Strong Hydrogen Bonding in Gas-Phase Anions. An Ion Cyclotron Resonance Determination of Fluoride Binding Energetics to Brønsted Acids from Gas-Phase Fluoride Exchange Equilibria Measurements

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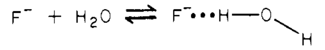
Abstract: Ion cyclotron resonance fluoride-transfer equilibrium measurements have been carried out with a wide range of Brønsted acids and accurate binding energies of F^- to these species obtained. For a homologous series of compounds such as aliphatic alcohols, a linear correlation between fluoride binding energies and gas-phase acidity is obtained. For diverse functional groups, the correlation between acidity and fluoride affinity breaks down. Hydrogen-bond energies to fluoride for all species studied with a known gas-phase acidity have been obtained to reveal that, as previously predicted, FHF^- has the strongest known hydrogen bond. The value determined for $D(F^-–HF)$ of 39 ± 1 kcal mol^{-1} is in good agreement with early predictions based on lattice-energy estimates and with ab initio calculations carried out by Noble and Kortzeborn. Also notable is the hydrogen-bond strength of 21.1 kcal mol^{-1} in $FHCN^-$, a species only recently observed by Ault.

Determinations of gas-phase acidities over the past decade using techniques such as high-pressure mass spectrometry (HPMS),[2-5] flowing afterglow (FA),[6,7] and ion cyclotron resonance spectroscopy (ICR)[8,9] have provided a wealth of information on the intrinsic stabilities of gas-phase anions. Frequently the relative order of stability of various acid functional groups in the gas phase is very different from that observed in solution from either equilibrium or kinetic acidity determinations. The reasons for such differences may be largely understood by considering the effects due to ion–solvent and ion-pair interactions that occur in the transfer of ions from the gas phase to solution. Briefly, anions derived from different functional groups will exhibit vastly different charge delocalization and, as a result, will have very different magnitudes of interaction with either solvent molecules or counterions. Since such interactions usually play a dominant role in the determination of solution-phase acidities, differences in gas-phase and solution-phase acidities are not unexpected. Thus, factors such as extensive resonance charge delocalization that are acid strengthening in the gas phase can frequently bring about acid weakening in solution due to more unfavorable solvation.

In order to understand the transition from the gas-phase behavior of ions to the solution-phase behavior of ions, it is of considerable interest to examine the intermediate situation of a partially solvated gas-phase ion. A number of investigations of the thermochemistry and mechanisms of reaction of such partially solvated ions have recently been carried out by several investigators. The available thermochemical data is however more extensive for positive-ion systems such as partially solvated oxonium[10-16] or ammonium ions.[17-22] For negative ions the data of Kerbarle on the interactions of halide,[23-25] hydroxide,[26] and cyanide ions[27] with hyrogen-bonding molecules is the most extensive and systematic to date.

Because of its small size and high electronegativity, the fluoride ion is expected to interact very strongly with potentially hydrogen-bonding molecules. This expectation is borne out by the fact that relatively few studies of clustering energetics of F^- have been carried out since the large binding energies entailed would demand high temperatures for observation of equilibrium under normal-pressure conditions of the HPMS experiment.[23] The only quantitative determinations of absolute fluoride binding energies to date have been those for H_2O[25] (eq 1) and CH_3CN[27] (eq 2).


(1)

$$F^- + CH_3CN \rightleftharpoons [FCH_3CN]^- \qquad (2)$$

In addition to these absolute measurements from HPMS clustering equilibria studies, the relative fluoride binding energies of acetic and propionic acids have been determined from bimolecular fluoride exchange equilibria[28] (eq 3). Due to the paucity of

$$CH_3CO_2HF^- + C_2H_5CO_2H \rightleftharpoons C_2H_5CO_2HF^- + CH_3CO_2H \qquad (3)$$

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accurate absolute fluoride binding data and in view of the importance of such data in understanding the solvation process, we have undertaken the present study of fluoride binding energetics using techniques developed in this laboratory[29] and elsewhere[30] for the bimolecular generation of fluoride adducts. For the Brønsted acids employed in the present study, adducts with fluoride lead to production of species that may be regarded as hydrogen bonded, and the hydrogen-bond strengths of such species are generally in excess of 20 kcal mol^{-1}. Such hydrogen-bond strengths are typical of the class of hydrogen bonds known either as "strong" or "very strong" hydrogen bonds. The strongest possible hydrogen-bonded species has usually been postulated to be the bifluoride ion,[31] FHF^-, with estimates for the hydrogen-bond strength, (eq 4), ranging from 30 kcal mol^{-1} [23] to 62 kcal mol^{-1}.[32]

$$F^- + HF \rightleftharpoons FHF^- \qquad (4)$$

Recent ab initio calculations, however, have suggested that the hydrogen-bond strength in adducts of F^- and strong acids may possess a stronger hydrogen bond.[33] Thus it was of particular interest in our study to determine the fluoride affinity of HF and to relate the fluoride affinities of this and other species to the hydrogen-bond strengths and so determine a scale of hydrogen-bond energies.

Experimental Section

All experiments were conducted at ambient temperature with an ICR spectrometer of basic Varian V-5900 design extensively modified to permit ion-trapping experiments.[34] Details of the design and operation of the trapped-ion ICR technique and conventional ICR single- and double-resonance experiments have been described in detail previously.[35,36]

All liquid samples were commercial products of highest purity obtainable. Methyl mercaptan, hydrogen sulfide, sulfur dioxide, sulfur tetrafluoride, sulfuryl fluoride, fluoroform, and hydrogen fluoride were obtained from Matheson of Canada Ltd. Carbonyl fluoride, phosphorus trifluoride, sulfur oxyfluoride, tetrafluorodimethyl ether, pentafluoroethane, 1,1,1-trifluoroethylamine, 1,1,2-trifluoroethane, trifluoroethylene, and *tert*-butyl fluoride were obtained from P.C.R. Inc. Nitrogen trifluoride was purchased from Air Products and Chemicals Inc. Hydrogen cyanide was synthesized by condensing gaseous HCl into a concentrated aqueous solution of KCN. The resulting gaseous sample contained traces of water but no other impurities. Ketene was synthesized with a homemade ketene generator by the pyrolysis of acetone vapor on a heated Nichrome filament.

All samples were degassed by several freeze–pump–thaw cycles before use.

The Monel inlet system used for HF experiments was conditioned for several days with HF before use. No impurities were detected in the HF samples used.

A typical fluoride transfer equilibrium experiment for compounds with a greater fluoride affinity than methanol involved preparation of a 6:1 mixture of methyl formate and NF_3. This mixture was admitted to the ICR cell region through a high-vacuum leak valve to a pressure of approximately 2×10^{-6} torr. Dissociative electron capture by NF_3 produced F^- which subsequently reacts via the carbon monoxide elimination reaction (eq 5), previously reported by Riveros,[30] to yield an adduct of F^-

$$F^- + HCO_2CH_3 \rightarrow F^-\cdots HOCH_3 + CO \qquad (5)$$

with methanol. A mixture of the two potential fluoride acceptor molecules, prepared with accurately known partial pressure ratios by using a Validyne AP-10 absolute pressure gauge on a Monel vacuum line was then leaked into the ICR cell region through a second leak valve to a pressure of 2×10^{-6} to 4×10^{-6} torr. In the case of less volatile compounds or highly reactive compounds such as HF, the single component was admitted through one leak valve with the appropriate accurately prepared ternary mixture being admitted through the other. In such experiments, pressure ratios of fluoride acceptors were determined from ion gauge current readings calibrated against an MKS Instruments Model 170 M Baratron capacitance manometer.

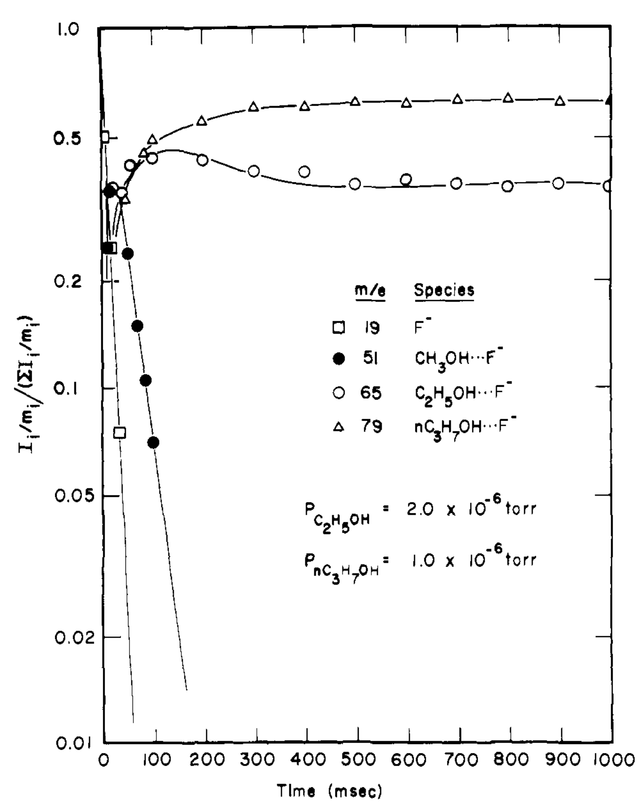


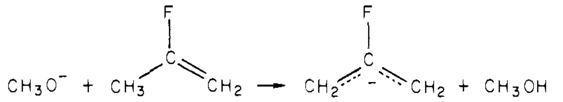
Figure 1. Variation of relative ionic abundances with time in a 1:6:5:10 mixture of $NF_3/HCO_2CH_3/n\text{-}C_3H_7OH/C_2H_5OH$ at a total pressure of 4.4×10^{-6} torr following a 5-ms, 70-eV electron beam pulse.

At the pressures typically used, $CH_3OH\cdots F^-$ produced in reaction 5 will have reacted completely via F^- transfer to the fluoride acceptors within 100 ms. Equilibrium fluoride transfer between the two Brønsted acids under study was usually then reached within the next 200–500 ms, and relative ionic abundances were monitored for at least twice the length of time needed for steady state to be established. A typical experiment is shown in Figure 1 for fluoride transfer equilibrium between ethanol and propanol (eq 6). Equilibrium constants were then calculated from

$$C_2H_5OH\cdots F^- + n\text{-}C_3H_7OH \rightleftharpoons n\text{-}C_3H_7OH\cdots F^- + C_2H_5OH \qquad (6)$$

the experimentally observed steady-state ionic abundances and the manometrically determined neutral pressure ratios.

For species of lower fluoride binding energy than methanol, fluoride ion adducts were generated from ion-molecule reactions in methyl nitrite–2-fluoropropene mixtures.[29] Methoxide ion, CH_3O^-, generated by dissociative electron impact in CH_3ONO, reacts with 2-fluoropropene to generate the 2-fluoroallyl anion (eq 7). This anion may be also formally

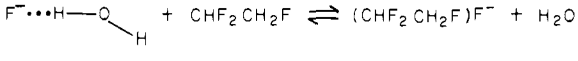


$$CH_3O^- + CH_3C(F)=CH_2 \rightarrow CH_2\cdots C(F)\cdots CH_2^- + CH_3OH \qquad (7)$$

regarded as the Lewis acid–base adduct of allene. From the previously determined gas-phase acidity of 2-fluoropropene,[29] a fluoride binding energy of 15 kcal mol^{-1} may be inferred for allene. Thus compounds with a fluoride affinity greater than this may be generated by simple fluoride transfer (eq 8). A typical experiment is shown in Figure 2 for fluoride

$$C_3H_4F^- + AH \rightarrow AH\cdots F^- + CH_2{=}C{=}CH_2 \qquad (8)$$

transfer in water-1,1,2-trifluoroethane mixtures (eq 9). Note that in the



$$F^-\cdots H-O(H) + CHF_2CH_2F \rightleftharpoons (CHF_2CH_2F)F^- + H_2O \qquad (9)$$

figure shown, equilibrium has not yet been attained. Relative pressures

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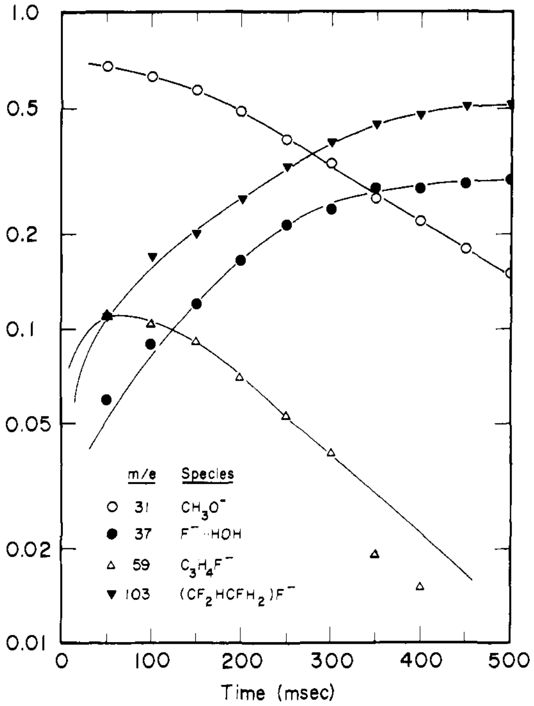
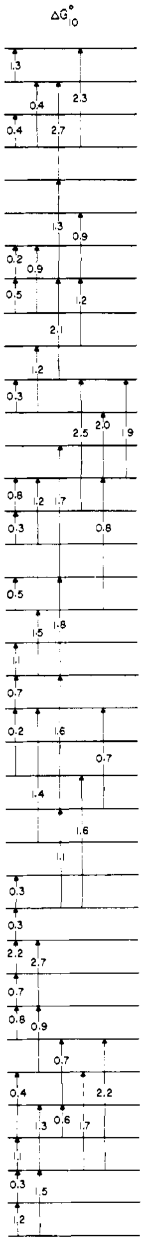


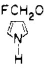
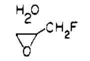
Figure 2. Variation of relative ionic abundances with time in a 1:10:6:7 mixtue of $CH_3ONO/CH_3CFCH_2/CF_2HCFH_2/H_2O$ at a total pressure of 1.2×10^{-6} torr following a 5-ms, 70-eV electron beam pulse.

of the fluoride-donating reagents and Brønsted acids and total pressures are similar to those described above for acids binding F^- more strongly than methanol.

Although attainment of a persistent steady state was taken to be the initial indication that thermochemical equilibrium had been established, this condition was also verified by a number of other methods. (i) The ratio of pressures of the fluoride acceptor molecules was varied over as large a range as practicable. Confirmation of equilibrium was taken to be an equilibrium constant invariant with changes in neutral pressures. (ii) Multiple overlap experiments were carried out so that the free energy difference in fluoride attachment of any two compounds could be verified by at least two independent routes. (iii) Double-resonance experiments were done at long reaction times to verify the occurrence of reaction in both forward and reverse directions. (iv) In many cases, ion ejection experiments at long reaction times were carried out to determine the equilibrium constant from the ratio of forward and reverse rate constants: $K_{eq} = k_f/k_r$.[28,37] This technique is illustrated in Figure 3 for fluoride transfer equilibrium in HF–HCN mixtures.

Table I, Standard Free Energies and Enthalpies of Binding of Fluoride Ion to Brønsted and Selected Lewis Acids[a]



Compound	$-\Delta G°_{11}$	$-\Delta S°_{11}$	$-\Delta H°_{11}$	$D(A-F^-)$	$\Delta H°_{acid}$
HCO_2H	20.0	6.8	20.0	45.3	345.2
SO_2	18.8	5.6	20.5	43.8	
CH_3CO_2H	18.4	8.2	20.8	44.1	348.5
SF_4	18.1	8.2	20.5	43.8	
COF_2	15.8	11.6	19.3	42.6	
ϕOH	15.4	8.9	18.1	41.3	349.8
HCN	14.8	4.8	16.2	39.5	353.1
PF_3	14.5	8.1	16.9	40.2	
HF	13.9	4.5	15.2	38.5	371.5
CF_3CH_2OH	13.0	9.4	15.8	39.1	364.4
SOF_2	12.1	6.7	14.1	37.4	
$(CH_2F)_2CHOH$	11.8	9.1	14.5	37.8	364.9
H_2S	10.9	1.3	11.3	34.6	353.4
$(CHF_2)_2O$	9.8	9.8	12.7	36.0	
SO_2F_2	9.5	10.1	12.5	35.8	
CH_2CO	9.3	9.1	12.0	35.3	
CH_3SH	9.2	5.85	10.9	34.2	359.0
CH_2FCH_2OH	8.9	8.8	11.5	34.8	371.0
	8.5	8.1	10.9	34.2	360.7
$t\text{-}C_4H_9OH$	7.4	8.7	10.0	33.3	373.3
$n\text{-}C_3H_7OH$	6.6	8.0	9.0	32.3	374.7
$i\text{-}C_3H_7OH$	6.6	8.2	9.0	32.3	374.1
$n\text{-}C_4H_9OH$	6.4	8.5	8.9	32.2	374.0
C_2H_5OH	6.0	7.5	8.2	31.5	376.1
ϕNH_2	5.3	8.8	7.9	31.2	367.1
C_2F_5CN	5.2	5.4	6.8	30.1	
CH_3OH	4.7	5.2	6.3	29.6	379.2
C_2F_5H	4.4	9.2	7.1	30.4	372.6
$CF_3CH_2NH_2$	2.2	8.6	4.8	28.1	
CF_3H	1.5	7.7	3.8	27.1	375.6
CF_2HCH_2F	0.7	8.5	3.2	26.5	37.2
C_2F_3H	0.6	8.2	3.0	26.3	37.2
H_2O	0.0	0.0	0.0	23.3	390.7
	0.3	6.3	2.2	25.5	
$(CH_3)_3CCHO$	-1.3	8.8	1.3	24.6	38.5
ϕCH_2F	-1.6	9.2	1.1	24.4	37.7
$t\text{-}C_4H_9F$	-2.8	6.2	-1.0	22.3	

[a] All values in kcal mol^{-1}.

Results

Standard free energy changes, $\Delta G_{10}°$, for each of the fluoride exchange equilibria examined are summarized in Table I. These

$$AF^- + B \rightleftharpoons BF^- + A \qquad (10)$$

data thus provide a quantitative relative scale of free energies of binding from Brøsted acids less acidic than water to those of acidity in the vicinity of formic acid. In order to provide a quantitative assessment of the free energies of binding of fluoride to each of the compounds in Table I, we also included the free energy changes for fluoride attachment relative to that of water, $-\Delta G_{11}°$. The absolute value of free energy of binding of fluoride

$$F^-\cdots H{-}O{-}H + A \rightleftharpoons AF^- + H_2O \qquad (11)$$

to each of the compounds, $\Delta G_{12}°$, may thus be obtained by adding

$$A + F^- \rightleftharpoons AF^- \qquad (12)$$

the value of $\Delta G_{11}°$ to the known free energy of binding of fluoride to water, $\Delta G_1°$. Entropy changes, $\Delta S_{11}°$, have also been calculated from statistical thermodynamic considerations of the translational and rotational contributions to the overall entropy change. The translational component of $\Delta S_{11}°$ may be readily determined from eq 13. Rotational contributions to the overall entropy change

$$\Delta S_{11}°(\text{trans}) = \frac{3}{2}R \ln \left(\frac{m_{H_2O}m_{AF^-}}{m_{H_2OF^-}m_A} \right) \qquad (13)$$

were calculated from eq 14, where $[I_AI_BI_C]$ is the product of the three principle moments of inertia of the species involved and σ

$$\Delta S_{11}°(\text{rot}) = \frac{1}{2}R \ln \left(\frac{[I_AI_BI_C]_{H_2O}[I_AI_BI_C]_{AF^-}}{[I_AI_BI_C]_{F^-H_2O}[I_AI_BI_C]_A} \right) + R \ln \left(\frac{\sigma_{F^-H_2O}\sigma_A}{\sigma_{H_2O}\sigma_{AF^-}} \right) \qquad (14)$$

are the rotational symmetry numbers. Geometries used to calculate moments of inertia of the neutral molecules were all well-known. For water,[38,39] alcohol,[40] and carboxylic acid, fluoride

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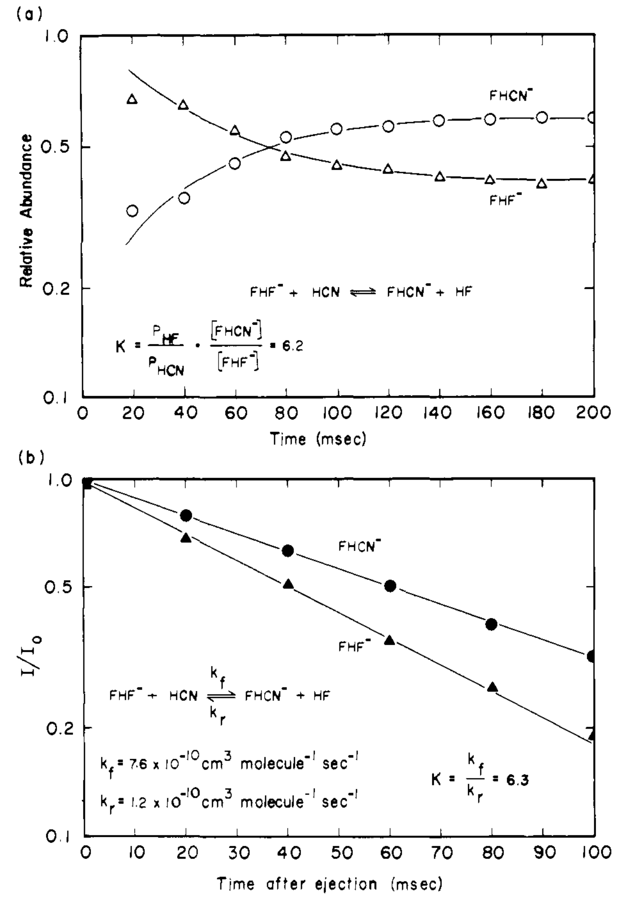

Figure 3. (a) Variation of relative intensities of fluoride adducts of HF and HCN a 1:6:28:7 mixture of $NF_3/HCO_2CH_3/HF/HCN$ at a total pressure of 4.2×10^{-6} torr following a 5-ms, 70-eV electron beam pulse. (b) Variation of intensity of FHF^- ($FHCN^-$) following continuous ejection of $FHCN^-$ (FHF^-) after equilibrium has been established in the mixture in (a) above.

adduct geometries available from ab initio calculations were used. For adducts of carbon acids, linear C–H–F bond distances of 2.70 Å were used by analogy to the ab initio determination of the geometries of the adducts of F^-–CH_3CN[41] and F^-–C_2H_4.[40] Overall vibrational contributions to the entropy change, $\Delta S_{11}°$, involving Brønsted acids were assumed to be negligible since the vibrational modes introduced by the addition of F^- were expected to contribute only a small amount of the overall entropies and should contribute similar amounts to all species, leading to an overall $\Delta S_{11}°$(vib) of nearly zero. Thus $\Delta S_{11}°$ was obtained by a summation of values from eq 13 and 14.

In the case of inorganic species participating in fluoride transfer equilibria such as SO_2, COF_2, PF_3 and SOF_2, entropies of the fluoride adducts FSO_2^-, COF_3^-, PF_4^-, and SOF_3^- were taken to be those of the isoelectronic neutrals F_2SO, CF_4, SF_4, and SF_4, respectively, with appropriate corrections for symmetry number differences.

Values of $\Delta H_{11}°$ are also included in Table I, calculated from the experimentally determined $\Delta G_{11}°$ and estimated $\Delta S_{11}°$. These values are in turn used to derive the overall fluoride affinities, $\Delta H_{12}°$, of each of the compounds investigated. The basis for the conversion of the relative fluoride affinity scale to an absolute one is 2-fold. First, Kebarle's value of 23.3 kcal mol⁻¹ for the enthalpy of attachment of F^- to water, $\Delta H_{11}°$,[23] was used together with the ladder of equilibrium measurements in Table I to provide an absolute scale of values of $\Delta H_{12}°$. Second, the absolute value of the fluoride affinity of ketene was established from the gas-phase acidity of acetyl fluoride as 35.7 kcal mol⁻¹.[42] The fluoride affinity of ketene relative to the scale of values in Table I was established from $\Delta G°$ for the equilibria of eq 15 and 16. This resulted in

$$CH_2COF^- \; SO_2F_2 \rightleftharpoons SO_2F_3^- + CH_2CO \qquad (15)$$

$$CH_2COF^- + (CHF_2)_2O \rightleftharpoons [(CHF_2)_2O]F^- + CH_2CO \qquad (16)$$

values of $\Delta G_{11}°$ of −9.3 kcal mol⁻¹ and $\Delta S_{11}°$ of −9.1 cal K⁻¹ mol⁻¹. Taken together with the value for fluoride affinity of water of 23.3 kcal mol⁻¹, the fluoride affinity of ketene may be calculated from the value of $\Delta H_{11}°$ of −12.0 kcal mol⁻¹ to be 35.3 kcal mol⁻¹. These two independent methods of establishing the absolute value of the fluoride affinity scale are thus seen to be in excellent agreement.

Also included for comparison in Table I are the values of the gas-phase acidity, $\Delta H_{17}°$ of each of the compounds studied, where available.

$$HA \rightleftharpoons H^+ + A^- \qquad (17)$$

In the case of many of the compounds studied with gas-phase acidities greater than that of HF such as carboxylic acids, phenols, and fluorinated alcohols, an HF displacement reaction (eq 18)

$$R_1HF^- + R_2H \rightleftharpoons R_1HR_2^- + HF \qquad (18)$$

occurred in competition with fluoride exchange.[28] These reactions were in general slower than the fluoride exchange but lead to some uncertainty in the determination of steady-state equilibrium constants. In such cases the time-delayed ion ejection method proved particularly valuable in determining the equilibrium constants from the rate constant ratio k_f/k_r.

Discussion

Strong Hydrogen Bonding. Recently, convincing arguments have been advanced for the separation of hydrogen bonds into two categories: weak or normal hydrogen bonds and strong or very strong hydrogen bonds.[47] Weak hydrogen bonds are generally regarded as those in which the proton involved may be clearly defined as being significantly more strongly covalently bound to one of the participants in the bond and may be designated A–H···B to indicate a much stronger A–H bond than B–H bond. The proton potential for such bonds is either a symmetric or asymmetric double minimum, depending upon the nature of A and B, with sizable barrier minima. Most, if not all, hydrogen bonds between neutrals fall in this category. In strong hydrogen bonds the proton is best regarded as being shared to a considerable extent by both of the participants in the bond and the designation A···H···B is usually used. The proton potential in this case is either a single-minimum potential well or a double-minimum potential well with a low barrier. Such strong hydrogen bonds are the rule for complexes in which one of the participants has unit charge. For example, ab initio calculations show that for both $H_5O_2^+$[48] and HF_2^-[48] single-minimum potential wells exist with an O–O distance of 2.38 Å and an F–F distance of 2.22–2.28 Å, respectively.

Emsley has further suggested that a bond strength in excess of 12 kcal mol⁻¹ be taken as the dividing line between weak and strong hydrogen bonds.[47] In defining the hydrogen-bond energy for the compounds investigated in the present work, care must

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Table II. Hydrogen-Bond Energies in Fluoride-Brønsted Acid Adducts

species less acidic than HF		species more acidic than HF	
compound (HA)	hydrogen-bond energy $D(F^- -HA)$, kcal mol^{-1}	compound (HA)	hydrogen-bond energy $D(F^- -HA)$, kcal mol^{-1}
t-C_4H_9F	22.3	$PhNH_2$	26.8
$PhCH_2F$	24.4	C_4NH_5	23.5
$(CH_3)_3CCHO$	24.6	CH_2FCH_2OH	34.3
$\overline{CH_2CH}CH_2F$	25.5	CH_3SH	21.7
H_2O	23.3	H_2S	16.5
C_2F_3H	26.3	$(CH_2F)_2CHOH$	31.2
CF_2HCFH_2	26.5	CF_3CH_2OH	32.0
CF_3H	27.1	HCN	21.1
$CH_3CH_2NH_2$	28.1	PhOH	19.6
C_2F_5H	30.4	CH_3CO_2H	21.1
CH_3OH	29.6	$(CF_3)_2C(CH_3)OH$	26
C_2H_5OH	31.5	HCO_2H	19.0
n-C_3H_7OH	32.3	$(CF_3)_2CHOH$	25
i-C_3H_7OH	32.3	$(CF_3)_3COH$	17
n-C_4H_9OH	32.2		
t-C_4H_9OH	33.3		
$(CF_2H)_2O$	35.9		

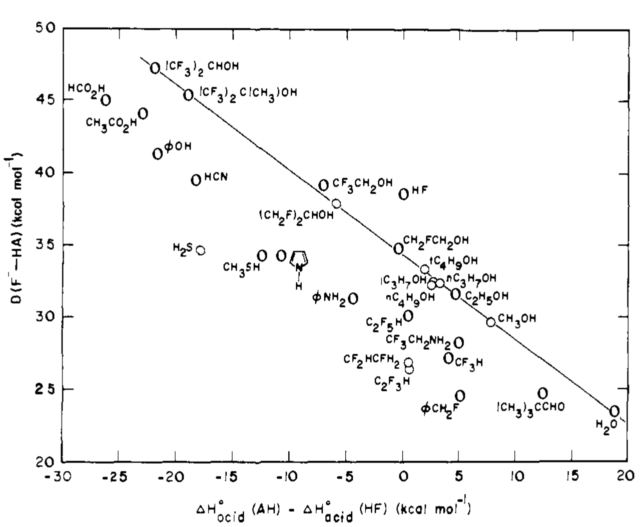

Figure 4. Correlation of fluoride binding energies with gas-phase acidity or Brønsted acids.

be taken to distinguish between the fluoride affinity and the hydrogen-bond energy. For compounds of lower gas-phase acidity than HF, the two quantities are synonymous. However, for compounds of greater gas-phase acidity than HF, a lower energy dissociation pathway then exists (eq 19) and the hydrogen-bond

$$A\cdots H\cdots F^- \rightarrow A^- + HF \qquad (19)$$

energy, $\Delta H_{19}°$ is taken to be $D(A^- -HF)$, which differs from the fluoride affinity of AH by an amount equal to the difference in gas-phase acidities of AH and HF. Hydrogen-bond energies, thus defined, are summarized in Table II for each of the Brønsted acids investigated for which gas-phase acidities are known.

Alcohol-Fluoride Hydrogen Bonds. It has previously been demonstrated by Kebarle[23] that for a series of anions, BHA^-, the dissociation energy $D(B^- -HA)$ may be expected to increase with increasing acidity of AH and to increase with increasing basicity of B^-. The data obtained for fluoride affinities of alcohols in the present work, shown in Figure 4, demonstrate that for a homologous series of gas-phase acids this relationship is a linear one over a very large acidity range. This linear correlation also provides support for the concept of a single minimum or double minimum with low-barrier proton potential. If a double-minimum potential well with a sizable barrier were appropriate for these systems, then for alcohols less acidic than HF the form $AH\cdots F^-$ would be the lower minimum and for alcohols more acidic than HF the form $A^-\cdots HF$ would be the lower minimum. Thus after passing through the acidity of HF, a fundamental change in the nature of the bonding would occur and a linear correlation of alcohol acidities with fluoride binding energies would not be expected to occur. Since such a correlation does exist, there is a clear indication that no significant change in the nature of the bonding occurs, implicating either a single-minimum proton potential or a double-minimum potential with a sufficiently low barrier that the proton may pass easily over it. Thus a change in the acidity of the alcohol more likely involves only a shift in electron density along the O–H–F axis with the minimum lowering and shifting slightly toward oxygen with increasing alcohol acidity.

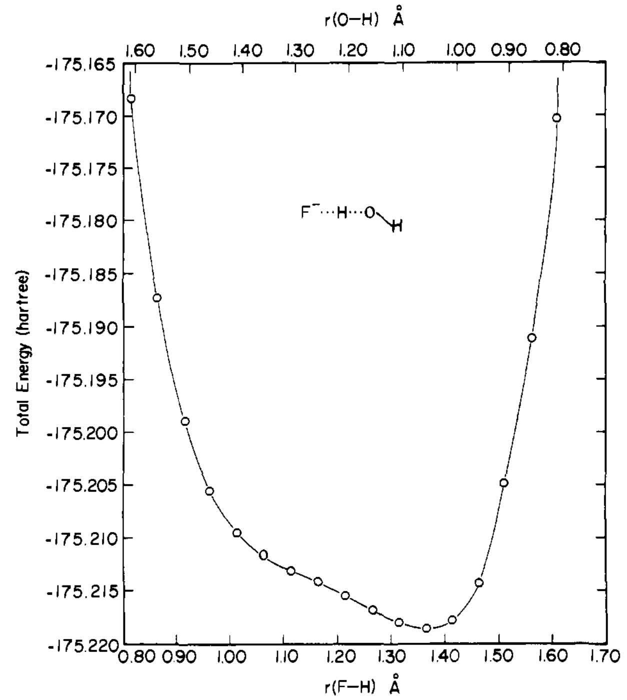

Figure 5. Proton potential for the hydrogen-bonded adduct of F^- and H_2O obtained at a total O–F separation of 2.52 Å.

This situation is illustrated in Figure 5 for the $F^- -H_2O$ adduct for which accurate ab initio calculations have been carried out.[38,40] Employing an equilibrium O–F distance of 2.51 Å,[40] we have carried out ab initio calculations using the GAUSSIAN70 program package employing a 4-31 G basis set and varied the position of the proton along the O–F axis. As can be seen from the plot, a single minimum is observed, even though the acidities of water and HF differ by 20 kcal mol^{-1}.

The slope of 0.5 for the plot in Figure 4 is also of interest. The change in fluoride binding energy is equal to one-half the difference in gas-phase acidity. This slope is very similar to that recently obtained by us for the variation of hydrogen-bond energies in assymmetric proton-bound dimers of oxygen n-donor bases with the difference in gas-phase basicity of the participant bases. In this case all hydrogen-bond strengths were in the vicinity of 30 kcal mol^{-1}. It would appear then that this might be a further experimental indication of the presence of strong hydrogen bonding; i.e., a variation of hydrogen-bond strength with acidity or basicity of the conjugate base, which yields a slope of 0.5. Such a result presumably indicates a nearly equal sharing of the proton. These results are in sharp contrast to the situation for complexes of substituted pyridinium ions with water,[17] which shows a slope of only 0.12 for a plot of pyridinium ion acidity vs. hydrogen-bond energy to water. In this case the overall bond energies are much weaker (10–15 kcal mol^{-1}) and the smaller slope may be indicative of more localized protons.

Carboxylic Acid and Phenol Hydrogen Bonds to Fluoride Ion. A correlation of fluoride binding energies with gas-phase acidity for most of the compounds investigated is shown in Figure 4. It is immediately apparent from this plot that all of the other organic acid functional groups lie below the alcohol line. Only HF has a fluoride affinity greater than that of alcohols of comparable gas-phase acidity. Significantly, both carboxylic acids and phenols, also oxygen-based acids, lie below the alcohol correlation line. This is presumably due to the fact that unlike alkoxide ions, which have a highly localized negative charge, carboxylate and phenolate ions are appreciably stabilized by charge delocalization giving rise to their enhanced gas-phase acidities. In the production of the adducts of F^- with carboxylic acids and phenols, however, the covalent strong hydrogen bond forces the negative charge on the oxygen acid fragment to be largely localized on the oxygen atom of the OH group. Recent ab initio calculations have in fact shown that the fluoride adducts of formic and acetic acids have greater negative charge on the hydroxylic oxygen than in either the neutral carboxylic acids or carboxylate ions.[33] This bears out our conjecture that no appreciable resonance charge delocalization can occur in the fluoride adducts of carboxylic acids or phenols. This loss of resonance stabilization in the fluoride adducts relative to carboxylate or phenolate anions results in a reduction of fluoride binding energy relative to that expected on the basis of the alcohol acidities. This may be regarded as due to the fact that in the fluoride adducts of carboxylic acids and phenols only the inductive component of the acidity is operable. This situation may thus be regarded as an example of *inhibition of resonance by solvation* and serves to provide a key to understanding the frequently observed differences between relative acidity orderings in solution and the gas phase.

Fluoride Hydrogen Bonds to Sulfur, Nitrogen, and Carbon Acids. Gas-phase acidity studies have previously demonstrated that sulfur, nitrogen, and carbon acids are much more acidic in the gas phase than might have been anticipated on the basis of their solution-phase pK_a values.[3,4,9] For example, in aqueous solution methanol is weaker in acidity than methyl mercaptan by only 1.3 pK_a units (1.8 kcal mol^{-1}), while in the gas phase the acidity difference is 20 kcal mol^{-1}. Similary, although cyclopentadiene is 4.5 pK_a units (6.1 kcal mol^{-1}) weaker in acidity than trifluoroethanol in aqueous solution, in the gas phase the carbon acid is 7 kcal mol^{-1} more acidic than the alcohol. The fluoride binding energies reported here for such compounds appear to be more indicative of their solution-phase acidities than gas-phase acidities. For example, methyl mercaptan has a fluoride affinity of about 22 kcal mol^{-1} while the fluoride affinity of trifluoroethanol is about 32 kcal mol^{-1} and that of cyclopentadiene is too low to allow detection of the fluoride adduct by us (<15 kcal mol^{-1}). This situation is quite representative of carbon acids where the acid strength is achieved primarily through resonance charge delocalization, which is eliminated or at least drastically inhibited in the fluoride adduct relative to the carbanion. In contrast, carbon acids that achieve their acid strength through inductive effects are not so drastically affected. For example, although 2-propanol and fluoroform have comparable gas-phase acidities, their solution-phase pK_a's differ by roughly 10 units, with CF_3H the weaker acid. Consistent with this, the fluoride affinity of CF_3H is some 5.2 kcal mol^{-1} less than that of 2-propanol; however, the reduction is not nearly so drastic as that for cyclopentadiene.

All attempts to correlate the gas-phase fluoride binding energies of the diverse functional groups investigated with some solution-phase property were unsuccessful. Exceedingly poor correlation was found with pK_a's of the acids, AH, Hammet σ and σ_I parameters of the substituents A, or NMR chemical shifts of the acidic protons.

An observation, based on the rather limited data available, would appear to be that the order of fluoride binding energies for a series of acids, AH, of comparable gas-phase acidity should be in the order of the group electronegativities of A. For example, with Pauling's method,[49] the electronegativity of the *n*-PrO′ group may be calculated to be 3.5, while that of CF_3 to be 3.0. Thus even though 1-propanol and fluoroform are species of comparable gas-phase acidity, the more electronegative group binds fluoride more strongly. There is insufficient experimental thermochemical data to calculate group electronegativities for other species; however, with use of electronegativity values of the heteroatoms involved, it would be predicted that for species of comparable gas-phase acidity, the order of fluoride binding energies should be oxygen acids > nitrogen acids > sulfur acids > carbon acids. This order appears to be at least qualitatively borne out by our data. It is noteworthy that electronegativity arguments predict that HF will bind F^- more strongly than oxygen acids, which is also observed.

Fluoride Affinities of HF and HCN. The hydrogen-bond energy in the bifluoride ion has generally been postulated to be the strongest of all possible hydrogen bonds. Previous experimental values for this quantity, $\Delta H_4°$, lead to a bewildering range of choices due, in large measure, to the approximations inherent in each of the determinations. Waddington has obtained values ranging from 58 ± 5[50] to 60.2 kcal mol^{-1} [32] for $D(F^-{-}HF)$ on the basis of crystal lattice energies of solid alkali metal bifluorides computed by summing point-charge electrostatic contributions and adding dispersion and higher order corrections using classical empirical formulas. Harrell and McDaniel[51] have measured $\Delta H_{20}°$ for eq 20 and compute a value of 37 kcal mol^{-1} for $D(F^-{-}HF)$ on the basis of the assumption that the crystal lattice energies of the fluoride and bifluoride salts are roughly equal.

$$N(CH_3)_4{}^+F^-(s) + HF(g) \rightarrow N(CH_3)_4{}^+HF_2{}^-(s) \quad (20)$$

Jenkins and Pratt[52] have rejected this assumption and have approximated the crystal lattice energy difference on the basis of the corresponding difference between $N(CH_3)_4{}^+Cl^-$ and $N(CH_3)_4{}^+HCl_2{}^-$ of 7 kcal mol^{-1} to give $D(F^-{-}HF)$ of 44 kcal mol^{-1}. They have also attempted to correct Waddington's data by recalculating repulsion contributions to alkali metal bifluoride crystal lattice energies on the basis of an empirical method of obtaining the charge distribution in FHF^-. In so doing, they obtain a value of $D(F^-{-}HF)$ of 42 kcal mol^{-1}. Most recently, Harmon[53] has discussed the relative hydrogen-bond strengths in alkali metal bifluorides and tetralkylammonium bifluorides and concludes that Harrel and McDaniel's assumption cannot be correct because of changes in lattice energies due to lattice expansion and because of hydrogen-bonding interactions between cation and anion. They thus claim that a value considerably greater than that of Harrel and McDaniel is indicated.

There are similarly a variety of theoretical calculations available for $D(F^-{-}HF)$. The most reliable of these give values from as low as 40 kcal mol^{-1} obtained by Noble and Kortzeborn[54] to values in the 51–52.5 kcal mol^{-1} range obtained by Almlof,[55,56] Kollman and Allen,[48] and Emsley.[57] The largest basis set employed was that of Noble and Kortzeborn, giving the lowest hydrogen-bond energy.

The experimental value of $D(F^-{-}HF)$ of 38.6 kcal mol^{-1} obtained in the present work represents the first completely experimental determination of the bifluoride hydrogen-bond energy. It is seen to be in excellent agreement with the theoretical value of Noble and Kortzeborn and with experimental value predicted by Harrel and McDaniel. It is significant to note that if the experimental determination of $\Delta H_{20}°$ is correct, then the assumption of nearly equal crystal lattice energies of $N(CH_3)_4{}^+F^-$ and $N(CH_3)_4{}^+HF_2{}^-$ is a good one. The agreement with Jenkins and Pratt's treatment of Waddington's data is also very good. We thus feel confident that a hydrogen-bond energy of 39 ± 1 kcal

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mol^{-1} for the bifluoride ion is quite reliable..

It is of interest in this connection to examine the enthalpy change for the formation of the assymmetrical proton-bound dimer, FH_2O^-, given by eq 21. In previous work, we concluded

$$FHF^- + HOH_2O^- \rightarrow 2FH_2O^- \qquad (21)$$

that the enthalpy change for this type of reaction is close to zero for strong-hydrogen-bonded systems and approximately equal to the enthalpy in transfering a proton from the strong acid to the anion of the weaker acid (−10.3 kcal in this case) for a weak-hydrogen-bonded system. From a simple thermochemical cycle, we calculate a value of $\Delta H_{21}° = -1.9$ kcal, close to what we would expect from our previous conclusion that the $R-O-H-F^-$ system was a strong-H-bonded one. Alternatively by setting $\Delta H_{21}° = 0$, one can calculate an expected upper limit to the value of $D(F^- - HF)$ of 40.9 kcal from previously measured dissociation energies of $F-H_2O^-$ and $OH(H_2O)^-$.[20] This estimate is in good agreement with our directly measured value.

As demonstrated by the data in Figure 3, the fluoride affinities of HF and HCN are very nearly equal. However, the lower energy dissociation pathway for $FHCN^-$ (eq 22) gives rise to a hydrogen-bond energy in $FHCN^-$ of only 21 kcal mol^{-1}. The chemical stability of this adduct has recently been demonstrated by Ault[58] who has succeeded in synthesizing and characterizing $FHCN^-$ in low-temperature matrices. In contrast to results reported previously by Sullivan and Beauchamp,[59] we do not see the HF displacement reaction (eq 23) producing the bicyanide ion. In their study, $FHCN^-$ had been generated by fluoride transfer from FSO_2^- (eq 24) formed from dissociative electron attachment to SO_2FCl. However, the data of Table I reveal that this reaction is endothermic by 4 kcal mol^{-1}, implying that the FSO_2^- formed from SO_2FCl has some internal excitation that is transferred to some extent to $FHCN^-$ subsequently permitting eq 23 to occur. The extreme slowness of eq 23 observed by Sullivan and Beauchamp is further evidence that this process may be an endothermic reaction. Our results thus indicate that $D(CN^- - HCN)$ is less than $D(CN^- - HF)$, although the difference is probably small.

$$FHCN^- \rightarrow CN^- + HF \qquad (22)$$

$$FHCN^- + HCN \nrightarrow H(CN)_2^- + HF \qquad (23)$$

$$FSO_2^- + HCN \rightarrow FHCN^- + SO_2 \qquad (24)$$

Conclusion

The results presented here demonstrate that a quantitative fluoride affinity scale for Brønsted acids has been established. The ordering of fluoride affinities of various functional groups provides a rational basis for understanding the ability of these groups to solvate anions. The data also provide some basis for understanding the differences in gas-phase and solution acidity behavior that are frequently observed. Within a homologous series of acids, it has been demonstrated that a correlation of gas-phase acidity and fluoride affinity exists. For different functional group types, however, such a correlation completely breaks down. For different acid types, a dependence of fluoride binding energy on electronegatively of the heteroatom involved is implicated. Finally, and perhaps most significantly, the hydrogen-bond energy in the bifluoride ion has been determined to be 38.6 kcal mol^{-1}, in good agreement with selected experimental and theoretical studies.

Acknowledgment. Financial support of the National Sciences and Engineering Research Council Canada (NSERC) is gratefully acknowledged. We thank M. Roy for the synthesis of ketene and for calculations of moments of inertia and geometries of fluoride adducts.

Registry No. F^-, 16984-48-8; HCO_2H, 64-18-6; SO_2, 7446-09-5; CH_3CO_2H, 64-19-7; SF_4, 7783-60-0; COF_2, 353-50-4; PhOH, 108-95-2; HCN, 74-90-8; PF_3, 7783-55-3; HF, 7664-39-3; CF_3CH_2OH, 75-89-8; SOF_2, 7783-42-8; $(CH_2F)_2CHOH$, 453-13-4; H_2S, 7783-06-4; $(CHF_2)_2O$, 1691-17-4; SO_2F_2, 2699-79-8; CH_2CO, 463-51-4; CH_3SH, 74-93-1; CH_2FCH_2OH, 371-62-0; t-C_4H_9OH, 75-65-0; n-C_3H_7OH, 71-23-8; i-C_3H_7OH, 67-63-0; n-C_4H_9OH, 71-36-3; C_2H_5OH, 64-17-5; $PhNH_2$, 62-53-3; C_2F_5CN, 422-04-8; CH_3OH, 67-56-1; C_2F_5H, 354-33-6; $CF_3CH_2NH_2$, 753-90-2; CF_3H, 75-46-7; CF_2HCH_2F, 430-66-0; C_2F_3H, 359-11-5; H_2O, 7732-18-5; $(CH_3)_3CCHO$, 630-19-3; $PhCH_2F$, 25496-08-6; t-C_4H_9F, 353-61-7; 1-*H*-pyrrole, 109-97-7; (fluoromethyl)oxirane, 503-09-3.

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Reversible Oxidation and Rereduction of Entire Thin Films of Transition-Metal Phthalocyanines

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Abstract: Thin films (1000–2000 Å thick) of iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) phthalocyanines (Pc) on gold or indium oxide electrodes undergo stoichiometric oxidation and rereduction. Except for FePc and CoPc, the process is essentially reversible. Chronocoulometry showed that ZnPc films oxidized to the extent of 1.21 electrons per ZnPc molecule; CoPc required 1.92 electrons per molecule. Charge compensation is attained upon oxidation by uptake of anions from the electrolyte and by expulsion of anions upon reduction. Auger electron spectrometry allowed detection of the ions and characterization of their distributions. In partially oxidized films, the anions appear to be homogeneously distributed. Oxidation seems to proceed at all grains with equal probability, with anions entering and departing along grain boundaries. Smaller anions allow full oxidation at rapid rates; larger ones inhibit the oxidation with respect to rate. Optical spectroscopy showed evidence for reorganization of the crystalline lattices. The rereduced form is not the same as the original material, but it can be restored to the original form by annealing at 125 °C. In cyclic oxidations and rereductions, there is a gradual loss of charge-consuming ability, apparently related to electrical isolation of small domains, perhaps grains. The oxidations and rereductions are electrochromic, and the various color changes are described.

Phthalocyanines have received much attention recently in a wide range of contexts,[1] particularly as thin films. Their catalytic properties, principally in the electroreduction of O_2, have been studied extensively.[2-6] A large volume of related research has

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