Fluoride Ion Affinity of Some Lewis Acids[1]

J. C. Haartz*[2] and Darl H. McDaniel

Contribution from the Department of Chemistry, The University of Cincinnati, Cincinnati, Ohio 45221. *Received April 30, 1973*

Abstract: The negative ion icr spectra of SO_2, HCl, HBr, BCl_3, BF_3, PF_5, SiF_4, AsF_5, SF_6, and combinations thereof were studied at various electron energies and pressures in an effort to obtain evidence for ion-molecule reactions yielding halide ion adducts. Only primary negative ions were observed with pure samples except for the previously reported SiF_5^-, BF_4^-, and AsF_6^- and the additional species $Si_2F_8^-$ and $B_2F_7^-$. Addition of SF_6 greatly enhanced halide adduct formation and was utilized in the reaction mixtures for all systems investigated. The relative order of fluoride ion affinity has been found to be: SF_4, $SF_5\cdot < SO_2$, HCl, $AsF_3 < SiF_4 < BF_3 < PF_5 < BCl_3 < AsF_5$. Fluoride ion affinities of these compounds and the enthalpies of formation of the corresponding fluoroanions have been estimated.

G. N. Lewis proposed that one of the operational criteria of an acid be that a stronger acid be able to displace a weaker acid from its acid–base complexes. Accordingly, reaction 1 should permit the order of

$$A' + B{:}A \longrightarrow B{:}A' + A \qquad (1)$$

acid strength of A and A′ to be assigned as A′ > A. The study of a sufficient number of such displacement reactions should allow an ordering of the strengths of acids in a given series toward a particular base.

Alternatively, and more quantitatively, the enthalpy change accompanying reaction 2 may be measured for a

$$A + B \longrightarrow B{:}A \qquad (2)$$

series of acids and a reference base. By the law of Hess, and the assumption that the displacement that occurs has a negative ΔH_{rxn}, the order of acidity toward the reference base may be taken as the order of exothermicity of reaction 2.

In practice reaction 1 or 2 most frequently has been chosen as a reaction occurring in solution, occasionally with an insoluble product or reactant or both; acidity orders have also been inferred from a variety of indirectly related properties such as solubilities or sublimation temperatures. Obviously, in such cases differences in solvational energies of products and reactants, or lattice energy effects, or both, may obscure intrinsic differences in acidity. To further complicate the picture, it is often assumed that the order of acid strength will be independent of the reference base. Within the last several decades it has been shown that the order of acid strengths is affected by the reference base chosen.[3]

The results of previous investigations of the relative acidities of some inorganic halides toward fluoride ion are summarized in Table I. These studies have utilized a variety of approaches and fluoride donors. It is obvious from the lack of agreement among these studies that there is a need for an acidity scale which is free of dependence on extraneous factors and which accurately reflects the inherent acidity of these compounds. The gas phase ion affinity (IA), defined as the negative enthalpy change for the reaction

$$A_{(g)} + X^-_{(g)} \longrightarrow AX^-_{(g)} \qquad (3)$$

should provide such a scale. We wish to report the determination by ion cyclotron resonance (icr) spectroscopy of the fluoride ion affinities of a series of Lewis acids.

Experimental Section

The compounds used were commercially available and all were degassed by several freeze–pump–thaw cycles at 77°K. In the case of gases, purification by preliminary distillations in a vacuum line was utilized when positive ion spectra of the compounds indicated impurities.

The icr spectrometer[4] used in this investigation was the ICR-9 manufactured by Varian.[5] Spectra were obtained under steady-state pressure conditions resulting from a constant leak of the compounds into the cell while pumping. Pressures in the cell were determined from the Vac-ion pump current which was accurate to approximately an order of magnitude and was shown to be linear with pressure. A check of these measured pressures using a Granville-Phillips ionization gauge indicated that the measured pressures were low by a factor of 2 but were self-consistent. Thus, pressure changes could be determined more accurately than absolute pressure. Mixtures of compounds were used by utilizing the dual inlet system of the instrument or were prepared with a desired mole per cent composition utilizing a vacuum line.

In the icr spectrometer, single resonance spectra are simply mass spectra of the ions present. Detection of these ions is based on the absorption of energy from an oscillating electric field by an ion in resonance. To detect the absorption, modulation of the ion density is effected by modulating one of several parameters (source region drift voltage, magnetic field, the frequency of the marginal oscillator, the trapping potential, electron energy) which affects the absorption of power from the marginal oscillator. For this study, single resonance spectra were recorded using electron energy modulation (eem)[4c,d] and magnetic field sweep with the marginal oscillator frequency fixed at values in the range 90–153.5 kHz. All icdr spectra were recorded using constant magnetic field and observing oscillator frequency. The irradiating frequency was swept and maintained at the minimum amplitude needed to detect reactions. The electron energy used was the minimum required for observation of negative ion species (usually less than 10 eV).

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* Address correspondence to this author at: Aerospace Research Laboratories (LJ), Wright-Patterson Air Force Base, Ohio 45433.

[1] Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., 1972.

[2] Abstracted from the Ph.D. Dissertation of J. C. H., University of Cincinnati, 1972.

[3] For examples of steric effects of the reference base, see H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," Vol. 1, F. C. Nachod and E. A. Braude, Ed., Academic Press, New York, N. Y., 1955, Chapter 14; for electrical effects see R. G. Pearson in "Survey of Progress in Chemistry," Vol. 5, A. F. Scott, Ed., Academic Press, New York, N. Y., 1969.

[4] For a detailed description of instrumentation and techniques see (a) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); (b) G. C. Goode, R. M. O'Malley, A. J. Ferrer-Correia, and K. R. Jennings, *Chem. Brit.*, 7, 12 (1971); (c) J. M. S. Henis and W. Frasure, *Rev. Sci. Instrum.*, **39**, 1772 (1968); (d) R. T. McIver, Jr., *Rev. Sci. Instrum.*, 41, 126 (1970).

[5] Varian Associates, Palo Alto, Calif.

Table I. Lewis Acidity Orders from Previous Studies

Order	Fluoride donor	Ref	Method
$BF_3 > TaF_5 > NbF_5 > TiF_4 > PF_5 > SbF_3 > WF_6 \gg SiF_4 \sim CrF_3$	HF + xylene	*a*	Solvent extraction of $ArH^+MF_{n+1}^-$
$AsF_5 \sim BF_3{}^g > PF_5 \sim WF_6 > NbF_5 \sim TaF_5 > SiF_4 \sim SbF_3 \sim CrF_3$	MF and/or HF	*b*	Solubility of MF or Lewis acid
$SbF_5 > AsF_5 > BF_3 > PF_5$	CF_3SF_3	*c*	Decomposition pressure
$AsF_5 > PF_5 > BF_3$	MF_{x+1}^- in CH_2Cl_2	*d*	Displacement reaction
$SbF_5 > AsF_5 \gg PF_5 \sim BF_3$	HF	*e*	Cryoscopy, conductivity
$AsF_3 > BF_3 > SiF_4 > AsF_5 > PF_5 > PF_3$	SF_6^-	*f*	Rate of F^- transfer

[a] D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, **73**, 2013 (1951); D. A. McCaulay, W. S. Higley, and A. P. Lien, *ibid.*, **78**, 3009 (1956). [b] Reference 29a. [c] Reference 30. [d] Reference 27. [e] Reference 28. [f] Reference 9. [g] The BF_3, PF_5 order is reversed in a later solvolysis study using different methods, ref 29b.

Table II. Double Resonance Results

Reaction	dk/dE_{ion}
1. $SF_5^- + SO_2 \rightarrow SO_2F^- + SF_4$	–
2. $SF_5^- + BF_3 \rightarrow BF_4^- + SF_4$	–
3. $SF_5^- + HCl \rightarrow HClF^- + SF_4$	–
4. $SF_5^- + HBr \rightarrow HBrF^- + SF_4$	–
5. $SF_5^- + PF_5 \rightarrow PF_6^- + SF_4$	–
6. $SF_6^- + SO_2 \rightarrow SO_2F^- + SF_5$	–
7. $SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$	–
8. $SF_6^- + BF_3 \rightarrow BF_4^- + SF_5$	–
9. $SF_6^- + HCl \rightarrow HClF^- + SF_5$	–
10. $SF_6^- + HBr \rightarrow HBrF^- + SF_5$	–
11. $SF_6^- + BCl_3 \rightarrow BCl_3F^- + SF_5$	–
12. $SF_6^- + AsF_5 \rightarrow AsF_6^- + SF_5$	–
13. $SF_6^- + PF_5 \rightarrow PF_6^- + SF_5$	*a*
14. $SF_6^- + AsF_3 \rightarrow AsF_4^- + SF_5$	–
15. $HClF^- + SiF_4 \rightarrow SiF_5^- + HCl$	–
16. $HClF^- + HBr \rightarrow HBrF^- + HCl$	–
17. $HClF^- + SO_2 \rightarrow SO_2F^- + HCl$	*b*
18. $HClF^- + HCl \rightarrow ClHCl^- + HF$	–
19. $AsF_4^- + AsF_5 \rightarrow AsF_6^- + AsF_3$	–
20. $AsF_4^- + BF_3 \rightarrow BF_4^- + AsF_3$	–
21. $AsF_4^- + SiF_4 \rightarrow SiF_5^- + AsF_3$	–
22. $PF_6^- + SiF_4 \rightarrow SiF_5^- + PF_5$	+
23. $PF_6^- + BCl_3 \rightarrow BCl_3F^- + PF_5$	–
24. $PF_6^- + AsF_5 \rightarrow AsF_6^- + PF_5$	–
25. $PF_6^- + BF_3 \rightarrow BF_4^- + PF_5$	*b*
26. $SiF_5^- + PF_5 \rightarrow PF_6^- + SiF_4$	–
27. $SiF_5^- + BF_3 \rightarrow BF_4^- + SiF_4$	–
28. $SiF_5^- + AsF_5 \rightarrow AsF_6^- + SiF_4$	–
29. $SiF_3^- + SiF_4 \rightarrow SiF_5^- + SiF_2$	–
30. $BF_4^- + SiF_4 \rightarrow SiF_5^- + BF_3$	+
31. $BF_4^- + PF_5 \rightarrow PF_6^- + BF_3$	–
32. $BF_4^- + BCl_3 \rightarrow BCl_3F^- + BF_3$	–
33. $BF_4^- + AsF_5 \rightarrow AsF_6^- + BF_3$	–
34. $BCl_3F^- + BF_3 \rightarrow BF_4^- + BCl_3$	+
35. $BCl_3F^- + PF_5 \rightarrow PF_6^- + BCl_3$	+
36. $AsF_6^- + PF_5 \rightarrow PF_6^- + AsF_5$	*b*
37. $AsF_6^- + BF_3 \rightarrow BF_4^- + AsF_5$	*b*
38. $AsF_6^- + SiF_4 \rightarrow SiF_5^- + AsF_5$	*b*

[a] Pressure study established exothermicity of this reaction (the closeness of the masses of SF_6^- and PF_6^- made double resonance difficult). [b] Reaction not observed in icdr experiment.

Results

The negative ions produced by SO_2, HCl, HBr, BCl_3, BF_3, PF_3, PF_5, SiF_4, AsF_5, SF_6, and combinations thereof were studied at various electron energies and pressures in an effort to observe ion–molecule reactions (imr) yielding halide ion adducts. Although adducts such as CCl_3^-, HX_2^-, and SO_2X^- have been reported[6] as the result of solid–gas interactions, initial efforts to obtain negative ion–molecule reactions in the gas phase resulting in halide adducts met with little success. The pure compounds, or mixtures thereof, in the gas phase at low pressures either (1) do not give rise to these species, (2) produce them in undetectably small amounts, or (3) the species have such short lifetimes that they are not observed under the operating conditions of the icr. Only primary negative ions were observed with pure samples except for the previously reported formation of SiF_5^- in SiF_4,[7] BF_4^- in BF_3,[8] and AsF_6^- in AsF_5[9] and the additional species[10] $Si_2F_8^-$ and $B_2F_7^-$. Attempts to utilize these adducts as reagents for fluoride transfer reactions to other compounds were of limited success. The addition of a second compound to the icr cell resulted in a decrease in the intensities of the previously observed adducts and the formation of barely discernible concentrations of additional adducts. However, addition of SF_6 greatly enhanced halide ion adduct formation and therefore was utilized in the reaction mixtures for all systems investigated.

Table II presents the reactions which may be inferred from the icdr spectra for the mixtures investigated. The icdr data exhibit a high degree of redundancy in terms of observing ion transfers which could have been inferred from combinations of other observed reactions. This redundancy was deliberately introduced in order to firmly establish a scale of relative Lewis acidities which would not depend on a single experiment; the set is self-consistent. From these data, the relative order of the fluoride ion affinity determined is given in Table III.

Table III. Relative Order of Acidity

$M_{(g)} + F^-{}_{(g)} \longrightarrow MF^-{}_{(g)}$
$SF_4, SF_5\cdot < SO_2 < HCl, AsF_3 < SiF_4 < BF_3 < PF_5 < BCl_3 < AsF_5$

Most of this work was carried out using inorganic fluorides since some difficulty arises due to exchange reactions which occur spontaneously on mixing fluorides with other halogen compounds. For example, a mixture of BCl_3, AsF_5, and SF_6 yields the expected AsF_4^- and AsF_6^- but not BCl_3F^-. Instead, other unexpected adducts including BF_4^-, $BClF_3^-$, and AsF_3Cl^- were observed, and the relative intensities of these

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(6) (a) Sr. R. M. Dieters and D. H. McDaniel, *J. Amer. Chem. Soc.*, 88, 2607 (1966); (b) D. H. McDaniel and R. Valleé, *Inorg. Chem.*, 2, 996 (1963); (c) G. Jander and H. Mesech, *Z. Phys. Chem., Abt. A*, 183, 121 (1938).

(7) K. A. G. MacNeil and J. C. J. Thynne, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 455 (1970).

(8) (a) K. A. G. MacNeil and J. C. J. Thynne, *J. Phys. Chem.*, **74**, 2257 (1970); (b) J. A. Stockdale, D. R. Nelson, F. J. Davis, and R. N. Compton, *J. Chem. Phys.*, **56**, 3336 (1972).

(9) (a) T. C. Rhyne and J. G. Dillard, *Inorg. Chem.*, **10**, 730 (1971); (b) T. C. Rhyne, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 1971.

(10) (a) The analogous $Ge_2F_8^-$ species has recently been reported by P. W. Harland, S. Cradock, and J. C. J. Thynne, *Int. J. Mass Spectrom. Ion Phys.*, **10**, 169 (1972); (b) the $B_2F_7^-$ has been reported previously only in solution or in solid derivatives; see ref 27 and K. Sukumarabandhu, Ph.D. Dissertation, University of Cincinnati, 1972.

peaks increased proportionately to the time the mixture was in the cell. The neutral precursors of these adducts undoubtedly resulted from chemical reactions between the neutral molecules BCl_3 and AsF_5. Ruff and Paulett[11] have shown that in an equilibrium mixture of $AsCl_3$ and AsF_3, the compounds $AsClF_2$ and $AsFCl_2$ are present; the same exchange reactions also occur in mixtures of PCl_3 and AsF_3 as well as in mixtures of BCl_3 and BF_3.[12] Since BCl_3F^- does not occur in mixtures of BCl_3 and AsF_5, it was not possible to directly establish the order of relative acidity toward F^- for these two compounds. However, since it is possible to observe the endothermic transfer of F^- from BCl_3F^- to PF_5 but not from AsF_6^- to PF_5 (the reverse reactions have both been shown to be exothermic), we have tentatively assigned AsF_5 as the most acidic compound of the series investigated.

Our data do not permit a direct positioning of SO_2 in the acidity series. Inferential reasoning places the SO_2 acidity as slightly less than that of HCl in the following manner. The SO_2F^- species is presumed to have been produced from the reaction of SO_2 with SF_6^- since the latter was present in all of these experiments, and the reaction is exothermic. Other experiments[13] have shown SO_2F^- is produced *via* a rapid reaction with SF_6^-. The observation of the adduct SO_2F^- in the presence of HCl but not in the presence of BF_3 was taken to indicate that the fluoride ion affinity of SO_2 is much less than that of BF_3. Further, icdr data do not indicate any reaction occurring between SO_2F^- and HCl and $HClF^-$ and SO_2; failure to observe transfer of F^- from SO_2F^- may be due to the low concentration of SO_2F^- produced in these mixtures. A similar reason, however, cannot be given for the failure of $ClHF^-$ to transfer F^- to SO_2, and accordingly HCl is tentatively assigned a higher acidity toward F^- than SO_2. Alternatively, the failure to observe icdr spectra in these cases may be due to an exothermicity large enough to cause dissociation of the product ion before it reaches the analyzer region of the spectrometer.

Thermodynamic Considerations

If the fluoride ion affinity of several of the acids listed in Table III could be established, then it would be possible to bracket the remaining fluoride affinities or, at least, to establish upper or lower limits.

The fluoride ion affinity of BF_3 may be obtained from the heat of dissociation of $KBF_{4(s)}$ (29 kcal/mol),[14] the lattice energy of KF (194 kcal/mol),[15] and the lattice energy of KBF_4 (152 kcal/mol).[16] The affinity thus calculated is 71 kcal/mol.[17]

The fluoride ion affinity of HCl may be obtained from the energy released in proton transfer[18] ($PA(F^-) - PA(Cl^-) = 36$ kcal/mol) and the energy of the $F–H–Cl^-$ hydrogen bond (10 kcal/mol),[19] giving a value of 46 kcal/mol.

The fluoride ion affinity of SF_4 and SF_5 may be calculated from the appropriate energy cycles.

$$\begin{tikzcd}
\mathrm{SF_5\cdot + F^-} \arrow[r, "\mathrm{IA}"] & \mathrm{SF_6^-} \arrow[d, "\mathrm{EA(SF_6)}"] \\
\mathrm{SF_5\cdot + F\cdot + e} \arrow[u, "\mathrm{EA(F)}"] & \mathrm{SF_6 + e} \arrow[l, "D_0\mathrm{(SF_6–F)}"']
\end{tikzcd}$$

$$\mathrm{IA(SF_5\cdot) = EA(SF_6)} + D\mathrm{(SF_5–F) - EA(F)}$$

$$\begin{tikzcd}
\mathrm{SF_4 + F^-} \arrow[r, "\mathrm{IA}"] & \mathrm{SF_5^-} \arrow[d, "\mathrm{EA(SF_5\cdot)}"] \\
\mathrm{SF_4 + F\cdot + e} \arrow[u, "\mathrm{EA(F)}"] & \mathrm{SF_5\cdot + e} \arrow[l, "D_0\mathrm{(SF_4–F)}"']
\end{tikzcd}$$

$$\mathrm{IA(SF_4) = EA(SF_5\cdot) + D(SF_4–F) - EA(F)}$$

The data of Kay and Page[20] ($EA(SF_6) = 33.2$ kcal/mol, $EA(SF_5\cdot) = 84.4$ kcal/mol, $D_0(SF_5–F) = 86.1$ kcal/mol, and $D_0(SF_4–F) = 35.1$ kcal/mol) coupled with the value of 79.5 kcal/mol for the EA(F),[21] yield values of 40.0 and 39.8 kcal/mol for the $IA(SF_4)$ and $(SF_5\cdot)$, respectively. However, recent mass spectrometric studies give $EA(SF_6) \geq 13.8$ kcal/mol[13], $D_0(F_5S–F) \leq 78$ kcal/mol,[22] and thus $IA(SF_5\cdot) = 12.3$ kcal/mol. These same groups[13,22] report values of $EA(SF_5\cdot) \geqq 64.6$ and $\sim$78.1 kcal/mol. These electron affinities coupled with the Kay and Page value[20] of $D_0(SF_4–F)$ give values of $IA(SF_4) = 20.2$ and 33.7. Our icdr data place an upper limit of 46 kcal/mol on the $IA(SF_4)$ which is compatible with all of the calculated values. However, the $\Delta H_f(SF_4) = -208$ kcal/mol calculated[23] from the Kay and Page data is out of line with the other reported values[23] (-161.8, -179, and -185.2 kcal/mol). Using the value $IA(SF_4) \leq 46$ kcal/mol from our icdr data, $\Delta H_f°(SF_6) = -291.8$ kcal/mol,[24] $D(F_2) = 37.0$ kcal/mol,[25] and the data of Lifshitz, *et al.* ($D_0(F_5S^-–F) = 25.3$ kcal/mol), from the processes

$$SF_6^- \longrightarrow SF_5^- + F\cdot$$

$$SF_5^- \longrightarrow SF_4 + F^-$$

we obtain $\Delta H_f°(SF_4) \leq -191$ kcal/mol, in good agreement with the values quoted above.[23]

Our icdr data place the IA of SiF_4 between that of BF_3 and that of HCl, *i.e.*, at 58 ± 12 kcal. Coupled with the $\Delta H_f°(SiF_{4(g)}$, 298.16°K) $= -386$ kcal/mol this leads to $\Delta H_f°(SiF_5^-{}_{(g)}) = -505$ kcal/mol. This value is considerably higher than the previously established[26]

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[11] J. K. Ruff and G. Paulett, *Inorg. Chem.*, **3**, 998 (1964).

[12] R. F. Porter, D. R. Bidinosti, and K. F. Watterson, *J. Chem. Phys.*, **36**, 2104 (1962).

[13] C. Lifshitz, T. O. Tiernan, and B. M. Hughes, *J. Chem. Phys.*, in press.

[14] J. H. deBoer and J. A. M. Van Liempt, *Recl. Trav. Chim. Pays-Bas*, **46**, 124 (1927).

[15] D. Cubicciotti, *J. Chem. Phys.*, 34, 2189 (1961).

[16] A. P. Altshuller, *J. Amer. Chem. Soc.*, **77**, 6187 (1955).

[17] This value differs from that of Altshuller, ref 16, because of changes in the accepted values of EA(F) and the $\Delta H_f(BF_3)$; a value of 76 kcal/mol has been given by T. C. Waddington, *Advan. Inorg. Chem. Radiochem.*, **1**, 158 (1959).

[18] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

[19] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **70**, 543 (1966); this value was estimated from the shift in the ν_{H-F} on formation of $ClHF^-$. It is in agreement with the upper limit of 14 kcal obtained from our icdr observation of (exothermic) reaction 18 and an enthalpy of the $ClHCl^-$ bond of 14 kcal/mol (ref 6b). It is also in agreement with the value of 10 kcal/mol obtained from an empirical equation of Sr. Rose Mary Deiters (Ph.D. Dissertation, University of Cincinnati, 1967).

[20] J. Kay and F. M. Page, *Trans. Faraday Soc.*, **60**, 1042 (1964).

[21] R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, 38, 1540 (1963).

[22] R. K. Curran, *J. Chem. Phys.*, **34**, 1069 (1961).

[23] See P. A. G. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, *J. Chem. Thermodyn.*, **2**, 71 (1970), for the experimental basis for the -161.8 kcal/mol value and literature references and error estimates for the other values and for calculations from the Kay and Page data.

[24] P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, *Trans. Faraday Soc.*, **62**, 558 (1966).

[25] C. J. Schexnayder, Jr., NASA TN D-1791, 1963.

[26] J. C. J. Thynne and K. A. G. MacNeil, *Inorg. Chem.*, **9**, 1946 (1970).

upper limit of $\Delta H_f°(SiF_5^-) \leqq -583$ kcal. From the icdr reaction 29 the IA of SiF_2 must be less than that of SiF_4. If the value of 118 kcal/mol is taken for $D(SiF_2\text{–}F)$,[27] then the $EA(SiF_3) \leqq 23$ kcal/mol, a value considerably less than the 77 kcal/mol reported.[28]

The above and similar data are summarized in Table IV. Where there was a choice to be made, we have used data derived from the values obtained by Lifshitz *et al.*, as their data appear by themselves and in conjunction with our calculations to be more consistent with other determinations of the quantities. The SF_6^- ion produced in the icr spectrometer is a species of longer half-life and lower energy than that produced in more conventional mass spectrometers.[29]

Table IV. Heats of Formation and Fluoride Ion Affinities (kcal/mol)

MF_n	$\Delta H_f°_{298°K}$-($MF_{n(g)}$)	IA(MF_n)	$\Delta H_f°(MF_{n+1}^-)$	Other reported values[p]
SF_6	−291.8[a]	(See text)	(See text)	
SF_5	−234.6[b]	12.3	−305.6	
SF_4	≤ -191[c]	<46	−298.8	−304[q]
HCl	−22.1[d]	46	−129	
HBr	−8.7[d]	53	−122	
SO_2	−70.9[d]	$12.3 < IA < 46$	$-142 > \Delta H_f > -177$	
SiF_4	−386[e]	$46 < IA < 71$	$-493 > \Delta H_f > -518$	≤ -457,[j] ≤ -583[l]
SiF_2	−139[f] (−118[l])	<71	> −271	−328[l]
BF_3	−271.6[g]	71	−413	−406,[m] ≤ -343,[j] ≤ -357[n]
BCl_3	−96.5[d]	>71	≤ -238	≤ -156[o]
PF_5	−380.8[h]	>71	≤ -512	≤ -452[j]
PF_3	−228.8[h]	>12.3[k]	≤ -300[k]	≤ -291[j]
AsF_5	−295.5[i]	>71	≤ -427	≤ -378[j]
AsF_3	−220[d]	$71 > IA > 10$	$-291 > \Delta H_f > -352$	≤ -298[j]

[a] Reference 24. [b] Reference 13. [c] See text. [d] D. R. Stull, E. F. Westrum, Jr., and G. S. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969. [e] D. D Wagman, W. H. Evans, V. P. Parker, I. Harlow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **422**, 270 (1968). [f] J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971); T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964), the value is −140. [g] G. K. Johnson, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, **70**, 1 (1966). [h] G. K. Johnson, J. G. Malm, and W. N. Hubbard, *J. Chem. Thermodyn.*, **4**, 879 (1972). [i] P. A. G. O'Hare and W. N. Hubbard, *J. Phys. Chem.*, **69**, 4358 (1965). [j] Rhyne and Dillard's values (ref 9) recalculated using $\Delta H_f(SF_6^-)$ given here (see text). [k] Based on reaction observed by Rhyne and Dillard and the IA of SF_5 given here (see text). [l] Reference 26. [m] Reference 17. [n] Reference 8a. [o] Reference 8b. [p] Except as noted, not necessarily based on ΔH_f of neutrals used here. [q] Reference 9a.

Discussion

The gas phase acidity order found in this study agrees well with the results of several solution studies for the compounds common to both studies (see Tables I and III). The agreement with the solution study of Brownstein[30] is not too surprising since the solvent used in that study was CH_2Cl_2, a relatively nonsolvating solvent in which the acid–base behavior found might be expected to approach that found in the gas phase. Polynuclear complex formation is known[31] to take place with SbF_5 and AsF_5 in HF at moderate concentration; nevertheless, there is fair agreement with several of the acidity orders found in studies in which HF was used as a solvent, particularly that of Clifford, *et al.*[32] Decomposition pressures[33] of $CF_3SF_2^+MF_{n+1}^-$ salts place BF_3 above PF_5 in acidity, but this may be explained by the higher lattice energy of the BF_4^- salt.

Although SF_4 was not included in any of the studies summarized in Table I, it is expected to be a weaker fluoride ion acceptor than the other compounds investigated. Other studies have shown[34] that SF_4 forms addition compounds with BF_3, AsF_3, PF_5, AsF_5, and SbF_5 which may be formulated as $SF_3^+MF_{m+1}^-$ salts. Since SF_4 does not act as an acid toward itself ($SF_3^+SF_5^-$ does not occur), SF_4 may be assumed to be a weaker acid than the acceptor compounds mentioned above.

The lack of agreement between this study and the previous gas phase study is disappointing unless the differences in the experiments are considered. The previously determined gas phase order[9b] (see Table I) was based on the magnitude of the reaction cross section at 100° for the transfer of F^- from SF_6^- to the neutral compounds

$$SF_6^- + MF_n \longrightarrow SF_5\cdot + MF_{n+1}^-$$

while the present work is based on observations of the energy dependence of the rate of the displacement reactions measured at ambient temperature (see Table II). We do not feel that rates of displacement reactions *per se* are necessarily related in a direct fashion to acidities.

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