J. Am. Chem. Soc. 1987, 109, 6230–6236

Hydrogen Bonding in Gas-Phase Anions. The Energetics of Interaction between Cyanide Ion and Brønsted Acids Determined from Ion Cyclotron Resonance Cyanide Exchange Equilibria

J. W. Larson and T. B. McMahon*

Contribution from the Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

Received January 21, 1987

Abstract: Pulsed ion cyclotron resonance spectroscopic techniques have been used to examine cyanide-exchange equilibria between pairs of Brønsted acids. A bimolecular method for the generation of these cyanide adducts at low pressure in the gas phase has been demonstrated. The accumulation of multiple-overlap cyanide-exchange equilibria involving a large number of pairs of Brønsted acids has allowed construction of an accurate relative scale of hydrogen bond energies to cyanide ion. Use of the known absolute value of the binding energy of CN$^-$ to H_2O allows conversion of the relative scale to an absolute one. Cyanide is demonstrated to be similar to chloride ion in its hydrogen-bonding properties. Data for F$^-$, Cl$^-$, CN$^-$, I$^-$, and RO$^-$ hydrogen bond interactions have been used to formulate a general empirical equation for prediction of anion–Brønsted acid interaction energies. This equation, for the first time, takes account of the electronegativity of the participants in the hydrogen bond.

The study of energetics of interaction of gas-phase ions with either single or small numbers of solvent molecules has provided a new and illuminating perspective for the understanding of bulk solvation of ions by both protic and aprotic solvents.[1] Recent contributions from this[2-7] and other[8-13] laboratories for the interaction of anions with single molecules of hydrogen-bonding solvent species have shown, from comparisons with solution-phase solvation energies, that an extended network of hydrogen-bonded solvent molecules must surround small anions in solution. In addition, a number of important differences have been shown to exist between the behavior of the smaller, more basic, alkoxide and fluoride ions and that of the larger, less basic chloride and iodide ions. For example, RO$^-$[12,13] and F$^-$[3] species form stronger hydrogen bonds with a pronounced dependence on the gas-phase acidity of the Brønsted acid substrate. In contrast, Brønsted acid adducts of Cl$^-$[6,9] and I$^-$[10] have considerably weaker hydrogen bonds with a much less pronounced dependence on gas-phase acidity. In particular the energetics of interaction of I$^-$ with adducts are almost constant with no clear trend of increasing bond strength with increasing gas-phase acidity of the substrate. This contrasting behavior for these simple anions reflects the extent to which the hydrogen bonds have covalent as well as electrostatic behavior or, in other terms, the extent to which the hydrogen atom is shared by the anion, X$^-$, and the conjugate base of the Brønsted acid, RH. In the case of fluoride[3] and alkoxide[12,13] adducts the anion binding energies increase by roughly 50% of the increase in the acidity of RH. Such a relationship is indicative of a broad single minimum potential well for the proton in which large-amplitude proton motion between the two heavy-atom centers is energetically feasible.[14] In the case of the more weakly basic anions the proton potential well is steeper and narrower with the proton significantly displaced toward the Brønsted acid side of the molecule in cases where the Brønsted acids are more weakly acidic than HX. In such cases the hydrogen bonds are decidedly weaker and have a much greater fraction of electrostatic relative to covalent character. Due to the larger radii of the chloride and iodide ions they are, however, much better able to participate in multiple site interactions with the Brønsted acid substrate.

The present study of energetics of interaction of cyanide with Brønsted acids has been undertaken because of the potentially very different nature of CN$^-$ relative to the halide and alkoxide ions. Cyanide is frequently classed as a pseudo-halide because of the similar chemical behavior of CN and CN-containing compounds to those of halogens. For example, the group electronegativity and electron affinity of CN are very similar to those of the halogens,[15] and HCN is a weak solution acid much like HF. Considerable attention has in fact recently been focused on the acid properties of HCN since it has been termed a "normal" acid in aqueous solution unlike other carbon acids.[16] This conclusion infers that little change in electron delocalization or geometry occurs in proceeding from HCN to CN$^-$ and that a large fraction of the negative charge must remain localized. The basis for these arguments is the fact that rate constant for proton exchange in aqueous HCN solutions and the rate of proton abstraction by CN$^-$ are very much greater than those for any other carbanion or charge-delocalized species. This would also appear to be supported by gas-phase data as well since proton abstraction by CN$^-$ and from HCN are observed to be very fast, usually proceeding at, or near, the collision rate.[17,18] In the gas phase, as well as solution, charge-delocalized ions such as enolates react much more slowly,[19a] although other solution-phase carbanions, such as those derived from deprotonation of acetylenes and nitriles, which are far more charge localized, do react quite rapidly.[9b]

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(1) See, for example: Kebarle, P.; Davidson, W. R.; Sunner, J.; Meza-Hojer, S. *Pure Appl. Chem.* **1979**, *51*, 63.

(2) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 5848.

(3) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944.

(4) Larson, J. W.; McMahon, T. B. *Can. J. Chem.* **1984**, *62*, 675.

(5) Larson, J. W.; McMahon, T. B. *J. Phys. Chem.* **1984**, *88*, 1083.

(6) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 517.

(7) Larson, J. W.; McMahon, T. B. *Inorg. Chem.* **1984**, *23*, 2029.

(8) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139.

(9) French, M. A.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1982**, *60*, 1907.

(10) Caldwell, G.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 967.

(11) Keesee, R. G.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1980**, *74*, 139.

(12) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660.

(13) (a) Mautner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525. (b) Mautner, M. *J. Am. Chem. Soc.* **1986**, *108*, 6189. (c) Mautner, M.; Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6687.

(14) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

(15) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: London, 1976.

(16) (a) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117. (b) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7126.

(17) Mackay, G. I.; Betowski, L. D.; Payzant, J. P.; Schiff, H. I.; Bohme, D. K. *J. Phys. Chem.* **1976**, *80*, 2919.

(18) Betowski, D.; Mackay, G. I.; Payzant, D.; Bohme, D. *Can. J. Chem.* **1975**, *53*, 2365.

(19) (a) Farneth, W.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. (b) Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354.

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These observations would thus suggest that CN^- should be a reasonably good hydrogen-bonding entity in the gas phase.

In contrast to this behavior suggesting that CN^- has a highly localized negative charge is the observation that CN^- is an ambident nucleophile able to react at either the carbon or nitrogen sites.[20] This conclusion is, however, complicated by the fact that in solution the reactive cyanide species may in fact be a contact or solvent-separated ion pair or a CN^- hydrogen bonded to the solvent species. In solvents of low polarity CN^- reacts as an ion pair or more highly associated ionic species. In protic solvents the solvent molecule may hydrogen bond to one or both of the sites in CN^-. Thus if one site of the CN^- ion is more highly associated with either a cation or a solvent molecule, the other site will be the more reactive. In support of a real ambident reactivity for an isolated cyanide ion are the recent ab initio calculations of Marynick[21] and Jorgensen.[22] In Lewis acid adducts of CN^- such calculations show that there is very little difference in binding energy between the carbon and nitrogen sites with BH_3, $B(CH_3)_3$, and BF_3.[21] Similarly for the hydration of CN^- by a single water molecule minimal differences in binding energy at the carbon and nitrogen sites were found.[22] These solution-phase experiments and ab initio calculations thus suggest that a significant degree of ambident character involving the carbon and nitrogen sites of CN^- is in fact present.

In the present paper we report a means whereby cyanide adducts of Brønsted acids may be readily produced by a bimolecular reaction sequence under the low-pressure conditions of an ion cyclotron resonance spectrometer. The adducts thus produced are allowed to participate in cyanide-exchange equilibria between pairs of Brønsted acids. From a series of exchange equilibria involving many Brønsted acids a scale of hydrogen bond energies to cyanide ion has been developed. These energetics allow considerable insight into the nature of hydrogen bonds involving CN^-.

Experimental Section

All experiments were carried out at ambient temperature (25 °C) with an ion cyclotron resonance (ICR) spectrometer of basic Varian design extensively modified to permit ion-trapping experiments. Details of the design and operation of both conventional drift and trapped-ion ICR experiments have been described elsewhere.[23,24]

Ethyl cyanoformate (99%) was obtained from Aldrich Chemical Co. Hydrogen cyanide was prepared by condensation of gaseous HCl into a concentrated aqueous solution of KCN. All other materials were commercial samples of highest purity obtainable and were used without further purification with the exception of degassing prior to use by successive freeze-pump-thaw cycles.

Results

A. Negative Ion Chemistry of Ethyl Cyanoformate. The negative ion mass spectrum of the commercial sample of ethyl cyanoformate obtained below 10^{-6} Torr in the ICR consists of 80% Cl^- and 20% CN^-. A positive ion mass spectrum revealed that the source of the chloride ion is a less than 10% impurity of ethyl chloroformate in the vapor phase. Due to the higher vapor pressure of ethyl chloroformate relative to ethyl cyanoformate the impurity level in the liquid phase should be less than that in the vapor phase. It is apparent therefore that the chloroformate ester has a much larger dissociative electron attachment cross section than the cyanoformate ester (eq 1). Attempts to further purify the sample were unsuccessful in producing a chloride free negative ion mass spectrum. Fortunately the presence of the large intensity of this impurity ion was of no consequence since both Cl^- and CN^- readily participate in a nucleophilic displacement reaction to yield the cyanoformate ion (eq 2). This reaction is thus entirely analogous to that used previously to generate the chloroformate ion. Other

$$XCO_2C_2H_5 \xrightarrow{e^-} X^- + CO_2C_2H_5 \qquad (1)$$
$$X = Cl, CN$$

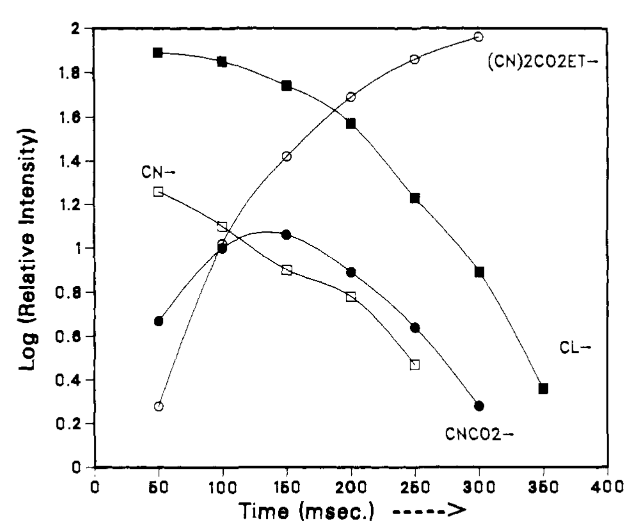

Figure 1. Variation of relative negative ion abundances with trapping time following a 5-ms, 70-eV ionizing electron beam pulse in $NCCO_2C_2H_5$ at a pressure of 1.5×10^{-6} Torr.

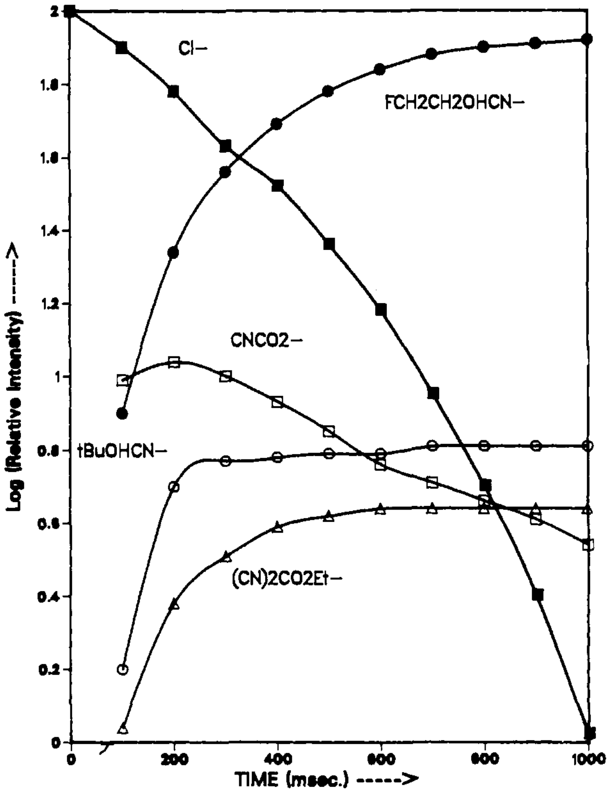

Figure 2. Variation of relative negative ion abundances with trapping time following a 5-ms, 70-eV ionizing electron beam pulse in a 3.3:1:4 mixture of $t\text{-}C_4H_9OH{:}FCH_2CH_2OH{:}NCCO_2C_2H_5$ at a total pressure of 1.8×10^{-6} Torr.

$$X^- + NCCO_2C_2H_5 \rightarrow NCCO_2^- + C_2H_5X \qquad (2)$$

anions were also reacted with the cyanoformate ester. Both fluoride and alkoxide ions were successful in generation of $CNCO_2^-$, but bromide ion was unreactive.

The variation of relative ionic abundances with trapping time for ethyl cyanoformate is shown in Figure 1. As can be seen, at long trapping times the cyanoformate ion reacts further to yield the dicyanoalkoxide ion (eq 3).

$$NCCO_2^- + NCCO_2C_2H_5 \rightarrow (NC)_2CO_2C_2H_5^- + CO_2 \quad (3)$$

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[20] Reutov, O. A.; Beletskaya, I. P.; Kurts, A. L. *Ambident Anions*; Michael, J. P., translator; Consultants Bureau: New York, 1983.

[21] Marynick, D. S.; Throckmarton, L.; Bacquet, R. *J. Am. Chem. Soc.* **1982**, *104*, 1.

[22] Gao, J.; Garner, D. S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4784.

[23] McMahon, T. B.; Beauchamp, J. L. *Rev. Sci. Instrum.* **1973**, *43*, 509.

[24] Lehman, T. A.; Bursey, M. M. *Ion Cyclotron Resonance Spectroscopy*; Wiley-Interscience: New York, 1976.

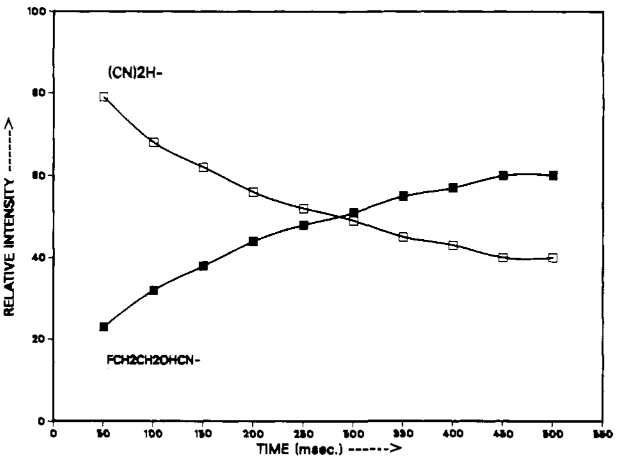

Figure 3. Variation of relative intensities of cyanide adducts of HCN and FCH_2CH_2OH with time in a 5.3:1:3 mixture of $HCN:FCH_2CH_2OH:NCCO_2C_2H_5$ at a total pressure of 1.5×10^{-6} Torr.

In the presence of Brønsted acids, AH, which bind cyanide more strongly than CO_2 or the cyanoformate ester, further CN^- transfer is observed to yield a hydrogen-bonded adduct (eq 4 and 5). The data shown in Figure 2 illustrate the results of cyanide transfer when a mixture of 2-fluoroethanol and *tert*-butyl alcohol is added

$$NCCO_2^- + AH \rightarrow NC^- \text{--} HA + CO_2 \qquad (4)$$

$$(NC)_2CO_2C_2H_5 + AH \rightarrow NC^- \text{--} HA + NCCO_2C_2H_5 \qquad (5)$$

to the ethyl cyanoformate in the spectrometer. As outlined below both CO_2 and $NCCO_2C_2H_5$ have cyanide binding energies in the vicinity of 15 kcal mol^{-1}. For compounds binding cyanide more strongly than this cyanide transfer was usually fast and cyanide-exchange equilibria were readily established. However, many compounds of interest had cyanide binding energies below those of CO_2 and $NCCO_2C_2H_5$, and as a result special measures were employed to minimize the abundance of the $(NC)_2CO_2C_2H_5^-$ ion. These involved use of a 10% CCl_4 in $CNCO_2C_2H_5$ mixture as the initial chemical ionization reagent gas to take advantage of the very large dissociative electron attachment cross section of CCl_4. This allowed the pressure of $NCCO_2C_2H_5$ to be maintained at a very low level while still permitting a usable $NCCO_2^-$ signal to be obtained. In this way it was found possible to employ endothermic cyanide transfer to species such as H_2O from $NCCO_2^-$ in order to extend the scale of cyanide binding energies. It was very important to be able to do this since the only absolute cyanide binding energy measured to date was that for H_2O and hence this would allow conversion of the relative scale of CN^- binding energies to an absolute one. In the case of cyanide transfer to H_2O the $NCCO_2^-$ signal dominates at all reaction times. Since the free-energy change at 298 K for CN^- transfer from CO_2 to H_2O is greater than 2 kcal mol^{-1} it seems probable that production of a sizable fraction of the $NC(H_2O)^-$ may be taking place from hot $NCCO_2^-$. However, with the low pressures of $NCCO_2C_2H_5$ employed CN^--transfer equilibria could be observed since the CN^--exchange process was fast compared to CN^- transfer to the cyanoformate ester. Adducts with CN^- binding energies even below that of H_2O (13.8 kcal mol^{-1}), such as $NCCH_3Cl^-$, could be observed, again likely from hot $NCCO_2^-$, although in these cases equlibria were not examined.

B. Cyanide-Transfer Equilibrium Measurements. The techniques of anion-exchange equilibria and methods used to derive thermochemical data have been described in detail previously.[3] A typical cyanide-exchange equilibrium experiment is shown in Figure 3 for a mixture of 2-fluoroethanol and hydrogen cyanide. From the steady-state ratio of cyanide-adduct abundances established after 500 ms of trapping time the equilibrium constant for eq 6 may be calculated as 0.25. If, after equilibrium is established, one of the cyanide adducts is selectively and continuously ejected from the ICR cell and the intensity of the other adduct monitored as a function of time after ejection, the rate constant for cyanide transfer in one direction may be obtained. If this experiment is repeated for the opposite reaction direction and the other rate constant determined the equilibrium constant may then be calculated from the ratio of forward and reverse rate constants. This experiment, shown in Figure 4, for the $HCN-FCH_2CH_2OH$ mixture above yields an equilibrium constant of 0.27 in excellent agreement with that determined from the steady-state ionic abundances. The rate constant data show that cyanide transfer is a relatively fast reaction allowing cyanide-exchange equilibrium to be usually established within 300–500 ms at pressures in the 10^{-6} Torr range.

$$(CN)_2H^- + FCH_2CH_2OH \rightleftarrows FCH_2CH_2OHCN^- + HCN \qquad (6)$$

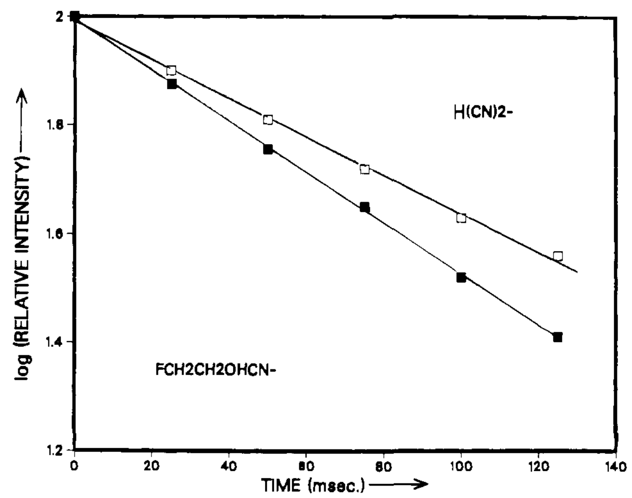

Figure 4. Variations of the intensities of $H(CN)_2^-$ ($FCH_2CH_2OHCN^-$) with time following continuous ejection of $FCH_2CH_2OHCN^-$ ($(CN)_2H^-$) after equilibrium has been established in the mixture in Figure 3.

Although attainment of a persistent steady-state ratio is taken as initial evidence that equilibrium has been established, confirmation is also sought in several ways: (1) The calculated equilibrium constant must be shown to be invariant with the neutral pressure ratio used. Minimum differences in pressure ratio of a factor of 5 are typically sought. (2) Multiple overlap experiments are carried out, as outlined in Table I, in which the free-energy difference in cyanide binding for any two compounds can be calculated from a sum of several free-energy differences for many compounds. Such "closed" thermochemical cycles ensure internally self-consistent data. (3) Double-resonance experiments are carried out at long trapping times to qualitatively ensure that cyanide transfer is occurring in both forward and reverse equilibrium directions. This verifies that a true equilibrium is being observed rather than a static steady state. (4) In many cases ion-ejection experiments, such as that in Figure 4, are carried out to allow determination of forward and reverse rate constants thus permitting a confirmatory calculation of the equilibrium constant.

Standard free-energy changes, $\Delta G°_7$, for cyanide-exchange equilibrium, eq 7, may be calculated from eq 8. These values also

$$R_1HCN^- + R_2H \rightleftarrows R_2HCN^- + R_1H \qquad (7)$$

$$\Delta G°_7 = -RT \ln K_7 \qquad (8)$$

given in Table I have a maximum uncertainty of ±0.2 kcal mol^{-1}.

C. Absolute Cyanide Binding Energies. The data outlined in Table I yield accurate relative cyanide binding energies; however, the only absolute cyanide binding energy to have been previously experimentally determined is that for H_2O-CN^- obtained from a pulsed electron beam high-pressure mass spectrometric study[25] of the equilibrium in eq 9a. The value of $\Delta H°_9$ at 298 K of 13.8 kcal mol^{-1} provides an absolute anchor point at the lower end of

$$CN^- + H_2O \rightleftarrows CN(H_2O)^- \qquad (9a)$$

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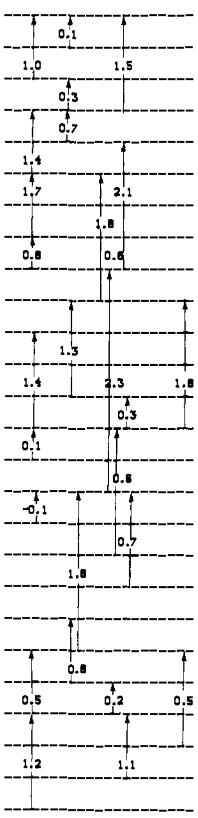
(25) Waddington, T. C. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 157.

Table I. Thermochemical Data Derived for Cyanide Adducts of Brønsted Acids[a]

ACID(AH)	$-\Delta G^\circ_7$	$-\Delta G^\circ_{10}$	$-\Delta S^\circ_{10}$	$-\Delta H^\circ_{10}$
CF3COCF2H		17.9	26.4	25.8
(CF3)2(CH3)COH		17.8	26.4	25.7
(CF3)2CHOH		16.8	26	25
CF3CH2OH		16.4	26.1	24.6
(CH2F)2CHOH		15.8	26.0	23.5
(CF2H)2O		15.1	26	22
HCN		13.7	26.9	21.7
CLCH2CH2OH		13.5	25.5	21.1
FCH2CH2OH		12.9	25.3	20.4
CH3COCF3		12.9	25.3	20.4
H2S		12.4	23.8	19.8
PYROLLE		12.3	23.8	19.5
CF3OCF2H		11.3	24.9	18.7
CF2HCFH2		11.0	24.8	18.4
CHCL3		10.8	24.8	18.2
t-C4H9OH		10.7	24.8	18.1
i-C3H7OH		10.7	24.8	18.1
CHCL2F		10.4	24.7	17.8
NCCO2C2H5		10.0	24.5	17.4
C2H5OH		10.0	24.5	17.4
CF3H		9.6	24.4	17.0
CH3OH		9.2	24.3	16.5
CH3CN		9.1	24.3	16.4
CH2CL2		9.0	24.2	16.3
CH3COCH3		8.0	22.5	14.7
H2O		7.9	19.8	13.8

[a] All ΔG° and ΔH° values in kcal mol^{-1}; ΔS° values in cal mol^{-1} K^{-1}.

the CN^- binding energy scale for the relative cyanide affinities obtained here.

A second absolute anchor point toward the upper end of the CN^- affinity scale is obtained from the data of Mautner for eq 9b for which a value of ΔH°_{10} of −20.7 kcal mol^{-1} has been determined.[26] Free-energy changes determined from the cyanide-exchange equilibria (eq 7) examined here are combined with entropy changes, ΔS°_{10}, for individual cyanide attachment reactions estimated by an approximate statistical thermodynamic method outlined previously,[3] employing translational and rotational partition functions. These values, also summarized in Table I, have a maximum uncertainty of approximately ±5 cal mol^{-1} K^{-1}. Values of ΔH°_{10} are obtained from eq 11 by employing the relative cyanide binding free energies, ΔG°_7, referenced to the value for H_2O, ΔG°_9, and the entropy estimates, ΔS°_{10}. The values of ΔH°_{10} given in Table I have an uncertainty of approximately ±2 kcal mol^{-1} based on the uncertainties in ΔH°_9, ΔS°_{10}, and ΔG°_7. The experimental difference in cyanide affinities of H_2O and HCN from high-pressure mass spectrometric experiments is thus seen to be well-reproduced by the present ICR determinators.

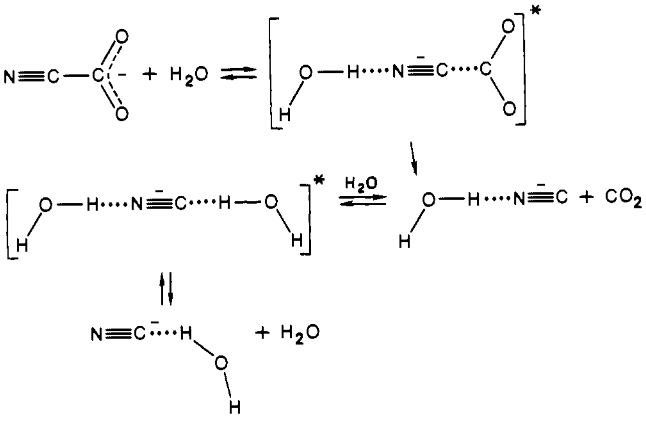
$$CN^- + HCN \rightleftarrows H(CN)_2^- \qquad (9b)$$

$$RH + CN^- \rightleftarrows RHCN^- \qquad (10)$$

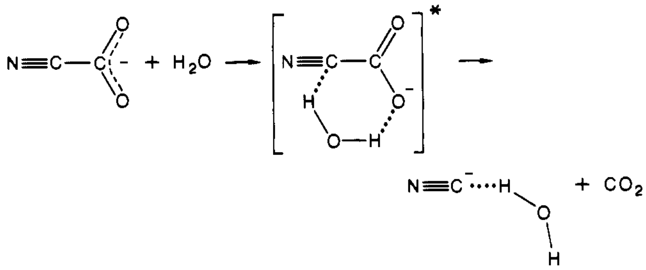
Discussion

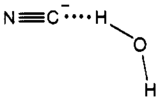
The structure of the cyanide adducts examined in the present work is by no means certain. Cyanide, being a well-known ambident nucleophile, may bind through either the carbon or nitrogen sites in forming hydrogen bonds. Using high-level ab initio calculations Jorgensen[22] has examined the binding of H_2O to both the carbon and nitrogen sites of CN^-. At the 6-31G(d) level (formerly denoted 6-31G*) Mulliken population analysis gives the charge on carbon to be −0.35 and that on nitrogen −0.65. At this level of calculation the carbon-bonded form (I) is favored by 1 kcal mol^{-1} over the nitrogen-bonded isomer (II). Addition of diffuse functions at the 6-31+G(d) level (6-31+G*) reverses this to a 1 kcal mol^{-1} preference for hydration at nitrogen. Addition of electron correlation (MP2/6-31+G(d)) reduces this to a 0.5 kcal mol^{-1} preference for nitrogen hydration. Despite the slight basis set dependence of which site is favored for hydration of CN^- it is clear that qualitatively both sites are comparable in binding energy and therefore structures for all adducts studied here involving both C and N binding must be considered possible.

Scheme I



Scheme II

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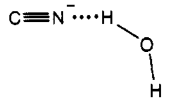
II

Consideration of the mechanism for addition of CN^- to each of the Brønsted acids and subsequent exchange of CN^- would indicate that in fact both possible structures are likely present. When H_2O is used as a typical substrate the mechanism outlined in Scheme I is illustrative. The species initially formed by CN^- transfer from $NCCO_2^-$ may be the nitrogen-bonded form if the intermediate produced is one in which CN^- bridges H_2O and CO_2. This species may then transfer cyanide to another water molecule by an intermediate in which CN^- bridges two water molecules. Thus after a sufficient number of CN^--exchange events have occurred an equilibrium distribution of carbon and nitrogen hydrogen-bonded forms should be present.

The mechanism for CN^- transfer from $CNCO_2^-$ to H_2O may also initially produce a hydrated ion bound through carbon via a carboxylate hydrogen bonded mechanism as shown in Scheme II. Subsequent exchange of H_2O via the process shown in Scheme I would then also lead to a mixture of C- and N-bonded hydrates. Alternatively an exchange mechanism may operate as in Scheme III whereby no change in the original site of binding occurs in which case only the nitrogen- or carbon-bonded form initially produced by the mechanisms in either Scheme I or Scheme II would be present.

In order to probe the relative probabilities of Schemes I and III for CN^- exchange, ab initio calculations for the two possible

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(26) Caldwell, G.; Kebarle, P., cited as private communication in ref 12.

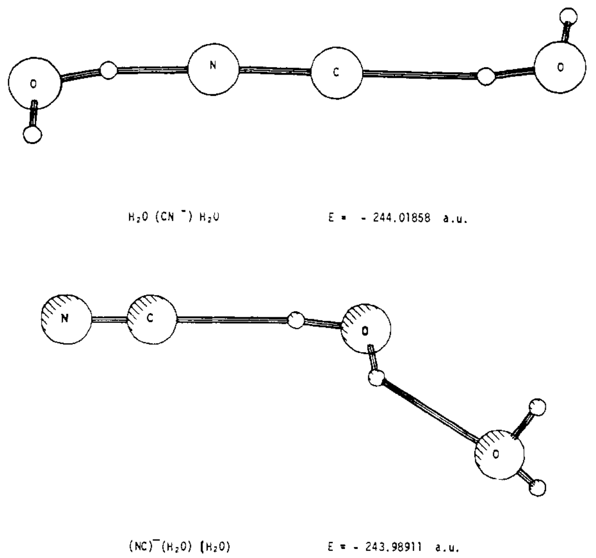
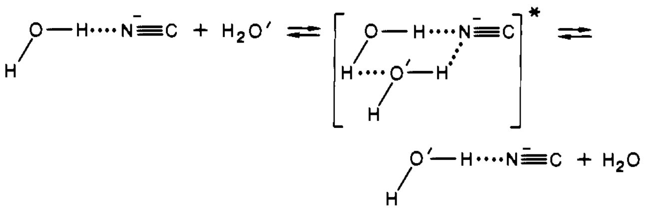


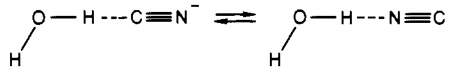
Figure 5. Structures of intermediates involved in transfer of CN^- between a pair of water molecules obtained from ab initio calculations employing a 4-31G basis set.

Scheme III



intermediates involved in CN^- exchange were performed. The optimized geometries obtained at the 4-31G level of calculation are illustrated in Figure 5. Although this basis set does not quantitively reproduce absolute ion–molecule interaction energies, the relative energies are probably sufficiently disparate (18.5 kcal mol^{-1}) to allow the qualitative conclusion that $H_2O(CN^-)H_2O$ is more stable than $(CN^-)(H_2O)(H_2O)$ and that therefore Scheme I represents the more probable mechanism for CN^- exchange. Thus an equilibrium mixture of nitrogen- and carbon-bonded adducts of CN^- is likely present in all of the CN^- Brønsted acid adducts examined here.

A further possibility has been suggested by a referee in which a unimolecular isomerization of the carbon- and nitrogen-bound cyanide complexes occurs (eq 11). In view of the very high barriers to unimolecular isomerization for $CN^-(BX_3)$ complexes found by Marynick,[21] we consider that this mechanism for the hydrogen-bonded complexes examined here is unlikely.



$$\mathrm{HO{-}H{\cdots}C{\equiv}N^-} \rightleftharpoons \mathrm{HO{-}H{\cdots}N{\equiv}C} \quad (11)$$

Data previously obtained from this laboratory for binding of F^- and Cl^- to Brønsted acids revealed several interesting trends.[3,6] Fluoride ion binding energies were found to correlate extremely well with gas-phase acidities within a given functional group series such as alcohols. A similar examination of chloride ion binding energies as a function of gas-phase acidity revealed that even within the alcohol functional group series a notable deviation from linear correlation occurred. Those compounds exhibiting deviations were found to be primarily those able to undergo interaction at more than one site in the molecule,[5] that is molecules with more than one acidic site. This extra interaction has the result of enhancing the chloride ion binding energy relative to that expected from either the gas-phase acidity or fluoride ion binding energy data.

A comparison of cyanide binding energy data to either fluoride or chloride binding energy data for the same series of compounds should then provide insights into the nature of CN^- interactions with Brønsted acids. Since the ionic radius of CN^- is very similar to that of Cl^- a similar tendency to undergo multiple site interactions might be expected. Further, since charge may be distributed on two centers, both of them first-row atoms, an enhanced ability to undergo multiple-site interaction relative even to chloride might be possible. In addition the greater basicity of CN^- relative to Cl^- would suggest that stronger interactions for cyanide should occur than for chloride but the interactions should be weaker than those for fluoride. Conversely if the charge in cyanide is significantly delocalized much weaker interactions than anticipated on the basis of its basicity should result.

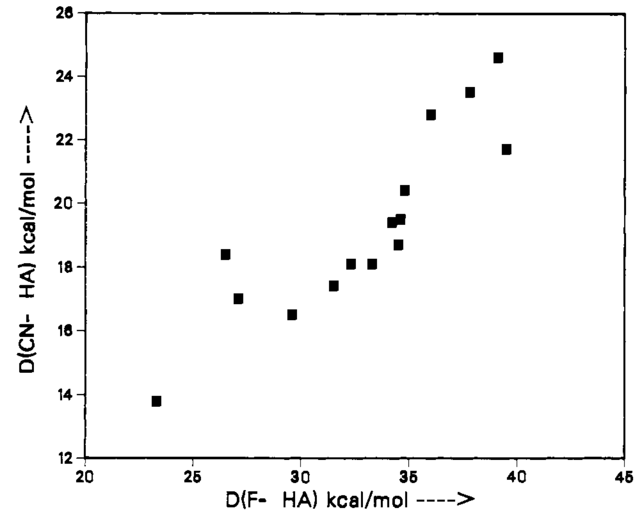


Figure 6. Variation of gas-phase cyanide binding energies with fluoride binding energies for Brønsted acids.

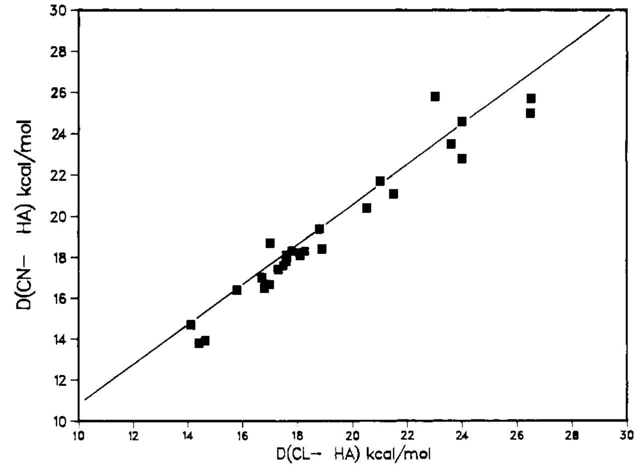


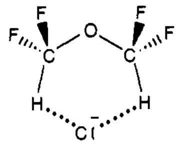
Figure 7. Variation of gas-phase cyanide binding energies with chloride binding energies for Brønsted acids.

A comparison of fluoride and cyanide binding energies is shown in Figure 6. This plot is very reminiscent of that obtained previously comparing fluoride and chloride binding energy data since in several cases cyanide binding is apparently enhanced relative to that anticipated from the fluoride data. A comparison of chloride and cyanide binding energy data shown in Figure 7 shows an excellent correlation (eq 12), suggesting that the atomic

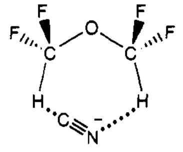
$$D(CN^- \text{---} HA) = 0.97D(Cl^- \text{---} HA) + 1.23 \text{ kcal mol}^{-1} \quad (12)$$

chloride ion and diatomic cyanide ion are similar in their binding properties despite the very large difference in gas-phase basicities of the two anions. In this connection it is interesting to recall that the thermochemical radius of chloride is 1.81 Å while that of cyanide is 1.82 Å.[25]

Only three compounds give significant deviations from the otherwise linear correlation of chloride and cyanide binding energies. The deviation of $(CHF_2)_2O$ from the correlation is immediately noteworthy since this species has been previously identified as being able to chelate both F^- and Cl^- through the two acidic hydrogens. Evidently the cyanide ion for reasons of geometry or charge dispersal is not as readily able to chelate as is chloride. The roughly 7 kcal mol^{-1} enhancement in binding energy for attachment of Cl^- to $(CHF_2)_2O$ (III) relative to CHF_2OCF_3 is reduced to a 4 kcal mol^{-1} enhancement of the CN^- adduct of $(CHF_2)_2O$ (IV). A similar explanation may be advanced for chloride and cyanide adducts of $(CF_3)_2CHOH$.

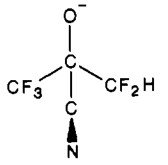


III

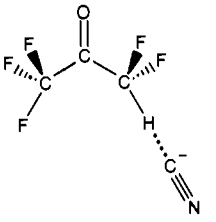


IV

The deviation of CF_3COCF_2H from the correlation of cyanide and chloride ion binding energies is in the opposite direction of those for $(CHF_2)_2O$ and $(CF_3)_2CHOH$; that is the cyanide binding energy is greater than that predicted by the correlation of eq 12. In addition it may be noted that the binding energy of CN^- to CF_3COCF_2H is very similar to those for the aprotic carbonyl Lewis acids COF_2, CF_3CFO, and CF_3CF_2CFO. As a result it may be possible that the cyanide adduct of CF_3COCF_2H is in fact the more conventionally accepted tetrahedral alkoxide structure, V, rather than the hydrogen bonded form, VI, found in fluoride and chloride adducts of CHF_2COCF_3.



V



VI

From an examination of trends in hydrogen bond energies of F^-, Cl^-, and CN^- from this laboratory[2-7] and for I^-,[10] alkoxides (RO^-),[12,13] and others from other laboratories it is evident that in addition to the dependence on acidities of HX and HY the hydrogen bond strength in anions XHY^- is also dependent upon the electronegativity of the heteroatoms in X and Y involved in hydrogen bond formation.[6,12] In order to quantify this dependence and to develop a capability for prediction of unknown anionic hydrogen bond strengths an empirical relation, eq 13, was formulated where $\chi(X)$ and $\chi(Y)$ are the electronegativities of X and Y, respectively. Values of anion binding energy obtained

$$D(X^- \cdots HY) = (443 - D(Y^- - H^+))\left[\frac{\chi(X) + \chi(Y)}{12} + \frac{D(X^- - H^+)}{300} - 1.4\right] \tag{13}$$

from this relationship are shown in Table II and compared to the experimentally determined values. For the halide ions, CN^-, NO_2^-, and NO_3^- it can be seen that eq 13 very accurately reproduces the experimental data with an average deviation of about 2–3 kcal mol^{-1}.

Table II. Comparison of Anion–Brønsted Acid Interaction Energies from Experiment and Equation 13

$X^- \cdots HY$		$D(X^- - HY)$, kcal mol^{-1}	
X^-	Y	expt[d]	eq 13
F^-	H_2O	23	24
	$HOCH_3$	30	28
	$HOtC_4H_9$	33	31
	$HOCH_2CF_3$	39	36
	$HOCOCH_3$	44	43
	H_2S	35	34
	HCN	39	34
	HCF_3	27	26
	HCHFPh	24	25
	HF	39	36
Cl^-	H_2O	14	14
	$HOCH_3$	17	16
	$HOtC_4H_9$	18	18
	$HOCH_2CF_3$	24	21
	$HOCOCH_3$	24	25
	HOCOH	26	26
	$HOC(CF_3)_2(CH_3)$	27	24
	$H\text{-}CH_2COCH_3$	14	14
	H·Ph	10	9
	HCN	21	17
	HF	22	22
	H_2S	12	17
	HCl	23	26
CN^-	H_2O	14	14 (14)
	$HOCH_3$	18	17 (17)
	$HOCH_2CF_3$	25	22 (21)
	$HOC(CF_3)_2CH_3$	27	25 (24)
	HCF_3	18	14 (13)
	HCH_2COCH	17	15 (14)
	HCH_2COCF_3	22	19 (18)
	HCN	23	18 (18)
	H_2S	21	18 (18)
	HF	21	23 (23)
Br^-	H_2O	13	11
	$HOCH_3$		13
	$HOCOCH_3$	21	20
	HOCHO	22	21
	HF	17	19
	HCl	20	21
	HBr	21	21
	HI	25	19
I^-	H_2O	10	8
	$HOCH_3$	11	10
	$HOCOCH_3$	17	15
	HF	15	14
	HCl	14	15
	HBr	16	14
	HI	17	12
HO^-	H_2O	27[b]	25
CH_3O^-	H_2O	24[b]	23
	$HOCH_3$	29[b]	27
	$HOtC_4H_9$	31[b]	30
$t\text{-}C_4H_9O^-$	$HOCH_3$	25[b]	26
PhC_2^-	$HOCH_3$	21[c]	21
$CF_3CH_2O^-$	HF	32	31
$CH_3CO_2^-$	HF	21	27

[a] Unless otherwise indicated all data are taken from the following: Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data*, in press. [b] Reference 13a. [c] Data from ref 12 corrected by new data in ref 13a.

In the case of CN^- the binding energies were calculated from eq 13 for interaction through both the carbon and nitrogen sites. Nitrogen–hydrogen bonded energetics are shown in parentheses. The value of gas-phase acidity of HNC necessary to determine these latter values is taken as 338.5 kcal mol^{-1}, that is nearly 15 kcal mol^{-1} more acidic than HCN, based on an appearance energy determination of $\Delta H_f°$(HNC) by Lifshitz[27] and by ab initio calculation.[28] Once again it is noteworthy that hydrogen bond energies to both carbon and nitrogen are comparable as a consequence of the cancellation of effects due to the greater acidity of HNC relative to HCN but greater electronegativity of N relative to C. For anions which are extensively charge delocalized such as acetate ($CH_3CO_2^-$), eq 13 overestimates the experimentally determined hydrogen bond energy because of the inhibition of resonance stabilization of the anion when the addition of the hydrogen-bonding substrate forces the negative charge to be localized at a single site. The difference between the calculated and experimental hydrogen bond energies in such cases may be used to infer the magnitude of the contribution to the acidity of the parent acid through resonance delocalization of charge.

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(27) Lifshitz, C.; Gotchiguian, P.; Roller, R. *Chem. Phys. Lett.* **1983**, *95*, 106.

(28) Pearson, P. K.; Schaefer, H. F.; Wahlgren, U. *J. Chem. Phys.* **1975**, *62*, 350.

Table III. Energetics of Association of Solvated Anions, $A^-(RH)_n$, with Brønsted Acids Calculated from Equation 14[a]

	$A^- = Cl^-$						$A^- = F^-$			
	RH = H_2O		RH = HCl		RH = CH_3CN		RH = H_2O		RH = HF	
	eq 14	expt	eq 14	expt	eq 14	expt	eq 14	expt	eq 14	ab initio
$\Delta H°_{0,1}$	14	14	26	24	13	13	24	23	36	53
$\Delta H°_{1,2}$	11	13	17	15	10	12	20	17	27	32
$\Delta H°_{2,3}$	9	12	11	12	8	11	16	14	21	25
$\Delta H°_{3,4}$	8	8	7	10	6	6	13	14	16	17

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

For clusters of hydroxide ion and alkoxide ions there are two possible sets of data to be used for comparison with eq 13. The first of these is due to Bartmess et al.,[12] which reports RO^----HOR′ binding energies from ICR exchange equilibria relative to a value for CH_3O^----$HOCH_3$ of 21.8 kcal mol^{-1} based on unpublished high-pressure mass spectrometric work by Kebarle.[26] The second, very recent data set is a high-pressure mass spectrometric study by Mautner and Sieck[13] in which the CH_3O^----$HOCH_3$ interaction is determined to be 28.8 kcal mol^{-1}. The value for this hydrogen bond energy predicted by eq 13 is 27 kcal mol^{-1}, in excellent agreement with the latter determination. Similarly, data for other alkoxides and hydroxide with alcohols and H_2O give excellent agreement with Mautner's data. Accordingly these are the experimental values reported in Table II. In a series of ab initio calculations of single hydration energies of anions Jorgensen[22] has obtained a CH_3O^----H_2O interaction energy of 25.8 kcal mol^{-1} at the highest level of calculation used. This agrees reasonably well with that predicted by eq 13 of 23 kcal mol^{-1}.

It is evident therefore that eq 13 correctly predicts absolute magnitudes of hydrogen bond strengths in anions as well as the qualitative behavior of increasing hydrogen bond strength with more acidic acceptors and/or more basic donors. In addition unlike previous empirical equations it provides quantitative predictions for a variety of heteroatoms in the complexes by introduction of a dependence on the electronegativity of the hydrogen bonding heavy atoms.

Addition of solvent molecules to an anion reduces the basicity relative to the free anion. Equation 13 may thus be employed to calculate successive solvation energies in an iterative fashion by calculation of a new $D(Y^-{-}H^+)$ from the sum of the previous solvation energies as in eq 14. In this way the data shown in Table III are obtained for a variety of Cl^- and F^- clusters and may be compared with experiment. The agreement may be seen to be

$$D(A^-(RH)_n{-}H^+) = D(A^-{-}H^+) + \sum_{j=1}^{n-1} \Delta H_{j-1,j} \qquad (14)$$

moderately good considering the several steps involved in the calculation, which successfully reproduces the qualitative behavior of decreasing successive interaction energetics with increasing number of solvent molecules added.

Conclusions

A method of bimolecular generation of cyanide adducts of Brønsted acids at low pressures has been demonstrated. This method, involving negative ion–molecule reaction sequences in ethyl cyanoformate, has been used as a means of determination of relative cyanide binding energies to Brønsted acids from examination of cyanide-exchange equilibria. The cyanide binding energies thus obtained are observed to very closely parallel those of chloride adducts. This may be rationalized in terms of the greater basicity but increased charge delocalization of the cyanide ion and in addition the lower electronegativity of the hydrogen bonding site relative to chloride. These data, coupled with previous work for F^- and Cl^- binding from this laboratory as well as data for HO^- and RO^- binding from other workers may be used to formulate an empirical equation for prediction of anion–Brønsted acid hydrogen bond energies. The empirical formula developed attempts for the first time to include effects due to the electronegativity of the atomic sites involved in the hydrogen bond as well as the more usual contributions due to the acidity of the conjugate acids. This equation very accurately reproduces experimental data as well as showing predictive abilities for energetics of higher order clusters.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged as is the assistance of J. Fisher, H. Gamble, and C. Allison in carrying out calculations and preparation of figures.

Registry No. $NCCO_2C_2H_5$, 623-49-4; HCN, 74-90-8; KCN, 151-50-8; HCl, 7647-01-0; $(NC)_2CO_2C_2H_5^-$, 109909-15-1; CCl_4, 56-23-5; $NCCO_2^-$, 109909-16-2; CN^-, 57-12-5; CF_3COCF_2H, 431-71-0; $(CF_3)_2(CH_3)COH$, 1515-14-6; $(CF_3)_2CHOH$, 920-66-1; CF_3CH_2OH, 75-89-8; $(CH_2F)_2CHOH$, 453-13-4; $(CF_2H)_2O$, 1691-17-4; $ClCH_2CH_2OH$, 107-07-3; FCH_2CH_2OH, 371-62-0; CH_3COCF_3, 421-50-1; H_2S, 7783-06-4; CF_3OCF_2H, 3822-68-2; CF_2HCFH_2, 430-66-0; $CHCl_3$, 67-66-3; t-C_4H_9OH, 75-65-0; i-C_3H_7OH, 67-63-0; $CHCl_2F$, 75-43-4; C_2H_5OH, 64-17-5; CF_3OH, 1493-11-4; CH_3OH, 67-56-1; CH_3CN, 75-05-8; CH_2Cl_2, 75-09-2; CH_3COCH_3, 67-64-1; H_2O, 7732-18-5; HF, 7664-39-3; $HOCOCH_3$, 64-19-7; HCHFPh, 350-50-5; HOCOH, 64-18-6; H-Ph, 71-43-2; HBr, 10035-10-6; HI, 10034-85-2; F^-, 16984-48-8; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; HO^-, 14280-30-9; CH_3O^-, 3315-60-4; t-$C_4H_9O^-$, 16331-65-0; PhC_2^-, 20404-08-4; $CF_3CH_2O^-$, 24265-37-0; $CH_3CO_2^-$, 71-50-1; pyrrole, 109-97-7.