

# Fluoride and Chloride Affinities of Main Group Oxides, Fluorides, Oxofluorides, and Alkyls. Quantitative Scales of Lewis Acidities from Ion Cyclotron Resonance Halide-Exchange Equilibria

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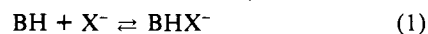
**Abstract:** Accurate binding energies of fluoride and chloride ions to a wide variety of Lewis acids including oxides, fluorides, oxofluorides, and alkyl derivatives of boron, carbon, silicon, phosphorus, arsenic, and sulfur have been determined with ion cyclotron resonance halide-exchange equilibrium techniques. Magnitudes of chloride and fluoride binding energies are discussed in terms of periodic trends, substituent effects, scales of Lewis acid hardness and softness, and empirical correlations. The limited data reveal no strong motivation for definitions of a hard-soft character for Lewis acids and bases in the gas phase. Useful new thermochemical data are derived for complex anions which are used to estimate crystal lattice energies for salts of complex chloro and fluoro anions. Implications for new synthetic targets and potential catalytic agents are discussed.

The introduction, by Lewis, of the electron pair acceptor-electron pair donor definitions of acids and bases,<sup>1</sup> respectively, as an adjunct to his theory of the electron pair bond<sup>1,2</sup> marked an important conceptual departure in the chemist's view of acids and bases. Unfortunately it remained until molecular orbital theories of bonding were introduced and widely accepted<sup>3</sup> for the Lewis concept of acids and bases to be given credence. Part of the reason for this slow acceptance was the reluctance on the part of practicing chemists to abandon the central role of the proton as the "acid principle". This reluctance arose primarily because of the almost universal practice of carrying out acid-base reactions in protic, ionizing solvents, where it was always energetically favorable for a proton transfer of some kind to occur. This difficulty was largely overcome when the use of highly purified, dry, aprotic, nonionizing solvents became practical. Another objection to the Lewis theory of acids and bases arose because of the perceived inability to formulate either a quantitative or qualitative ordering of Lewis acid-base strength. These objections were satisfied by the arguments arising naturally from molecular orbital theory and covalent bonding that Lewis acid-base strengths must be defined with respect to a specific reference species and a quantitative order of Lewis acid or base strengths may be obtained from the relative stabilities of adducts formed with the given reference species. It follows immediately from this view that different orders of acid-base strengths are possible and indeed probable as the reference species is changed.<sup>4</sup> Since all protic species can in principle act as electron pair acceptors or donors, it is important to note that protic (Brønsted) acids and bases are merely an important subset of Lewis acids and bases.<sup>5,6</sup>

An important related theory of acids and bases which appears to be especially applicable to gas-phase ion-molecule interactions is that due to Usanovich<sup>7,8</sup> in which acid-base properties are associated with coordinate unsaturation. In this formalism acids are coordinatively unsaturated species containing electropositive atoms which tend to combine with negatively charged species and, conversely, bases are coordinatively unsaturated entities containing electronegative atoms which tend to combine with positively charged species. As special examples Usanovich cited the halogen acids which may act in a Brønsted sense by giving up a proton or in the more general sense by combining with anions such as in the formation of  $FHF^-$ . In addition coordinately unsaturated acid "anhydrides" such as  $CO_2$  and  $SO_3$  are cited because of their ready ability to combine with anions.

In previous work from this laboratory, absolute binding energies for fluoride<sup>9,10</sup> and chloride<sup>11,12</sup> ions to Brønsted acids were re-

ported, eq 1. As seen from the Lewis acidity definition, these



binding energies are a measure of the stability of adducts in which an electron pair donor,  $X^-$ , forms a coordinate bond to an electron pair acceptor, BH. According to the Usanovich definition the Brønsted acid BH is coordinatively unsaturated where the electropositive hydrogen atom is coordinately saturated by dicoordination. The stability of the adducts  $BHX^-$  thus provide a quantitative measure of the Lewis acidities of BH. While the Lewis acidities of BH in general parallel the gas-phase Brønsted acidities, as measured by  $\Delta H_1^\circ$  and  $\Delta H_2^\circ$ , respectively, important reversals do occur, particularly when the acid functional group type is varied. These reversals provide valuable information



regarding the nature of the  $BHX^-$  hydrogen bond. It is important to note that it is only because the Brønsted acid-base definitions have a constant reference species ( $H^+$ ) that one unique quantitative acidity-basicity scale results in a fixed solvent. However, even a minor solvent change can result in an entirely different qualitative ordering of acidities and basicities by effectively changing the solvated nature of the reference  $H^+$ . This is effectively the same situation as changing the reference species for a Lewis acid-base scale.

In the present work we wish to report ion cyclotron resonance measurements of thermal fluoride- and chloride-exchange equilibria involving pairs of Lewis acids, eq 3. From the thermo-



chemical data derived from these equilibrium measurements, scales of relative Lewis acidities toward the reference bases  $F^-$  and  $Cl^-$  have been constructed. From selected cases where absolute  $F^-$  and  $Cl^-$  binding energies are accurately known, these relative scales have been converted to absolute binding energy data for  $F^-$  and  $Cl^-$  adducts of main group oxides, fluorides, oxofluorides, and alkyl

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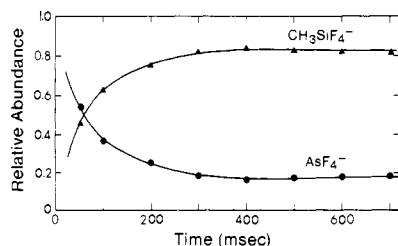
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**Figure 1.** Variation of relative abundances for fluoride adducts of  $\text{AsF}_3$  and  $\text{CH}_3\text{SiF}_3$  with time following a 5-ms, 70-eV electron beam pulse in a 1:4:6.5 mixture of  $\text{CH}_3\text{SiF}_3/\text{SF}_6/\text{AsF}_3$  at a total pressure of  $4.0 \times 10^{-6}$  torr.

derivatives. These data provide, for the first time, absolute Lewis acidity data for a sufficient number of compounds in the gas phase to allow discussion of substituent effects, periodic trends, and effects of reference base. In addition the data allow deduction of thermochemistry of novel anionic species, suggest new possible synthetic targets, provide insight into the catalytic activity of simple salts, and yield further understanding of structure and bonding in main group compounds.

### Experimental Section

All experiments were conducted at ambient temperature with an ICR spectrometer of basic Varian V5900 design extensively modified to permit routine operation in both conventional drift and trapped-ion modes.<sup>13</sup> Details of the design and operation of trapped-ion ICR techniques and conventional ICR single- and double-resonance experiments have been described extensively elsewhere.<sup>14,15</sup>

All samples used were commercial materials of the highest purity obtainable. Trace amounts of  $\text{SO}_2$  were found to be present in  $\text{SO}_2\text{F}_2$ .  $\text{AsF}_3$  was condensed into a vessel containing sodium fluoride to remove HF impurities. Fuming sulfuric acid was used as a source of  $\text{SO}_3$ . Prior to use, all gas-handling vacuum lines and sample vessels were thoroughly conditioned with  $\text{SF}_4$  or  $\text{COF}_2$  to passivate all surfaces. After such conditioning no significant  $\text{FHF}^-$  or  $\text{SiF}_5^-$  signals were detectable in negative ion mass spectra after long trapping times. All samples were thoroughly degassed by successive freeze-pump-thaw cycles prior to use.

A typical anion-transfer equilibrium experiment involved the introduction of a halide donor precursor into the high vacuum ICR cell region to a pressure of  $10^{-7}$ – $10^{-6}$  torr. Fluoride ion donors used included  $\text{SF}_6^-$  from  $\text{SF}_6$ ,<sup>16</sup>  $\text{SF}_4^-$  from  $\text{SF}_4$ ,  $\text{CF}_3\text{O}^-$  from  $\text{CF}_3\text{OF}$ ,<sup>17</sup>  $\text{CH}_3\text{OH}-\text{F}^-$  from a mixture of  $\text{NF}_3$  and  $\text{HCO}_2\text{CH}_3$ ,<sup>18</sup> and  $\text{CH}_2\text{CFCH}_2^-$  from a mixture of  $\text{CH}_3\text{O}^-$  and  $\text{CH}_2\text{CF}=\text{CH}_2$ .<sup>17</sup> Chloride donors included  $\text{SO}_2\text{Cl}^-$  from  $\text{SO}_2\text{Cl}_2$ <sup>19</sup> and  $\text{ClCO}_2^-$  from  $\text{ClCO}_2\text{CH}_3$ .<sup>12</sup> A mixture of two anion receptor molecules, prepared with accurately known partial pressure ratios using a Validyne AP-16 absolute pressure gauge, was then admitted to the ICR cell through an independent leak valve to a pressure of  $1 \times 10^{-6}$  to  $5 \times 10^{-6}$  torr. An equilibrium constant for halide exchange,  $K_3$ , could be readily determined by monitoring the steady-state ratio of  $\text{L}_1\text{X}^-$  and  $\text{L}_2\text{X}^-$  intensities as a function of trapping time in the ICR cell, provided that (i) the anion donor had a lower halide affinity than either  $\text{L}_1$  or  $\text{L}_2$ , (ii)  $\text{L}_1$  and  $\text{L}_2$  had halide affinities within  $\sim 2$  kcal mol<sup>-1</sup> of each other, and (iii) the halide-exchange reaction was sufficiently rapid. A typical normalized abundance curve for ionic intensities as a function of trapping time is shown in Figure 1 for a mixture of  $\text{SF}_6$ ,  $\text{AsF}_3$ , and  $\text{CH}_3\text{SiF}_3$ .

The equilibrium constant for halide exchange can then be calculated from the experimentally observed steady-state ionic abundance ratio and the manometrically determined partial pressure ratio, eq 4.

$$K_3 = \frac{[\text{L}_2\text{X}^-]P_{\text{L}_1}}{[\text{L}_1\text{X}^-]P_{\text{L}_2}} \quad (4)$$

Attainment of a persistent steady state was taken as initial evidence that thermal equilibrium had been established. This condition was ver-

**Table I.** Standard Free Energy (kcal mol<sup>-1</sup>), Enthalpy (kcal mol<sup>-1</sup>) and Entropy (cal mol<sup>-1</sup> K<sup>-1</sup>) Data Relevant to Fluoride Binding to Lewis Acids

Compound	$\Delta G_3^\circ$	$-\Delta G_3^\circ$	$-\Delta S_3^\circ$	$-\Delta H_3^\circ$	$\Delta H_f^\circ(\text{MF}^-)$ (kcal mol <sup>-1</sup> )
$\text{B}(\text{Et})_3$		43.5	25	51.0	-148.6
$\text{SiMeF}_3$	0.5 <sup>a</sup>	43.0	25	50.5	
$\text{CF}_3\text{COCF}_3$	2.0	41.6	27	49.7	
$\text{AsF}_3$	0.6	41.0	24	48.2	-328.1
$\text{PF}_3\text{O}$	0.9	40.1	26	47.9	-403.4
$\text{BMe}_3$	2.2	39.7	25	47.2	-136.8
$\text{CF}_3\text{CF}_2\text{COF}$	0.4 <sup>a</sup>	38.8	28	47.2	
$\text{CF}_3\text{COF}$	3.5	37.2	28	45.6	
$\text{CFOCFO}$	1.6	37.0	29	45.7	
$\text{SO}_2$	0.6	36.6	24	43.8	-174.6
$\text{SF}_4$	0.4 <sup>b</sup>	36.2	25	43.8	-291.0
$\text{COF}_2$	2.7	33.9	29	42.6	-255.2
$\text{PF}_3$	1.3 <sup>b</sup>	32.6	25	40.2	-325.0
$\text{SiMe}_3\text{F}$	1.1	31.6	22	38.2	
$\text{SOF}_2$	1.6	30.2	24	37.4	
$\text{SO}_2\text{F}_2$	2.5 <sup>b</sup>	27.6	27	35.8	-279.1
$\text{tBuOH}$	2.1 <sup>b</sup>	25.5 <sup>b</sup>	26	33.3	
$\text{COS}$		24.6	24	31.8	-124.7
$\text{CO}_2$	0.5	24.5	24	31.7	-185.6
$\text{CS}_2$	1.9	24.1	24	31.3	-63.2
$\text{SiMe}_4$	0.4	23.6	21	29.9	-147.0
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CN}$	1.7	23.6	24	30.8	
$\text{CF}_3\text{CF}_2\text{CN}$	0.8	23.1	24	30.3	
$\text{MeOH}$	0.5	22.8 <sup>b</sup>	23	29.6	
$\text{CF}_3\text{CN}$	0.3	21.9	24	29.2	
$\text{H}_2\text{O}$	0.9	18.1 <sup>c</sup>	17.3 <sup>c</sup>	23.3 <sup>c</sup>	

<sup>a</sup> Reference 30. <sup>b</sup> Reference 10. <sup>c</sup> Standard reference value (ref 20).

ified by (i) determinations that the calculated equilibrium constant was independent of both total pressure and partial pressure ratio, (ii) multiple overlap equilibrium experiments that resulted in closed thermochemical cycles to give an internally consistent "ladder" of anion affinities, (iii) double-resonance experiments at long trapping times to verify the occurrence of reaction in both forward and reverse directions, and (iv) time delayed ion ejection experiments in selected cases to determine rate

$$K_3 = k_f/k_r \quad (5)$$

constants in both forward and reverse directions to establish that  $K_3$  calculated from eq 5 was identical with that calculated from eq 4.

### Results

**1. Thermal Equilibrium Measurements.** The free energy changes for halide transfer, eq 3, can be calculated from the measured equilibrium constants by using the standard thermochemical equation, (6). The individual fluoride-transfer free

$$\Delta G_3^\circ = -RT \ln K_3 \quad (6)$$

energies,  $\Delta G_3^\circ$ , are reported in Table I, and the chloride-transfer free energies are reported in Table II. It should be noted that the individual free energy changes shown in these tables represent roughly one-half of the total number of equilibria involving these compounds. Chloride- and fluoride-transfer equilibrium constants involving a large number of Bronsted acids<sup>10,11</sup> and the compounds in Tables I and II were also determined concurrently and provide further validation of  $\Delta G_3^\circ$  and other thermochemical quantities derived. The maximum uncertainty in each of the individual values of  $\Delta G_3^\circ$  is placed at  $\pm 0.2$  kcal mol<sup>-1</sup> based on the large number of closed thermochemical cycles examined.

Absolute values of free energies of binding of  $\text{F}^-$  and  $\text{Cl}^-$ ,  $\Delta G_7^\circ$ , to the Lewis acids studied were obtained from the relative free energies,  $\Delta G_3^\circ$ , and the known free energies of binding of  $\text{F}^-$  to

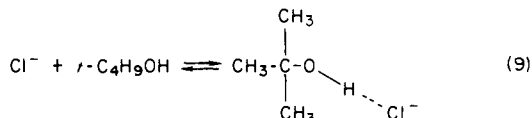
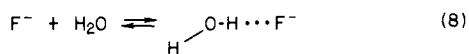
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**Table II.** Standard Free Energy (kcal mol<sup>-1</sup>), Enthalpy (kcal mol<sup>-1</sup>) and Entropy (cal mol<sup>-1</sup> K<sup>-1</sup>) Data Relevant to Chloride Binding to Lewis Acid

Compound	$\Delta G_3^\circ$	$-\Delta G_7^\circ$	$-\Delta S_7^\circ$	$-\Delta H_7^\circ$	$\Delta H_f^\circ(\text{MCL}^-)$ (kcal mol <sup>-1</sup> )
BF <sub>3</sub>		19.3	23	26.0	-353.3
AsF <sub>3</sub>		18.6	24	25.8	-301.7
SiCl <sub>4</sub>		17.6	22	24.2	-237.2
BEt <sub>3</sub>		17.2 <sup>a</sup>	22	23.8	-117.4
SiF <sub>4</sub>		16.8	22	23.4	-237.2
CF <sub>3</sub> COCF <sub>3</sub>		16.3	22	22.9	
SO <sub>2</sub>		14.7 <sup>a</sup>	21	20.9	-147.7
CF <sub>3</sub> COC <sub>2</sub>		11.2	22	17.8	
SOF <sub>2</sub>		10.2	23	17.1	
CF <sub>3</sub> COF		10.1	22	16.7	
CHF <sub>3</sub>		9.8 <sup>a</sup>	23	16.7	
SiMeF <sub>3</sub>		9.5	22	16.1	
PF <sub>3</sub>		9.2 <sup>a</sup>	21	15.5	-296.3
MeOCOC <sub>2</sub>		7.8	21	14.1	
PF <sub>3</sub> O		7.6	21	13.9	-365.4
COF <sub>2</sub>		6.6	20	12.5	-221.1
COC <sub>2</sub>		6.5	20	12.5	-121.0
MeC <sub>2</sub>		6.1 <sup>a</sup>	20	12.2	
CS <sub>2</sub>		5.7	20	11.7	-39.6
CO <sub>2</sub>		2.5 <sup>b</sup>	20 <sup>b</sup>	8.5 <sup>b</sup>	-158.4

<sup>a</sup>Reference 12. <sup>b</sup>Reference 31.

H<sub>2</sub>O<sup>20</sup> ( $\Delta G_8^\circ = -18.1$  kcal mol<sup>-1</sup>) and Cl<sup>-</sup> to *t*-C<sub>4</sub>H<sub>9</sub>OH<sup>21</sup> ( $\Delta G_9^\circ = -11.1$  kcal mol<sup>-1</sup>). Other Bronsted acids with known halide



ion binding free energies were also incorporated into the relative scales shown in Tables I and II, and the data remained internally consistent.

The entropies of binding of halide ions to the Lewis acids,  $\Delta S_7^\circ$ , can be estimated by three methods: (i) the entropy of LX<sup>-</sup> is set equal to the known entropy of an isoelectronic neutral molecule with small corrections for translational entropy differences and symmetry difference; (ii) the entropy of LX<sup>-</sup> is calculated by using statistical thermodynamic methods where the geometry of L in LX<sup>-</sup> is assumed to be unchanged and the A-X<sup>-</sup> force constants are estimated from the dissociation energy;<sup>22</sup> and (iii) in a few cases, rigorous statistical thermodynamic calculations of the entropy can be carried out when the geometries of LX<sup>-</sup> and the vibrational frequencies are known from some combination of crystallographic and spectroscopic experiments on either crystalline salts of LX<sup>-</sup> or matrix isolated LX<sup>-</sup>. All three methods give gratifyingly good agreement. For example for SO<sub>2</sub>F<sup>-</sup>,  $\Delta S_7^\circ$  is calculated to be -27, -23, or -26<sup>23</sup> cal mol<sup>-1</sup> K<sup>-1</sup> using (i), (ii), and (iii) above, respectively. Similarly for CF<sub>3</sub>O<sup>-</sup>,  $\Delta S_7^\circ$  can be calculated to be -31, -26, and -30,<sup>24</sup> or -29<sup>25</sup> cal mol<sup>-1</sup> K<sup>-1</sup>,

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fluoride affinity order, L-R	$D(\text{L-F}^-)$ , kcal mol <sup>-1</sup>	$\Delta H_f^\circ(\text{LF}^-)$ , kcal mol <sup>-1</sup>
PF <sub>3</sub> ≥ SO <sub>3</sub>	85 ± 10	-522
SO <sub>3</sub> ≤ PF <sub>3</sub>		
SO <sub>3</sub> ≥ BF <sub>3</sub>	78 ± 10	-233
SO <sub>3</sub> ≥ SiF <sub>4</sub>		
BF <sub>3</sub> ≤ SO <sub>3</sub>	72 ± 5	-403
BF <sub>3</sub> ≥ SiF <sub>4</sub>		
CH <sub>3</sub> OBF <sub>2</sub> ≥ HCl	62	
SiF <sub>4</sub> ≤ BF <sub>3</sub>		
SiF <sub>4</sub> ≥ HCl		
SiF <sub>4</sub> ≥ (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> BF	60 ± 4	-506
SiF <sub>4</sub> ≥ (CH <sub>3</sub> O) <sub>2</sub> BF		
SiF <sub>4</sub> ≥ (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B		
HCl	60 ± 2	-142
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> BF ≤ SiF <sub>4</sub>	58 ± 5	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> BF ≥ (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B		
(CH <sub>3</sub> O) <sub>2</sub> BF ≤ SiF <sub>4</sub>		
(CH <sub>3</sub> O) <sub>2</sub> BF ≤ HCl	52 ± 5	
(CH <sub>3</sub> O) <sub>2</sub> BF ≥ AsF <sub>3</sub>		
(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> B ~ SO <sub>2</sub>	44 ± 3	
(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> B > (CH <sub>3</sub> O) <sub>3</sub> B		
(CH <sub>3</sub> O) <sub>3</sub> B < SO <sub>2</sub>		
(CH <sub>3</sub> O) <sub>3</sub> B ~ OCF <sub>2</sub>	42 ± 3	
(CH <sub>3</sub> O) <sub>3</sub> B > PF <sub>3</sub>		
CF <sub>3</sub> NO < H <sub>2</sub> O	<23	
Xe < H <sub>2</sub> O	<23	

respectively. The entropies thus determined are also reported in Tables I and II.

The enthalpy changes,  $\Delta H_7^\circ$ , which give the halide ion bond dissociation energies in LX<sup>-</sup> can be then readily calculated from eq 10. These values are also given in Tables I and II. The

$$\Delta H_7^\circ = \Delta G_7^\circ + T\Delta S_7^\circ = -D(\text{L-X}^-) \quad (10)$$

uncertainty in  $\Delta H_7^\circ$  values includes the experimental uncertainty in determination of  $\Delta G_3^\circ$  values, the uncertainty in estimation of  $\Delta S_7^\circ$ , probably about ±3 cal mol<sup>-1</sup> K<sup>-1</sup>, and the uncertainty in thermochemistry of the reference neutrals and anions. These thus combine to render  $\Delta H_7^\circ$  values accurate to within a maximum absolute uncertainty of ±2 kcal mol<sup>-1</sup>.

**2. Bracketing Experiments.** For several of the compounds of interest in this study, thermal equilibrium halide transfer could not be observed due either to fast reactions competing with halide transfer or to the fact that the compound of interest was above the range of the ladders in Tables I and II in halide affinity. In such cases the occurrence or nonoccurrence of a halide-transfer reaction, verified by ICR double-resonance and/or ion ejection experiments, was used to establish a qualitative order of halide ion affinities. The results of such bracketing experiments are summarized in Table III as well as thermochemical inferences drawn from them.

The value of  $D(\text{SiF}_4-\text{F}^-)$  of 62 ± 4 kcal mol<sup>-1</sup> is obtained from an extrapolation of the fluoride affinity measurements of (CH<sub>3</sub>)<sub>n</sub>SiF<sub>4-n</sub> compounds in which a regular increase of 7 ± 1 kcal mol<sup>-1</sup> in fluoride affinity is observed for every substitution of F for CH<sub>3</sub> and the observation that FHCl<sup>-</sup> transfers F<sup>-</sup> to SiF<sub>4</sub>. The fluoride affinity of HCl is accurately known from thermal equilibrium measurements of the Cl<sup>-</sup> binding energy to HF and the known gas-phase acidity difference between HF and HCl.<sup>11</sup>

Both (CH<sub>3</sub>O)<sub>3</sub>BF<sup>-</sup> and (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>BF<sup>-</sup> undergo reactions in mixtures containing fluoride donor precursors to yield ions of the

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type  $(\text{RO})_2\text{BF}_2^-$  and  $\text{ROBF}_3^-$ , thus preventing fluoride-exchange equilibrium from occurring. The values for fluoride affinity of boron compounds were selected assuming constant substituent effects, a measured value for  $(\text{CH}_3\text{O})_3\text{B}$ , and a value for  $\text{BF}_3$  consistent with lattice energy calculations and ICR double-resonance experiments.

The fluoride affinities of  $\text{SO}_3$  and  $\text{PF}_5$  were based primarily on lattice energy calculations to be discussed below.

**3. Enthalpies of Formation of Complex Anions.** Values of  $\Delta H_f^\circ$  ( $\text{LX}^-$ ) in the gas phase may be calculated from eq 11 using  $\Delta H_f^\circ(\text{F}^-)$  of  $-59.9 \text{ kcal mol}^{-1}$ <sup>26</sup> and  $\Delta H_f^\circ(\text{Cl}^-)$  of  $-55.9 \text{ kcal mol}^{-1}$ <sup>27-29</sup> and standard sources of thermochemical data for neutral molecules.

**4. Comparison of Present Results with Literature Data.** Very little data of a quantitative nature are available for the binding energies of  $\text{F}^-$  and  $\text{Cl}^-$  to Lewis acids. Haartz and McDaniel<sup>16</sup>

$$\Delta H_f^\circ(\text{LX}^-) = \Delta H_f^\circ(\text{L}) + \Delta H_f^\circ(\text{X}^-) - \Delta H_7^\circ \quad (11)$$

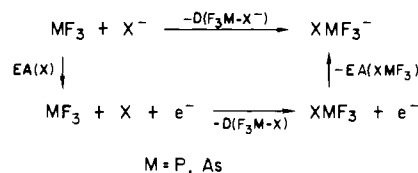
have carried out a number of fluoride- and chloride-transfer reactions using conventional ICR techniques and arrived at a qualitative relative ordering of halide binding energies including some Lewis acids. Murphy and Beauchamp have observed fluoride-transfer reactions for fluoride adducts of substituted boranes<sup>26,27</sup> and silanes.<sup>30</sup> Using a value for  $D(\text{SF}_4-\text{F}^-)$  of  $54 \pm 15 \text{ kcal mol}^{-1}$ , they arrived at a qualitative fluoride binding energy scale which was obviously limited by the large uncertainty of the reference data for  $\text{SF}_5^-$ . There have been some data obtained from direct clustering of halide ions with Lewis acids by using high-pressure mass spectrometric techniques. Keesee, Lee, and Castleman<sup>31</sup> have measured anion binding energies for  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_2^-$ , and  $\text{SO}_3^-$  to  $\text{SO}_2$  and  $\text{CO}_2$ . Wlodek et al.<sup>32</sup> have used a similar technique to study the binding of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  to  $\text{SO}_2$ .

Some data are also available for halide affinities from experimental determinations of electron affinities, appearance potentials, and collisional and photodissociation of anions. These methods often provide only upper or lower limits due to difficulties in accurately determining thresholds for these processes.

**(a)  $\text{SF}_5^-$ .** The electron affinity of  $\text{SF}_5$  has been the subject of a number of investigations yielding values variously of 63,<sup>33</sup> 65,<sup>34</sup> 64,<sup>35</sup>  $\geq 78$ ,<sup>36</sup> and  $84$ <sup>37</sup>  $\text{kcal mol}^{-1}$ . These data taken with  $\Delta H_f^\circ(\text{SF}_5)$  of  $-232 \pm 5 \text{ kcal mol}^{-1}$ <sup>38</sup> and  $\Delta H_f^\circ(\text{SF}_4)$  of  $-187 \pm 6$ <sup>27</sup>  $\text{kcal mol}^{-1}$  lead to a fluoride affinity of  $\text{SF}_4$  ranging from 48 to 69  $\text{kcal mol}^{-1}$ . Our value obtained in the present work of 44  $\text{kcal mol}^{-1}$  supports the lower electron affinity determinations of Compton<sup>33</sup> and Lifschitz<sup>35</sup> although the large uncertainties in the enthalpy data for  $\text{SF}_4$  and  $\text{SF}_5$  make a definitive assessment impossible.

**(b)  $\text{SO}_2\text{F}^-$ .** An early determination by Franklin<sup>39</sup> of the appearance potential of  $\text{SO}_2\text{F}^-$  from  $\text{SO}_2\text{F}_2$  led to a fluoride affinity of  $\text{SO}_2$  of 40  $\text{kcal mol}^{-1}$  in good agreement with the value of 44  $\text{kcal mol}^{-1}$  determined here. However, the earlier work was based on a value of  $\Delta H_f^\circ(\text{SO}_2\text{F}_2)$  of  $-205 \text{ kcal mol}^{-1}$ <sup>39</sup> which has since been replaced by a more reliable calorimetric value of  $-183.4 \text{ kcal mol}^{-1}$ .

#### Scheme I



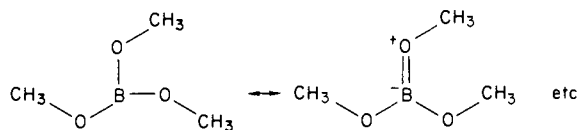
$\text{mol}^{-1}$ ,<sup>40</sup> Thus the early appearance potential value of 2.3–2.5 eV<sup>39,41</sup> actually leads to a fluoride affinity of  $\text{SO}_2$  or 17  $\text{kcal mol}^{-1}$ . Such a value is impossibly low since  $\text{FSO}_2^-$  would then be expected to transfer  $\text{F}^-$  to weakly acidic species such as  $\text{H}_2\text{O}$  and  $\text{CO}_2$  which it clearly does not. This low value is also inconsistent with the relative ease of synthesis and stability of  $\text{SO}_2\text{F}^-$  salts. Wang and Franklin<sup>41</sup> have speculated that  $\text{SO}_2\text{F}^-$  formed by electron impact from  $\text{SO}_2\text{F}_2$  may be produced in an electronically excited state. Our data support this conjecture and lead to an energy level for the excited state 1.2 eV above the ground state. Additional evidence for an excited state of  $\text{SO}_2\text{F}^-$  comes from the fact that Sullivan and Beauchamp<sup>19</sup> observe that  $\text{SO}_2\text{F}^-$  formed from electron impact on  $\text{SO}_2\text{F}_2$  undergoes  $\text{F}^-$  transfer to both  $\text{PF}_3$  and  $\text{HCN}$ . In our experiments in which  $\text{FSO}_2^-$  is produced by fluoride transfer to  $\text{SO}_2$ , no exothermic transfer of  $\text{F}^-$  to  $\text{PF}_3$  or  $\text{HCN}$  is observed.

**(c)  $\text{SO}_2\text{Cl}^-$ .** The value of 14.7  $\text{kcal mol}^{-1}$  for the free energy of binding of  $\text{Cl}^-$  to  $\text{SO}_2$  obtained in the present work is in excellent agreement with the directly measured values of 14.9<sup>31</sup> and 14.2<sup>42</sup>  $\text{kcal mol}^{-1}$  obtained from clustering equilibria measurements.

#### Discussion

**Periodic Trends and Substituent Effects on Lewis Acidities.** A comparison of the data in Tables I–III reveals that in all cases,  $\text{F}^-$  is bound more strongly than  $\text{Cl}^-$  to Lewis acids with fluoride affinities generally being at least twice the corresponding chloride affinities. This result is expected from the small size of the fluoride ion, the greater covalent bond energy of fluoride to all elements, and the previously observed greater basicity of  $\text{F}^-$  toward  $\text{H}^+$  and all hydrogen-bonding Bronsted acids.<sup>10,11</sup>

When substitution is carried out at the atom in the Lewis acids to which covalent binding occurs, the substituent effect is qualitatively similar to that observed for the proton acidities of Bronsted acids. The order of increasing acidity of  $\text{CH}_3 < \text{F} < \text{CF}_3 < \text{CF}_3\text{CF}_2$  holds for binding to both  $\text{F}^-$  and  $\text{Cl}^-$  as the reference base. Unlike in Bronsted acids, the  $\text{CH}_3\text{O}$  substituent in boron compounds weakens the Lewis acidity relative to  $\text{CH}_3$ . For example,

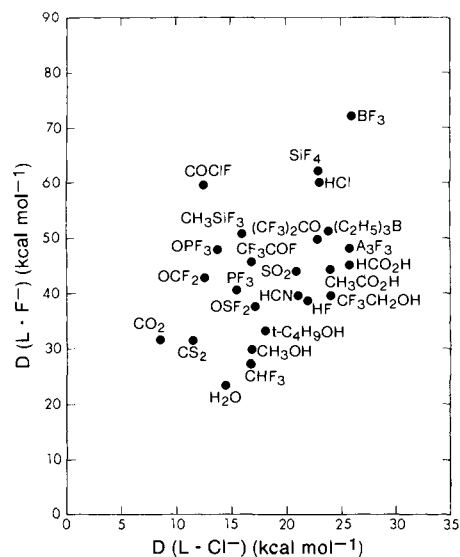


$(\text{CH}_3\text{O})_3\text{B}$  is observed to be roughly 6  $\text{kcal mol}^{-1}$  weaker in acidity toward  $\text{F}^-$  than  $(\text{CH}_3)_3\text{B}$ . This is due to the strong  $\pi$ -donor interaction between oxygen lone pairs and the vacant p orbital on boron which cancels any favorable inductive effect of the more electronegative  $\text{CH}_3\text{O}$  group.

A comparison of the oxides, fluorides, and oxofluorides of sulfur and phosphorus is most puzzling. The two hexavalent compounds of sulfur have both the highest ( $\text{SO}_3$ ) and lowest ( $\text{SO}_2\text{F}_2$ ) fluoride affinities in the sulfur series, while among the tetravalent species  $\text{SOF}_2$  has a lower fluoride affinity than either  $\text{SF}_4$  or  $\text{SO}_2$  which are identical in Lewis acidity toward  $\text{F}^-$ . Neither the number of contributing valence bond structures nor the formal charge on sulfur appear to have any correlation with relative fluoride affinity. It may be noteworthy, however, that the highest fluoride affinities are associated with tetrahedral anions ( $\text{SO}_3\text{F}^-$ ,  $\text{SO}_2\text{F}^-$ ) while the lowest are those associated with tetrahedral neutral molecules

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**Figure 2.** Scatter diagram for fluoride ion affinities vs. chloride ion affinities for Lewis acids and selected Bronsted acids.

( $\text{SO}_2\text{F}_2$ ,  $\text{SOF}_2$ ). Apparently there may be some special stability associated with tetrahedral compounds of sulfur, oxygen, and fluorine. Octahedral coordination may also impart a special stability to species since, despite many attempts using fluoride donors of very low fluoride binding energy, no addition of  $\text{F}^-$  to  $\text{SF}_6$  to yield  $\text{SF}_7^-$  could be achieved. In addition, in the phosphorus series of compounds,  $\text{PF}_5$  has the highest fluoride affinity of any compound which we have investigated while  $\text{PF}_3$ , which goes from tetrahedral to square-pyramidal geometry upon  $\text{F}^-$  addition, has the lowest fluoride affinity in the series. The tetrahedral molecule  $\text{OPF}_3$ , which results in a trigonal-bipyramidal anion  $\text{OPF}_4^-$ , is intermediate in fluoride affinity although it lies much closer to  $\text{PF}_3$  than to  $\text{PF}_5$ . Although there are no gas-phase data available, it is known that NSF readily forms a fluoride adduct (tetrahedral  $\text{NSF}_2^-$ ) with  $\text{HgF}_2$  whereas  $\text{NSF}_3$  does not.<sup>43</sup> Despite this interesting correlation between structure and stability, we are not aware of any firm theoretical basis for it.

$\text{AsF}_3$  and  $\text{PF}_3$  provide the only pair of compounds which allow deduction of group trends in Lewis acidity. Toward both  $\text{F}^-$  and  $\text{Cl}^-$ ,  $\text{AsF}_3$  exhibits the greater acidity. This trend may be understood through the thermochemical cycle shown in Scheme I where the halide ion binding energy is given by eq 12. From

$$D(\text{F}_3\text{M-X}^-) = \text{EA}(\text{XMF}_3) + D(\text{F}_3\text{M-X}) - \text{EA}(\text{X}) \quad (12)$$

known trends in bond dissociation energy, the As-X bonds will be weaker than P-X bonds,<sup>44</sup> and as a result it must be the case that the electron affinities of the  $\text{XAsF}_3$  radicals are significantly greater than their  $\text{XPF}_3$  analogues.

**Comparison of Chloride and Fluoride Affinities.** Fluoride affinities are plotted vs. chloride affinities in Figure 2 for all the common Lewis acids studied as well as selected Bronsted acids. While there is a general trend toward parallel increases in acid strength toward the reference bases  $\text{F}^-$  and  $\text{Cl}^-$ , the scatter in the plot is seen to be extremely large. It is scatter such as this which has frustrated most efforts to develop quantitative scales of Lewis acid strength.

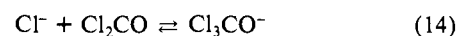
For purposes of discussion the  $\text{Cl}^-$  affinities will be treated as "normal" Lewis acidities for the species examined, and interpretation will be sought for the unusual order of  $\text{F}^-$  affinities. While this choice is arbitrary, it is justified by the practice of solution-phase chemists of treating  $\text{F}^-$  as an unusual nucleophile by virtue of its very small size and high electronegativity. In the plot of Figure 2, any compound to the "northwest" of another

represents a reversal in Lewis acidity order from  $\text{Cl}^-$  to  $\text{F}^-$ . Thus, for example, while  $\text{PF}_3$  has a greater  $\text{Cl}^-$  affinity than  $\text{OPF}_3$ , the  $\text{F}^-$  affinity of  $\text{OPF}_3$  is 8 kcal mol<sup>-1</sup> greater than that of  $\text{PF}_3$ .

The first general trend of note in Figure 2 is the fact that relative to the alcohol series of Bronsted acids, the Lewis acids have much greater fluoride affinities than the chloride affinities would initially indicate. This is very likely predominantly due to the fact that halide addition to Lewis acids results in strong covalent bond formation, and while the hydrogen bond energies of  $\text{F}^-$  and  $\text{Cl}^-$  to Bronsted acids differ by only 10–15 kcal mol<sup>-1</sup>, the covalent bond energies to B, C, Si, P, As, and S may differ by as much as 50 kcal mol<sup>-1</sup>.

Especially notable among the Bronsted acids is HCl with a much greater  $\text{F}^-$  affinity than its  $\text{Cl}^-$  affinity would predict. The interpretation in this case is the fact that  $\text{FHCl}^-$  produced by  $\text{F}^-$  addition to HCl will in actuality resemble a  $\text{Cl}^-$ -HF adduct; that is, a significant extent of proton transfer has occurred during adduct formation. Thus, the high  $\text{F}^-$  affinity of HCl is in fact due to the large gas-phase acidity difference between HF and HCl which, in turn, is largely a result of the significantly greater H-F relative to H-Cl covalent bond strength (33 kcal mol<sup>-1</sup>).

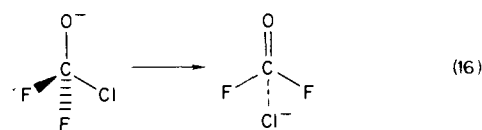
An interesting series of halide binding energies is that of the carbonyl halides. The chloride affinities of both  $\text{COF}_2$  and  $\text{COCl}_2$  have been directly measured to be 12.4 kcal mol<sup>-1</sup>, eq 13 and 14.



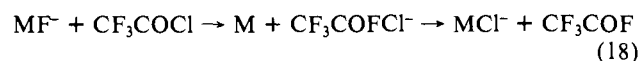
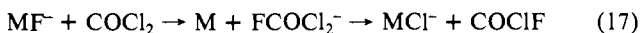
The anion resulting from  $\text{Cl}^-$  addition to  $\text{F}_2\text{CO}$  can also be prepared from  $\text{F}^-$  addition to carbonyl chlorofluoride,  $\text{COClF}$ , eq 15. If  $\Delta H_f^\circ(\text{COClF})$  is taken as 102 kcal mol<sup>-1</sup>, the average of that for  $\text{COCl}_2$  and  $\text{COF}_2$ ,<sup>45</sup> then the fluoride affinity of  $\text{COClF}$ ,  $-\Delta H_{15}^\circ$ , can be calculated to be 57.6 kcal mol<sup>-1</sup>. Taking the



chloride affinity of  $\text{COClF}$  to be 12.5 kcal mol<sup>-1</sup>, equal to that of  $\text{COF}_2$  and  $\text{COCl}_2$ , a point for  $\text{COClF}$  may then also be plotted in Figure 2 which can be seen to indicate an anomalously high fluoride affinity for  $\text{COClF}$ . This result provides some insight into the nature of binding of  $\text{F}^-$  and  $\text{Cl}^-$  to carbonyl compounds.  $\text{F}^-$  binds to the carbonyl group via a strong covalent bond whereas it seems likely that  $\text{Cl}^-$  is bound in a far more predominantly electrostatic fashion. Thus, when  $\text{F}^-$  is added to  $\text{COClF}$ , the resulting anion likely rearranges to a structure resembling an ion-dipole complex of  $\text{Cl}^-$  and  $\text{COF}_2$ , eq 16. Such a transfor-



mation will be driven by the  $\pi$ -bond formation of the carbonyl group and the exothermic electron transfer from O to Cl. This result can be seen to be directly analogous to that for HCl where  $\text{F}^-$  additions resulted in a significant rearrangement of the covalent bond structure and an anomalously high  $\text{F}^-$  affinity. This conjecture is supported by studies of  $\text{F}^-$  addition to  $\text{COCl}_2$  and  $\text{CF}_3\text{COCl}$ <sup>46</sup> which resulted in subsequent transfer of only  $\text{Cl}^-$ , eq 17 and 18. In neither case could reversible  $\text{F}^-$  transfer be obtained.



In addition in argon matrix isolation experiments using the salt-molecule technique, Ault's attempts<sup>24</sup> to prepare  $\text{COF}_2\text{Cl}^-$  from  $\text{CsF}$  and  $\text{COClF}$  resulted in some  $\text{COF}_2 + \text{CsCl}$  formation

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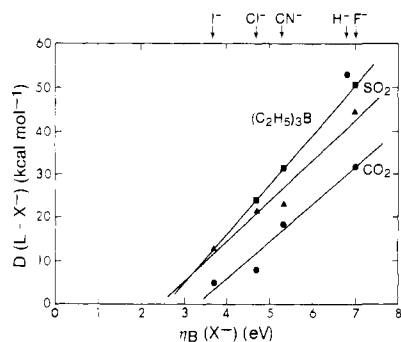


Figure 3. Variation of anionic binding energies as a function Lewis base hardness ( $\eta_B$ ) for the Lewis acids  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $(\text{C}_2\text{H}_5)_3\text{B}$ .

as well as an additional unidentified product.

**Hard and Soft Acid-Base Theory (HSAB).** Pearson<sup>4,47</sup> has proposed that acids and bases may be classified as either *hard* or *soft* to account for the wide variability of strength of binding in acid-base adducts. The formalism was adopted that hard acids bind most favorably to hard bases, principally by electrostatic interaction, while soft acids bind most favorably to soft bases, principally by covalent interaction. Hard bases are defined as those with small size, low polarizability, high negative charge density, and high  $\text{p}K_a$ . More recently, Parr and Pearson<sup>48</sup> have devised an absolute hardness scale based on eq 19 where  $\eta_B$  is the hardness of the base,  $I_B$  is the ionization potential of B, and  $E_B$  is the electron affinity of B. From data for a variety of species

$$\eta_B = \frac{1}{2}(I_B - E_B) \quad (19)$$

using this definition of hardness,  $\text{F}^-$  is seen to be the hardest common base ( $\eta_{\text{F}^-} = 7.0$ ) with  $\text{Cl}^-$  having an  $\eta$  value of 4.7, while still being defined qualitatively as a hard base.

For several of the Lewis acids examined in the present work, binding energy data are also available for  $\text{CN}^-$ ,<sup>74</sup>  $\text{I}^-$ ,<sup>50,51</sup> and, to a limited extent,  $\text{H}^-$ <sup>52</sup> adducts. These data and those in Tables I and II may be used to construct the plot of Lewis base hardness vs. anion binding energy for adducts of  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $(\text{C}_2\text{H}_5)_3\text{B}$  shown in Figure 3. The straight lines drawn represent least-squares fits to the data points for  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{CN}^-$ , and  $\text{I}^-$ . The points for the  $\text{H}^-$ - $\text{CO}_2$  adduct and  $\text{H}^-$ - $\text{SO}_2$  adduct (not shown) are omitted from the fit since the  $\text{H}^-$  binding energies appear to bear no relation to the assigned hardness value. Although there appears to be some predictive power associated with these hardness values for determining anion binding energies, it is important to note that an equally good, or better, correlation can be obtained between the anion binding energies,  $D(\text{L}-\text{X}^-)$ , and the gas-phase proton affinities of the anions,  $\text{X}^-$ . It is also noteworthy that a positive slope is obtained for the three Lewis acids in Figure 3 despite the fact that a wide range of base hardness values is used and despite the fact that the Lewis acids range from hard ( $\text{CO}_2$ ) to borderline soft acids ( $\text{SO}_2$ ,  $(\text{C}_2\text{H}_5)_3\text{B}$ ). It might have been expected that as acid hardness decreased, the slope of the line in Figure 3 would decrease or even become negative. From the limited data presented here, this is seen not to be the case. Future studies will center on Lewis base interactions with very soft acids to determine if this behavior is general.

It is of interest to examine the enthalpy changes associated with anion switching reactions for a number of Lewis acids, L, relative to a fixed reference acid such as  $\text{CO}_2$ , eq 20. Since  $\text{F}^-$  is known

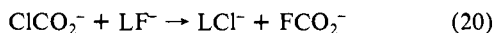


Table IV. Enthalpy Changes,  $\Delta H_{20}^\circ$ , for the Anion Switching Reaction  $\text{ClCO}_2^- + \text{LF}^- \rightleftharpoons \text{LCI}^- + \text{FCO}_2^-$

L	$\Delta H_{20}^\circ$	L	$\Delta H_{20}^\circ$
$\text{BF}_3$	25.6	$\text{CO}_2$	0
$\text{SiF}_4$	14.3	$\text{SO}_2$	-0.4
$\text{CH}_3\text{SiF}_3$	11.1	$\text{AsF}_3$	-0.9
$\text{B}(\text{OCH}_3)_3$	10.7	$\text{OsF}_2$	-3.0
$\text{OPF}_3$	10.7	$\text{CS}_2$	-3.7
$\text{OCF}_2$	6.8	$\text{HCN}$	-5.3
$\text{CF}_3\text{COF}$	5.6	$\text{HF}$	-6.5
$\text{B}(\text{C}_2\text{H}_5)_3$	3.9	$\text{CHF}_3$	-13.0
$(\text{CF}_3)_2\text{CO}$	3.5	$\text{H}_2\text{O}$	-14.4
$\text{PF}_3$	1.4		

Table V. Kroeger-Drago Parameters Used to Model Enthalpies of Lewis Acid Base Adduct Formation in Terms of Electrostatic ( $e$ ), Covalent ( $c$ ), and Electron-Transfer ( $t$ ) Contributions

	$e$	$c$	$t$
Bases			
$\text{F}^-$	6.154	34.768	1.108
$\text{Cl}^-$	5.111	2.730	17.508
$\text{I}^-$	4.517	-2.502	19.608
$\text{CN}^-$	5.420	2.585	18.949
$\text{H}^-$	5.334	-267.005	175.307
Acids			
$t\text{-C}_4\text{H}_9\text{OH}$	3.747	0.408	0.010
$\text{BF}_3$	2.000	1.668	0.914
$\text{SO}_2$	3.777	0.721	0.010
$\text{H}_2\text{O}$	1.649	0.372	0.196
$\text{CHCl}_3$	2.247	0.010	0.267
$\text{B}(\text{CH}_3)_3$	8.590	1.601	0.292

to be a harder base than  $\text{Cl}^-$ , the relative magnitudes of  $\Delta H_{20}^\circ$  should give a qualitative measure of the relative hardness of Lewis acids, L, with the hardest acids giving the most positive  $\Delta H_{20}^\circ$  values and the softest acids giving the lowest (most negative) values of  $\Delta H_{20}^\circ$ . Values of  $\Delta H_{20}^\circ$  for a number of Lewis acids are listed in Table IV in order of decreasing hardness according to this definition. Most of these results are in qualitatively satisfactory agreement with those hardness and softness classifications based on solution-phase data. For example, the hardest species are  $\text{BF}_3$  and  $\text{SiF}_4$ , which satisfy the qualitative criteria of hard acids of low polarizability, small size, high positive charge density at the acceptor site, and low electronegativity of the acceptor atom. Also among the hardest acids thus classified are other boron- and silicon-containing species as well as the series of carbonyl compounds. It is interesting to note that the order of Lewis acid strength of the carbonyl compounds, as measured by both  $\text{F}^-$  and  $\text{Cl}^-$  binding energies, is  $\text{CF}_2\text{O} > \text{CF}_3\text{COF} > (\text{CF}_3)_2\text{CO}$ . This result may be understood in terms of the lower polarizability of  $\text{CF}_2\text{O}$  and higher positive charge density at the carbon in  $\text{CF}_2\text{O}$  relative to the  $\text{CF}_3$  substituted analogues. Also understandable on a similar basis is the greater hardness of  $\text{PF}_3$  relative to  $\text{AsF}_3$  and of  $\text{CO}_2$  relative to  $\text{CS}_2$ . Some of the data, however, do not agree with the qualitative assignments of relative hardness and softness previously assigned to them on the basis of solution-phase data. For example,  $\text{CO}_2$  is seen to be comparable to  $\text{SO}_2$  in value for  $\Delta H_{20}^\circ$  whereas in solution  $\text{CO}_2$  is classified as a hard acid while  $\text{SO}_2$  is a borderline acid between hard and soft. In addition solution-phase data place  $\text{B}(\text{C}_2\text{H}_5)_3$  as a borderline acid whereas the present data place it harder than  $\text{CO}_2$ . All the hydrogen bonding acids listed in Table IV are indicated to be quite soft while previous assignments categorized them as hard.

These disagreements thus raise some question of the suitability of attempting to apply a HSAB interpretation to gas-phase ion-neutral interactions. In addition to the above inconsistencies, the usual interpretation of the nature of binding in HSAB theory is not in agreement with our gas-phase findings. For example, although hard acid-hard base interactions are supposed to be largely electrostatic in nature, our findings for  $\text{F}^-$  interactions with both supposedly hard and soft acids indicate substantial covalent binding, such as in  $\text{BF}_3$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{HF}$  adducts. In contrast,

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**Table VI.** Enthalpies of Lewis Acid–Base Adduct Formation ( $-\Delta H_{22}^\circ$ ) Calculated from the Kroeger–Drago Equation (Eq 22) and from Experiment<sup>a</sup>

acid	base				
	H <sup>-</sup>	F <sup>-</sup>	Cl <sup>-</sup>	CN <sup>-</sup>	I <sup>-</sup>
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH	-87	37.3 (33.3) <sup>b</sup>	20.4 (18.1) <sup>d</sup>	21.6 (19.2) <sup>c</sup>	16.1 (12.1) <sup>f</sup>
BF <sub>3</sub>	-274	71.3 (72) <sup>c</sup>	30.8 (26.0) <sup>c</sup>	32.5	22.7
SO <sub>2</sub>	-170 (>53)	48.3 (43.8) <sup>c</sup>	21.4 (20.9) <sup>c</sup>	22.5 (23.3) <sup>e</sup>	15.4 (12.9) <sup>g,h</sup>
H <sub>2</sub> O	-56 (~10)	23.3 (23.3) <sup>b</sup>	12.9 (14.4) <sup>d</sup>	13.6 (16.6) <sup>e</sup>	10.4 (10.1) <sup>f</sup>
CHCl <sub>3</sub>	56.2	14.5	16.2 (18.1) <sup>d</sup>	17.3	15.4 (14) <sup>h</sup>
(CH <sub>3</sub> ) <sub>3</sub> B	-330	108.9 (47.2) <sup>c</sup>	53.4 (~24) <sup>c</sup>	56.2 (~30) <sup>e</sup>	40.5

<sup>a</sup>All values in kcal mol<sup>-1</sup>. <sup>b</sup>Reference 40. <sup>c</sup>This work. <sup>d</sup>Reference 11. <sup>e</sup>Reference 74. <sup>f</sup>Reference 49. <sup>g</sup>Reference 31. <sup>h</sup>Reference 50.

for the softer bases, Cl<sup>-</sup> and I<sup>-</sup><sup>49,50</sup> indications are that binding to both hard and soft acids is predominantly electrostatic in nature.

A further point of departure between HSAB theory and gas-phase ion–molecule interaction energetics involves H<sup>-</sup>. In derivation of absolute hardness values, a hardness value for H<sup>-</sup> of 6.8 is obtained relative to a value for F<sup>-</sup> of 7.0. Pearson<sup>48</sup> chooses to treat H<sup>-</sup> as an exception to the derived values of  $\eta$  since solution-phase data always consider H<sup>-</sup> to be a very soft base. The soft nature of H<sup>-</sup> is intuitively puzzling, however, since it has small size, exceedingly low polarizability, and very high negative charge density. The limited gas-phase data available for H<sup>-</sup> indicate that it should in fact be considered to be harder than F<sup>-</sup>. For example, the binding energy of H<sup>-</sup> to CO<sub>2</sub> is known to be 53 kcal mol<sup>-1</sup>,<sup>51</sup> more than 20 kcal mol<sup>-1</sup> greater than the F<sup>-</sup>–CO<sub>2</sub> interaction energy. In addition, ion cyclotron resonance experiments establish that H<sup>-</sup> is bound even more strongly to SO<sub>2</sub><sup>52</sup> and to (CF<sub>3</sub>)<sub>2</sub>CO<sup>53</sup> and that it is able to hydrogen bond to binary hydrides, producing species such as H<sub>3</sub>O<sup>+</sup> and NH<sub>4</sub><sup>+</sup>. It therefore seems reasonable to treat H<sup>-</sup> in the gas phase as a hard base.

A good deal of the disagreement of reactivity trends for anions between the gas phase and solution is likely due to varying extents of solvation of the anions. It is hoped that in the future we will be able to obtain sufficient data for interactions with very soft acids and to subsequently assess more thoroughly the suitability of gas-phase scales of hardness and softness.

**Quantitative Binding Energy Predictions.** Many attempts have been made to obtain quantitative relationships between strength of binding in a Lewis acid–base adduct and some intrinsic properties of the acid and base. Among the earliest, and perhaps most insightful from the point of view of gas-phase interaction energetics, was that due to Drago,<sup>54</sup> eq 21, where  $\Delta H_{21}^\circ$  represents the binding energy of an acid, A, to a base, B, and  $e$  and  $c$  represent the ability of the species to participate in electrostatic and covalent bonding, respectively. More recently this equation has been

$$-\Delta H_{21}^\circ = e_A e_B + c_A c_B \quad (21)$$

expanded by Kroeger and Drago<sup>55</sup> to include a contribution,  $t$ , to account for the tendency to undergo electron transfer upon adduct formation, eq 22. On the basis of available data, these

$$-\Delta H_{22}^\circ = e_A e_B + c_A c_B + t_A t_B \quad (22)$$

authors have assigned values of  $e$ ,  $c$ , and  $t$  to a number of Lewis acids and bases. The values assigned are summarized in Table V and have been used to calculate the energies of binding summarized in Table VI. Also included in Table VI, where available, are the experimental binding energies. For the comparison of predicted and experimental values, it can be seen that for F<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup>, and CN<sup>-</sup>, very good agreement is obtained for BF<sub>3</sub>, SO<sub>2</sub>, and hydrogen bonding acids H<sub>2</sub>O, *t*-C<sub>4</sub>H<sub>9</sub>OH, and CHCl<sub>3</sub>. The agreement for B(CH<sub>3</sub>)<sub>3</sub> is very poor with the predicted values exceeding experimental by more than a factor of 2. However, while the  $e$ ,  $c$ , and  $t$  parameters for most acids were assigned on the basis of known gas-phase ion–neutral interaction energies, those for B(CH<sub>3</sub>)<sub>3</sub> were assigned on the basis of poorly defined neu-

tral–neutral interaction energies. Thus on the basis of new gas-phase ion–molecule data, a reassignment of  $e$ ,  $c$ , and  $t$  parameters for B(CH<sub>3</sub>)<sub>3</sub> would likely be in order.

In most serious disagreement with experimental results are the data for H<sup>-</sup> binding. The predictions suggest that no adducts of H<sup>-</sup>, with the exception of that with CHCl<sub>3</sub>, will be bound. This is obviously incorrect since gas-phase ion–molecule reactions place the H<sup>-</sup>–SO<sub>2</sub> binding energy at greater than 51 kcal mol<sup>-1</sup>,<sup>52</sup> and H<sup>-</sup>–H<sub>2</sub>O<sup>56–59</sup> is known to be bound by roughly 10 kcal mol<sup>-1</sup>. There is also good reason to expect that H<sup>-</sup> will be very strongly bound to BF<sub>3</sub> and B(CH<sub>3</sub>)<sub>3</sub> and by analogy to H<sub>2</sub>O; H<sup>-</sup> should be bound to *t*-C<sub>4</sub>H<sub>9</sub>OH by greater than 10 kcal mol<sup>-1</sup>. Examination of the  $e$ ,  $c$ , and  $t$  parameters reveals that the negative binding energies for H<sup>-</sup> are due to the large negative  $c_H$  factor, indicating that H<sup>-</sup> has no tendency to undergo covalent bonding. This is known definitely not to be the case in gas-phase ion–molecule interactions particularly for species such as HCO<sub>2</sub><sup>-</sup> and HSO<sub>2</sub><sup>-</sup>. A reassignment of  $e$ ,  $c$ , and  $t$  parameters for H<sup>-</sup>, therefore, definitely seems appropriate.

An examination of the relative magnitudes of  $e$ ,  $c$ , and  $t$  parameters for the Lewis bases in Table IV reveals trends that are difficult to rationalize on the basis of gas-phase data. All of the  $e$  values seem reasonable (with the possible exception of that for H<sup>-</sup>) with a slight decrease in  $e$  as anionic size increases. The decreasing values of  $c$  with F<sup>-</sup> > Cl<sup>-</sup> > CN<sup>-</sup> are also reasonable; however, negative values of  $c$  for I<sup>-</sup> and H<sup>-</sup> seem completely unjustified. Lastly the order of the values of  $t$  is completely reversed (with the exception of that for H<sup>-</sup>) from that expected. Species with the greatest electron affinity would be expected to exhibit the least tendency to transfer electron density. Thus, the very low value of  $t_F$  seems inconsistent with much greater values of  $t$  for Cl<sup>-</sup>, I<sup>-</sup>, and CN<sup>-</sup> which have comparable electron affinity values.

Studies of binding energies of many anions with Lewis acids are continuing with the eventual aim of a rational equation to model Lewis acid–base interactions.

**Lattice Energies of Salts of Complex Anions and Catalytic Activity of MF Salts.** Many of the fluoride adducts, AF<sup>-</sup>, of species investigated here with fluoride affinities greater than 40 kcal mol<sup>-1</sup> have been synthesized by addition of acids, A, to alkali or tetraalkylammonium fluoride salts, MF. The enthalpy change for this process,  $\Delta H_{23}^\circ$ , is given by eq 24 where  $\Delta U$  is the difference



in crystal lattice energies of MAF and MF ( $U_{\text{MF}} - U_{\text{MAF}}$ ) and  $\Delta H_7^\circ$  is the enthalpy change for fluoride addition to gaseous A.

$$\Delta H_{23}^\circ = \Delta U = \Delta H_7^\circ \quad (24)$$

Experimentally determined values for  $\Delta H_{23}^\circ$  and the values of  $\Delta H_7^\circ$  determined in the present work may then be used to calculate  $\Delta U$ , and from the known crystal lattice energies of MF salts, the crystal lattice energy of the MAF salts can be calculated. These latter data can in turn be used to calculate the effective

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**Table VII.** Lattice Energies of MAF Salts and Effective Radii of AF<sup>-</sup> Ions Derived from Experimental Determinations of  $\Delta H_{23}^\circ$  and  $\Delta H_7^\circ$ <sup>a</sup>

M <sup>+</sup>	AF <sup>-</sup>	$-\Delta H_{23}^\circ$	$-\Delta H_7^\circ$ <sup>l</sup>	$\Delta U$	$U_{MF}$	$U_{MAF}$	$r_{AF^-}$ , Å
Cs <sup>+</sup>	SF <sub>5</sub> <sup>-</sup>	11 <sup>b,e</sup>	44	33	167	124	2.2
(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	SF <sub>5</sub> <sup>-</sup>	12 <sup>c,f</sup>	44	32			
K <sup>+</sup>	SO <sub>2</sub> F <sup>-</sup>	18 <sup>g</sup>	44	26	186	160	1.8
K <sup>+</sup>	AsF <sub>4</sub> <sup>-</sup>	15 <sup>b,h</sup>	48	33	186	153	2.1
Cs <sup>+</sup>	AsF <sub>4</sub> <sup>-</sup>	16 <sup>b,h</sup>	48	32	167	135	2.2
K <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	40 <sup>d,i</sup>	71	31	186	155	2.0
Cs <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	47 <sup>d,i</sup>	73	26	167	141	2.0
K <sup>+</sup>	SO <sub>3</sub> F <sup>-</sup>	48 <sup>d,j</sup>	78	30	186	156	2.0
K <sup>+</sup>	PF <sub>6</sub> <sup>-</sup>	41 <sup>c,k</sup>	84	43	186	143	2.3
Cs <sup>+</sup>	PF <sub>6</sub> <sup>-</sup>	50 <sup>c,k</sup>	86	36	167	141	2.3

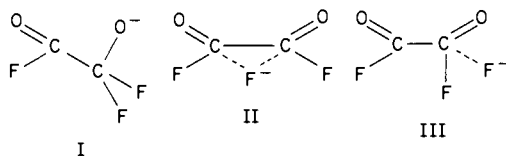
<sup>a</sup>All values in kcal mol<sup>-1</sup> unless otherwise indicated. <sup>b</sup>Estimated from decomposition pressure and  $\Delta S_{23}^\circ = -35$  cal mol<sup>-1</sup> K<sup>-1</sup>. <sup>c</sup>Calculated from  $\ln f$  vs.  $1/T$  data. <sup>d</sup>Calorimetric determination. <sup>e</sup>Reference 67. <sup>f</sup>Reference 68. <sup>g</sup>Reference 69. <sup>h</sup>Reference 70. <sup>i</sup>Reference 71. <sup>j</sup>Reference 72. <sup>k</sup>Reference 73. <sup>l</sup>This work.

radii of the AF<sup>-</sup> anions from Kapustinskii's equation (eq 25),<sup>58</sup> where  $z_1$  and  $z_2$  are both unity (the charge of the ions) and  $r$  corresponds to the effective ionic radius. Experimental values

$$U = \frac{n287z_1z_2}{r_{M^+} + r_{AF^-}} \left( 1 - \frac{0.347}{r_{M^+} + r_{AF^-}} \right) \quad (25)$$

of  $-\Delta H_{23}^\circ$ ,  $-\Delta H_7^\circ$ , known crystal lattice energies of the MF salts and consequently derived values for  $\Delta U$ , the crystal lattice energy of MAF salts, and the effective radii of AF<sup>-</sup> are all summarized in Table VII. In the cases of SO<sub>3</sub> and PF<sub>5</sub> where no accurate value of  $\Delta H_7^\circ$  was obtained in the present work, values of  $r_{AF^-}$  were estimated at 2.0 and 2.3 Å, respectively, and used to calculate  $\Delta U$  and subsequently  $\Delta H_7^\circ$  values, the fluoride affinity.

Many of the anions studied here such as OPF<sub>4</sub><sup>-</sup>, PF<sub>4</sub><sup>-</sup>, OSF<sub>3</sub><sup>-</sup>, SO<sub>2</sub>F<sub>3</sub><sup>-</sup>, FCO<sub>2</sub><sup>-</sup>, and CF<sub>3</sub>CFN<sup>-</sup> have not been observed as crystalline salts. Rough lattice energy estimates indicate that alkali cation salts of these species should be formed exothermically via eq 23, particularly if large cations such as Cs<sup>+</sup> are used. Attempted synthesis of OPF<sub>4</sub><sup>-</sup> and PF<sub>4</sub><sup>-</sup> salts has led to disproportionation reactions, however.<sup>7</sup> It is noteworthy that the matrix isolation technique of Ault<sup>24</sup> where crystal lattice energy difference problems are avoided has resulted in the successful synthesis of FCO<sub>2</sub><sup>-</sup> and should prove valuable to obtain other complex anions. The fluoride adduct of oxalyl fluoride might be of particular interest since three feasible structures (I–III) are possible.



Spectroscopic detection of the F<sup>-</sup>(FCOCOF) anion in argon matrices could lead to a definitive structural proof for this anion.

In addition to being synthetically and structurally interesting the complex fluoro and chloro anions studied here are of potential interest as intermediates in reactions in which alkali halides are used as catalytic agents.<sup>60–63</sup> For example, eq 26–28 are reactions catalyzed by CsF or NaF<sup>59,64–69</sup> in which the fluoride adducts are proposed as intermediates in the reactions.

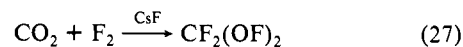
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The anion affinities determined in the present work provide many examples of further reagents which might undergo novel reactions catalyzed by fluoride and chloride salts.<sup>65</sup>

### Conclusion

A general method has been presented whereby fluoride and chloride adducts of main group compounds may be readily generated by bimolecular gas-phase ion–molecule reactions. When ion cyclotron resonance halide-exchange equilibria measurements have been used, accurate absolute binding energies of F<sup>-</sup> and Cl<sup>-</sup> to a variety of oxide, oxofluoride, fluoride, and alkyl derivatives of boron, carbon, silicon, phosphorus, arsenic, and sulfur have been obtained. These data define scales of Lewis acidity of these compounds toward the reference Lewis bases F<sup>-</sup> and Cl<sup>-</sup>, revealing no strong correlation of Lewis acid strength toward these two bases. The data also reveal that no strong motivation exists for the definition of absolute scales of hardness and softness for gas-phase ion–molecule interactions. The multiparameter approach of Kroeger and Drago for prediction of interaction energetics has been shown to be useful for the binding energies of halides and CN<sup>-</sup> toward a number of Lewis and Bronsted acids, however, the interaction of H<sup>-</sup> is not yet well modeled nor are the interactions of any anions toward organoboranes. New thermochemical data for complex anions have been shown to be useful for calculation of crystal lattice energies of salts of these anions, and new synthetic routes and potential catalytic agents are suggested.

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**Registry No.** B(Et)<sub>3</sub>, 97-94-9; SiMe<sub>3</sub>, 373-74-0; CF<sub>3</sub>COCF<sub>3</sub>, 684-16-2; AsF<sub>3</sub>, 7784-35-2; PF<sub>3</sub>O, 13478-20-1; BMe<sub>3</sub>, 593-90-8; CF<sub>3</sub>CF<sub>2</sub>COF, 422-61-7; CF<sub>3</sub>COF, 354-34-7; CFCFO, 359-40-0; SO<sub>2</sub>, 7446-09-5; SF<sub>4</sub>, 7783-60-0; COF<sub>2</sub>, 353-50-4; PF<sub>3</sub>, 7783-55-3; SiMe<sub>2</sub>F, 420-56-4; SOF<sub>2</sub>, 7783-42-8; SO<sub>2</sub>F<sub>2</sub>, 2699-79-8; *t*-BuOH, 75-65-0; COS, 463-58-1; CO<sub>2</sub>, 124-38-9; CS<sub>2</sub>, 75-15-0; SiMe<sub>4</sub>, 75-76-3; CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CN, 375-00-8; CF<sub>3</sub>CF<sub>2</sub>CN, 422-04-8; MeOH, 67-56-1; CF<sub>3</sub>CN, 353-85-5; BF<sub>3</sub>, 7637-07-2; SiCl<sub>4</sub>, 10026-04-7; SiF<sub>4</sub>, 7783-61-1; CF<sub>3</sub>COCl, 354-32-5; CHF<sub>3</sub>, 75-46-7; MeOCOCl, 79-22-1; COCl<sub>2</sub>, 75-44-5; MeCl, 74-87-3; PF<sub>5</sub>, 7647-19-0; SO<sub>3</sub>, 7446-11-9; CH<sub>3</sub>OBf<sub>2</sub>, 381-59-9; (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>BF, 367-45-3; (CH<sub>3</sub>O)<sub>2</sub>BF, 367-46-4; (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>B, 150-46-9; (CH<sub>3</sub>O)<sub>3</sub>B, 121-43-7; CF<sub>3</sub>NO, 334-99-6; Cs<sup>+</sup>SF<sub>5</sub><sup>-</sup>, 52653-08-4; (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>SF<sub>5</sub><sup>-</sup>, 94295-12-2; K<sup>+</sup>SO<sub>2</sub>F<sup>-</sup>, 94295-08-6; K<sup>+</sup>AsF<sub>4</sub><sup>-</sup>, 28174-28-9; Cs<sup>+</sup>AsF<sub>4</sub><sup>-</sup>, 76759-36-9; K<sup>+</sup>BF<sub>4</sub><sup>-</sup>, 14075-53-7; Cs<sup>+</sup>BF<sub>4</sub><sup>-</sup>, 18909-69-8; K<sup>+</sup>SO<sub>3</sub>F<sup>-</sup>, 94295-09-7; K<sup>+</sup>PF<sub>6</sub><sup>-</sup>, 17084-13-8; Cs<sup>+</sup>PF<sub>6</sub><sup>-</sup>, 16893-41-7; AsF<sub>4</sub><sup>-</sup>, 42847-14-3; OPF<sub>4</sub><sup>-</sup>, 36580-97-9; SO<sub>2</sub>F<sup>-</sup>, 22539-11-3; SF<sub>5</sub><sup>-</sup>, 31140-82-6; CF<sub>3</sub>O<sup>-</sup>, 57178-38-8; PF<sub>4</sub><sup>-</sup>, 25443-47-4; OSF<sub>3</sub><sup>-</sup>, 94295-11-1; FCO<sub>2</sub><sup>-</sup>, 67228-77-7; B(Et)<sub>3</sub>F<sup>-</sup>, 63599-31-5; BMe<sub>3</sub>F<sup>-</sup>, 63599-30-4; COSF<sup>-</sup>, 94295-05-3; CS<sub>2</sub>F<sup>-</sup>, 94295-06-4; SiMe<sub>4</sub>F<sup>-</sup>, 51108-61-3; BF<sub>3</sub>Cl<sup>-</sup>, 36503-32-9; SiCl<sub>5</sub><sup>-</sup>, 22795-18-2; SiF<sub>4</sub>Cl<sup>-</sup>, 94347-09-8; COCl<sub>3</sub><sup>-</sup>, 94295-07-5; CH<sub>3</sub>SiF<sub>4</sub><sup>-</sup>, 44244-53-3; B(OCH<sub>3</sub>)<sub>3</sub>F<sup>-</sup>, 76791-10-1; (CF<sub>3</sub>)<sub>2</sub>COF<sup>-</sup>, 44967-50-2; HCNF<sup>-</sup>, 94347-83-8; HF<sub>2</sub><sup>-</sup>, 18130-74-0; CF<sub>3</sub>COF<sub>2</sub><sup>-</sup>, 94295-10-0; Cl<sup>-</sup>, 16887-00-6; F<sup>-</sup>, 16984-48-8.

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