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Reactions of Gaseous Inorganic Negative Ions. IV. Arsenic Trifluoride and Arsenic Pentafluoride[1,2]

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The ion–molecule reactions of negative ions from SF_6 with AsF_3 yield the AsF_4^- secondary ion. The magnitude of the reaction cross sections is consistent with the fluoride ion acceptor ability of AsF_3. In pure AsF_5 the secondary ions AsF_5^- and AsF_6^- are produced by reaction with AsF_4^-. In mixtures of SF_6 and AsF_5 the dominant secondary ion is AsF_6^-. The reaction cross sections and rate constants are presented as a function of repeller voltage.

Introduction

Recent studies[4-6] of the gas-phase negative ion chemistry of inorganic fluorides have shown that negative ions produced from sulfur hexafluoride react with nonmetal fluorides, AF_n, to form secondary negative ions of the type $[AF_{n+1}]^-$. The process for the formation of the secondary ions involves transfer of a fluoride ion from SF_6^- to the nonmetal fluoride according to the general reaction

$$SF_6^- + AF_n \rightarrow [AF_{n+1}]^- + SF_5 \qquad (1)$$

Reactions in which $AF_n = PF_3, PF_5, BF_3, SiF_4, POF_3$, and PSF_3 have been reported.[4-6] Similar reactions in which the secondary ion $[AF_{n+1}]^-$ is formed by the reaction

$$SiF_3^- + SiF_4 \rightarrow SiF_5^- + SiF_2 \qquad (2)$$

have also been observed.[7,8]

Previous studies have demonstated the importance of fluoride ion transfer processes in describing the gas-phase chemistry of nonmetal fluoride systems. The similarity of the gas-phase behavior of these systems to that observed in solution has prompted studies of other inorganic fluorides in an effort to understand the kinetics of fluoride ion transfer processes and, ultimately, to correlate molecular parameters such as size, polarizability, and dipole moment with the acceptor ability of the nonmetal fluoride. In this paper the reactions of negative ions in arsenic(III) and arsenic(V) fluorides and in mixtures of the materials with SF_6 will be presented.

Arsenic trifluoride has frequently been used as a nonaqueous solvent.[9] The pure liquid has a fairly high conductivity[10] which apparently arises from self-ionization of the type

$$2AsF_3 \rightarrow AsF_2^+ + AsF_4^- \qquad (3)$$

The ability of AsF_3 to act as a fluoride ion acceptor in solution is evidenced by its exothermic reactions with metallic fluorides (KF, RbF, CoF, and TlF) to form $MAsF_4$ salts.[11,12] The importance of size and polarizing power of the cation in such a complex has been alluded to,[12] and the failure to observe $LiAsF_4$ and $NaAsF_4$ has been cited[12] as evidence for the importance of such factors in determining reactivity. From ^{19}F chemical shift data[13] it is noted that the shift for AsF_3 is greater than that for AsF_5. The relative magnitudes of the shifts suggest[14] that the As–F bond in AsF_3 is more ionic than in AsF_5. In addition the average AsF bond dissociation energy[15] is some 20 kcal/mol greater for AsF_3 than for AsF_5.

The acid-base properties of group V pentahalides and particularly AsF_5 have been discussed in several publications.[16-19] It is evident[16-18] that the relative acidities are in the order $SbF_5 > AsF_5 > PF_5$. In anhydrous HF the $As_2F_{11}^-$ anion is the dominant species[17] as demonstrated from ^{19}F nmr measurements.

Gas-phase measurements of the rate of fluoride ion transfer to AsF_3 and AsF_5 are independent of many of the factors which complicate measurements in condensed-phase systems. A determination of the rate of reaction and measurement of the reaction cross section with a common fluoride ion donor under similar reaction conditions should enable meaningful comparisons of the acceptor properties of AsF_3 and of AsF_5 with those of previously studied[5,6] nonmetal fluorides. In addition, an investigation of reactions of the AsF_3 molecule ($\mu_0 = 2.81$ D)[20] and AsF_5 ($\mu_0 = 0$) should provide an indication of the contributions of permanent dipole moment to reactivity toward the F^- donor.

Experimental Section

The compounds used in this study were obtained from commercial sources. SF_6 was found to be of sufficient purity for use as supplied by the manufacturer (Matheson Gas Co.). AsF_3 (Ozark-Mahoning) required purification to remove significant amounts of SiF_4. The SiF_4 impurity was removed by repeated trap-to-trap vacuum distillation at −63°. The final AsF_3 was at least 99% pure and was stored in a stainless steel cylinder.

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

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Arsenic pentafluoride was contaminated with $AsOF_3$. Although $AsOF_3$ has a much higher boiling point than AsF_5, the much broader liquid range of $AsOF_3$ complicates the separation process. Repeated passes of the material through a U tube cooled by a chloroform slush (−63°) resulted in gradual removal of $AsOF_3$ until the remaining AsF_5 was found to be of satisfactory purity (~98%) for use in these studies.

The high-pressure mass spectrometer, associated apparatus, and the computerized data acquisition system used in this investigation have been described previously.[5,21] 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. For these experiments the ion source temperature was maintained at approximately 100° for all measurements of ionization efficiency curves and for rate studies.

The ion source required extensive conditioning (8–12 hr) before consistent ion current measurements could be obtained when the arsenic compounds were introduced into the spectrometer. This behavior is apparently the result of reaction of the fluoride with the surfaces in the instrument although colloidal carbon was present on these surfaces. In accordance with similar behavior observed with various fluorine-containing molecules,[22] these surfaces become passivated by extended contact with the compound. Once the instrument was passivated as described above, mass spectra of AsF_3 and AsF_5 were consistent and reproducible unless the source was removed for cleaning or a different compound was introduced into the instrument.

Ion currents were measured using a Faraday cup collector or an electron multiplier which had been calibrated for negative ions using the Faraday cup. A correction[23] was made for loss of SF_6^- *via* autodetachment as described previously.[5] The specific rate constant is evaluated from the expression

$$k = \frac{i}{i_s + i_p}\left[\frac{1}{nt}\right]$$

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

$$t = \left[\frac{2dm_i}{eE}\right]^{1/2}$$

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. The reaction cross section, Q_R, was calculated from the expression

$$Q_R = \frac{i_s}{i_p}\left[\frac{1}{nd}\right]$$

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.

Results

Low-Pressure Studies. The low-pressure mass spectra (10^{-6}–10^{-7} Torr) indicate that the dominant ions in AsF_3 are F^- and AsF_2^- with resonance maxima at approximately 10.8 and 5.8 eV, respectively. In AsF_5 the important ions at low pressure are F^-, AsF_4^-, and AsF_5^-. The AsF_4^- and AsF_5^- ions are formed at near-zero electron energy while F^- is produced at about 10 eV by resonance-capture processes. The formation of AsF_4^- and AsF_5^- will be discussed later in this paper and in more detail in a subsequent paper.[24] In both compounds the fluoride ion was the most abundant ion in the spectrum. These observations are in agreement with the preliminary report by Saalfeld[25] of the negative ions formed in AsF_3 and AsF_5 at low pressure.

High-Pressure Studies. AsF_3. No negative ions were detected at near-zero electron energies when pure AsF_3 was introduced into the mass spectrometer. However, when SF_6 was added to AsF_3 the secondary ion AsF_4^- was observed in the energy region where SF_6^- and SF_5^- are formed in large abundance by resonance electron capture.[26] The ionization efficiency curves for SF_6^- and AsF_4^- are identical, identifying SF_6^- as the precursor ion for the formation of AsF_4^-. The AsF_4^- ion is formed by a bimolecular process since the ion current for AsF_4^- exhibits a second-order pressure dependence. A plot of ion current ratio ($i_s/(i_s + i_p)$), as a function of AsF_3 pressure shown in Figure 1, supports the bimolecular collision process between SF_6^- and AsF_3 according to eq 4. This process is similar to that observed for re-

$$SF_6^- + AsF_3 \rightarrow AsF_4^- + SF_5 \qquad (4)$$

actions of SF_6^- with other nonmetal fluorides,[4–6] and comparison of rate data obtained for each of these systems should be of interest since the reactant ion, the energy of the reactants, and the ion source conditions are similar for each of the measurements involved. The reaction cross sections and rate constants as a function of repeller voltage are presented in Table I.

AsF_5. When AsF_5 is introduced into the ion source at high pressure the ions AsF_4^-, AsF_5^-, and AsF_6^- are formed at near-zero electron energy. Examination of the ionization efficiency curves shown in Figure 2 for AsF_4^-, AsF_5^-, and AsF_6^- reveals that all are formed at the same electron energy and the widths of all resonance curves are approximately equal. The reaction for the formation of AsF_4^- is the dissociative electron-capture process

$$AsF_5 + e^- \rightarrow AsF_4^- + F \qquad (5)$$

AsF_5^- may be formed by resonance electron capture

$$AsF_5 + e^- \rightarrow AsF_5^- \qquad (6)$$

a charge-transfer ion–molecule reaction

$$AsF_4^- + AsF_5 \rightarrow AsF_5^- + AsF_4 \qquad (7)$$

or an atom-transfer ion–molecule reaction

$$AsF_4^- + {}^{\ddagger}AsF_4{*}F \rightarrow {}^{\ddagger}AsF_4 + AsF_4{*}F^- \qquad (8)$$

The formation of AsF_6^- is probably *via* the reaction

$$AsF_4^- + AsF_5 \rightarrow AsF_6^- + AsF_3 \qquad (9)$$

AsF_5^- is not selected as the primary ion for reaction 9 because the AsF_5^- and AsF_6^- ions are of approximately the same relative intensity over the pressure region studied. On the other hand, the intensity of AsF_4^- is more than 25 times that of either AsF_5^- or AsF_6^-, a value typical of primary: secondary ion ratios.

Figure 3 shows the variation with pressure of the ion current ratios for the ion pairs AsF_4^-–AsF_5^- and AsF_4^-–AsF_6^-. At low pressures the ratios describing the AsF_5^- and AsF_6^- ion current behavior increase linearly with increasing AsF_5

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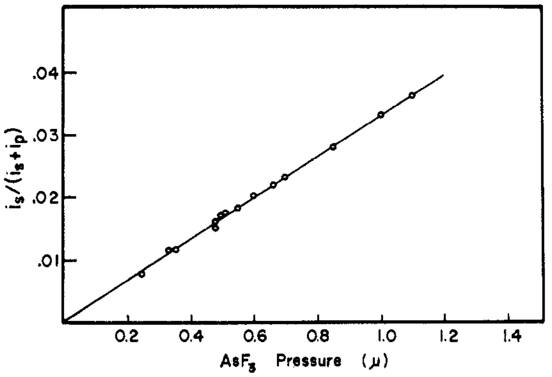

Figure 1. Ion current ratio as a function of AsF_3 pressure in SF_6-AsF_3 mixtures for the reaction $SF_6^- + AsF_3 \rightarrow AsF_4^- + SF_5$.

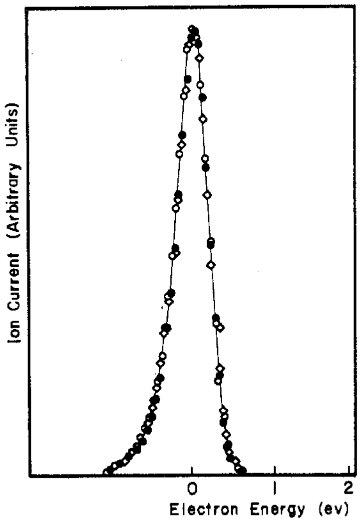

Figure 2. Ionization efficiency curves for ions formed in pure AsF_5: ●, AsF_4^-; ◇, AsF_5^-; ○, AsF_6^-. (All curves are scaled to the same ordinate value by the computer program.)

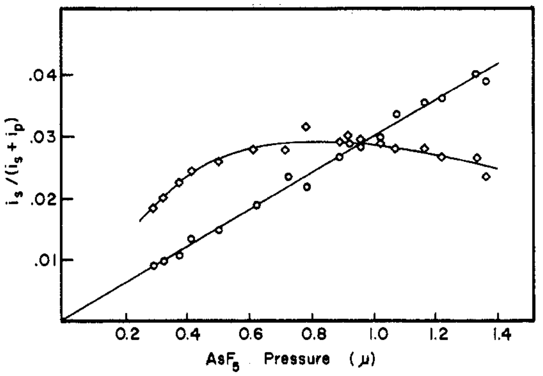

Figure 3. Ion current ratios for AsF_5^- and AsF_6^- in pure AsF_5 as a function of pressure: ◇, AsF_5^-; ○, AsF_6^-.

Table I. Reaction Rate Constants and Reaction Cross Sections Determined as a Function of Repeller Voltage for the Reaction $SF_6^- + AsF_3 \rightarrow AsF_4^- + SF_5$

Repeller voltage, E_R, V	$10^{10}k$, cm^3/molecule sec	Q, $Å^2$/molecule	Repeller voltage, E_R, V	$10^{10}k$, cm^3/molecule sec	Q, $Å^2$/molecule
1.5	4.34	100.7	3.0	4.49	73.7
2.0	4.22	84.7	3.5	4.59	69.7
2.5	4.38	78.7	4.0	4.61	65.5

pressure. This result indicates that AsF_5^- may be formed *via* a secondary process in addition to the resonance-capture process. Since the ionization efficiency curve for AsF_5^- coincides with that of AsF_4^-, the ion-molecule process for AsF_5^- formation is suggested to be either reaction 7 or 8. It is impossible under the experimental conditions employed to distinguish between reactions 7 and 8. At pressures exceeding 0.5 μ of AsF_5 the AsF_5^-:AsF_4^- ion current ratio levels off and proceeds to drop slowly, suggesting that the cross section for the formation of AsF_5^- *via* a secondary process decreases dramatically and that AsF_5^- formed by charge transfer or atom transfer is destroyed by some process not operable at lower AsF_5 pressure. The mechanism for destruction of AsF_5^- is likely collisional detachment by AsF_5

$$AsF_5^- + AsF_5 \rightarrow 2AsF_5 + e^- \qquad (10)$$

although an ion-molecule reaction (eq 11) could be possible.

$$AsF_5^- + AsF_5 \rightarrow AsF_6^- + AsF_4 \qquad (11)$$

Since the initial formation of AsF_5^- is pressure dependent (pseudo first order), corresponding to a bimolecular process, reaction 11 would require consecutive bimolecular collisions if this were contributing to the formation of AsF_6^-. This process is not likely since much higher pressures are normally required. In addition no change in slope of the curve for the formation of AsF_6^- is observed in the region where AsF_5^- is diminishing. If reaction 11 does contribute to the formation of AsF_6^-, the amount of AsF_6^- formed is insignificant compared to that resulting from other pathways of formation. Therefore reaction 11 is eliminated from consideration as a means of destruction of AsF_5^- and the loss of AsF_5^- is ascribed to collisional detachment.

An alternate possibility for the AsF_5^- ion current behavior is that the per cent ion current for AsF_5^- is really invariant over the pressure range studied and that the initial linear behavior is only an apparent variation because of the precision in ion current measurement. The ion current measurements and the linear behavior observed were reproducible to within at least 5% over a period of several months and replicate measurements.

AsF_6^- ion formation obeys a second-order pressure dependence over the entire range studied, and the correspondence of the ionization efficiency curve with that for AsF_4^- identifies reaction 9 as the dominant process for formation of AsF_6^- in pure AsF_5. The rate constants and reaction cross sections for AsF_5^- and AsF_6^- formation as a function of repeller potential are summarized in Table II.

Since secondary ions are observed in the high-pressure negative ion mass spectrum of pure AsF_5, the identification of ion-molecule reactions with SF_6^- was more difficult. When SF_6^- was added to AsF_5, the secondary ion AsF_6^- was observed to increase in abundance while AsF_4^- and AsF_5^- showed no corresponding increase. This behavior suggested that the ion-molecule reaction

$$SF_6^- + AsF_5 \rightarrow AsF_6^- + SF_5 \qquad (12)$$

occurs in mixtures of SF_6 and AsF_5 and that charge transfer between SF_6^- and AsF_5 does not take place. The ionization efficiency curves for the formation of negative ions in the low-energy region are presented in Figure 4 for a mixture of SF_6 and AsF_5. Since the SF_6^- curve is coincident with the curves for all ions containing arsenic, positive identification of reaction 12 was accomplished by monitoring the variation in AsF_6^- ion current upon addition of SF_6 at low electron energies.

Figure 5 shows the variation of AsF_6^- ion current ratio in mixtures of SF_6 and AsF_5 as a function of AsF_5 pressure. The points designated by circles are the calculated ratios for

Table II. Reaction Cross Sections for the Formation of Secondary Ions in Pure AsF_5 as a Function of Repeller Voltage for the Reactions $AsF_4^- + AsF_5 \rightarrow AsF_5^- + AsF_4$; $AsF_4^- + AsF_5 \rightarrow AsF_6^- + AsF_3$

	Q, Å²/molecule			Q, Å²/molecule	
E_R, V	AsF_5^-	AsF_6^-	E_R, V	AsF_5^-	AsF_6^-
1.5	138.7	110.5	3.0	87.8	60.5
2.0	105.6	78.2	3.5	85.8	55.4
2.5	97.0	66.8	4.0	84.1	51.1

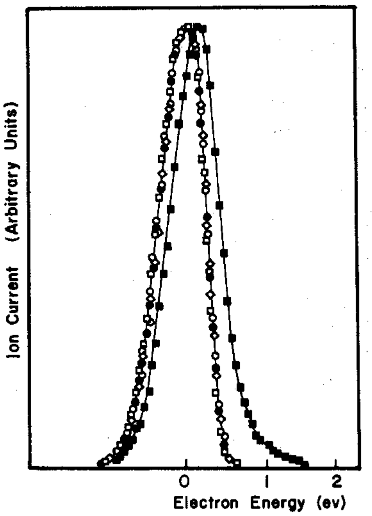

Figure 4. Ionization efficiency curves for ions formed in SF_6–AsF_5 mixtures: ●, AsF_4^-; ◇, AsF_5^-; ○, AsF_6^-; □, SF_6^-; ■, SF_5^-.

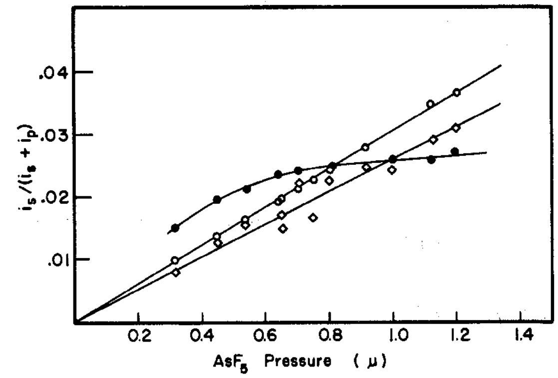

Figure 5. Ion current ratios as a function of AsF_5 pressure in SF_6–AsF_5 mixtures: ●, AsF_5^-:AsF_4^- ratio (reaction 7, 8); ○, AsF_6^-:AsF_4^- ratio (reaction 9); ◇, AsF_6^-:SF_6^- ratio (reaction 12).

reaction 9 based on the measured cross section for the ion-molecule reaction in pure AsF_5. The calculated AsF_6^- ion current due to reaction 9 was subtracted from the measured ion current and the ion current ratio due to reaction 12 was calculated. The reaction cross sections for the reactions in pure AsF_5 are summarized in Table II. The rate constants and cross section for the reaction of SF_6^- with AsF_5 are presented in Table III.

Table III. Reaction Cross Sections for the Formation of Secondary Ions as a Function of Repeller Voltage for the Reaction $SF_6^- + AsF_5 \rightarrow AsF_6^- + SF_5$

E_R, V	$10^{10}k$, cm³/molecule sec	Q, Å²/molecule	E_R, V	$10^{10}k$, cm³/molecule sec	Q, Å²/molecule
1.5	3.12	72.4	3.0	2.10	34.7
2.0	2.76	55.8	3.5	2.15	32.7
2.5	2.20	39.6	4.0	2.13	30.4

Correcting for the lifetime of the primary and secondary negative ions is important in the calculations of the reaction cross sections and the rate constants. The measured SF_6^- ion current was corrected as before.[5] AsF_5^- is a temporary negative ion whose autodetachment lifetime has not been measured. If the lifetime is approximately equal to that of the isoelectronic ion SF_4^- ($\tau \approx 10$ sec),[27] then the cross section for reaction 7 or 8 would be larger than reported here since the collected AsF_5^- ion current was not corrected for autodetachment. Similarly the autodetachment lifetimes of AsF_4^- and AsF_6^- are also unknown and could not be measured in this study. Although it is recognized[23] that the autodetachment lifetime increases with decreasing ion energy and is directly related to the number of degrees of freedom in the ion, no correction was made for the measured AsF_4^- and AsF_6^- ion currents. If such corrections are significant, then the reaction cross sections for AsF_4^- and AsF_6^- formation *via* reactions 4 and 12, respectively, would be larger. Furthermore the cross section for AsF_4^- formation would be increased to a greater extent than that for AsF_6^- since the AsF_4^- lifetime would be expected to be shorter due to a smaller number of degrees of freedom.

Discussion

A comparison with previous studies[5] indicates that the cross section for formation of PF_4^- *via* a process analogous to reaction 4 is about a factor of 0.03 lower than that observed for the formation of AsF_4^-. The principal differences between these two group V trifluorides are the size of the central atom and the magnitude of the dipole moment, $\mu_0(PF_3) = 1.03$ D[28] and $\mu_0(AsF_3) = 2.81$ D.[20] It may be suggested that the enhanced reactivity of AsF_3 may be the result of one or both of these factors.

The increased size of the arsenic atom gives rise to a trifluoride which is larger and more polarizable than PF_3 which would enhance the probability of AsF_4^- formation. However, the difference in polarizability is not sufficient to account for the large difference in Q. In addition the reorganization energy required to alter the valence electronic sttructure from tetrahedral AsF_3 to a trigonal-bipyramidal structure for AsF_4^- is probably less for AsF_3. Thus in the reaction with SF_6^-, transfer of F^- is not sufficient to produce the trigonal-bipyramidal geometry assumed for PF_4^- but sufficient energy is supplied for AsF_4^- formation. Such a prediction suggests that the promotion energy for phosphorus must be significantly larger than that for arsenic. It is not reasonable that the promotion energies would be significantly different and certainly not different enough to account for the large differences in cross section. In addition, if the promotion energy is supplied by SF_6^-, then the cross section for PF_4^- should increase with increasing ion energy. This behavior is not in agreement with the experimental results.[5]

The relative magnitude of the reaction cross sections are related to the values of the dipole moments although not directly. The order of the cross section is in agreement with the prediction of Moran and Hamill.[29] However, the primary ion energies in this study are usually too large for the "lock in" dipole model to be important. Furthermore, in previous studies,[5] the magnitude of the dipole was found to influence the reaction cross section in an unpredictable manner.

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In summary the large difference in reaction cross section for AsF_4^- and PF_4^- formation remains unexplained. Studies are in progress to determine the variation in reaction cross section for other congener pairs of groups V and VI nonmetals.

The reaction cross section at 2.0-V repeller voltage for AsF_6^- formation *via* reaction 12 is greater by about a factor of 4 than the value measured[5] for the formation of PF_6^-. For the group V pentafluorides the polarizability and size of the central atom must be the dominant parameter influencing the reaction since each molecule has a zero dipole moment. That the cross section for AsF_6^- formation is greater than that for PF_6^- production is consistent with the known[16-18] Lewis acidities and reflects the significance of fluoride ion transfer processes in determining acidities of nonmetal fluorides.

The cross section for the reactions studied here exhibit a decrease in magnitude with increasing ion energy, an effect which is characteristic of exothermic reactions. The reactions involving SF_6^- are therefore shown to be exothermic, and thermochemical calculations of the approximate ionic heats of formation of the secondary ions may be carried out since $\Delta H(\text{reaction}) \geqslant 0$. However, since no measurements of internal energy or kinetic energy of the reactants or products were carried out in this study, the values obtained here represent upper limits.

The primary ion AsF_4^- is formed by reaction 5. From the appearance potential of AsF_4^-, AP = ~0, the heat of formation of AsF_4^- is −315 kcal/mol. The value $\Delta H_f(AsF_4^-)$ may also be evaluated from an ion-molecule process (reaction 4). The heats of formation of SF_6^- and SF_5 have been previously evaluated[5] as −289 and −234 kcal/mol, respectively. The heat of formation of the reactant AsF_3 is given[30] as −220.04 kcal/mol, so that $\Delta H_f(AsF_4^-) = -275$ kcal/mol. This latter value is more positive than the value calculated from reaction 5. That the $\Delta H_f(AsF_4^-)$ calculated from the ion-molecule reaction is greater than that evaluated from reaction 5 suggests that AsF_4^- is formed with significant excess energy in the ion-molecule process.

If the value $\Delta H_f(AsF_4^-) = -315$ kcal/mol is used in reaction 9, $\Delta H_f(AsF_6^-)$ is calculated to be −391 kcal/mol. On the other hand, $\Delta H_f(AsF_6^-)$ is evaluated as −351 kcal/mol from reaction 12. This result again suggests that in the ion-molecule reaction the products are produced with significant quantities of excess energy.

The gaseous heats of formation were obtained from the references cited (in kcal/mol): AsF_3, −220;[30] AsF_5 −296;[15] SF_6^-, −289;[5] SF_5, −234;[5] F, 19.[30]

Experiments to measure the kinetic energies of primary and secondary ions are in progress so that more exact determinations of heats of formation of negative ions may be obtained.

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Registry No. SF_6^-, 12206-92-7; AsF_3, 7784-35-2; AsF_4^-, 42847-14-3; AsF_5, 7784-36-3.

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Interhalogen Fluorosulfates and Triatomic Interhalogen Cations of Iodine, Bromine, and Chlorine[1]

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The synthesis of interhalogen fluorosulfates of the two types IX_2SO_3F and I_2XSO_3F, with X = Br or Cl, is accomplished by the oxidative addition of the corresponding halogen or interhalogen molecules to iodine(I) fluorosulfate. The vibrational spectra are interpreted in terms of ionic solids with evidence for strong anion-cation interaction. All compounds behave as strong bases in HSO_3F as shown by conductometric studies, giving rise to the solvated interhalogen cations ICl_2^+, IBr_2^+, I_2Cl^+, and I_2Br^+. The identity of these cations is confirmed by their electronic spectra in HSO_3F, HSO_3CF_3, and 96% H_2SO_4.

Introduction

Interhalogen cations have received considerable attention in previous years,[2] where they have been studied in the solid state or in solution of strong protonic acids. The abstraction of halide ions from interhalogens by suitable Lewis acids has been the main synthetic route to compounds containing such cations. Obviously this method is limited in its application by the number of known stable interhalogens and the small number of suitable Lewis acids strong enough to affect halide ion transfer without side reactions, such as halogen exchanges. The route is very successful in the preparation of compounds containing fluoro cations, where BF_3, SbF_5, and AsF_5 can be used as Lewis acids. Of the cations formed by the heavier halogens Cl, Br, and I, only ICl_2^+ [3] and very recently I_2Cl^+ [4,5] and $IBrCl^+$ [5b] have been characterized as $SbCl_6^-$ [3,5] or as $AlCl_4^-$ salts.

In a recent preliminary communication[6] we have drawn

(1) Presented at the 7th International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July 15-20, 1973.

(2) R. J. Gillespie and M. J. Morton, *Quart. Rev., Chem. Soc.*, 25, 553 (1971).

(3) C. G. Vonk and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, 78, 913 (1959).

(4) D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, *J. Chem. Soc., Chem. Commun.*, 779 (1972).

(5) (a) J. Shamir and M. Lustig, *Inorg. Nucl. Chem. Lett.*, 8, 985 (1972); (b) J. Shamir and M. Lustig, *Inorg. Chem.*, 12, 1108 (1973).

(6) For a preliminary account see P. A. Yeats, W. W. Wilson, and F. Aubke, *Inorg. Nucl. Chem. Lett.*, 9, 209 (1973).