to explain the otherwise rare occurrence of a radical cation and neutral resulting from closed-shell ion and neutral reactants. The CID-MIKES spectrum of this ion also supports the structure proposed above. Cleavage of the C–N bond results in peaks of comparable intensity at *m/z* 15 (CH_3^+) and *m/z* 34 (NFH^+). Loss of HF + H results in a broad major peak at *m/z* 28 ($HCNH^+$) with smaller contribution at *m/z* (H_2CNH^+) from loss of HF and *m/z* 27 (HCN^+) from loss of HF + H_2.

Further experiments are planned to attempt to generate selectively $^3NF_2^+$ to establish the different reactivity of the possible electronic states of the difluoronitrenium ion.

Conclusion

Ion cyclotron resonance, high-pressure mass spectrometric, and collision-induced decomposition experiments as well as ab initio calculations have been used to investigate the gas-phase ion–molecule reactions occurring in nitrogen trifluoride–methane mixtures. The major feature of this chemistry is the production of nitrogen protonated hydrogen cyanide from the reaction of both NF_2^+ and NF_3H^+ with methane. In the former case a probable mechanism involving C–H bond insertion of the carbene-like cation NF_2^+ has been proposed consistent with each of the types of experimental data obtained. Protonated NF_3 has been strongly suggested to be a fluorine protonated species which reacts via NF_2^+ transfer to CH_4 in a manner exactly analogous to that of naked NF_2^+. The potential energy surface has been qualitatively explored using ab initio calculations which show that the proposed intermediates and transition states are energetically feasible. A difference in reactivity of $^1NF_2^+$ and $^3NF_2^+$ has been proposed based on the appearance of a radical cation product, CH_3NFH^+.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. The assistance of Dr. A. Young of the Ontario Regional Ion Chemistry Laboratory is also acknowledged as is that of Professor T. H. Morton and D. Stams of the University of California, Riverside, for facilitating use of the San Diego State Super Computer Center.

Gas-Phase Lewis Acid–Base Interactions. An Experimental Determination of Cyanide Binding Energies from Ion Cyclotron Resonance and High-Pressure Mass Spectrometric Equilibrium Measurements

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Abstract: Both ion cyclotron resonance and high-pressure mass spectrometric equilibrium techniques have been used to investigate the binding energies of anions to a variety of Lewis acids. From an analysis of the enthalpy changes associated with CN^- binding it is evident that in cases of relatively weak binding considerable freedom of rotational motion of CN^- in the complex may be retained. Ab initio calculations and experiment suggest that binding through both the N and C sites of CN^- is nearly equally favorable in some cases. In contrast to results previously obtained for Brønsted acids which showed that CN^- and Cl^- bind nearly identically, the present data for Lewis acids show many cases where cyanide is much more favorably bound than chloride, a consequence of enhanced covalent binding of the CN^- complexes. New Kroeger Drago parameters derived for CN^- support the importance of covalent binding in cyanide adducts. Correlations of binding energy of anions to Lewis acids with the anion proton affinity show excellent linear relationships which may be used to predict binding energetics for new anions.

Since the introduction by Lewis of the electron pair acceptor–electron pair donor definition of acids and bases,[1] chemists have attempted to develop quantitative Lewis acidity and basicity scales. These attempts have been largely frustrated by the failure of a given series of Lewis acids to display the same qualitative order of binding strength toward different bases. The realization that such a constant ordering of strengths is not possible came as an outgrowth of a better understanding of bonding interactions.[2] As a result, in 1965 Drago and Wayland[3] formulated an equation predicting acid–base interaction energetics based on the ability of both acid and base to participate in electrostatic and covalent interactions. From examination of a large number of interactions, *E* (electrostatic) and *C* (covalent) parameters were assigned to species such that the strength of interaction between acid (A) and base (B) is given by eq 1. A similar, more qualitative theory, the hard–soft Acid–Base (HSAB) principle, was advanced at roughly the same time by Pearson,[4] in which acids and bases were classified as either "hard" or "soft" with the general formalism that hard–hard or soft–soft acid–base interactions are more favorable than hard–soft interactions. In effect this principle also recognizes the simple idea that individual electrostatic and covalent interactions are highly idiosyncratic.

$$-\Delta H_{A-B} = E_A E_B + C_A C_B \qquad (1)$$

Each of these, and similar, theories suffers from the significant disadvantage that they are formulated largely on the basis of solution-phase interactions. Thus interactions of species, particularly ionic ones, with solvent can disguise the magnitude of interaction of that species with its acid or base substrate counterpart. For this reason gas-phase acid–base interaction energetics are particularly valuable since the intrinsic, electronic nature of

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the interaction is revealed and can then be meaningfully theoretically modeled.

We have recently developed the first quantitative scales of binding energetics of both F^- and Cl^- with a sufficient number of Lewis acids to deduce substituent effects, periodic trends, and effect of reference base on the interaction.[5] These data have in turn allowed an assessment of the generality of the various theories of acid–base interaction when extended to gas-phase interactions. While revealing, these data were limited in dealing only with spherical, monoatomic halide ions. In order to expand the data base and gain a more complete understanding of these interactions, we have carried out the measurements outlined in the present manuscript for cyanide ion–Lewis acid interactions.

Even though it is frequently classified as a pseudo-halide,[6] cyanide differs from F^- and Cl^- in being diatomic and also ambident, that is it is able to coordinate acids through either the carbon or nitrogen site. For example, Marynick[7] has shown that the interactions of CN^- with BH_3, BF_3, and $B(CH_3)_3$ are comparable in energy through either C or N binding although a significant barrier exists for their interconversion. However, cyanide is known to have a thermochemical radius of 1.82 Å,[8] nearly identical with that of Cl^-, and in a recent publication we have shown that toward a wide variety of Brønsted acids cyanide binds with a strength nearly identical with that for the corresponding Cl^- adduct.[9] In each case, however, CN^- is binding to a nearly constant reference acid (A–H), although the environment of the hydrogen bond is somewhat variable. Our analysis of the hydrogen bond energetics, however, suggested that the similarity of CN^- to Cl^- was a result of a cancellation of factors associated with the different H^+–CN^- and H^+–Cl^- heterolytic bond dissociation energies and the different electronegativities of carbon (or nitrogen) and chlorine. Therefore, it might be anticipated that cyanide and chloride would not reveal similar characteristics in binding to Lewis acids.

Mautner et al.[18] have recently examined the binding of CN^- to HCN using both ab initio calculations and high-pressure mass spectrometric experiments. From the data obtained for both single and multiple solvation of CN^- by HCN, these authors have suggested that CN^- exhibits a nearly spherical character in its binding to HCN. This is in accord with our own previous conclusion that CN^- and Cl^- exhibit nearly identical behavior in their binding to Brønsted acids in general,[9] which can be attributed to the nearly identical ionic radii of the two anions participating in interactions which are predominantly electrostatic in character. It was of considerable interest in the present work therefore to determine whether the similarity between CN^- and Cl^- interactions is retained in situations where the interaction of CN^- with a substrate becomes more covalent and somewhat stronger.

The data obtained in the present work involves examination of two types of gas-phase ion–molecule equilibria. The first of these, bimolecular cyanide exchange equilibrium (eq 2), was

$$L_1CN^- + L_2 \rightarrow L_2CN^- + L_1 \qquad (2)$$

examined by pulsed ion cyclotron resonance spectrometry. In previous work for F^- and Cl^- the $\Delta G°$ data obtained were converted to $\Delta H°$ data using assumptions regarding the entropy changes for halide transfer which appeared to be quite accurate. As outlined below, it was anticipated that CN^- to Lewis acid interactions might involve significantly greater negative entropy changes than observed for F^- and Cl^-. For this reason pulsed ionization high-pressure mass spectrometric measurements of termolecular cyanide clustering equilibria (eq 3) were also carried

$$CN^- + L \rightarrow LCN^- \qquad (3)$$

out over a sufficiently large temperature range to allow both $\Delta H°_3$ and $\Delta S°_3$ to be determined. These two types of data taken together allowed construction of the CN^- binding energy scale described here.

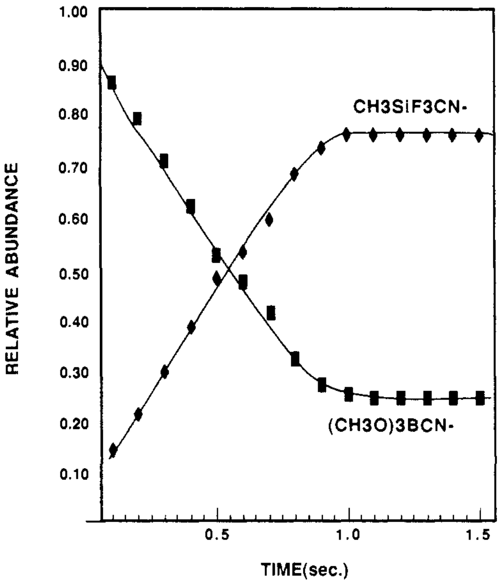

Figure 1. Variation of relative ionic abundances as a function of time in an ICR experiment following a 5-ms, 70-eV, electron beam pulse in a 1:6.1:7.1 mixture of $(CH_3)_3OB$: $(CN)CO_2C_2H_5$ at a total pressure of 2.0×10^{-6} torr.

Experimental Section

All ICR experiments were carried out at ambient temperature (25 °C) using a pulsed ion cyclotron resonance spectrometer of dual region cell design capable of both conventional drift and trapped ion ICR experiments.[10] Details of the technique have been described in detail elsewhere.[11]

Pulsed ionization high-pressure mass spectrometric experiments were performed on an instrument recently constructed at the University of Waterloo.[12] High-pressure mass spectrometric techniques have been recently reviewed.[13]

In both types of experiment cyanide ion was generated by dissociative electron attachment to ethyl cyanoformate (eq 4). In ICR experiments

$$\text{NÇ}CO_2C_2H_5 + e^- \rightarrow CN^- + CO_2C_2H_5 \qquad (4)$$

the CN^- thus formed reacts subsequently with the parent ester via nucleophilic displacement to generate cyanoformate, $NCCO_2^-$ (eq 5), which

$$CN^- + NCCO_2C_2H_5 \rightarrow NCCO_2^- + C_2H_5CN \qquad (5)$$

served as a bimolecular cyanide donor to the desired Lewis acid substrate. Under conditions of the HPMS experiments direct clustering of CN^- to the parent ester occurred, and this species also served as a CN^- source for the Lewis acid substrates (eq 6) in addition to the direct clustering (eq 3).

$$(CN)_2CO_2C_2H_5^- + L \rightarrow LCN- + NCCO_2C_2H_5 \qquad (6)$$

In some cases N_2O was also introduced to produce OH^- which also reacted rapidly with the ethyl cyanoformate to generate $NCCO_2^-$. Ethyl cyanoformate (99%) was obtained from Aldrich Chemical Co. All other Lewis acids were commercialy available materials 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

Cyanide exchange equilibrium measurements for pairs of Lewis acids (eq 2) were carried out using ion cyclotron resonance spectroscopy, as described previously for pairs of Brønsted acids. A typical cyanide exchange equilibrium experiments is shown in

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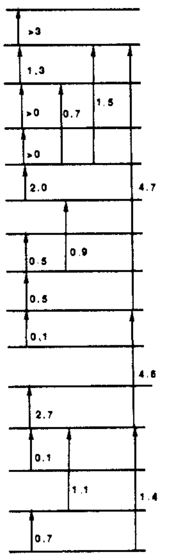
Table I. Thermochemical Data Derived from Examination of Equilibria Involving Cyanide Binding to Lewis Acids

COMPOUND	ΔG (2)	ΔG°_{298}	ΔS°_{298}	ΔH°_{298}
$(C_2H_5)_3B$		>22	36	>33
SiF_4		18.3	30	27.2
CF_3CF_2CFO		17.2	35	27.6
SF_4		16.9	30	25.8
AsF_3		16.6	28	24.9
OPF_3		14.6	30	23.5
CF_3CFO		14.2	35	24.6
CH_3SiF_3		13.7	30	22.6
SO_2		13.2	28.4	21.7
OCF_2		13.1	35	23.5
$(CH_3O)_3B$		10.7	35	19.6
CO_2		8.0	31.5	17.3
$(CH_3)_2SiF_2$		7.9	30	16.8
OSF_2		6.9	30	15.8
PF_3		6.4	30	15.3

[a] ±0.2 kcal mol^{-1}. [b] ±0.5 kcal mol^{-1}. [c] ±2 cal mol^{-1} K^{-1}. [d] ±1 kcal mol^{-1}.

Figure 1 for a mixture of methyltrifluorosilane and trimethyl borate, (eq 7). From the manometrically prepared known neutral

$$NCB(OCH_3)_3^- + F_3SiCH_3 \rightarrow NCSi(CH_3)F_3^- + B(OCH_3)_3 \quad (7)$$

partial pressure ratio and the relative anionic abundances at equilibrium, the equilibrium constants for cyanide exchange, K_2, could then be accurately experimentally determined. The free energy change, ΔG°_2, for cyanide exchange could then be readily obtained from (eq 8). In addition to mixtures containing two

$$\Delta G^\circ_2 = -RT \ln K_2 \quad (8)$$

Lewis acids, mixtures consisting of Lewis acids and Brønsted acids were also examined in order that the scale of Lewis acid cyanide binding free energies could be related to those of the protic species previously determined. It is of some interest to note that the approach to equilibrium steady-state ionic abundances took considerably longer when both species involved were Lewis acids than when one of the equilibrium participants was a protic acid. In all cases double resonance experiments established the occurrence of reaction in both forward and reverse reaction directions, however. The free energy changes directly obtained between pairs of Lewis acids are summarized in Table I. Absolute free energies of attachment of CN$^-$ to the Lewis acids, ΔG°_3, were initially assigned on the basis of the only previously determined cyanide clustering equilibrium, that to H_2O (eq 9).[14] The value

$$CN^- + H_2O \rightarrow CN(H_2O)^- \quad (9)$$

of ΔG°_9 of −7.9 kcal mol^{-1} and equilibria relating Brønsted acid cyanide energetics to those for Lewis acids allowed initial assignment of values of ΔG°_3 also given in Table I.

In previous studies of F$^-$ and Cl$^-$ clustering to Lewis acids, entropies of association, ΔS°_3, had been estimated from the known entropy of the gaseous halide ion and neutral Lewis acid and estimates of the entropy of the new anionic adduct from either the known entropy of an isoelectronic neutral analogue or statistical thermodynamic calculations where sufficient data were available. When similar isoelectronic calculations were carried out for CN$^-$, it was evident that instead of the ~25 cal mol^{-1} K^{-1} entropy loss usually obtained for clustering of the halide ions, for association reactions of CN$^-$ with Lewis acids the entropy changes were usually in the −30 to −35 cal mol^{-1} K^{-1} range. In order to experimentally verify that such entropy changes were, in fact, reasonable, high-pressure mass spectrometric (HPMS) investigations of the energetics of association of CN$^-$ with several Brønsted and Lewis acids were carried out. For example, the variation of CN$^-$ and CNCO$_2^-$ abundances as a function of time after initial ionization is shown in Figure 2. This type of data taken over a wide temperature range allows construction of a plot of equilibrium constant K_3 versus reciprocal temperature, shown in Figure 3, from which accurate values of ΔH°_3 and ΔS°_3 can be obtained. The data obtained for CN$^-$ clustering with CO_2 (eq 10) give ΔH°_{10} of −17.4 kcal mol^{-1} and ΔS°_{10} of −31.5 cal mol^{-1}

$$CN^- + CO_2 \rightarrow NCCO_2^- \quad (10)$$

K^{-1}. Using group equivalent and bond additivity methods,[15] the entropy of $CH_2C(CN)F$ can be estimated and from this the entropy for isoelectronic NCCO$_2^-$, determined to be 67.2 cal mol^{-1} K^{-1}. In this way,[15] taking $S^\circ(CN^-)$ as 47.0 cal mol^{-1} K^{-1} and $S^\circ(CO_2)$ as 51.1 cal mol^{-1} K^{-1}, ΔS°_{10} can be estimated to be −31 cal mol^{-1} K^{-1}, in excellent agreement with the experimental determination. In similar fashion values of ΔH°_3 and ΔS°_3 were obtained for $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, CH_3SiF_3, PF_3, and CF_3CF_2CFO. These data, when combined with the ICR CN$^-$ exchange equilibrium data, ΔG°_2, allowed assignment of the set of values, ΔG°_3, ΔS°_3, and ΔH°_3 given in Table I.

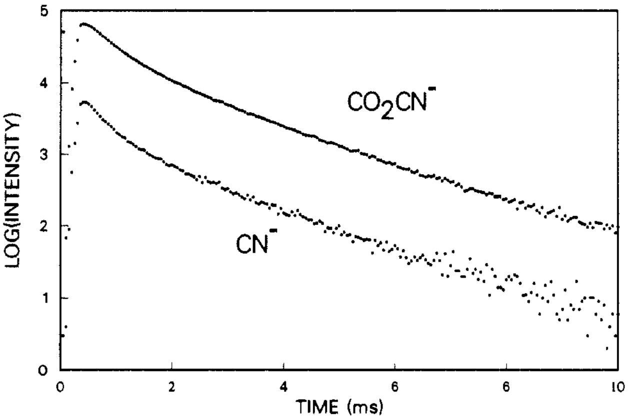


Figure 2. Variation of absolute ionic abundance as a function of time in a high-pressure mass spectrometric experiment following a 50 μs, 2000-eV electron beam pulse in a mixture of $(CN)CO_2C_2H_5$:CO_2:CH_4 at a total ion source pressure of 5.0 torr at 55 °C.

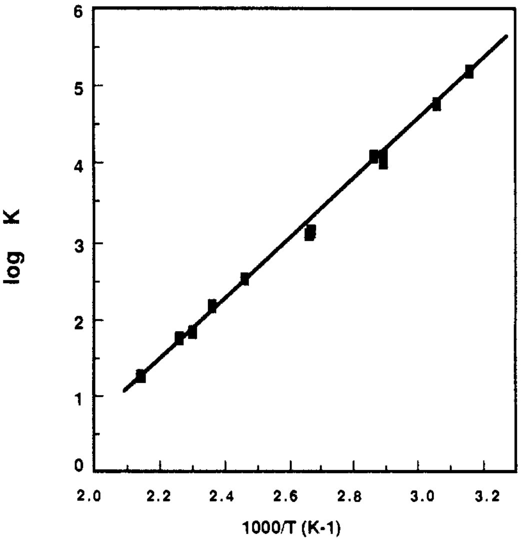


Figure 3. van't Hoff plot for the clustering reaction of CN$^-$ onto CO_2.

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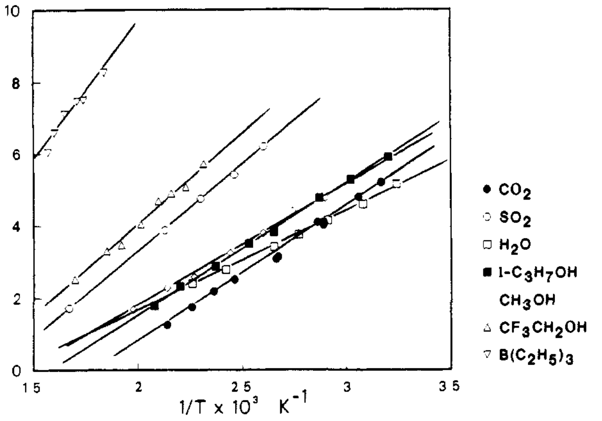

Figure 4. van't Hoff plots for the clustering reactions of CN^- onto a variety of Lewis and Brønsted acids.

Table II. Thermochemical Data Derived from CN^- Clustering Equilibria Measurements: $LCN^- \rightarrow L + CN^-$

L	$\Delta G°_{298}$ (kcal mol^{-1})	$\Delta H°$ (kcal mol^{-1})^b	$\Delta S°$ (cal mol^{-1} K^{-1})^c
$B(Et)_3$	27.6	35.9	28
CF_3CH_2OH	15.1	24.0	30
SO_2	13.4	21.7	28
i-C_3H_7OH	9.0	16.7	26
CH_3OH	8.8	15.7	23
CO_2	7.9	17.3	31.5
H_2O	7.3	12.7	18

[a] ±0.2 kcal mol^{-1}. [b] ±0.8 kcal mol^{-1}. [c] ±2 cal mol^{-1} K^{-1}.

In order to ensure that cyanide binding energies previously assigned for Brønsted acids were accurate, the clustering of CN^- to H_2O was reexamined using our pulsed ionization high-pressure mass spectrometer. In addition the binding to isopropyl alcohol was also examined in order to compare $\Delta S°$ changes for clustering to other hydrogen bonding acids to those for Lewis acids. Equilibrium data for all of the termolecular clustering equilibria examined are shown in Figure 4 and the thermochemical data derived are summarized in Table II.

Discussion

1. The Nature of Binding of CN^-. Each of the Lewis acids involved in the present study has been examined previously in determinations of fluoride and chloride binding energies to Lewis acids. The plot of fluoride versus cyanide binding energies in Figure 5 shows a moderately good qualitative correlation between these two quantities. The plot of chloride versus cyanide energies, Figure 6, exhibits considerably more scatter, however. These plots do reveal that CN^- is *always* more weakly bound than F^- to Lewis acids while it is either more strongly bound than or comparable to Cl^- in binding to Lewis acids. These data are initially somewhat surprising in view of our previous observation that Cl^- and CN^- binding energies to Brønsted acids are almost always nearly identical to within 1–2 kcal mol^{-1}. From this it had been postulated that since chloride was felt to interact predominantly electrostatically with Brønsted acids and since fluoride had a substantial covalent component in its hydrogen binding interactions, then cyanide would therefore also participate in interactions with Brønsted acids of a predominantly electrostatic nature. If this were the case, however, it would be anticipated that CN^- and Cl^- should interact similary with Lewis acids, a phenomenon which is not observed.

A convenient means of assessing electrostatic and covalent components of molecular interactions has been devised by Kroeger and Drago[16] in the form of a three-component equation (eq 11),

$$\Delta H° = e_A e_B + c_A c_B + t_A t_B \qquad (11)$$

which expresses the enthalpy of interaction between an acid A

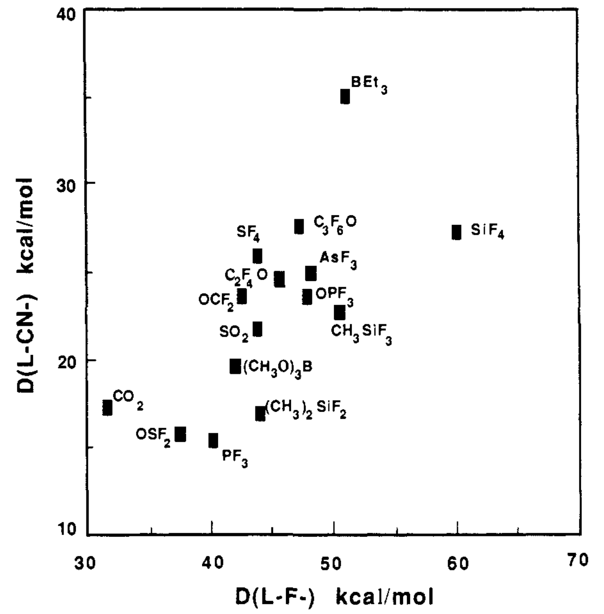

Figure 5. Variation of cyanide binding energies with fluoride binding energies for selected Lewis acids.

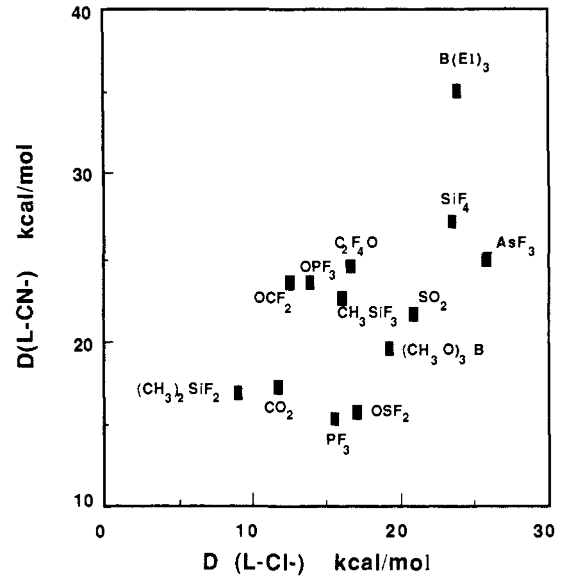

Figure 6. Variation of cyanide binding energies with chloride binding energies for selected Lewis acids.

Table III. Kroeger–Drago Parameters for Anions

anion	e	c	t
H^-	5.334	−267.005	125.307
F^-	6.154	34.768	1.109
Cl^-	5.111	2.730	17.508
I^-	4.517	−2.502	19.608
HO^-	6.599	34.817	2.394
NO_2^-	5.896	3.396	18.200
CN^-	2.71	15.72	12.14

and a base B, such as eq 3, in terms of electrostatic (e), covalent (c), and electron transfer (t) components. The values of e, c, and t derived by Kroeger and Drago for a number of anions are summarized in Table III. From these data it can readily be seen that toward a given Lewis acid fluoride will have a slightly stronger electrostatic interaction than chloride, a consequence of its smaller size, but will have a substantially larger covalent interaction. The relative magnitudes of the electron transfer parameters might indicate that Cl^- could approach F^- in binding due to such interactions but for all Lewis acids for which data are available of the size of the t parameter is such that this effect makes only a

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(16) Kroeger, M. K.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 3250.

Table IV. Enthalpy Changes for the Hypothetical Exchange Reaction: $LCl^- + CN^- \rightarrow LCN^- + Cl^-$

L	ΔH°_{12} (kcal mol^{-1})[a]	L	ΔH°_{12} (kcal mol^{-1})[a]
PF_3	0.2	CH_3SiF_3	−6.5
OSF_2	1.3	CF_3CFO	−7.9
$(CH_3)_2SiF_2$	~−8	OPF_3	−9.6
CO_2	−5.6	A_5F_3	1.1
$(CH_3O)_3B$	−0.4	SiF_4	−3.8
OCF_2	−11.0	$(C_2H_5)_3B$	−12.1
SO_2	−0.8		

[a] ±1 kcal mol^{-1}.

Table V. Kroeger–Drago Covalent Interaction Energies (C_AC_B) and Entropies of Association of Selected Compounds Binding to CN^-

compound (A)	C_A	$C_AC_{CN^-}$ (kcal mol^{-1})	ΔS°_3 (cal mol^{-1} K^{-1})
H_2O	0.37	5.8	17.9
CH_3OH	0.41	6.4	23.4
i-C_3H_7OH	0.47	7.4	26.2
SO_2	0.72	11.3	28.4
CF_3CH_2OH	0.81	12.7	29.7
CO_2	0.87	13.7	31.5

small contribution to the overall interaction energy.

The original *e*, *c*, and *t* parameters derived by Kroeger and Drago for CN^- were stated to be tentative due to data being available for only one ion–molecule interaction, presumably CN^-–H_2O. We have thus rederived *e*, *c*, and *t* parameters for CN^- based on our new CN^-–H_2O and CN^-–SO_2 high-pressure mass spectrometric determinations reported here and the CN^-–t-C_4H_9OH interaction energy based on the value of 16.7 kcal mol^{-1} determined here for CN^-–i-C_3H_7OH and the previous ICR observation that CN^- interacts equally well with i-C_3H_7OH and t-C_4H_9OH. Using these data, values of *e*, *c*, and *t* for CN^- of 2.71, 15.72, and 12.14 are obtained. These values are in sharp contrast to those obtained for Cl^- in Table III of 5.111, 2.730, and 17.508 for *e*, *c*, and *t*, respectively, indicating that contrary to the previous deduction that CN^- behaves like Cl^- in interacting with substrates principally by electrostatic interaction, in fact, CN^- undergoes a substantial degree of covalent interaction with substrates. This difference between Cl^- and CN^- is most dramatically revealed in the comparison of binding energy data for Cl^- and CN^- to the Lewis acids SO_2 and CO_2. While both anions bind equally well to SO_2, the CN^--CO_2 interaction is found to be substantially greater than the Cl^-–CO_2 interaction energy. Since CO_2 has no permanent dipole moment, the electrostatic component of its interaction with anions is expected to be substantially reduced relative to SO_2. For CN^- this does not have as serious consequences as for Cl^- since the former participates more covalently in its interactions. This diversity in Cl^- and CN^- binding to Lewis acids can be seen to be present in many cases as the data shown in Table IV for the hypothetical exchange reaction (eq 12) reveal.

$$LCl^- + CN^- \rightarrow LCN^- + Cl^- \qquad (12)$$

For CO_2, F_2CO, CF_3CFO, CH_3SiF_3, SiF_4, OPF_3, $(CH_3O)_3B$, and $(CH_3)_3B$, the value of ΔH°_{12} is substantially negative. In each of these cases the reason must be that CN^- is participating in a much more favorable covalent interaction with the Lewis acid. However, in several cases there is no appreciable difference between CN^- and Cl^- binding energies such as for SO_2, OSF_2, PF_3, and AsF_3. In each of these cases the site of binding of the anionic bases is an atom bearing a nonbonding lone pair. It thus seems probable that the repulsion between this lone pair and the approaching CN^- prevents an optimal covalent bond formation giving rise to a reduction in the overall CN^- interaction energy. Significantly, $B(OCH_3)_3$ also falls in this latter group indicating that a substantial back-donation of electron density from the oxygens to boron is occurring limiting the ability of CN^- to covalently bind to the boron center.

Further insight into the nature of binding of the CN^- ion with both Brønsted and Lewis acids may be found in a comparison of the entropies of association of CN^- and the apparent covalent component of the interaction energy. These data, summarized in Table V, show that the stronger the covalent component of the interaction the more negative is the entropy of association. This is in contrast to data for monoatomic ions such as F^-, Cl^-, and I^- which show no systematic variation of entropy of association with the strength of the interaction. This variation of ΔS° for the diatomic anion CN^- would thus suggest an increased loss of degree of freedom in the association complex as the strength of interaction increases. A seemingly logical deduction from this is that in the weakly bound complexes such as those with H_2O and CH_3OH the CN^- may have retained a significant degree of rotational freedom, that is, the CN^- is behaving much like a spherical monoatomic anion, while in the more strongly covalently bound adducts such as with CO_2 this rotational freedom is lost. In intermediate cases a rather large amplitude low-frequency bending motion may contribute to a somewhat enhanced entropy of the CN^- complex. This conjecture is supported to a certain extent by *ab initio* calculations of binding of CN^- to H_2O and HF which show very little difference in binding energy to the carbon and nitrogen sites of CN^-. In addition the *side-on* structure of CN^-–HF has been calculated[17] to be only 12 kcal mol^{-1} higher in energy, thus suggesting that the potential energy surface for rotational motion of CN^- in hydrogen bonded complexes may be very flat near the minimum. In the HF case the total binding energy to CN^- of 39.5 kcal mol^{-1} has a substantial covalent character. In contrast for a much more weakly bonded system such as CN^-–H_2O where the overall covalent contribution is quite weak, it would be anticipated that the potential energy surface for rotation of CN^- will be even flatter than the CN^-–HF case, and in fact practically free rotation of the CN^- may occur. High-quality ab initio calculations to test this hypothesis would thus be very desirable. This type of calculation has been carried out for the $(CN)_2H^-$ anion at the MP2/6-31+G**[18] in which a barrier of only 2.3 kcal mol^{-1} was found for the rotation of CN^- relative to HCN where the binding energy at the minimum $CN^-\cdots HCN$ structure is calculated to be 21.0 kcal mol^{-1}, in excellent agreement with the experimentally determined value of 20.7 kcal mol^{-1}. It would thus appear that for CN^- interacting with H_2O, CH_3OH, and i-C_3H_7OH where the values of ΔS° for the association reaction are low that relatively free rotation of CN^- in the complex occurs. For more strongly hydrogen bonded complex such as CN^-, CF_3CH_2OH, and for Lewis acid adducts such as with SO_2 and CO_2, where the -ΔS° values are larger, drastically restricted or no rotation likely occurs. It is of interest to note that an analogous conclusion was reached in spectroscopic studies of vapor-phase KCN where in all but the $v = 0$ level of the ground-state free rotation of CN^- occurs.[19] In the case of many species a mixture of both nitrile and isonitrile anion structures may, in fact, be present.[9]

2. Implications for HSAB Theory. One of the principal tenets of the hard–soft Acid–Base theory is that acids and bases may be categorized as either hard or soft based on the nature of their interactions. It is accepted that soft acids bind most favorably to soft bases predominantly by covalent interaction, while hard acids bind most favorably to hard bases predominantly by electrostatic interaction. Either combination of hard–soft interaction is viewed as being less energetically faovrable. Based largely on solution-phase ion–ion interactions CN^- has been categorized as a soft base. This can be seen to be in accord with the conclusion of the previous section that CN^- does, in fact, participate in substantial covalent interaction, for example, much more so than does Cl^-. However, the prototypical hard base, F^-, is found to also participate in significant covalent binding. The behavior of CN^- toward CO_2 and SO_2 would seem to be consistent with predictions of HSAB theory since the CN^-–CO_2 interaction (soft–hard) is weaker than the CN^-–SO_2 interaction (soft–soft).

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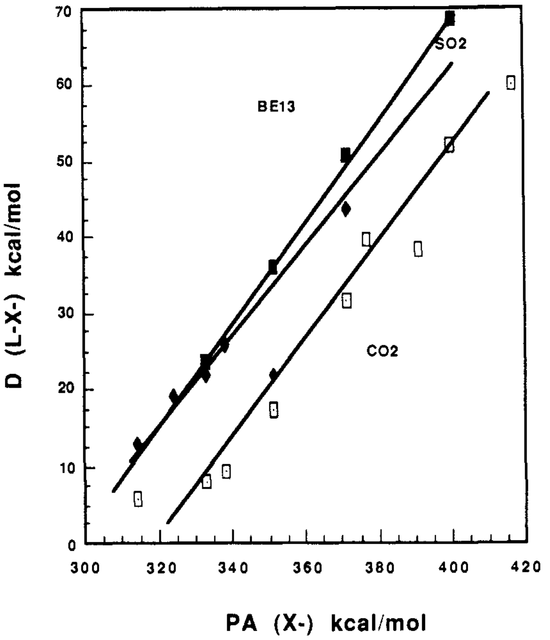


Figure 7. Variation of binding energies of anions to selected Lewis acids with anion proton affinity.

However, the F^-–CO_2 interaction (hard–hard) is found to be much weaker than the F^-–SO_2 interaction (hard–soft). These new data for CN^- Lewis acid interactions thus tend to reinforce our earlier conclusion that HSAB considerations based on solution-phase data are of limited applicability to gas-phase ion–neutral interaction energetics.

Parr and Pearson[20] have also recently attempted to formulate an absolute hardness parameter (η_B) for a base defined in terms of the ionization energy (I_B) and electron affinity (E_B) (eq 13).

$$\eta_B = \tfrac{1}{2}(I_B - E_B) \qquad (13)$$

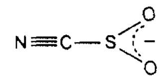
Thus species of high ionization energy and/or low electron affinity are predicted to be hard, while species of low ionization energy and/or high electron affinity are soft. Using this definition fluoride is found to be the hardest anionic base ($\eta_{F^-} = 7.0$) followed by hydride ($\eta_{H^-} = 6.8$), hydroxide ($\eta_{OH^-} = 5.6$), amide ($\eta_{NH_2^-} = 5.3$), and cyanide ($\eta_{CN^-} = 5.3$). The other halides, chloride, bromide, and iodide, have considerably lower hardness parameters at 4.7, 4.2, and 3.7, respectively. As noted previously for the series F^-, CN^-, Cl^-, and I^-, a *rough* correlation of anion binding energy with increasing hardness parameter is evident for CO_2, SO_2, and $(C_2H_5)_3B$. However, if other anionic bases such as H^-, CH_3^-, OH^-, CF_3^-, and NO_2^- are included, this apparent correlation disappears with OH^-, H^-, CH_3^-, and CF_3^-, all found to be bound far more strongly than the previous apparent correlation would have predicted. An additional apparent inconsistency is evident if the corresponding Lewis acid hardness values of CO_2 and SO_2 of 6.9 and 5.6, respectively, are used to attempt to rationalize results. Even though CO_2 is predicted to be "harder" than SO_2, it is bound much more weakly than SO_2 to the hardest Lewis bases F^-, H^-, and OH^-. Only for the CN^- ion, midway in hardness between F^- and I^-, is CO_2 found to be bound comparably to SO_2. Thus for the purposes of analysis of gas-phase ion–molecule interaction energies, these relative hardness parameters of CO_2 and SO_2 provide no insight.

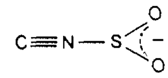
3. Correlations with Gas-Phase Basicity of Anions. A much better correlation of anion binding energies may be found from a comparison with gas-phase basicities of the anionic Lewis bases. A plot of anion–Lewis acid binding energy versus proton affinity of the anion, is shown in Figure 7 for CO_2, SO_2, and $(C_2H_5)_3B$. An excellent linear correlation of anion basicity and binding energies to CO_2 is immediately apparent and can be represented be eq 14. This relationship is remarkably similar to that observed

$$D(X^- - CO_2) = 0.58\,PA(X^-) - 181 \qquad (14)$$

previously by Squires et al.[21] for anion binding to $Fe(CO)_5$. In both instances anions are bound to a carbonyl carbon, and thus the similarity of binding likely gives rise to the similarity of the correlations. It also seems likely that this relationship will have some predictive power. Thus the binding energies in $HOCO_2^-$, $NH_2CO_2^-$, and $CH_3OCO_2^-$ can be predicted to be 44, 53, and 38 kcal mol^{-1}, respectively.

The correlation of the two parameters is also of interest for SO_2 although fewer data points are available for comparison. Most notably the CN^- data point falls far off the correlation line obtained for F^-, NO_2^-, Cl^-, Br^-, and I^-. It is interesting to note, however, that if the nitrogen basicity of CN^- is used instead of the carbon basicity, a much better agreement is obtained. This may then suggest that rather than the carbon bound anion (Ia) a nitrogen bound anion (Ib) is being generated. The acidities of


Ia


Ib

HNC and HCl are very similar, and thus it might be suggested that, in each of those cases in Table III where comparable Cl^- and CN^- binding energies are obtained, binding through nitrogen is occurring. A rationalization of this is not immediately apparent, however.

The data for Cl^-, F^-, and CN^- clustering onto triethylboron have been used by Squires[22] to extrapolate a value for the hydride affinity of $B(C_2H_5)_3$ of 69 ± 2 kcal mol^{-1} which appears quite reasonable. The predictive power of these plots of anion binding energy versus anion basicity can therefore be seen to be significant for obtaining estimates of new thermochemical data for novel anions.

Conclusion

The cyanide affinities of a number of main group oxides, fluorides, oxofluorides, and alkyls have been determined. A comparison with corresponding fluoride and chloride affinities reveals that with a few exceptions the cyanide binding energies are intermediate between those of F^- and Cl^-. In cases where the bonding of CN^- appears to be principally electrostatic, such as in weak hydrogen bond interactions and Lewis acids such as SO_2, OSF_2PF_3, and AsF_3, the binding energies are very nearly identical with those of Cl^-. In the case of the weakest interactions the entropy data indicate that the CN^- unit in the complex may, in fact, retain a considerable degree of rotational freedom. In general, however, for most Lewis acids cyanide ion involves a substantially greater covalent character than that of Cl^-, and, in fact, the difference in Cl^- and CN^- binding energies may be taken as a rough measure of the covalent component of the interaction. Using the data obtained here, new Kroeger–Drago parameters for CN^- and CO_2 have been derived. The analysis using these parameters gives good agreement with the qualitative separation of binding energy into the electrostatic and covalent components described. The data do not appear to be readily rationalized on the basis of HSAB theory. An excellent correlation of anion binding energies with anion basicity has been observed which can be used to predict new anion–Lewis acid interaction energetics.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. $(C_2H_5)_3B$, 97-94-9; SiF_4, 7783-61-1; CF_3CF_2CFO, 422-61-7; SF_4, 7783-60-0; AsF_3, 7784-35-2; OPF_3, 13478-20-1; CF_3CFO, 354-34-7; CH_3SiF_3, 373-74-0; SO_2, 7446-09-5; OCF_2, 353-50-4; $(CH_3O)_3B$, 121-43-7; CO_2, 124-38-9; $(CH_3)_2SiF_2$, 353-66-2; OSF_2, 7783-42-8; PF_3, 7783-55-3; CF_3CH_2OH, 75-89-8; *i*-C_3H_7OH, 67-63-0; CH_3OH, 67-56-1; H_2O, 7732-18-5; cyanide ion, 57-12-5; ethyl cyanoformate, 623-49-4.

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