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Trends in Gas-Phase Fluoride Ion Affinities of Main-Group Oxyfluorides and Fluoride Sulfides. Generation and Characterization of the Fluoride Adducts of FAsO, FPO, FPO_2, F_2SiO, F_4SO, FBO, F_2SiS, FPS, FAsS, F_2S_2, and S_2O by Ion Cyclotron Resonance Addition–Elimination Reactions

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Received May 5, 1987

Methods are described for the generation of a number of novel oxyfluoride and fluoride sulfide anions of main-group elements by gas-phase ion–molecule reaction sequences. The energetics of transfer of fluoride from these anions to a variety of Lewis acids have been investigated by using ion cyclotron resonance techniques. The data obtained are used to generalize periodic trends in fluoride ion binding energies of main-group oxides, fluorides, and oxyfluorides. The data reveal a pronounced tendency for tetrahedral and octahedral anions to exhibit a high degree of stability.

Introduction

The fluoride affinity (FA) of any acid species, A, may be defined as the enthalpy associated with the bond in AF^- adducts (eq 1). The first demonstration that exothermic fluoride transfer

$$AF^- \rightarrow A + F^- \qquad (1)$$

$$FA(A) = \Delta H^\circ_1 \qquad (2)$$

could be used to obtain relative Lewis acidities of main-group compounds toward F^- was made by Haartz and McDaniel,[1] who used ion cyclotron resonance (ICR) observations of fluoride transfer reactions (eq 3) to establish an order of fluoride affinities

$$A_1F^- + A_2 \rightarrow A_2F^- + A_1 \qquad (3)$$

of several Lewis and Brønsted acids. Subsequently similar ICR experiments involving compounds of boron,[2] silicon,[3] phosphorus,[4] and carbon[5] were carried out, which extended the range and expanded the scope of the qualitative relative fluoride ion binding energy scale. Attempts to determine accurate absolute fluoride ion affinities were made on the basis of lattice energy calculations,[6] appearance energies,[7] electron affinities and bond energies,[4,5] and extrapolation of values from hydrogen-bonded fluoride adducts. Due to inherent inaccuracies in each of the above methods, a semiquantitative scale of fluoride affinities for a few compounds was established with accuracies of 5–10 kcal mol^{-1}.

Although a few equilibrium measurements of fluoride ion exchange had been reported in these early gas-phase studies it was not until the recent exhaustive study of F^- and Cl^- transfer equilibria was carried out by Larson and McMahon[8-11] that a qualitative scale of F^- binding energies was established. The relative fluoride affinity scale obtained from the multiple overlap fluoride exchange equilibria measurements was converted to an absolute scale on the basis of two fluoride affinities that were felt to be well established. The first of these is the value of the binding energy of F^- to H_2O, which had been determined by high-pressure mass spectrometric clustering equilibrium measurements (eq 4).[12]

$$F^- + H_2O \rightleftarrows F^-(H_2O) \qquad (4)$$

This equilibrium was studied as a function of temperature thus allowing both ΔH°_4 and ΔS°_4 to be calculated. The F^-–H_2O binding energy of 23.3 kcal mol^{-1} was then used as an absolute anchor for the low end of the fluoride affinity scale. The second absolute fluoride affinity is taken from the known gas-phase acidity of acetyl fluoride, ΔH°_5,[13] which allows calculation of the fluoride affinity of ketene as 35.3 kcal mol^{-1} (eq 5). The equilibrium

$$CH_3COF \rightarrow CH_2COF^- + H^+ \qquad (5)$$

experiments very accurately reproduce the difference in the fluoride affinities of ketene and H_2O, lending confidence to the absolute assignments and the accuracy of the relative fluoride affinity measurements. In this way a scale of fluoride binding energies ranging from 20 to 55 kcal mol^{-1} has been established, which includes most commonly available main group oxides, fluorides and oxyfluorides.[10]

No gas-phase ion molecule experiments have been carried out for aluminum fluoride or other metal fluorides; however, they have been studied in a high-temperature Knudsen cell.[14-19] Thermodynamic calculations from the results of these experiments have led to values of fluoride affinity for seven metal fluorides including BeF_2 and AlF_3. Lattice energy calculations[10,20] are also a source of fluoride affinities although there continues to be a large uncertainty associated with assignment of partial charges to polyatomic ions.

In the present manuscript results are presented in which novel ions are generated by the isoelectronic replacement of F in a main-group polyfluoride by O^- or S^- via the reaction of either *tert*-butoxide (eq 6) or RS^- (eq 7) with the polyfluorides.[4,5,21] In

$$t\text{-}C_4H_9O^- + MF_n \rightarrow MF_{n-1}O^- + t\text{-}C_4H_9F \qquad (6)$$

$$RS^- + MF_n \rightarrow MF_{n-1}S^- + RF \quad R = H, CH_3 \qquad (7)$$

this way fluoride ion adducts of novel neutral molecules that are either commercially unavailable or, in several cases, previously

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unknown can be prepared. From observations of exothermic fluoride transfer from these novel anions to species of known fluoride affinity the fluoride affinities of these novel neutral molecules can usually be fairly accurately bracketed. In this way data have been obtained for the fluoride affinities of FBO, FAsO, FPO, FPO_2, F_2SiO, F_4SO, FPS, F_2S_2, FAsS, F_2SiS, and S_2O. In addition, use of a sample of F_4SO allowed determination of the equilibrium constant for fluoride exchange between F_4SO and SiF_4 to quantitatively determine the fluoride affinity of F_4SO.

These new values of fluoride affinity provide key data for interpretation of periodic trends in fluoride affinity of several main-group oxides, fluorides, oxyfluorides and fluoride sulfides.

Experimental Section

All experiments were carried out at ambient temperature with an ion cyclotron resonance spectrometer of basic Varian V5900 design extensively modified to permit operation in both drift and trapped-ion modes.[22] Details of the design and operation of trapped-ion ICR and conventional single- and double-resonance techniques have been described in detail elsewhere.[23,24]

All materials, except F_4SO, were commercial samples of highest purity available and were used without further purification. The sample of F_4SO was kindly provided by Professor J. Passmore of the University of New Brunswick.

Prior to use of reactive fluorides all sample vessels and inlet lines of the ICR vacuum system were conditioned with SF_4 to passivate the surfaces. Prior to use each sample was degassed by several freeze-pump-thaw cycles.

Negative ion reagents were generated by dissociative electron attachment and negative ion molecule reaction. Dissociative attachment to *tert*-butyl nitrite afforded excellent intensities of $t\text{-}C_4H_9O^-$ (eq 8).[25]

$$t\text{-}C_4H_9ONO \xrightarrow{e^-} t\text{-}C_4H_9O^- + NO \qquad (8)$$

In the absence of any other reactive material $t\text{-}C_4H_9O^-$ reacts with the parent nitrite to yield NO_2^- (eq 9). The very high cross section for

$$t\text{-}C_4H_9O^- + t\text{-}C_4H_9ONO \rightarrow NO_2^- + (t\text{-}C_4H_9)_2O \qquad (9)$$

production of $t\text{-}C_4H_9O^-$ from $t\text{-}C_4H_9ONO$ however allowed the nitrite pressure to be maintained very much below that of the fluoride neutral reactant, thus minimizing the occurrence of (9).

The sulfide anions were generated by proton abstraction from either H_2S or CH_3SH by F^- generated by dissociative electron attachment to NF_3 (eq 10 and 11).

$$NF_3 \xrightarrow{e^-} F^- + NF_2 \qquad (10)$$

$$F^- + RSH \rightarrow RS^- + HF \quad R = H, CH_3 \qquad (11)$$

Reaction of the alkoxide or sulfide ions with a main-group fluoride yielded the new oxyfluoride or fluoride sulfide anion of interest (eq 6 and 7). Subsequent fluoride-transfer reactions of these new anions with species of known fluoride affinity allow a limit to be placed on the fluoride affinity of the corresponding neutral since all ion molecule reactions observed must be exothermic or at least nearly thermoneutral. Occurrence of all reactions was verified by ICR double-resonance techniques.

Exothermic ion-molecule reactions in the gas phase normally proceed without any activation energy in the entrance channel. All of the exothermic reactions examined here proceed at or near the ion-molecule collision rate ($k = 10^{-10}$ cm^3 molecule^{-1} s^{-1}), indicating that the fluoride-transfer reactions involved in the present paper also proceed with no activation barriers.

Results

A. Oxyanions. 1. Boron Oxyfluoride (FBO). Variation of negative ion abundances as a function of trapping time for a mixture of BF_3 and $t\text{-}C_4H_9ONO$ is shown in Figure 1. The reaction sequence (eq 12-13) indicates that the fluoride affinity

$$t\text{-}C_4H_9O^- + BF_3 \rightarrow F_2BO^- + t\text{-}C_4H_9F \qquad (12)$$

$$F_2BO^- + BF_3 \rightarrow BF_4^- + FBO \qquad (13)$$

of FBO is less than that of BF_3. In order to further refine the limits of the fluoride affinity of FBO, BF_3 was mixed with other fluoride acceptors that were unreactive with $t\text{-}C_4H_9O^-$. This mixture was then admitted to the system where $t\text{-}C_4H_9ONO$ was present, and subsequent fluoride transfer from F_2BO^- to the new species was examined. In a 10:1 SO_2:BF_3 mixture no FSO_2^- was observed, implying that (14) is endothermic and that therefore

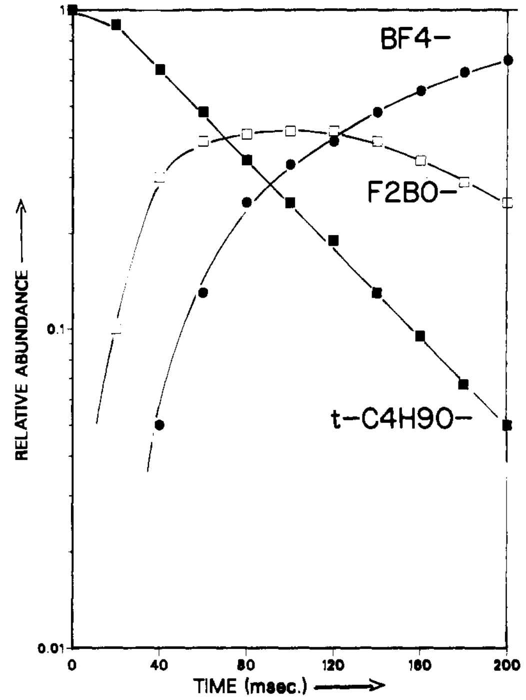

Figure 1. Variation of relative anionic abundances with time in a 1:1 mixture of $t\text{-}C_4H_9ONO$:BF_3 at a total pressure of 8×10^{-7} Torr following a 10-ms, 70-eV electron beam pulse.

$$F_2BO^- + SO_2 \rightarrow FSO_2^- + FBO \qquad (14)$$

the fluoride affinity of FBO is greater than that of SO_2. A similar experiment with triethylborane led to slow production of small amounts of $FB(C_2H_5)_3^-$ (eq 15), indicating an exothermic or nearly

$$F_2BO^- + B(C_2H_5)_3 \rightarrow FB(C_2H_5)_3^- + FBO \qquad (15)$$

thermoneutral reaction. The fluoride affinity of FBO may thus be bracketed as being between those of SO_2 and $B(C_2H_5)_3$ and is 48 ± 3 kcal mol^{-1}. Taking the Knudsen cell determination[26] of $\Delta H_f°$(FBO) of −144 ± 3 kcal mol^{-1}, a value of $\Delta H_f°(F_2BO^-)$ of −252 ± 6 kcal mol^{-1} may be calculated.

Several theoretical calculations have led to predictions of the heat of formation,[27] bond distances,[28] and ionization potential of FBO;[29] however, the only other quantity ever *experimentally* determined for this species is an infrared absorption band at 1900 cm^{-1} observed in high-temperature mixtures of BF_3 and O_2.[30]

2. Silicon Oxyfluoride (F_2SiO). The trifluorosilicate anion, F_3SiO^-, formed in (16), does not transfer F^- to SiF_4 (eq 17).

$$t\text{-}C_4H_9O^- + SiF_4 \rightarrow F_3SiO^- + t\text{-}C_4H_9F \qquad (16)$$

$$F_3SiO^- + SiF_4 \rightarrow SiF_5^- + F_2SiO \qquad (17)$$

$$F_3SiO^- + PF_5 \rightarrow PF_6^- + F_2SiO \qquad (18)$$

Further no fluoride transfer is observed from F_3SiO^- to PF_5, the compound that previously had been found to have the highest

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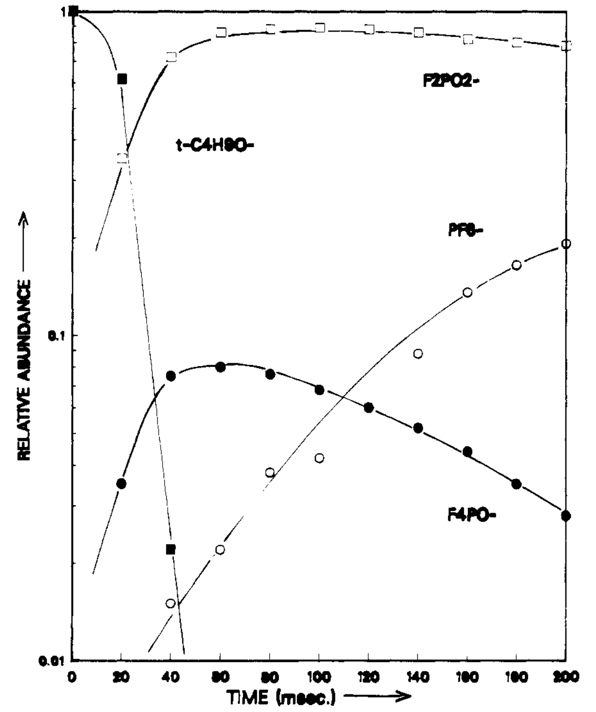

Figure 2. Variation of relative anionic abundances with time in a 5:3:2 mixture of $t\text{-}C_4H_9ONO{:}PF_5{:}OPF_3$ at a total pressure of 2×10^{-6} Torr following a 10-ms, 70-eV electron beam pulse.

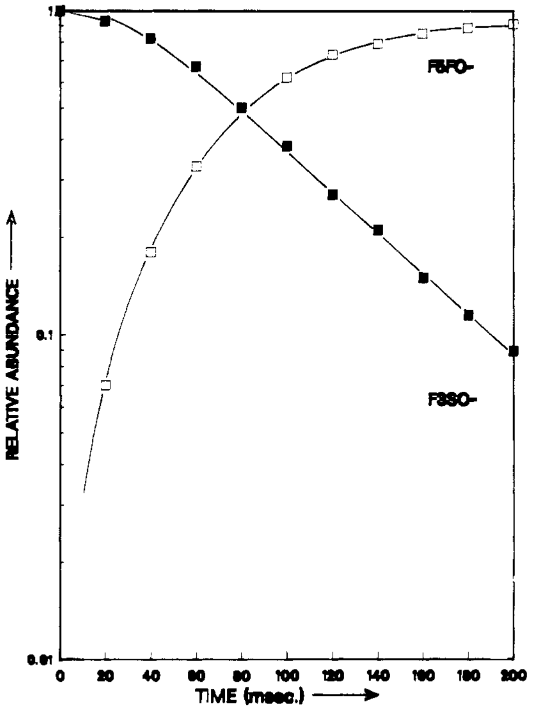

Figure 3. Variation of relative anionic abundances with time in OSF_4 at a pressure of 7×10^{-7} Torr following a 5-ms, 70-eV electron beam pulse.

fluoride affinity of any main-group species available to us. This establishes a probable fluoride affinity of F_2SiO in excess of 85 kcal mol^{-1}. On the basis of periodic trends discussed below, it is expected that the fluoride affinity of F_2SiO will be less than that of AlF_3 (120 kcal mol^{-1}),[14,18] allowing an estimate of 102 ± 17 kcal mol^{-1} to be made for the fluoride affinity of F_2SiO. An estimate of −231 ± 6 kcal mol^{-1} has been made for $\Delta H_f°(F_2SiO)$ based on comparisons of thermochemical data for SiF_4 and SiO_2.[31] This and the present fluoride affinity lead to a calculated value of −393 ± 23 kcal mol^{-1} for $\Delta H_f°(F_3SiO^-)$.

3. Phosphorus Dioxyfluoride (FPO_2). Reaction of $t\text{-}C_4H_9O^-$ with phosphoryl fluoride readily leads to the difluorophosphate anion (eq 19).[4] When a mixture of OPF_3 and PF_5 is introduced,

$$t\text{-}C_4H_9O^- + F_3PO \rightarrow F_2PO_2^- + t\text{-}C_4H_9F \qquad (19)$$

the variation of ion intensities as a function of time shown in Figure 2 results. The F_4PO^- produced in (20) readily transfers F^- to PF_5

$$t\text{-}C_4H_9O^- + PF_5 \rightarrow F_4PO^- + t\text{-}C_4H_9F \qquad (20)$$

$$F_4PO^- + PF_5 \rightarrow PF_6^- + F_3PO \qquad (21)$$

to yield PF_6^- (eq 21). This transfer can be seen from the decay in intensity of F_4PO^- in Figure 2 and also from double-resonance experiments. No evidence of F^- transfer from $F_2PO_2^-$ to PF_5 is seen. This FPO_2 molecule, which is isoelectronic with AlF_3, F_2SiO, and SO_3, may be estimated from periodic trends described below to have a fluoride affinity between those of SO_3 and F_2SiO, roughly 90 ± 15 kcal mol^{-1}.

Although FPO_2 is not a known neutral molecule, the anion, $F_2PO_2^-$, is well-known as a stable species.[32] This is undoubtedly the result of the large stabilization of the anion by F^- addition to FPO_2 as evidenced by the higher fluoride affinity.

4. Phosphorus Oxyfluoride (FPO). The difluorophosphite anion produced in (22)[4] does not subsequently transfer F^- to the parent

$$t\text{-}C_4H_9O^- + PF_3 \rightarrow F_2PO^- + t\text{-}C_4H_9F \qquad (22)$$

PF_3 or to SO_2 or $B(C_2H_5)_3$. It does however transfer F^- to SiF_4 (eq 23), allowing the fluoride affinity of FPO to be bracketed

$$F_2PO^- + SiF_4 \rightarrow SiF_5 + FPO \qquad (23)$$

between those of $B(C_2H_5)_3$ and SiF_4 at 56 ± 4 kcal mol^{-1}.

Neither the FPO molecule nor the F_2PO^- anion have been previously known as synthetically accessible species. The appreciable fluoride affinity of FPO would indicate that this F_2PO^- is significantly stabilized and would prove to be a good synthetic target.

5. Arsenic Oxyfluoride (FAsO). The difluoroarsenite anion is produced by (24). Subsequent fluoride transfer to AsF_3 is not

$$t\text{-}C_4H_9O^- + AsF_3 \rightarrow F_2AsO^- + t\text{-}C_4H_9F \qquad (24)$$

observed; however, F^- transfer to SiF_4 (eq 25) is seen. These

$$F_2AsO^- + SiF_4 \rightarrow F_5Si^- + FAsO \qquad (25)$$

observations allow determination of the fluoride affinity of FAsO as 54 ± 6 kcal mol^{-1}.

The only previous literature evidence for FAsO or F_2AsO^- is a solubility study of As_2O_3 in $HF\text{–}H_2O$ mixtures that suggests compound formation corresponding to either FAsO or F_2AsOH.[33]

6. Thionyl Tetrafluoride (F_4SO). The availability of a sample of F_4SO allowed completion of our earlier work, which had established quantitative fluoride affinities of all other known stable oxides, fluorides, and oxyfluorides of sulfur. Thionyl tetrafluoride has a large dissociative attachment cross section leading to good abundances of F_3SO^- under electron impact (eq 26). As shown

$$F_4SO \xrightarrow{e^-} F_3SO^- + F \qquad (26)$$

in Figure 3 the F_3SO^- anion efficiently transfers F^- to F_4SO to yield the octahedral F_5SO^- anion (eq 27). No F^- transfer from

$$F_3SO^- + F_4SO \rightarrow F_5SO^- + F_2SO \qquad (27)$$

F_5SO^- in mixtures with AsF_3 was observed; however, in the presence of SiF_4, equilibrium fluoride exchange was observed (eq 28) with an equilibrium constant, K_{28}, of 40 ± 5 obtained. This

$$F_5SO^- + SiF_4 \rightleftarrows F_5Si^- + F_4SO \qquad (28)$$

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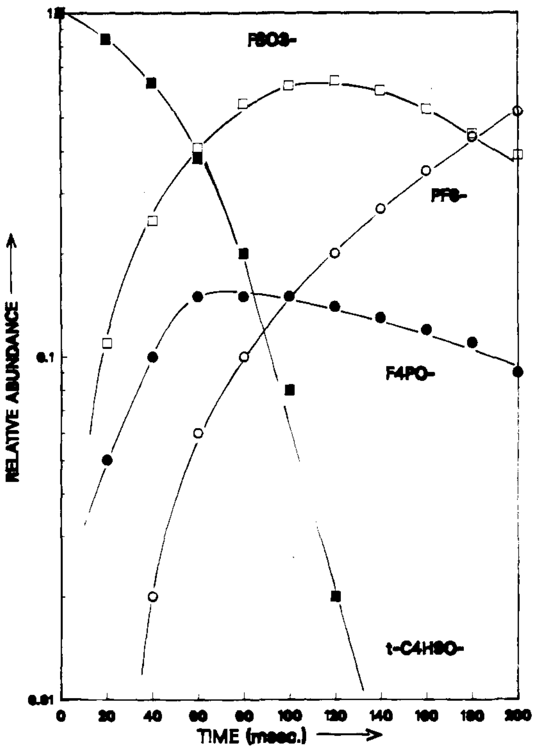


Figure 4. Variation of relative anion abundances with time in a 2:1:1 mixture of $t\text{-}C_4H_9ONO{:}PF_5{:}SO_2F_2$ at a total pressure of 2×10^{-6} Torr following a 10-ms, 70-eV electron beam pulse.

result establishes the fluoride affinity of F_4SO as 1.5 kcal mol^{-1} less than that of SiF_4 or 58 ± 2 kcal mol^{-1}.

7. Other Reactions of $t\text{-}C_4H_9O^-$. Several fluoride adducts that had previously been examined by F^- addition to stable neutral molecules were also prepared by reaction of *tert*-butoxide with an appropriate fluoride. These reactions (eq 29–33) resulted in

$$t\text{-}C_4H_9O^- + SF_4 \rightarrow F_3SO^- + t\text{-}C_4H_9F \quad (29)$$

$$t\text{-}C_4H_9O^- + F_2CO \rightarrow FCO_2^- + t\text{-}C_4H_9F \quad (30)$$

$$t\text{-}C_4H_9O^- + F_2SO \rightarrow FSO_2^- + t\text{-}C_4H_9F \quad (31)$$

$$t\text{-}C_4H_9O^- + SO_2F_2 \rightarrow FSO_3^- + t\text{-}C_4H_9F \quad (32)$$

$$t\text{-}C_4H_9O^- + PF_5 \rightarrow OPF_4^- + t\text{-}C_4H_9F \quad (33)$$

adducts that all transferred F^- consistent with the fluoride affinities previously deduced for the parent neutral molecules.[9] A typical example is shown in Figure 4, in which FSO_3^- formed via (32) and F_4PO^- formed via (33) each subsequently transfer F^- to PF_5, confirming the greater fluoride affinity of PF_5 relative to those of both OPF_3 and SO_3.

Attempts to produce F_2NO^- from NF_3 (eq 34) were unsuccessful presumably due to the absence of a suitable orbital on NF_3 for attack by the alkoxide. Reaction of *tert*-butoxide with oxalyl fluoride resulted in a fluoroglyoxalate anion (eq 35). However no subsequent fluoride-transfer reactions of this species were observed to produce either a C_2O_3 neutral species or a CO_2, CO pair.

$$t\text{-}C_4H_9O^- + NF_3 \rightarrow F_2NO^- + t\text{-}C_4H_9F \quad (34)$$

$$t\text{-}C_4H_9O^- + FCOCOF \rightarrow FCOCO_2^- + t\text{-}C_4H_9F \quad (35)$$

Attempts to generate F_2COCN^- by reaction of $t\text{-}C_4H_9O^-$ with CF_3CN (eq 36) were unsuccessful. However CN^- was produced, which could have resulted either from a direct nucleophilic displacement reaction to yield $t\text{-}C_4H_9OCF_3$ and CN^- or alternatively from decomposition of $NCCF_2O^-$ initially formed in (36) to F_2CO and CN^-. The cyanodifluoromethoxide anion has also been generated in separate studies of cyanide binding to Lewis acids,[34] which resulted in a binding energy of CN^- to CF_2O of 22 kcal mol^{-1}. Combining these data with available thermochemical data for CN^- and CF_3CN and group equivalent estimates of $\Delta H_f°(t\text{-}C_4H_9F)$ allows calculation of the enthalpy change of (36) of −41 kcal mol^{-1}. Thus the $NCCF_2O^-$ may have initially been produced with sufficient excitation to unimolecularly lose CN^-. Direct nucleophilic displacement is also estimated to be exothermic however.

$$t\text{-}C_4H_9O^- + CF_3CN \rightarrow NCCF_2O^- + t\text{-}C_4H_9F \quad (36)$$

The large dissociative attachment cross section of most main-group chlorides and bromides generally precludes observation of similar reactions for these other halogen species. In the case of $SiCl_4$, however, (37) was observed, resulting in the Cl_3SiO^- anion, which did not subsequently transfer Cl^- to $SiCl_4$.

$$t\text{-}C_4H_9O^- + SiCl_4 \rightarrow Cl_3SiO^- + t\text{-}C_4H_9Cl \quad (37)$$

B. Thio Anions. 1. Silicon Fluoride Sulfide (F_2SiS). Silicon tetrafluoride reacts with both HS^- and CH_3S^- to yield the trifluorothiosilicate anion, F_3SiS^- (eq 38). Fluoride transfer from this anion is not observed to either SiF_4 or BF_3 establishing the fluoride affinity of F_2SiS as greater than that of BF_3, 72 kcal mol^{-1}.

$$RS^- + SiF_4 \rightarrow F_3SiS^- + RF \quad (38)$$

2. Phosphorus Fluoride Sulfide (FPS). The difluorothiophosphinite anion, F_2PS^-, is generated from sulfide ions by (39).

$$RS^- + PF_3 \rightarrow F_2PS^- + RF \quad (39)$$

Fluoride transfer is not observed from F_2PS^- to either PF_3 or SO_2, but fluoride is observed to somewhat endothermically transfer to SiF_4 (eq 40). In addition transfer to BF_3 is found to be exothermic (eq 41). These results suggest limits for the fluoride affinity of FPS of 62 ± 5 kcal mol^{-1}.

$$F_2PS^- + SiF_4 \rightarrow SiF_5^- + FPS \quad (40)$$

$$F_2PS^- + BF_3 \rightarrow BF_4^- + FPS \quad (41)$$

3. Arsenic Fluoride Sufide (FAsS). The difluorothioarsenite ion, F_2AsS^-, is generated by (42) by reaction of either HS^- or CH_3S^- with AsF_3. Subsequent fluoride transfer is not observed to AsF_3 but is observed to SiF_4 (eq 43), which brackets the fluoride affinity of FAsS as 56 ± 6 kcal mol^{-1}.

$$RS^- + AsF_3 \rightarrow F_2AsS^- + RF \quad (42)$$

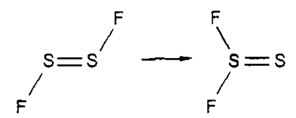
$$F_2AsS^- + SiF_4 \rightarrow SiF_5^- + FAsS \quad (43)$$

4. Thiothionyl Fluoride (F_2SS). The F_3SS^- anion is generated exothermically in (44) by both HS^- and CH_3S^-. Fluoride transfer is not observed from F_3SS^- to either CO_2 or H_2S but is observed to both F_2SO (eq 45) and SF_4. This establishes the fluoride affinity of F_2SS as less than that of F_2SO (37 kcal mol^{-1}) but greater than that of H_2S (35 kcal mol^{-1}), with a value of 36 ± 3 kcal mol^{-1}.

$$RS^- + SF_4 \rightarrow F_3SS^- + RF \quad (44)$$

$$F_3SS^- + F_2SO \rightarrow F_3SO^- + F_2SS \quad (45)$$

The S_2F_2 molecule is known to have two stable forms.[35] Difluorodisulfane, FSSF, slowly isomerizes to thiothionyl fluoride in the presence of alkali metals (eq 46). The more stable $F_2S{=}S$ is then almost certainly the species generated by (45).



(46)

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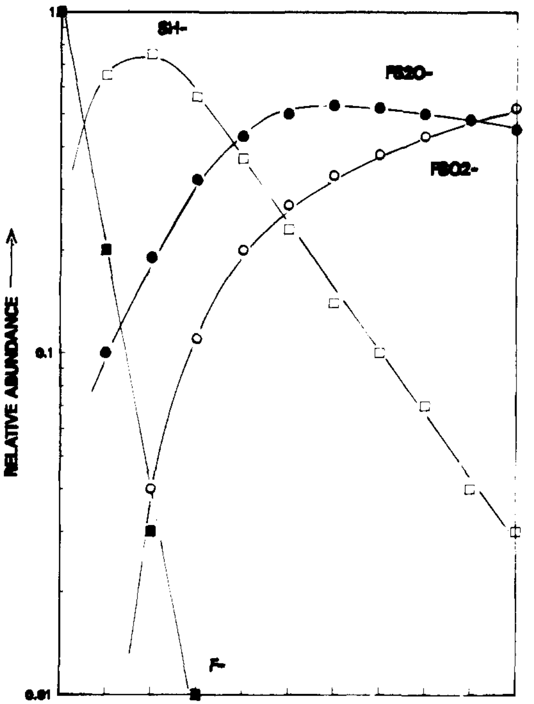


Figure 5. Variation of relative anion abundances with time in a 2.4:8.2:6.4:1.0 mixture of H_2S:NF_3:OSF_2:SO_2 at a total pressure of 1.8 × 10^{-6} Torr following a 10-ms, 70-eV electron beam pulse.

5. Disulfur Monoxide (S_2O). The FS_2O^- anion is generated by reaction of RS^- with F_2SO (eq 47).

$$RS^- + F_2SO \rightarrow FS_2O^- + RF \qquad (47)$$

Subsequent fluoride transfer is not observed to carbonyl fluoride but is observed to SO_2 (eq 48), as shown in Figure 5 suggesting

$$FS_2O^- + SO_2 \rightarrow FSO_2^- + S_2O \qquad (48)$$

limits of 44 ± 3 kcal mol^{-1} for the fluoride affinity of S_2O. The known $\Delta H_f°(S_2O)$[31] of −5 kcal mol^{-1} allows calculation of $\Delta H_f°(FS_2O^-)$ of −109 ± 5 kcal mol^{-1}.

Discussion

A summary of periodic trends in fluoride affinities of some first- and second-row oxides, fluorides and oxyfluorides is shown in Table I. It should be noted that in several cases there is as much as 20 kcal mol^{-1} difference between the values reported here and those obtained from lattice energy calculations.

The most interesting relationship immediately apparent is that of decreasing fluoride affinity in moving from left to right across the periodic table for an isoelectronic series. This trend also corresponds to a decrease in fluoride affinity with an increase in the electronegativity of the central atom to which the fluoride binds. Thus, as the electronegativity of the central atom increases in going from BeF_2 to the isoelectronic CO_2 or from SiF_4 to SO_2F_2, the fluoride affinity drops. Table I includes 13 possible pairs in which experimental data may be directly compared. All follow the simple rule that the more electropositive the central atom, the higher the fluoride affinity. On average the drop in fluoride affinity may be taken as 30 kcal mol^{-1} per atomic number for the first-row elements and about 15 kcal mol^{-1} for compounds with second-row elements as the central atom.

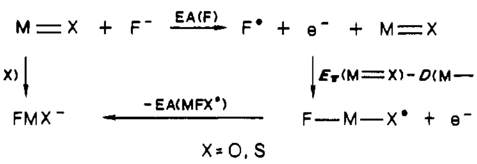
In moving down a group of the periodic table an increase in fluoride affinity is seen as the higher atomic weight central atom becomes more electropositive. Thus for example the fluoride affinity of AlF_3 is greater than that of BF_3, that of F_2SiO is greater than that of F_2CO, that of AsF_3 is greater than that of PF_3, and that of FPO_2 is greater than that of FNO_2. The magnitude of the increase is quite variable, however, with FPO and FAsO differing by only a few kilocalories per mole while BF_3 and AlF_3 differ by 50 kcal mol^{-1}.

Table I. Fluoride Affinities of First- and Second-Row Oxides, Fluorides, and Oxyfluorides[a]

group[b]					
II (2)	III (13)	IV (14)	V (15)	VI (16)	VII (17)
BeF_2	FBO	CO_2			
90[c]	50[d]	32[f]			
	BF_3	F_2CO	FNO_2		
	72[f]	93[f]	(8)[g]		
	AlF_3	F_2SiO	FPO_2	SO_3	
	120[c]	105[e]	90[e]	78[f]	
		F_2Si	FPO_6	SO_2	
		(67)[h]	56[d]	44[f]	
		SiF_4	F_3PO	F_2SO_2	$FClO_3$
		60[f]	48[f]	36[f]	(24)[g]
			PF_3	F_2SO	$FClO_2$
			40[f]	37[f]	(33)[g]
			PF_5	F_4SO	F_3ClO_2
			85[f]	58[e]	(31)[g]
				SF_4	F_3ClO
				44[f]	(30)[g]

[a] All values expressed in kcal mol^{-1} for $\Delta H°_1$. [b] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.) [c] References 14 and 18. [d] This work. Uncertainty is believed to be ±10 kcal mol^{-1}. [e] This work. ±2 kcal mol^{-1}. [f] Reference 9. [g] Extrapolated from isoelectronic series values. [h] Extrapolated value. Literature values range from less than that of SiF_4 to over 10 kcal mol^{-1}. See ref 1.

Scheme I



A comparison of the oxyanions and their isoelectronic thio anion analogues reveals another interesting trend. For example the fluoride affinity of FPO is bracketed by exactly the same limits as that of FPS. Similarly the fluoride affinities of F_2S_2 and F_2SO are found to be very similar as are those of S_2O and SO_2 and FAsO and FAsS. Thus it would appear that substitution of a sulfur for oxygen at either a phosphorus or sulfur center has an extremely small effect on the fluoride affinity. If this is a general trend carrying through the second-row oxides and sulfides, then it may be possible to generalize by inferring that the fluoride affinity of F_2SiS is comparable to that of F_2SiO and if the trend continues into the first row the fluoride affinities of FBO and FBS may be comparable as may those of F_2CO and F_2CS. It will remain for further thermochemical data for these latter thio anions to become available to test the validity of this conjecture. The similarity of fluoride affinities of the oxy and thio compounds may be qualitatively rationalized with reference to the thermochemical cycle outlined in Scheme I and summarized in (49). In general the

$$FA(M{=}X) = D(M{-}F) - E_\pi(M{=}X) - EA(F) + EA(MFX) \qquad (49)$$

value of D(M–F) can be considered to be roughly comparable for both oxo and thio compounds; however, the π-bond energies E_π will in general be much greater for the oxo compounds than for the thio analogues. This term alone would have the effect of greatly reducing the fluoride affinity of the oxo relative to the thio compound. In compensation for this is the fact that the electron affinities of the oxo radicals must be correspondingly greater than those of the thio radicals. This can be rationalized on the basis of the much greater ability of the oxo anion to undergo back-donation into vacant orbitals on the central atom to form M═O bonds with anionic charge delocalized onto the central atom. The effects of π-bond energy and electron affinity thus effectively cancel each other, resulting in comparable fluoride affinities for the M=O and M=S species.

In our previous contributions on fluoride affinities of main-group compounds,[10] we had noted that there appears to be a special stability associated with either tetrahedral or octahedral compounds of sulfur. Thus the tetrahedral molecule F_2SO, which gives rise to a square-pyramidal anion on F^- addition (F_3SO^-), has a low fluoride affinity while SO_2, which gives rise to the tetrahedral anion FSO_2^-, has a higher fluoride affinity. The new measurement of the fluoride affinity of F_4SO in the present work completes the series of oxides, fluorides, and oxyfluorides of sulfur, establishing the order $SO_3 > F_4SO > SO_2 > OSF_2 > F_2SO_2$ where the strongest three fluoride acceptors give rise to tetrahedral or octahedral anions while the weaker two are tetrahedral neutrals. The other results of the present work further support this observation and allow its extension to other main-group elements. For example the fluoride affinities of the phosphorus compounds PF_5, OPF_3, and FPO_2 might be expected to be in decreasing order on the basis of simple substituent effects. However the experimental values of 85 ± 10, 48, and 90 ± 15 kcal mol^{-1} respectively indicate that this is far from the case. It is noteworthy then that the compounds which give rise to the octahedral and tetrahedral anions, PF_6^- and $F_2PO_2^-$, respectively, have high fluoride affinities whereas the tetrahedral molecule OPF_3 has a much lower fluoride affinity. Similarly the tetrahedral PF_3 has a low fluoride affinity of 40 kcal mol^{-1} while the compound FPO, giving rise to the tetrahedral F_2PO^- anion, has a much higher fluoride affinity of 56 ± 4 kcal mol^{-1}. Thus the fluoride affinities of the oxyfluorides and fluorides of phosphorus bear no relation to the number of oxygens and fluorines but rather depend on the geometries of the anions and neutrals involved. Comparison with the series of sulfur compounds also reveals that there is no apparent preference for octahedral over tetrahedral configurations.

The present and previous data suggest that it is appropriate to define a *configuration number* as the number of atoms (or groups) plus lone electron pairs about a central atom. Even configuration numbers of 2, 4, or 6 can then be associated with linear, tetrahedral, or octahedral geometries. For all of the compounds of B, C, N, Si, R, S, and As examined, higher fluoride affinities are associated with species giving rise to anions with even configuration numbers while lower fluoride affinities are associated with neutral molecules with even configuration numbers.

It is interesting to note that attempts to prepare salts of the odd configuration anion F_4PO^- by conventional chemical means give rise instead to salts of the products of the disproportionation reaction (eq 50).[36] The fluoride affinity data reported here show

$$2F_4PO^- \rightarrow PF_6^- + F_2PO_2^- \qquad (50)$$

that this disproportionation reaction is exothermic by 76 kcal mol^{-1}.

In the light of the above arguments the relatively low fluoride affinity of the FBO molecule, of configuration number 2, can be understood. Taking the experimental value of $\Delta H_f°(BO_2^-)$ of −178 kcal mol^{-1},[37] the enthalpy change for the boron disproportionation reaction (eq 51) can also be calculated to be −60 kcal mol^{-1}. This value contrasts sharply with the isoelectronic neutral odd to even configuration number disproportionation reaction (eq 52) with an enthalpy change of +12 kcal mol^{-1}.[38] This latter comparison would indicate that it is a special stability of linear, tetrahedral, or octahedral *anions* that gives rise to the fluoride affinity orders rather than any special stability associated with configurations of the neutral molecules. Apparently, in some way, the electron deficiency that characterizes good Lewis acids is associated with an even configuration number of the anionic adduct.

$$2F_2BO^-(g) \rightleftarrows BO_2^-(g) + BF_4^-(g) \qquad (51)$$

$$2F_2CO(g) \rightleftarrows CO_2(g) + CF_4(g) \qquad (52)$$

Several values listed in Table I are based on extrapolation of the present experimental values to isoelectronic species. For example the value of 8 kcal mol^{-1} obtained for fluoride affinity of FNO_2 is on the order of a weak electrostatic interaction, indicating no significant degree of covalent binding is to be expected in $F_2NO_2^-$. This is consistent with the known nonexistence of tetrahedral anions of nitrogen.

The fluoride adducts of $FClO_2$ and F_3ClO are known in salts, but due to experimental difficulties associated with handling these species, no experimental fluoride affinity measurements have been attempted here.

Conclusions

The new fluoride affinities described here provide key data for interpretation of periodic trends in Lewis acidities of oxides, fluorides and oxyfluorides of boron, carbon, nitrogen, silicon, phosphorus, sulfur, and arsenic toward fluoride ion. For isoelectronic series the strongest Lewis acids are invariably those of the most electropositive central atoms on the left in the periodic table. Furthermore, among compounds of a single element the strongest Lewis acids are those of odd configuration numbers with either trigonal or trigonal-bipyramidal arrangements of atoms (or groups) and electron pairs about a central atom. For thio and oxy compounds of second-row elements the fluoride affinities appear to be comparable. This is a consequence of the greater π-bond energy associated with the oxy compounds as well as the greater electron affinity of the corresponding fluoro radical obtained by addition of F$^\bullet$ to the compound.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada is greatly acknowledged.

Registry No. FBO, 23361-56-0; F_2SiO, 14041-22-6; FPO_2, 36986-65-9; F_4SO, 13709-54-1; FPO, 82867-95-6; FAsO, 13464-52-3; F_2SiS, 110661-62-6; FPS, 55753-39-4; FAsS, 110661-63-7; F_2SS, 16860-99-4; S_2O, 20901-21-7; BF_3, 7637-07-2; t-C_4H_9ONO, 540-80-7; $B(C_2H_5)_3$, 97-94-9; $FB(C_2H_5)_3^-$, 63599-31-5; SO_2, 7446-09-5; SiF_4, 7783-61-1; F_3SiO^-, 69318-81-6; F_3PO, 13478-20-1; $F_2PO_2^-$, 20410-46-2; F_4PO, 36580-97-9; PF_3, 7783-55-3; F_2PO^-, 95357-81-6; AsF_3, 7784-35-2; F_2AsO^-, 110661-64-8; F_3SO^-, 86527-07-3; F_5SO^-, 17023-34-6; SF_4, 7783-60-0; F_2CO, 353-50-4; FCO_2^-, 67228-77-7; F_2SO, 7783-42-8; FSO_2^-, 22539-11-3; SO_2F_2, 2699-79-8; FSO_3^-, 15181-47-2; PF_5, 7647-19-0; NF_3, 7783-54-2; FCOCOF, 359-40-0; $FCOCO_2^-$, 110682-31-0; CF_3CN, 353-85-5; CN^-, 57-12-5; $NCCF_2O^-$, 110661-65-9; $SiCl_4$, 10026-04-7; Cl_3SiO^-, 104119-18-8; HS^-, 15035-72-0; CH_3S^-, 17302-63-5; F_2AsS^-, 110661-66-0; F_3SS^-, 110661-67-1; F_2BO^-, 36477-99-3.

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