively. The discrepancies probably lie in the fact that neither of the values obtained from the ion–molecule studies takes into account internal energy or kinetic energy of the reactants and products. It is well known that such contributions may be significant in negative ion formation and reaction processes. Investigations are in progress to determine the translational energy associated with secondary ion formation.

Acknowledgments.—We gratefully acknowledge the Research Corp. and the donors to the Petroleum Research Fund administered by the American Chemical Society for partial financial support and the National Science Foundation for providing funds to aid in purchasing the mass spectrometer. Special thanks are due Mr. Gerald Dulaney for his advice and assistance in programming the laboratory computer and interfacing it with the mass spectrometer and Mr. Don Bodell and Mr. Frank Shelor of the Virginia Polytechnic Institute Research Division machine shop for construction of the high-pressure ion source and pump housing.

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