Gas-Phase Bifluoride Ion. An Ion Cyclotron Resonance Determination of the Hydrogen Bond Energy in FHF^- from Gas-Phase Fluoride Transfer Equilibrium Measurements

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Gas phase ion–molecule clustering equilibria in recent years have provided valuable insights into the intrinsic Lewis acid–base behavior of isolated molecules.[2–4] It has generally been acknowledged that the strongest of all hydrogen bonds should be that in the bifluoride ion, FHF^-,[5] due to the high electronegativity and small size of fluorine and the large dipole moment of HF. However the measurement of the hydrogen bond energy in FHF^- has eluded persistent investigations for over 30 years.[6] Values for this quantity, defined as the negative of the enthalpy change for eq 1, have a variation of over 30 kcal mol^{-1} due in large part

$$F^-(g) + HF(g) \rightarrow FHF^-(g) \qquad (1)$$

to the approximations that have been inherent in the methods of determination and in experimental difficulties associated with handling HF. Early experimental determinations of $\Delta H_1°$ were based on lattice energy estimates for alkali metal bifluoride salts, $M^+HF_2^-(s)$, which yielded values ranging from 58 and 60.2 kcal mol^{-1} obtained by Waddington[7,8] to a low of 37 kcal mol^{-1} obtained by Harrell and McDaniel[9], who assumed that the crystal lattice energy of $NH_4^+HF_2^-$ was equal to that of $NH_4^+F^-$. Attempts to estimate the hydrogen bond energy in FHF^- from correlations of hydrogen bond strengths and vibrational frequencies for the hydrogen bond lead to the impossibly high value of 263 kcal mol^{-1}.[10] Recent ab initio quantum chemical calculations of the hydrogen bond energy in FHF^- also led to a wide range of values from as low as 40 kcal mol^{-1} obtained by Noble and Kortzeborn[11] to as high as 52.2 kcal mol^{-1} obtained by Kollman and Allen.[12] An early attempt by Kebarle[13] to correlate hydrogen bond energies of F^- to molecules AH in the gas phase with the gas-phase acidity of AH led to an estimate of $D(F^-{-}HF)$ of 30 ± 5 kcal mol^{-1}. In the present communication we report the first completely experimental determination of the hydrogen bond energy in gas-phase FHF^- that involves no underlying assumptions or approximations.

Adducts of F^- with hydrogen bonding molecules were readily generated from mixtures containing NF_3 and methyl formate in which the CO elimination reaction (eq 2) occurs to generate an

$$F^- + HCO_2CH_3 \rightarrow CH_3OHF^- + CO \qquad (2)$$

adduct of F^- with methanol.[14] For experiments involving species binding F^- less strongly than methanol, adducts were generated from mixtures containing methyl nitrite and 2-fluoropropene in which eq 3 occurs yielding a fluoride–allene adduct, the 2-fluoroallyl anion.[15] Subsequent reactions of either $F^-{\cdots}HOCH_3$

$$CH_3O^- + H_2C{=}C(F)CH_3 \rightarrow C_3H_4F^- + CH_3OH \qquad (3)$$

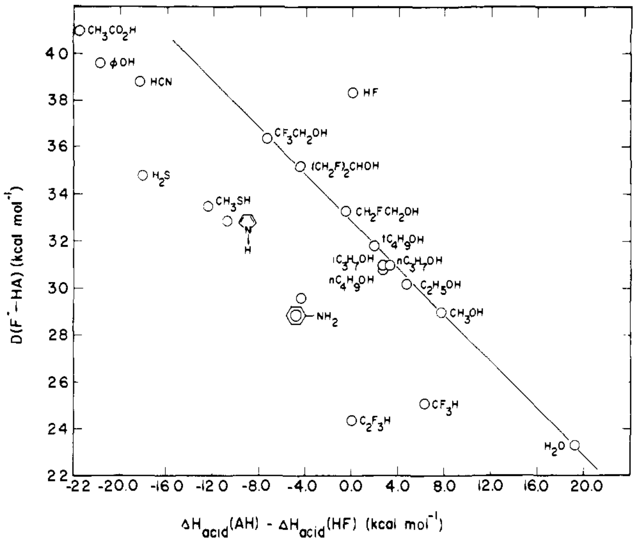

Figure 1. Correlation between fluoride binding energy and gas-phase acidity for a number of gas-phase Brønsted acids of various functional group types. Lewis acids and Brønsted acids with gas-phase acidities that are either unknown or less than that of water were also used to provide successive fluoride transfer equilibria for multiple overlap sequences used to construct the fluoride affinity scale.

or $C_3H_4F^-$ with species of greater fluoride binding energy than either methanol or allene, respectively, led readily to the production of a wide variety of fluoride adducts, and examination of subsequent fluoride transfer equilibria (eq 4) produced a scale of

$$AF^- + B \rightleftharpoons BF^- + A \qquad (4)$$

relative fluoride affinities. In general, as shown in Figure 1, for a homologous series of gas-phase Brønsted acids such as the alcohols an excellent correlation between fluoride binding energy and gas-phase acidity exists; however, for acids of different functional group type, the correlation completely breaks down.

In the course of our studies it was found possible to examine equilibrium fluoride transfer in mixtures containing HF and to thus accurately determine the fluoride binding energy of HF relative to a large number of fluoride donors. Fluoride transfer equilibria in HF–HCN- and HF–PF_3-containing mixtures (eq 5 and 6) were observed and used to establish the fluoride affinity of HF on the relative scale of fluoride binding energies.

$$FHF^- + HCN \rightleftharpoons FHCN^- + HF \qquad (5)$$

$$FHF^- + PF_3 \rightleftharpoons PF_4^- + HF \qquad (6)$$

The scale of accurate relative fluoride binding energies thus obtained was converted to a scale of absolute fluoride binding energies by two independent confirmations. First, the fluoride affinity of ketene was established from the gas-phase acidity of acetyl fluoride[16] as 35.7 kcal mol^{-1}, and the observation of the equilibrium constant for eq 7 and 8 were used to relate the fluoride affinity of ketene to the relative scale of fluoride affinities in the

$$CH_2COF^- + SO_2F_2 \rightleftharpoons SO_2F_3^- + CH_2CO \qquad (7)$$

$$CH_2COF^- + (CHF_2)_2O \rightleftharpoons [(CHF_2)_2O]F^- + CH_2CO \qquad (8)$$

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present work. This allows an absolute value of D(F$^-$–HF) of 39.1 kcal mol^{-1} to be established. Second, Kebarle's[13] value of 23.3 kcal mol^{-1} for D(F$^-$–H$_2$O) and the ladder of fluoride transfer equilibrium measurements of the present work establish an absolute value of D(F$^-$–HF) of 38.6 kcal mol^{-1}. These two independent methods of rendering our relative scale an absolute one are thus seen to be in excellent agreement.

We thus suggest that a new completely experimental value for D(F$^-$–HF) of 39 ± 1 kcal mol^{-1} (163 ± 4 kJ mol^{-1}) be adopted. It is interesting to note that this value is in best agreement with the lowest of the previous experimental determinations[8] based on crystal lattice energy assumptions and in excellent agreement with the ab initio quantum chemical calculations by Noble and Kortzeborn.[11]

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Opening of Epoxides with Trimethylsilyl Cyanide To Produce β-Hydroxy Isonitriles. A General Synthesis of Oxazolines and β-Amino Alcohols

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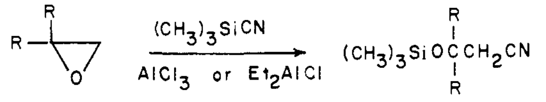
Recently, trimethylsilyl cyanide has been reported to react with epoxides under catalysis by aluminum chloride[1] or diethylaluminum chloride[2] to produce the trimethylsilyl ethers of β-hydroxy nitriles (eq 1). A type of general Lewis acid catalysis has been invoked to explain these transformations.[2] We now report (a) that catalysis of the addition of trimethylsilyl cyanide to epoxides with zinc iodide gives an entirely different product, namely, the trimethylsilyl ether of β-hydroxy isonitriles, and (b) that this highly stereospecific synthesis of β-hydroxy isonitriles provides ready access to stereospecifically substituted oxazolines and β-amino alcohols.

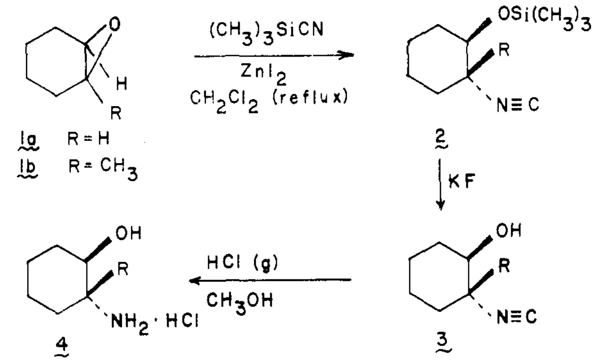


(1)

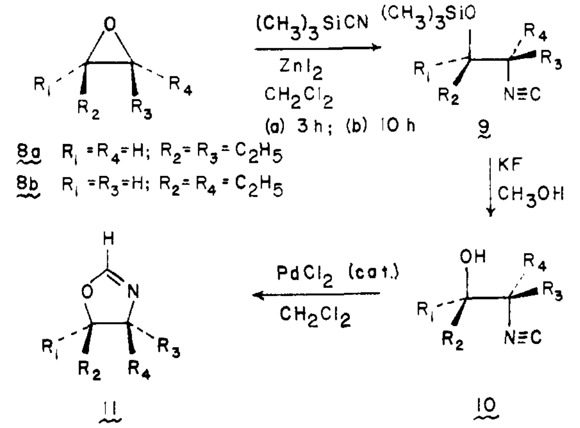
In a typical procedure, 1 equiv of cyclohexane epoxide (**1a**), Scheme I, was treated with 2 equiv of trimethylsilyl cyanide and a catalytic amount (0.5 mol%) of zinc iodide in refluxing methylene chloride for 4 h to give 73% of **2a**.[3] Removal of the trimethylsilyl protecting group from **2a** was accomplished with 3 equiv of potassium fluoride in methanol to give 98% of **3a**. The stereochemistry of the epoxide opening was shown to be trans through the hydrolysis of **3a** to the known amine hydrochloride, **4a**, in 88% yield, mp 174–175 °C (lit.[4] mp 176–177 °C).[5,6]

The same sequence of reactions that had been carried out on **1a** was performed on 1-methylcyclohexene epoxide (**1b**) in order to evaluate the regiospecificity of this useful isonitrile synthesis. Under the reaction conditions described above, **1b** gave 79% of **2b**. Both the stereospecificity and the regiospecificity of the opening of the epoxide moiety of **1b** were very clean. The regiospecificity was established through careful analysis of the proton-decoupled ^{13}C NMR spectrum of **2b**, which showed the quaternary carbon as a triplet of equal intensity peaks due to the coupling of this carbon with the nitrogen of the isonitrile group.[7] It is of particular significance that the regiospecificity of the zinc iodide catalyzed reaction[8] is the opposite of that reported[2] for the aluminum trichloride promoted reaction.[9]

Scheme I

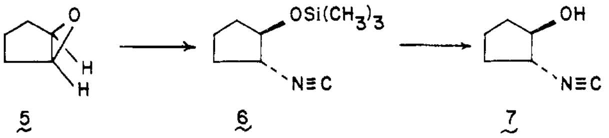


Scheme II



Deprotection of **2b** with potassium fluoride gave an 81% yield of **3b**. Hydrolysis of **3b** with methanolic hydrogen chloride produced **4b**, mp 199–202 °C, in 80% yield. The formation of the β-amino alcohol having the amino group on the tertiary carbon illustrates the synthetic potential of our reaction sequence for this class of compounds.

In a general extension of this new synthetic method, we treated cyclopentene epoxide (**5**) (eq 2) with trimethylsilyl cyanide in the presence of zinc iodide for 12 h to yield 77% of **6**. Deprotection of the hydroxyl moiety of **6** with potassium fluoride gave a 92% yield of **7**. The stereochemistry of **7** was established through the hydrolysis of **7** to the known *trans*-β-amino alcohol hydrochloride salt, mp 192.5–194.0 °C (lit.[10] mp 193–194 °C). In a similar series of reactions, *cis*-3-hexene epoxide (**8a**), was treated with trimethylsilyl cyanide in the presence of zinc iodide to give 82%



(2)

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[3] Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds. In all cases the spectral data (IR, NMR, etc.) were consistent with the assigned structures. All yields reported are of isolated, purified material.

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[5] The overall yield of **4a** from **1a** was 63%. This offers a very simple and highly stereospecific path to β-amino alcohols.

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[8] It should be noted that the opening of **1b** occurred faster than the opening of **1a**. With **1b** the reaction was complete in 3 h.

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