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Nucleophilic Addition–Elimination Reactions of Weak Bases with the Trifluoroarsonium Ion in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

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The gas-phase ion chemistry of AsF_3 has been investigated both by itself and in binary mixtures in which the $HAsF_3^+$ ion is produced. Reactions in AsF_3 alone lead to production of the tetrafluoroarsonium ion, AsF_4^+. Reaction of $HAsF_3^+$ with AsF_3 yields $As_2F_5^+$ via a nucleophilic addition of AsF_3 to $HAsF_3^+$ followed by rearrangement loss of HF. This reaction is found to be general for $HAsF_3^+$ with a large number of bases, B, giving rise to a number of novel ionic species of the form $BAsF_2^+$. In addition, the proton affinity (PA) of AsF_3 has been found to be 153 ± 2 kcal/mol and the order of gas-phase basicities of the group 5 trifluorides to be $NF_3 < AsF_3 < PF_3$. This ordering is interpreted in terms of a special stability for the HPF_3^+ ion.

Introduction

Recent studies in our laboratory have involved the construction of an accurate gas-phase basicity scale for compounds whose proton affinities (PA) lie in the moderately weakly basic range between carbon monoxide[1,2] and water.[3] The development of such a gas-phase basicity scale involves the examination of a large number of bimolecular proton-transfer equilibria such as reaction 1, where A and B are molecules

$$AH^+ + B \rightleftharpoons BH^+ + A \qquad (1)$$

of comparable proton affinity.[4-6] This work has been hampered by the small number of stable, readily available compounds which are sufficiently weakly basic to lie within the desired proton affinity range. The relatively few compounds which have been found to have appropriate gas-phase basicities however, have been, in general, inorganic oxides, fluorides, and oxofluorides of the main-group elements.[7-9] One such series of compounds investigated in detail in our laboratory is the group 5 trifluorides NF_3, PF_3, and AsF_3.

In the course of examination of the gas-phase ion chemistry of AsF_3, both by itself and with other weak bases, it was found that in no case could steady-state concentrations of protonated species be achieved. This was discovered to be due to the fact that the trifluoroarsonium ion, $HAsF_3^+$, was extremely reactive, both with AsF_3 and with other bases, by a channel other than simple proton transfer. These reactions were found to have the character of a nucleophilic addition of the weak base to the trifluoroarsonium ion followed by a unimolecular elimination of HF to yield a novel ionic species in which the weak base, B, was bound to the AsF_2^+ cation (reaction 2). This

$$HAsF_3^+ + B \rightarrow BAsF_2^+ + HF \qquad (2)$$

type of reaction is unprecedented in the ion chemistry of the other group 5 trifluorides where both HNF_3^+[7] and HPF_3^+[8] are found to be unreactive by any means other than proton transfer.

In addition to the novel reactivity of the trifluoroarsonium ion, it was found early in our work that the order of basicities of the group 5 trifluorides was also unusual, with proton affinity values increasing in the order $NF_3 < AsF_3 < PF_3$. Thus, in view of these unique features of the gas-phase ion chemistry of the AsF_3 system, it was deemed worthwhile to undertake an extensive systematic investigation of the nucleophilic addition–elimination reaction between weak bases and $HAsF_3^+$ and to determine, as accurately as possible, the gas-phase basicity of AsF_3.

Experimental Section

All experiments were carried out at ambient temperature by using an ion cyclotron resonance (ICR) spectrometer of basic Varian design, extensively modified to permit ion-trapping experiments.[10] Details of design, construction, and operation of trapped-ion ICR have been described in detail previously.[11,12]

Arsenic trifluoride, obtained from PCR Inc., was condensed into a vessel containing sodium fluoride to remove HF impurity in the AsF_3. Fresh AsF_3 samples were prepared daily by transferring material from this stock vessel to well-passivated glass bulbs. Remaining impurities of SiF_4 were finally removed by pumping on the sample at −84 °C (obtained by using an ethyl acetate slush bath). The resulting AsF_3 was analyzed mass spectrometrically in the ICR spectrometer, and this usually revealed little or no SiF_4 present.

Mixtures of methane and weak bases used were prepared in known ratio manometrically on a vacuum line. All gases used were obtained from commercial sources and, with the exception of AsF_3, were used without further purification other than degassing by freeze–pump–thaw cycles at 78 K.

Pressures in the ICR spectrometer were obtained from ion-pump current readings calibrated against an MKS Instruments Model 170M baratron capacitance manometer capable of pressure readings as low as 2×10^{-6} torr.

Results and Discussion

Gas-Phase Ion Chemistry of AsF_3. The 70-eV single resonance ICR spectrum of AsF_3 at 5×10^{-7} torr consists of four peaks: AsF_3^+ (27.5%), AsF_2^+ (62.6%), AsF^+ (5.4%) and As^+ (4.5%). No other reported mass spectrum of AsF_3 appears to be available in the literature for comparison. Significantly, no *m/e* 85 (SiF_3^+), diagnostic of SiF_4 impurity, was usually observed.

The variation of relative ionic abundances with time for ions derived from AsF_3 at 70 eV and 2.5×10^{-6} torr is shown in Figure 1. The only reactions observed observed to occur are (3)–(6), producing AsF_2^+, AsF_4^+, and $As_2F_5^+$. The rate

$$As^+ + AsF_3 \rightarrow AsF_2^+ + AsF \qquad (3)$$

$$AsF^+ + AsF_3 \rightarrow AsF_2^+ + AsF_2 \qquad (4)$$

$$AsF_2^+ + AsF_3 \rightarrow AsF_4^+ + AsF \qquad (5)$$

$$AsF_3^+ + AsF_3 \rightarrow As_2F_5^+ + F \qquad (6)$$

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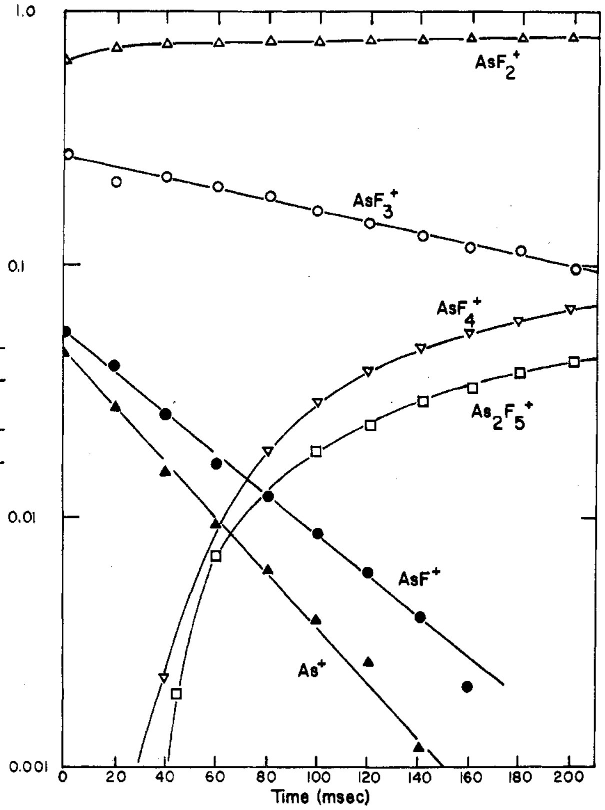


Figure 1. Variation of relative ionic abundances with time for AsF_3 at 2.5×10^{-6} torr following a 6-ms, 70-eV electron beam pulse.

constants obtained are $k_3 = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $k_4 = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $k_5 = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and $k_6 = 4.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Reaction 5, producing the tetrafluoroarsonium ion, is unique to the arsenic member of the group 5 trifluorides, although reaction 7 is observed to occur in PF_3–NF_3 mixtures to give the

$$PF_3^+ + NF_3 \rightarrow PF_4^+ + NF_2 \qquad (7)$$

tetrafluorophosphonium ion.[8] To date, no observation of the tetrafluoroammonium in the gas phase has been reported, although salts of this cation have been synthesized and characterized.[13,14] A reaction analogous to (7) producing AsF_4^+ is also observed in AsF_3–NF_3 mixtures.

Gas-Phase Basicity of AsF_3. The proton affinity of a base, B, defined as the negative of the enthalpy change for reaction 8, is a quantitative measure of the gas-phase basicity of B.

$$B + H^+ \rightarrow BH^+ \qquad (8)$$

Approximate gas-phase basicities of molecules are conveniently determined from ICR single and double resonance experiments[16,17] by observation of occurrence or nonoccurrence of exothermic proton transfer from protonated reference bases, of accurately known proton affinity, to the compound of interest. In favorable cases, where proton-transfer equilibrium (reaction 1) may be established, highly accurate *relative* proton affinities of bases may be obtained.[5,6]

As noted above, the reactivity of $HAsF_3^+$ precluded proton-transfer equilibrium measurements. The proton affinity of AsF_3 was therefore approximately determined to be 152 ± 3 kcal/mol on the bases of observation of proton transfer from protonated methyl fluoride, CH_3FH^+,[18] to AsF_3 (reaction 9) and observation of proton transfer from $HAsF_3^+$ to CF_2O (reaction 10).[19] Reference proton affinity data for bases in

$$CH_3FH^+ + AsF_3 \rightarrow HAsF_3^+ + CH_3F \qquad (9)$$

$$HAsF_3^+ + CF_2O \rightarrow CF_2OH^+ + AsF_3 \qquad (10)$$

the proton affinity range between CO and C_2H_4 are summarized in Table I.

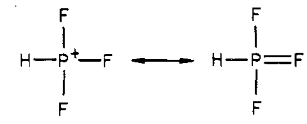
Table I. Gas-Phase Proton Affinities of AsF_3 and Reference Bases

base (B)	PA(B), kcal/mol	base (B)	PA(B), kcal/mol	base (B)	PA(B), kcal/mol
HCl	135,[a] 141[b]	AsF_3	153 ± 2[d]	$(CF_3)_2CO$	155.9[g]
CO	143[c]	SO_2F_2	154.8[f,g]	SO_2	(157.0)[f,g]
NF_3	148 ± 5[d]	CF_2O	155.1[g]	PF_3	158 ± 1[d,h]
CH_3F	153[e,f]	CF_3CFO	155.4[g]	C_2H_4	159[i]

[a] Reference 20. [b] Reference 3. [c] References 1 and 2. [d] This work. [e] Reference 18. [f] Reference 9. [g] Doiron, C. E.; McMahon, T. B., unpublished results (using a value of 157.0 kcal/mol for PA(SO_2) as suggested by Munson[9]). [h] Reference 8. [i] Reference 21.

It is of considerable interest to compare the basicity of AsF_3 to that of its group 5 homologues. Previous examinations of NF_3 allowed assignment of 150 ± 9 kcal/mol for the proton affinity[7] based on experiments placing the basicity between HCl[20] and C_2H_4.[21] We have refined the limits of basicity for NF_3 to 148 ± 5 kcal/mol on the basis of observation of proton transfer from HCO^+ to NF_3 and proton transfer from HNF_3^+ to CH_3F. Similarly for PF_3, the previously assigned value of 160 ± 5 kcal/mol for the proton affinity[8] has been improved to 158 ± 1 kcal/mol on the basis of observation of proton transfer from HSO_2^+ to PF_3 and failure to observe proton transfer from $C_2H_5^+$ to PF_3.

On the basis of previous observations of periodic trends in gas phase basicities,[11] it might normally be expected that the basicities of the group 5 trifluorides would change regularly proceeding down the group. The anomalous basicity order ($NF_3 < AsF_3 < PF_3$) is paralleled by an unusual order of ionization potentials for the same series of compounds[22] ($NF_3 > AsF_3 > PF_3$). In the case of ionization potentials, the phosphorus and arsenic compound orderings again appear to be transposed. These two observations can possibly be explained on the basis of the PF_3 and HPF_3^+ systems exhibiting a much greater tendency to participate in p_π–d_π overlap between fluorine 2p orbitals and empty 3d orbitals on phosphorus.[23-25] For example, the trifluorophosphonium ion, HPF_3^+, may be formally represented by valence-bond structures such as I which increase the stability of the ion and thus



I

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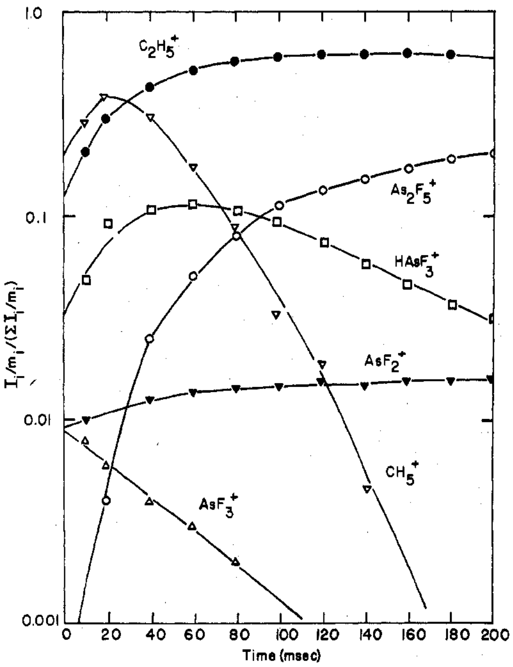
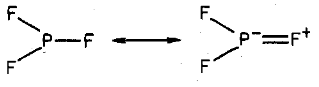


Figure 2. Variation of relative ionic abundances with time for a 1:1 mixture of CH_4 and AsF_3 at 2.6×10^{-6} torr total pressure following a 6-ms, 70-eV electron beam pulse. CH_3^+, CH_4^+, and the minor ions from AsF_3 and CH_4 are not shown.

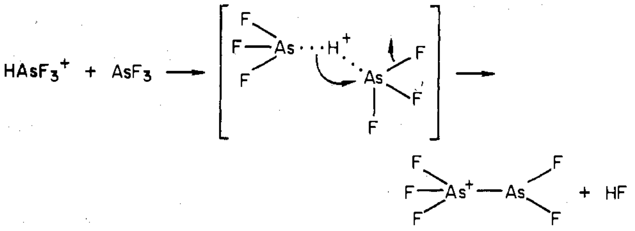
enhance the PF_3 proton affinity. Similarly, the low ionization potential of PF_3 might be explained by participation of charge-separated resonance structures such as II[25] in the



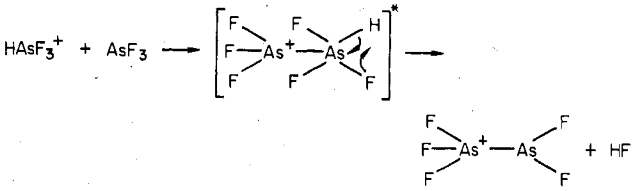
II

bonding of the neutral PF_3 molecule. Since PF_3 is well-known to be a good Lewis acid,[26] structures such as II might be regarded as an intramolecular donor–acceptor adduct. The increased electron density of phosphorus thus increases the availability of electrons, thereby lowering the ionization potential. Significantly, the increased availability of an electron pair will also increase the proton affinity. Since such effects due to p_π–d_π bonding will be a maximum for second-row atoms, these effects will be less pronounced for AsF_3, thus leading to an increased ionization potential and lower proton affinity for AsF_3. Similar arguments have been advanced to explain the basicity order of the group 5 trimethyl compounds of $(CH_3)_3P > (CH_3)_3N > (CH_3)_3As$.[27,28] More recently the basicities of the analogous triphenyl compounds have also been determined, and these show a similar proton affinity ordering to those of the trimethyl compounds with $Ph_3P > Ph_3N \simeq Ph_3As > Ph_3Sb$.[29] Again participation of the π electrons of the aromatic rings with empty 3d phosphorus orbitals should significantly enhance the basicity of triphenylphosphine. By comparison, the group 5 hydrides, where no such π-bonding effects are possible, show a regular decrease in proton affinities $(NH_3 > PH_3 > AsH_3)$[30,31] and the ionization potentials of PH_3 and AsH_3 are nearly identical.[32-34]

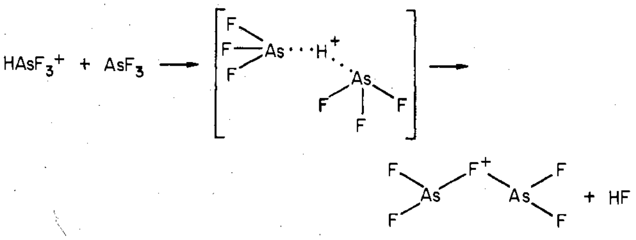
Scheme I



Scheme II



Scheme III



Reaction of the Trifluoroarsonium Ion with AsF_3. In mixtures of AsF_3 with other species in which the trifluoroarsonium ion, $HAsF_3^+$, is produced, this ion is found to undergo subsequent bimolecular reaction with AsF_3. For example, the variation of relative ionic abundances with reaction time for a 1:1 mixture of CH_4:AsF_3 at a total pressure of 2.6×10^{-6} torr and 70 eV is shown in Figure 2. Consistent with the observed proton affinity, AsF_3 is protonated by CH_5^+ but not by $C_2H_5^+$ (reaction 11).

$$CH_5^+ + AsF_3 \rightarrow HAsF_3^+ + CH_4 \qquad (11)$$

The disappearance of $HAsF_3^+$ is accompanied by appearance of an ion at *m/e* 245, corresponding to a species of molecular formula $As_2F_5^+$ (reaction 12). This reaction re-

$$HAsF_3^+ + AsF_3 \rightarrow As_2F_5^+ + HF \qquad (12)$$

quires the addition of AsF_3 to the trifluoroarsonium ion followed by loss of a molecule of HF. The ionic product, $As_2F_5^+$, may be formally regarded as an AsF_3 molecule bound to the Lewis acid AsF_2^+; however, it is of some interest to speculate on the details of the mechanism for this process and on the structure of $As_2F_5^+$.

One possible mechanism, shown in Scheme I, involves formation of a proton-bound dimer of AsF_3, followed by rearrangement loss of HF to give an ionic product with an As–As bond.

A second possible mechanism, Scheme II, requires attack of the As lone pair in AsF_3 at the As center of $HAsF_3^+$ to produce a pentavalent arsenic intermediate which subsequently loses HF to yield the same ionic product as that proposed in Scheme I.

Finally, a third possible mechanism suggests itself, based on the known tendency of arsenic and antimony to form

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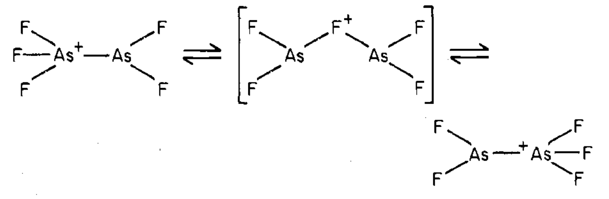
Table II. Nucleophilic Addition–Elimination Reactions of Weak Bases (B) with $HAsF_3^+$ Observed To Occur

	PA(B)[a]
$HAsF_3^+ + CO_2 \rightarrow O{=}C{=}O{-}AsF_2^+ + HF$	127[b,c]
$HAsF_3^+ + N_2O \rightarrow O{=}N{=}N{-}AsF_2^+ + HF$	139[c,d]
$HAsF_3^+ + CO \rightarrow O{=}C{-}AsF_2^+ + HF$	143[e]
$HAsF_3^+ + NF_3 \rightarrow F_3N{-}AsF_2^+ + HF$	148[f]
$HAsF_3^+ + CH_3F \rightarrow CH_3AsF_3^+ + HF$	153[g]
$HAsF_3^+ + AsF_3 \rightarrow As_2F_5^+ + HF$	153[f]
$HAsF_3^+ + CF_2O \rightarrow F_2C{=}O{-}AsF_2^+ + HF$	155[h]

[a] All values in kcal/mol. [b] Reference 36. [c] Bohme, D. K.; Fennelly, P.; Hemsworth, R. S.; Schiff, H. I. *J. Am. Chem. Soc.* 1973, *95*, 7512. [d] The bonding of N_2O to AsF_2^+ is presumed to be via the nitrogen rather than oxygen end of the molecule by analogy to transition-metal complexes where N_2O is a ligand. See: Bottomley, F.; Brooks, W. V. F. *Inorg. Chem.* 1977, *16*, 501. [e] References 1 and 2. [f] This work. [g] References 9 and 18. [h] Doiron, C. E.; McMahon, T. B., unpublished results.

fluorine bridging bonds.[35] As shown in Scheme III, the initial intermediate formed is identical with that in Scheme I. However, rearrangement loss of HF takes place via intramolecular nucleophilic attack by fluorine, resulting in a bridged fluoronium ion structure. Such a structure has a known analogy in the chemistry of SbF_3 where mixtures of SbF_3 and SbF_5 give salts of the form $Sb_2F_5^+Sb_2F_{11}^-$ which are shown to have a bridging fluoride in the $Sb_2F_5^+$ cation by X-ray crystallographic analysis.[36,37] Although no salts of $As_2F_5^+$ are known, it is not unreasonable to expect this ion to exhibit a similar structure to its congener $Sb_2F_5^+$. The possibility must also be considered that a bridged fluoronium ion in the gas phase is an intermediate between the two possible tautomeric forms of As–As bonded $As_2F_5^+$ (reaction 13). If such is the case, then all fluorines of the $As_2F_5^+$ cation would become equivalent.



(13)

Reaction of $HAsF_3^+$ with Weak Bases. Nucleophilic addition to $HAsF_3^+$ resulting in elimination of HF is not unique to AsF_3 as the nucleophile. A number of mixtures of n-donor bases with AsF_3 and CH_4 were examined, and in a great number of cases, the general reaction (2) was observed to occur. The reaction is similar to that producing $As_2F_5^+$ in the AsF_3 system with the exception that in this case the $BAsF_2^+$ adduct will almost certainly have the structure of an AsF_2^+ cation bound to the most basic site of the molecule B. Reactions of this type observed to occur are summarized in Table II.

The $BAsF_2^+$ adducts once produced can frequently participate in further reaction with AsF_3 (reaction 14) to also

$$BAsF_2^+ + AsF_3 \rightarrow As_2F_5^+ + B \qquad (14)$$

generate the $As_2F_5^+$ cation. This latter reaction is a nucleophilic displacement process in which a stronger base, AsF_3, displaces a weaker base, B, from the Lewis acid, AsF_2^+. A typical example is that shown in Figure 3 for a 3.5:3.5:1 mixture of CO_2, CH_4, and AsF_3 at a total pressure of 2.4×10^{-6} torr and 70 eV.

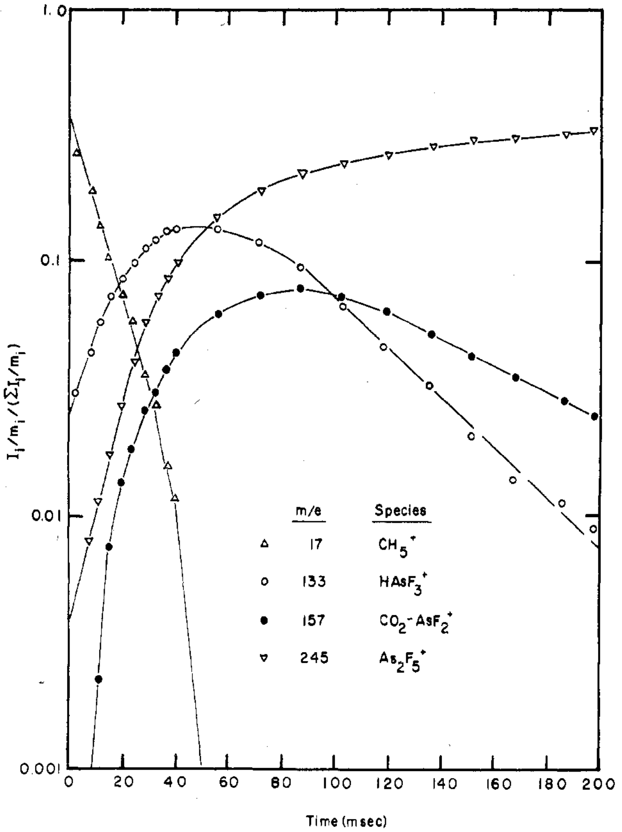


Figure 3. Variation of relative ionic abundances with time for a 3.5:3.5:1 mixture of CO_2, CH_4, and AsF_3 at 2.4×10^{-6} torr total pressure following a 6-ms, 70-eV electron beam pulse. Only CH_5^+ and ionic products derived from it are shown.

As an approximate guide to predicting the course of reaction in mixtures of bases with AsF_3 in which $HAsF_3^+$ is present, the following generalizations may be made.

(1) Addition of a base, B, to $HAsF_3^+$ may be followed by HF elimination if the internal excitation of the intermediate adduct is sufficient to overcome any activation barrier to HF loss. The amount of internal excitation in the intermediate $BHAsF_3^+$ species is equal to the binding energy of B to $HAsF_3^+$. This quantity is not known for any of the bases used; however, the relative order of binding energies to $HAsF_3^+$ may be expected to parallel approximately the order of proton affinities of the bases.[38] Thus, the binding energy of $HAsF_3^+$ to CO_2 (PA = 127 kcal/mol[39]) is sufficient to induce loss of HF (reaction 15), whereas the binding energies of $HAsF_3^+$ to N_2 (PA = 114 kcal/mol[39]) and Xe (PA = 114 kcal/mol[39]) are not (reactions 16 and 17). In all cases of addition of n-donor bases of proton affinity greater than that of CO_2 but less than that of AsF_3 to $HAsF_3^+$, HF elimination was observed.

$$HAsF_3^+ + CO_2 \rightarrow OCOAsF_2^+ + HF \qquad (15)$$

$$HAsF_3^+ + N_2 \nrightarrow N_2AsF_2^+ + HF \qquad (16)$$

$$HAsF_3^+ + Xe \nrightarrow XeAsF_2^+ + HF \qquad (17)$$

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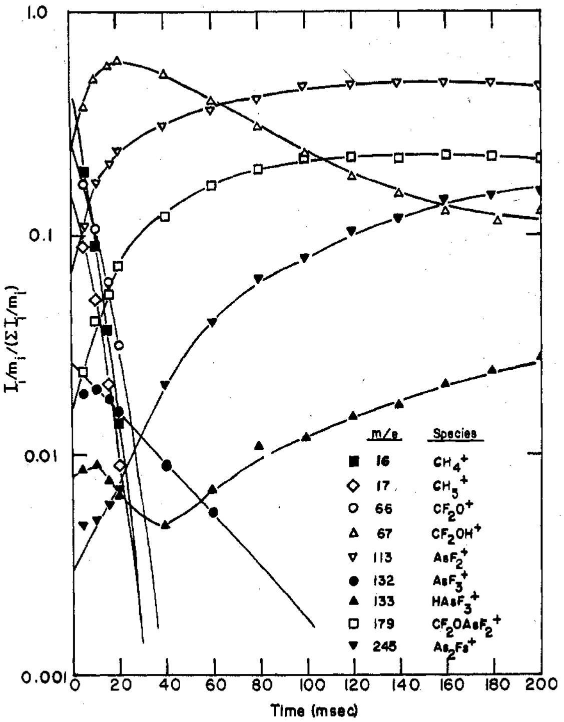


Figure 4. Variation of relative ionic abundances with time for a 3.8:3.1:1 mixture of CF_2O, CH_4, and AsF_3 at 7.5 × 10^{-6} torr total pressure following a 6-ms, 70-eV electron beam pulse.

(2) In cases where the proton affinity of the base, B, is greater than that of AsF_3, a competition between proton transfer from $HAsF_3^+$ to produce BH^+ and nucleophilic addition–elimination to produce $BAsF_2^+$ will occur. Such a situation is demonstrated by the variation of relative ionic abundances with the reaction time shown in Figure 4 for a 3.8:3.1:1 mixture of CF_2O, CH_4, and AsF_3 at 7.5 × 10^{-6} torr and 70 eV. In this case, both possible reaction channels occur, reactions 18 and 19 with proton transfer appearing to be slightly more dominant. In addition, CF_2OH^+ is also observed to react to produce $F_2CO{-}AsF_2^+$ (reaction 20). Here proton transfer is expected to be 2 ± 2 kcal/mol exothermic.

$$HAsF_3^+ + CF_2O \rightarrow CF_2OH^+ + AsF_3 \tag{18}$$

$$HAsF_3^+ + CF_2O \rightarrow F_2C{=}O{-}AsF_2^+ + HF \tag{19}$$

$$CF_2OH^+ + AsF_3 \rightarrow F_2C{=}O{-}AsF_2^+ + HF \tag{20}$$

At the relatively high pressures used in the CF_2O, CH_4, and AsF_3 mixture a further reaction channel (reaction 21) is also observable, leading to the slight increase in $HAsF_3^+$ intensity at longer reaction times.

$$As_2F_5^+ + CH_4 \rightarrow HAsF_3^+ + CH_3AsF_2 \tag{21}$$

When reactions of $HAsF_3^+$ with PF_3 were examined, only proton transfer was observed. In this case, the proton transfer is 5 ± 3 kcal/mol exothermic. The failure to observe $PF_3AsF_2^+$ indicates that, when a sufficiently exothermic proton transfer channel exists, the addition–elimination reaction will not compete favorably. This conclusion is supported by failure to observe any adducts $BAsF_2^+$ when the base used has a proton affinity greater than that of PF_3.

(3) In cases where B has a lower affinity for AsF_2^+ than does AsF_3, the general reaction (14) may be expected to occur. Again, as an approximate guide to the order of AsF_2^+ binding energies, the relative order of proton affinities may be used. This approximation assumes that the basicities of compounds toward Lewis acids such as AsF_2^+ will parallel the order of basicities toward the proton, H^+. While this may generally be true, some reversals do occur, particularly in instances where the proton basicities of B and AsF_3 are comparable. This is illustrated by the variation of relative ionic abundances with reaction time shown in Figure 5 for a 1:1 mixture of CH_3F and AsF_3 at 1.5 × 10^{-6} torr and 70 eV. Double-resonance experiments verify the greater proton affinity of AsF_3 over CH_3F. However, reaction 22 is also observed to be exothermic,

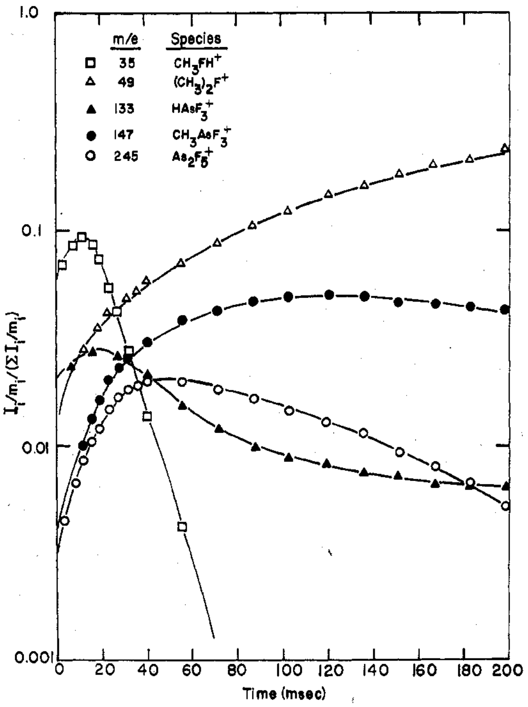


Figure 5. Variation of relative ionic abundances with time for a 1:1 mixture of CH_3F and AsF_3 at 1.5 × 10^{-6} torr total pressure following a 6-ms, 70-eV electron beam pulse. Only CH_3FH^+ and ionic products derived from it are shown.

$$As_2F_5^+ + CH_3F \rightarrow CH_3FAsF_2^+ + AsF_3 \tag{22}$$

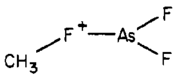
indicating that, toward the Lewis acid AsF_2^+, CH_3F has a greater basicity than AsF_3. The $CH_3FAsF_2^+$ ion is also formed in reaction 23 and is found to subsequently react with CH_3F

$$HAsF_3^+ + CH_3F \rightarrow CH_3FAsF_2^+ + HF \tag{23}$$

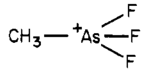
$$CH_3FAsF_2^+ + CH_3F \rightarrow CH_3FCH_3^+ + AsF_3 \tag{24}$$

via reaction 24 to produce the dimethylfluoronium ion.[18] This latter result also indicates that, toward the Lewis acid CH_3^+, CH_3F has a greater basicity than AsF_3. This then represents a second reversal of order of proton and Lewis basicities of the two compounds.

The structure of the $CH_3FAsF_2^+$ ion gives rise to some speculation also. By analogy to other observed reactions of the general type 2, it would be predicted that this ion would have structure III in which AsF_2^+ is bound to the most basic

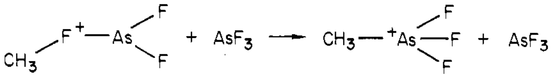


III



IV

site of CH_3F. However, another possible structure is IV in which a CH_3^+ cation is bound to the most basic site of AsF_3, the As lone pair. Structure III might also be regarded as CH_3^+ coordinated to a F lone pair which would be expected to be a less basic site of AsF_3 and hence an energetically less favorable species. Thus, it seems likely that, if III is, for kinetic reasons, the initially formed ion, a unimolecular isomerization to IV should occur if no activation barrier is involved. Alternatively, a bimolecular isomerization (reaction 25) could


(25)

III IV

also occur, making it extremely probable that any $CH_3FAsF_2^+$ observed at long reaction time has structure IV. This reaction is essentially a CH_3^+ transfer from a less basic to a more basic site of AsF_3.

Conclusion

The above results demonstrate that the trifluoroarsonium ion displays an unusual reactivity among its group 5 trifluoride congeners. The $As_2F_5^+$ adduct produced via nucleophilic addition–elimination rections with AsF_3 has a known analogy in synthetic inorganic chemistry in the $Sb_2F_5^+$ cation found in $Sb_2F_5^+Sb_2F_{11}^-$ which has been shown by crystallographic methods to have a bridging fluoronium ion structure. Our results indicate that such a structure for $As_2F_5^+$ is not unreasonable.

The reactions of bases with $HAsF_3^+$ also suggest that, by a judicious choice of reaction conditions to simulate the gas-phase conditions as closely as possible in synthetic experiments, a number of salts of unusual cations might be produced. For example, a mixture of AsF_3 and $HF–SbF_5$ might conceivably yield $As_2F_5^+Sb_2F_{11}^-$. In addition, in the presence of a large excess of another weakly basic species, salts such as $AsF_2CO^+Sb_2F_{11}^-$ might be produced.

Through our continuing studies of gas-phase basicities of inorganic main-group oxides, fluorides, and oxofluorides, we hope to develop further routes to novel gas-phase ionic species which can suggest synthetic pathways to new compounds which exhibit unusual bonding.

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Registry No. NF_3, 7783-54-2; AsF_3, 7784-35-2; PF_3, 7783-55-3; $HAsF_3^+$, 74203-18-2; $F_3NAsF_2^+$, 74203-19-3; AsF_5^+, 12446-59-2.

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Organometallic Gallium(I) Anions Prepared by a Reductive Elimination Reaction

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A series of ((trimethylsilyl)methyl)gallium(I) compounds, $M^IGa(CH_2SiMe_3)_2$ (M^I = Na, K) and $M^IGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (M^I = Li, Na), have been prepared and fully characterized by elemental analyses, cryoscopic molecular weight measurements in benzene solution, solubility properties, and infrared and ^1H and ^{13}C NMR spectral data. These novel compounds represent a new class of organometallic derivative, which incorporate low oxidation state, main-group, metallic anions. The preparative route to these organogallium(I) compounds involves an apparent reductive elimination reaction between $Ga(CH_2SiMe_3)_3$ with alkali-metal hydrides in benzene or dimethoxyethane. All available data including the high solubility in aliphatic and aromatic solvents, low melting points, and molecular weight measurements are consistent with the covalent molecular formulas $[KGa(CH_2SiMe_3)_2]_2$, $[NaGa(CH_2SiMe_3)_2]_3$, and $[LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe]_x$. Structures involving gallium–gallium bonds are proposed to account for observed molecular association and chemical properties.

Introduction

Organometallic compounds have been known for over 100 years. Much of the development of the chemistry of the transition-metal derivatives can be ascribed to the synthetic utility of redox reactions and metal carbonyl anions.[1] In contrast the chemistry of the organometallic derivatives of the main-group elements has focused on the properties and reactions of compounds with the metals in their highest oxidation states.[2] Consequently, the literature contains very few examples of well-defined, kinetically stable, low oxidation state organometallic compounds or of reactions in which the main-group metal in an organometallic derivative changes oxidation state. The compounds[3,4] $In(C_5H_5)$ and $Tl(C_5H_5)$ are the only examples of low oxidation state group 3 organometallic derivatives. Both of these compounds[5,6] exist in the solid state as linear polymers with the cyclopentadienyl ring exhibiting η^5 coordination. In group 4 chemistry, the unique low oxidation state compounds[7] $M^{IV}(CH(SiMe_3)_2)_2$ (M^{IV} = Ge, Sn, Pb) have been prepared and thoroughly characterized. An X-ray structural study[7] of the tin compound confirms a dimeric structure which has an apparent bent tin–tin double bond using the available electron pair and vacant orbital on each tin(II) atom.

The two potential routes to low oxidation state main-group organometallic compounds involve the alkylation of a low oxidation state halogen compound or the reduction of a high oxidation state organometallic derivative. The alkylation reaction has been applied to the syntheses of the $M^{IV}(CH(SiMe_3)_2)_2$ compounds from $M^{IV}Cl_2$ and the lithium alkyl.[7] In contrast the synthesis[3,8] of $In(C_5H_5)$ involves a reduction reaction since the starting material is $InCl_3$. The cyclopentadienide anion[8] is considered the reducing agent for $In(C_5H_5)_3$. Regrettably, both of these observed reactions are of limited use for the synthesis of other group 3 derivatives. The common low oxidation state halogen compounds incorporate the metal in both the low and high oxidation states,[9] for example, $Ga^+GaCl_4^-$.

The chemistry of the hydride derivatives of the heavier main-group metals suggests the potential occurrence of facile

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