brosylate) seems not to influence the isotope effects much,[2] the results may be attributed mainly to the difference in the participating group, methyl or phenyl.

In the case of **2**, moderately nucleophilic π electrons of the phenyl ring can interact directly with the α carbon displacing the leaving group oxygen; in the TS, the phenyl ring participates mainly via 1,3 through-space interaction (reflected in a stronger C_α–C_γ bond). On the other hand, since no mobile π electrons are available for **1**, less nucleophilic σ electrons of the C_β–C_γ bond should interact with the α carbon (weak C_β–C_γ bond), and the interaction in this case occurs predominantly through the C_α–C_β bond (stronger C_α–C_β bond). Thus it can be concluded that the major mode of the participation by the phenyl ring is bridging whereas that by the methyl group is hyperconjugation. Although no calculations have been carried out for solvolysis with participation by the most nucleophilic lone-pair electrons (*n* participation), it can be reasonably expected that the 1,3 interaction is even stronger in the TS with *n* participation than that with π participation and that the relative importance of bridging over hyperconjugation increases from σ to *n* through π participation, constituting a sort of spectrum.

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Registry No. 1 (X = *p*-nitrobenzenesulfonate), 13372-31-1.

Relative Bond Dissociation Energies for Two-Ligand Complexes of Ni^+ with Organic Molecules in the Gas Phase

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Abstract: Relative two-ligand dissociation enthalpies, $\delta D(\mathrm{Ni}^+\text{–}2L)$, for Ni^+ with 50 organic molecules are determined. A pulsed laser volatilization–ionization source is used to generate Ni^+ which can react with various neutrals to give $\mathrm{Ni(ligand)_2}^+$ species. Equilibrium constants are measured for the ligand-exchange reactions which occur when pairs of ligand molecules are present. Free energies for two-ligand exchange are obtained from the equilibrium constant for the reaction $\mathrm{Ni(A)_2}^+ + 2\mathrm{B} \rightleftarrows \mathrm{Ni(B)_2}^+ + 2\mathrm{A}$. The free-energy differences are added to give a scale of relative free energies for ligand exchange. These are converted to enthalpies to give $\delta D(\mathrm{Ni}^+\text{–}2L)$. Dependence of $\delta D(\mathrm{Ni}^+\text{–}2L)$ on functional groups and substituent effects is analyzed. The results for Ni^+ are compared to available results for other reference acids: H^+, Al^+, Mn^+, NO^+, Li^+, Co^+, Cu^+, and $CpNi^+$. The extensive data set for Ni^+ makes possible correlations which clearly demonstrate differences in bonding among different compound classes, in particular between oxygen compounds and alkenes, nitriles, sulfur bases, and other ligands capable of π-back-bonding. These comparisons show that Ni^+ is a substantially softer acid than NO^+, Li^+, Al^+, and H^+, slightly softer than Co^+ and $CpNi^+$, and slightly harder than Cu^+. The relative slopes of the correlation plots suggest that the average metal–ligand bonding distance for $\mathrm{Ni(ligand)_2}^+$ complexes is shorter than that for both Co^+ and Cu^+.

Ion cyclotron resonance (ICR) spectroscopy with a pulsed-laser volatilization–ionization source of atomic metal cations has recently been applied to measure relative gas-phase ligand-binding energies for various metal cations. One-ligand binding energies, $D(\mathrm{M}^+\text{–L})$, were obtained for Al^+ and Mn^+[2,3] while two-ligand binding energies, $D(\mathrm{M}^+\text{–2L})$, were measured for Cu^+ and Co^+.[4,5] These binding energies, which are essentially basicities with the metal cation as reference acid, are useful in evaluating the energetics of reaction processes and in developing models for understanding molecular interactions. In addition, comparisons between different scales can be quite informative and often reveal interesting points about metal–ligand interactions. In particular, correlations of the previously measured data sets for Al^+, Mn^+, Cu^+, and Co^+ have provided quantitative measures of hard and soft acid base concepts unencumbered by solvation and other complicating effects.[4,5] Ideally, basicity scales should be determined for the same set of ligands. The resulting comparisons would then have complete overlap of data. Normally, due to experimental constraints, data overlap is less than ideal and in some cases quite poor. As a result, comparisons among the previously determined data sets are often not totally satisfying in that they suggest the occurrence of interesting systematic effects while not providing sufficient evidence for them. For example, the data suggest that in a given correlation plot, molecules of different functional groups may in general fall on different lines.[2-5] Usually the lines obtained for various oxygen functionalities are not distinguishable. Data points for cyanides, amines, sulfur compounds, and alkenes generally deviate quite appreciably from the line for oxygen bases and appear to fall on lines of their own. With minor exceptions, however, the data sets in previous studies have been inadequate to show whether the data for each of these other functionalities do indeed fall on separate lines.

In the present paper we report determinations of relative binding energies of 50 organic molecules in two-ligand complexes with Ni^+. The data set of ligands studied is much larger than in previous studies. The ligands measured were chosen to give as much overlap with other data sets as possible. In particular, the question of separate correlation lines for different functionalities was addressed by including appropriate cyanide, amine, sulfur base, and alkene molecules as ligands. The results are compared to available gas-phase basicity scales for the other reference acids: H^+, Li^+, NO^+, Al^+, Mn^+, Co^+, Cu^+, and $CpNi^+$ ($Cp = \eta^5\text{-}C_5H_5$).

Experimental Section

Experiments were carried out by using ICR instrumentation and techniques which have been previously described.[2-7] The output of a pulsed YAG laser is focused onto a nickel wire target at the end of the ICR cell to produce atomic nickel cations. The mass spectrum for this

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(2) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1229, 1235.

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source with no added gases shows the five naturally occurring nickel isotopes in relative abundances of 69.6%, 24.0%, 1.0%, 4.1%, and 1.3% for masses 58, 60, 61, 62, and 64, respectively. This compares to the 68.3%, 26.1%, 1.1%, 3.6%, and 0.9% expected from their natural abundance. Ni^{2+} or Ni_2^+ were not observed. No evidence was seen for production of significant amounts of kinetically or electronically excited Ni^+. HCN was obtained by mixing NaCN and H_2SO_4 under vacuum. Other chemicals were from commercial sources and were degassed by repeated freeze–pump–thaw cycles before use. All experiments were carried out at an ambient temperature of 25 °C. Gas mixtures were prepared in the cell and partial pressures measured by difference as has been previously described.[2] Accuracy of pressure ratios is limited to about ±30% because the ion gauge is not individually calibrated for each gas.

Results

Ethyl chloride was used as a reagent for preparation of the complex $Ni(EtCl)(C_2H_4)^+$ which is formed in a rapid bimolecular reaction sequence. The reactions observed when Ni^+ is generated in the presence of EtCl are analogous to those previously described with Cu^+.[4] However, in contrast to the Cu^+ system, $Ni(EtCl)_2^+$ is not observed so $Ni(EtCl)(C_2H_4)^+$ is the only major product at long times. The molecules studied as ligands in this work readily displace EtCl and C_2H_4 to give $Ni(L)_2^+$ complexes. With many of the more strongly bound ligands, such complexes can be formed by direct condensation of the neutral molecule with Ni^+ and $Ni(ligand)^+$. Where these condensation reactions proceed rapidly under the experimental conditions of interest, use of EtCl was omitted. In all of the cases examined in this work, initial reactions proceeded rapidly to give two-ligand complexes of Ni^+. Further condensation steps to give $Ni(ligand)_3^+$ complexes occurred very slowly or not at all.

With two ligand molecules A and B present, initial reactions forming $Ni(ligand)_2^+$ complexes are followed by ligand-exchange reactions 1 and 2, M = Ni. The enthalpy expressions for these reactions follow from the definition of the heterolytic bond dissociation energy for a single ligand in a two-ligand complex (reaction 3). Overall, reactions 1 and 2 together result in the exchange of both ligands (reaction 4), where $D(M^+\text{–}2L)$ is the enthalpy for dissociation of both ligands in a two-ligand complex (reaction 5).

$$AMA^+ + B \overset{K_1}{\rightleftharpoons} AMB^+ + A \qquad (1)$$

$$\Delta H_1 = D(AM^+\text{–}A) - D(AM^+\text{–}B)$$

$$AMB^+ + B \overset{K_2}{\rightleftharpoons} BMB^+ + A \qquad (2)$$

$$\Delta H_2 = D(BM^+\text{–}A) - D(BM^+\text{–}B)$$

$$AMB^+ \rightarrow AM^+ + B \qquad \Delta H_3 \equiv D(AM^+\text{–}B) \qquad (3)$$

$$AMA^+ + 2B \overset{K_4}{\rightleftharpoons} BMB^+ + 2A \qquad (4)$$

$$\Delta H_4 = D(M^+\text{–}2A) - D(M^+\text{–}2B)$$

$$LML^+ \rightarrow M^+ + 2L \qquad \Delta H_5 \equiv D(M^+\text{–}2L) \qquad (5)$$

Figure 1 shows the variation of ion abundances with time for some of the species formed when Ni^+ is generated in the presence of n-BuOH and EtCHO: a sequence of reactions yields $Ni(n\text{-}BuOH)_2^+$, $Ni(n\text{-}BuOH)(EtCHO)^+$, and $Ni(EtCHO)_2^+$ as the final product ions in this system. Ligand-exchange reactions 1 and 2 for these ions with n-BuOH and EtCHO neutrals are shown by double-resonance experiments to be rapid and approach equilibrium. For typical total pressures of 3×10^{-6} torr, equilibrium is approached to within ±10% after approximately 120 ms following the formation of Ni^+. The equilibrium constants for reactions 1, 2, and 4 can be calculated from the ratios of ion abundances at long times and the measured partial pressures of n-BuOH and EtCHO. The equilibrium constants are conveniently expressed as free energies by using the relation $\Delta G° = -RT \ln K$.

Equilibria were measured for varous pairwise combinations of 52 organic molecules as ligands. Values for the free energy difference for exchange of both ligands, $\Delta G_{exchange}$, calculated from the measured equilibrium constants for reaction 4 are given in Table I. Each value represents the average of at least three determinations. The results are combined to give a scale of relative free energies for binding, $\delta\Delta G_{exchange}$. The zero of this scale is arbitrarily chosen by setting the value for C_2H_2 equal to zero. Redundant determinations within the scale provide an internal consistency check on the results. Agreement is found to within about ±0.2 kcal/mol. The major factor contributing to these differences is accuracy of pressure measurements.

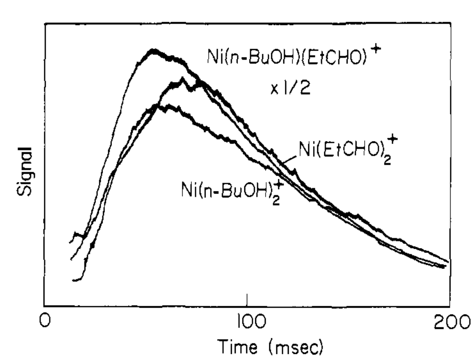
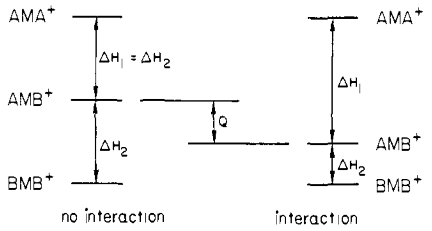


Figure 1. Variation of ion abundances with time typical of the equilibrium determinations of this study. When Ni^+ is generated in the presence of n-BuOH and EtCHO at a total pressure of 2×10^{-6} torr, initial reactions lead to the formation of three two-ligand complexes: $Ni(n\text{-}BuOH)_2^+$, $Ni(n\text{-}BuOH)(EtCHO)^+$, and $Ni(EtCHO)_2^+$. These ionic species undergo ligand-exchange reactions with the EtCHO and n-BuOH neutrals. Equilibrium is reached in this example after about 120 ms. The overall equilibrium constant for exchange of two EtCHO ligands for two n-BuOH molecules is calculated from the ratio of ion abundances and the pressures of the reactants at $K = 1.20$. The decrease in the signals at long times in this figure is due to ion loss from the ICR cell.

Scheme I



The measured equilibria for reaction 4 takes no account of the relative abundance of the mixed ligand species AMB^+. This abundance may be used to establish the values of the separate equilibria for reactions 1 and 2. This is conveniently expressed as an energy difference (Scheme I). If there were no interaction between the two ligand sites on the metal, then the enthalpies for reactions 1 and 2 would be equal, $\Delta H_1 = \Delta H_2$, defining a relative value for the enthalpy of the mixed species AMB^+ as the average of the enthalpies for the species AMA^+ and BMB^+. The actual relative enthalpy for AMB^+ is conveniently expressed as the deviation Q from this average value, where $Q = (\Delta H_2 - \Delta H_1)/2 = [D(AM^+\text{–}B) + D(BM^+\text{–}A) - D(AM^+\text{–}A) - D(BM^+\text{–}B)]/2$ (Scheme I). In terms of the equilibrium constants, Q is given as $Q = (1/2)RT \ln (K_1/4K_2)$; the factor of a quarter is a statistical correction arising because the mixed species can be formed in two ways as AMB^+ or BMA^+. Other entropy corrections cancel or are small and can be neglected.[8] Values of Q calculated from the measured equilibria among the 50 ligands studied are given in Table I. Note that $Q = (\Delta H_2 - \Delta H_1)/2$ is sometimes larger than $\Delta H_1 + \Delta H_2$; in these cases ΔH_1 and ΔH_2 are of opposite sign.

Discussion

Relative two-ligand dissociation enthalpies for $Ni(ligand)_2^+$ complexes, $\delta D(Ni^+\text{–}2L)$, are given in table I for the 50 molecules

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[8] Corrections for symmetry number changes cancel because Q is a difference.

Table I. Measured Free Energies for Exchange of Both Ligands, ΔG_{exch}, Measured Enthalpies of Stabilization of the Mixed-Ligand Species, Q, and Relative Two-Ligand Dissociation Enthalpies, $\delta D(\text{Ni}^+\text{-}2\text{L})$, for Two-Ligand Complexes of Ni$^+$ in the Gas Phase[a]

Ligand (L)	Measured ΔG_{exch} and Q								$\delta D(\text{Ni}^+\text{-}2\text{L})$[b]
Pyridine									28.65
	2.04	0.06							
i-PrNH$_2$									28.61
	0.74	0.16							
C_6H_5CN									25.87
	1.23	0.35							
EtNH$_2$									24.64
Me$_3$N									24.40
	1.31	0.19					1.07	0.12	
Me$_2$NH									24.17
					0.84	0.10			
n-PrCN									24.07
			0.74	-0.03					
EtCN									23.33
	1.20	0.19							
MeNH$_2$									22.13
					2.05	-0.12			
Et$_2$S									21.46
	1.14	0.07					0.18	0.20	
MeCN									21.28
	1.93	0.78							
i-Pr$_2$CO									19.35
	1.28								
t-BuCOMe									18.07
	0.71	-0.05							
Et$_2$CO									17.36
					0.54	0.51			
NH$_3$									16.82
	0.86	0.53							
MeNCS									16.52
					0.02	-0.27			
Me$_2$S									16.50
	0.83	0.36					2.29	-0.10	
MeCOEt									15.67
	0.54	0.06							
EtCO$_2$Et									15.13
	1.96	-0.10			2.13	0.10			
EtCO$_2$Me									13.17
	0.15	0.12							
Me$_2$CO									13.02
	1.81	0.18							
THF[c]									12.37
					0.57				
1,3-Butadiene									10.98[d]
							0.74	-0.65	
Benzene									10.91[d]
			1.39	-0.11					
t-BuCHO									11.63
			0.36	-0.27			0.72	-0.20	
Et$_2$O									11.27
					1.33	0.14			
MeCO$_2$Me									10.91
	1.47	-0.15							
EtSH									10.75
			0.35	1.18					
C_6H_5Cl									10.40
							1.60	0.08	
i-PrCHO									9.80
	1.43	-0.15							
HCN									9.26
					0.11	0.63			
n-PrCHO									9.15
					0.78	-0.19			
i-PrOH									8.37
							1.28	-0.02	
EtCHO									7.87
					0.11	-0.10			
n-BuOH									7.76
	1.31	-0.16					1.21		
MeSH									6.63
					0.52	-0.24			
n-PrOH									6.55
							0.44	1.18	
Me$_2$C=CH$_2$									5.28[d]
							1.00	1.42	
1,4-dioxane									4.28[d]
	2.27	-0.08			1.03	0.26			
EtOH									4.20
							0.46	0.09	
EtCH=CH$_2$									4.10
			0.06	1.18					
Me$_2$O									4.07
			0.33	-0.08					
MeCHO									3.74
							0.12	0.10	
HCO$_2$Me									3.62
					1.11	0.14			
Furan									2.96
	1.65	1.27							
MeCH=CH$_2$									2.42
	1.42	0.54							
Oxirane									1.26
					0.25	-0.07			
MeOH									1.00
	0.81	1.11							
Allene									-1.45[e]
	0.19	0.14							
C_2H_2									0.00

[a] All data in kcal/mol. [b] Values are relative to $\delta D(\text{Ni}^+\text{-}2C_2H_2) = 0$. Free energy differences, ΔG_{exch}, are added to give relative free energies $\delta\Delta G_{\text{exch}}$. These are converted to relative enthalpies, $\delta D(\text{Ni}^+\text{-}2\text{L})$, by assuming that entropy changes can be neglected except for corrections for symmetry number changes. [c] Tetrahydrofuran. [d] In converting the relative free energy to relative enthalpy, a correction of $T\Delta S = -0.82$ kcal/mol is made for isobutylene, 1,4-dioxane, C_6H_5Cl, and C_6H_6 to account for a decrease in symmetry number by a factor of 2 for each ligand molecule on formation of the Ni(ligand)$_2^+$ complex. [e] For allene a correction of $T\Delta S = -1.64$ kcal/mol is made to account for a decrease in symmetry number by a factor of 4 for each allene on formation of the Ni(ligand)$_2^+$ complex.

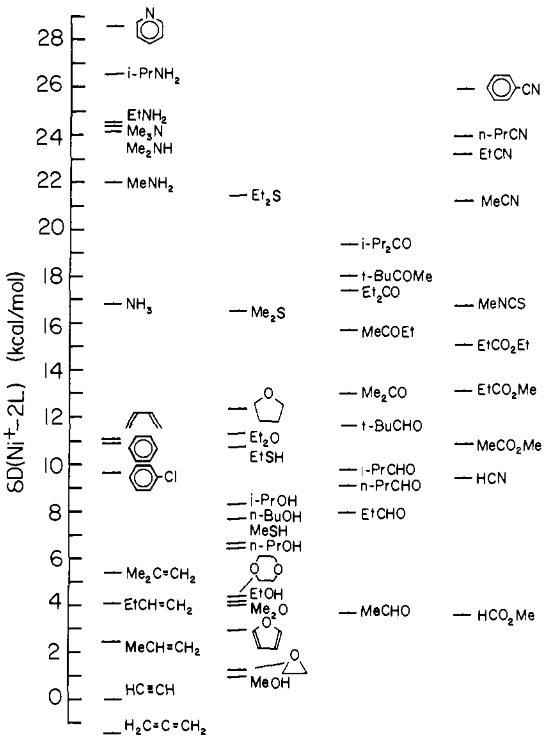

Figure 2. Relative two-ligand dissociation enthalpies for Ni$^+$, $\delta D(\text{Ni}^+\text{-}2\text{L})$, arranged by functional group. The value for acetylene is arbitrarily chosen as zero for this scale.

studied. The zero of this scale is chosen arbitrarily as $\delta D(\text{Ni}^+\text{-}2C_2H_2) = 0$. The absolute zero of this scale cannot be determined from the present work. The enthalpy scale is obtained from the free energy scale by assuming that entropy changes are small and tend to cancel so that they may be neglected except for corrections for symmetry changes.[4,9]

The symmetry correction is necessary when a ligand which has a symmetry number greater than one as a free molecule binds in the Ni(ligand)$_2^+$ complex so as to reduce its symmetry. This is clearly the case for 1,4-dioxane, C_6H_6, C_6H_5Cl, and isobutylene. All four of these lignds lose a twofold symmetry axis when binding to Ni$^+$. The relative free energy for 1,4-dioxane, C_6H_6, C_6H_5Cl, and isobutylene ($\delta\Delta G_{\text{exch}}$) is therefore corrected by adding $T\Delta S = -2RT \ln 2 = -0.82$ kcal/mol in calculating the relative enthalpy. Allene, when binding to Ni$^+$, loses both of its twofold symmetry axes. As a result, the relative free energy for allene must be corrected by adding $T\Delta S = -2RT \ln 4 = -1.64$ kcal/mol in order to obtain $\delta D(\text{Ni}^+\text{-}2C_3H_4)$ (Table I). No such symmetry correction is made for any of the other molecules studied as ligands in this work.[10]

It has been noted in a previous paper dealing with the two-ligand complexes of Cu$^+$,[4] that relative two-ligand dissociation energies, $\delta D(\text{M}^+\text{-}2\text{L})$, are not simply related to one-ligand dissociation energies, $\delta D(\text{M}^+\text{-L})$. There is no reason to expect that the bonding of one ligand to Ni$^+$ is independent of the other. For such complexes, in fact, the dissociation energy for the second ligand should be significantly less than that for the first: $D(\text{LNi}^+\text{-L}) < D(\text{Ni}^+\text{-L})$. A particular kind of nonideal behavior in bond enthalpies is demonstrated by the measured stabilization energies, Q, listed in Table I. Pairs of oxygen bases, together, show no stabilization of the mixed species. For pairs of oxygen bases with alkenes, however, the mixed species are stabilized by about 1.0 kcal/mol. A similar effect is observed for pairs of oxygen and sulfur bases as well as pairs of oxygen and nitrogen bases. These

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(9) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976; p 76.

(10) Symmetric ethers and ketones (Me$_2$O, Me$_2$CO, etc.), which have twofold axes as free molecules, are assumed to form Ni(ligand)$_2^+$ complexes with the Ni$^+$ on the symmetry axis of the ligand so that this symmetry is retained.

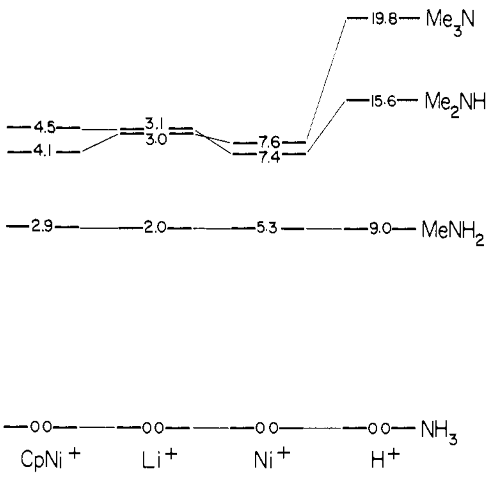

Figure 3. Methyl substituent effect in amines. Shown are the ligand-binding energies for NH_3, $MeNH_2$, Me_2NH, and Me_3N with four reference acids. The scale for each series is normalized to the difference in ligand-binding energy between the $MeNH_2$ and NH_3 complexes. The data for Ni^+ is for the dissociation of two ligands; the data for the other reference acids is for dissociation of one ligand.

effects have been reported in a previous paper where they are analyzed in detail.[11]

Relative two-ligand dissociation enthalpies for the 50 molecules studied in this work are plotted in Figure 2. Within each functional group series, alkyl substituent effects are apparent. Substitution of a larger alkyl group for a smaller one leads to a systematic increase in $\delta D(Ni^+\text{–}2L)$. Similar effects have been seen for proton affinities,[12,18] for one-ligand binding energies to Li^+,[13,14] Al^+,[2] Mn^+,[3] and NO^+[15] and for two-ligand binding energies to Co^+[5] and Cu^+.[4]

A related effect is apparent in the binding energies of methylamines, NH_3, $MeNH_2$, Me_2NH, and Me_3N. The proton affinities (PA) of these bases have been found to fall in the order $PA(NH_3) < PA(MeNH_2) < PA(Me_2NH) < PA(Me_3N)$,[12] increasing systematically with methyl substitution. A reversal in this order was found in measurements of one-ligand complexes with Li^+[14] and $CpNi^+$:[16] $D(M^+\text{–}NH_3) < D(M^+\text{–}MeNH_2) < D(M^+\text{–}Me_3N) < D(M^+\text{–}Me_2NH)$. The Ni^+ data is qualitatively like that found for H^+ and does not show such a reversal. A comparison of the various data sets is shown in Figure 3. The numbers are normalized to the difference in ligand-dissociation enthalpy between $MeNH_2$ and NH_3 for the various reference acids. Examination of Figure 3 reveals that, in spite of their *qualitative* agreement with the proton affinities, the Ni^+ results are in fact *quantitatively* similar to those seen for $CpNi^+$ and Li^+. The relative ligand dissociation enthalpy measured for $Ni(Me_3N)_2^+$ does not greatly differ from the value found for $Ni(Me_2NH)_2^+$. Simple electrostatic calculations on the origin of the partial inversion of the order observed for Li^+ complexes suggest that the major factor contributing to the effect is a large electrostatic repulsion between Li^+ and the methyl groups of Me_3N.[14] A similar, slightly weaker, repulsive term might then explain the Ni^+ data.

Bonding of ligands to Ni^+ involves both ionic and covalent contributions. Ionic effects include interaction of intrinsic and induced ligand dipoles with the charge on Ni^+. Covalent bonding can occur by delocalization of electrons from occupied ligand orbitals into empty 4s and 4p orbitals on Ni^+. This delocalization will be limited by repulsion by the electrons in the filled 3d and core orbitals. Covalent bonding can also occur by delocalization of 3d electrons on Ni^+ into unoccupied π^* or d-ligand orbitals, π-back-bonding. This can occur only for ligand molecules with suitable orbitals available.

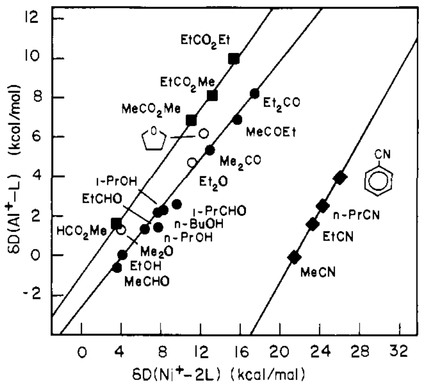

Figure 4. Comparison of the relative ligand dissociation enthalpies for Al^+ to relative two-ligand dissociation enthalpies for Ni^+. The upper solid line is a least-squares fit to the data for the four esters (■): $\delta D(Al^+\text{–}L) = 0.706\delta D(Ni^+\text{–}2L) - 0.97$ kcal/mol (correlation coefficient, $r = 0.998$). A least-squares fit to the data for ten oxygen bases (●) gives the middle line: $\delta D(Al^+\text{–}L) = 0.641\delta D(Ni^+\text{–}2L) - 3.1$ kcal/mol ($r = 0.984$). The three ether data points (○) are omitted from this linear regression because they appear to fall on a line of their own, which is not drawn. The lower solid line is a least-squares fit to the data for the four nitriles (◆) $\delta D(Al^+\text{–}2L) = 0.915\delta D(Ni^+\text{–}2L) - 19.7$ kcal/mol ($r = 0.997$).

Atomic nickel cation, Ni^+, has a ^2D ground state corresponding to an $[Ar](3d)^9$ configuration.[17] The next higher states, $[Ar](3d)^8(4s)$ ^4F at 1.0 eV and $[Ar](3d)^8(4s)$ ^2F at 1.7 eV, should not be involved in ligand bonding. No evidence was seen for participation of excited states in any of the observed chemistry of Ni^+.

Comparisons to Basicity Scales for Other Reference Acids. Comparison of the relative two-ligand dissociation enthalpies for Ni^+ with available results for other reference acids reveals some interesting points about the nature of metal–ligand bonding interactions. Figure 4 shows a plot of ligand binding energies to Al^+,[2] $\delta D(Al^+\text{–}L)$, vs. the results for Ni^+, $\delta D(Ni^+\text{–}2L)$. Due to the large Ni^+ data set it is possible to *clearly* distinguish systematic differences in bonding among compounds with different functional groups. Ten oxygen bases, including alcohols, ketones, and aldehydes, fall approximately on a single line. A least-squares fit to this data gives $\delta D(Al^+\text{–}L) = 0.641\delta D(Ni^+\text{–}2L) - 3.1$ kcal/mol (correlation coefficient, $r = 0.984$). The three ether data points are omitted from this line because they appear to fall on their own separate line (not drawn). A separate line of similar slope but offset by about 4 kcal/mol on the $D(Ni^+\text{–}2L)$ axis is defined by the four ester data points: $\delta D(Al^+\text{–}L) = 0.706\delta D(Ni^+\text{–}2L) - 0.97$ kcal/mol ($r = 0.998$). The offset of the ester correlation line can be interpreted as indicating a stronger interaction between Al^+ and esters than is observed for Ni^+. This observation may be related to an ability of the Al cation to bond more efficiently to the *two* oxygens of the ester group. The four nitriles fall on a third line which is offset from the oxygen base correlation line by about 16 kcal/mol on the $D(Ni^+\text{–}2L)$ axis: $\delta D(Al^+\text{–}L) = 0.915\delta D(Ni^+\text{–}2L) - 19.7$ kcal/mol ($r = 0.977$). It is interesting to note that cyanobenzene falls on the same correlation line as aliphatic nitriles. This implies that the bonding of cyanobenzene to Ni^+ and Al^+ is through the –CN functional group.

The sign of the offset of the nitrile-correlation line indicates that nitriles bond relatively more strongly to Ni^+ than to Al^+. This is consistent with the expectation that the comparatively soft acid Ni^+ should bond relatively more strongly than the hard acid Al^+

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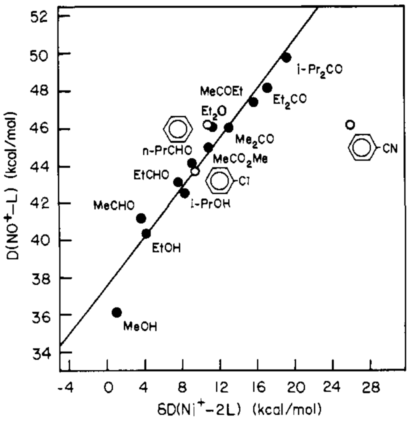

Figure 5. Comparison of ligand dissociation enthalpies for NO^+ to relative two-ligand dissociation enthalpies for Ni^+. The solid line is a least-squares fit to the data for 12 oxygen bases (●): $D(NO^+–L) = 0.655\delta D(Ni^+–2L) + 37.6$ kcal/mol ($r = 0.938$).

to soft bases such as nitriles compared to hard bases such as the oxygen compounds.

Results qualitatively very similar to those obtained in the comparison of Al^+ and Ni^+ data sets are seen when plotting ligand binding energies to Mn^+,[3] $\delta D(Mn^+–L)$, vs. the results for Ni^+, $\delta D(Ni^+–2L)$ (not shown). Fourteen oxygen compounds including alcohols, ketones, aldehydes, and ethers fall on one line. A least-squares fit gives $\delta D(Mn^+–L) = 0.491\delta D(Ni^+–2L) + 3.1$ kcal/mol ($r = 0.954$). Separate lines are seen for esters: $\delta D(Mn^+–L) = 0.484\delta D(Ni^+–2L) + 4.70$ kcal/mol and nitriles $\delta D(Mn^+–L) = 0.607\delta D(Ni^+–2L) - 4.5$ kcal/mol ($r = 0.998$).

Figure 5 shows a comparison of NO^+[15] and Ni^+ binding energy scales. The 12 oxygen bases show a reasonably good linear correlation. A least-squares fit to the data gives $D(NO^+–L) = 0.655\delta D(Ni^+–2L) + 37.6$ kcal/mol ($r = 0.938$). Benzene and chlorobenzene fall on or very close to the oxygen base correlation line. Cyanobenzene, in contrast, falls off this line bonding much more strongly to Ni^+. In comparing Al^+ and Ni^+ basicity scales, cyanobenzene was found to be a soft ligand, falling on the line with aliphatic nitriles. Figure 5 further demonstrates that cyanobenzene does not behave like benzene or chlorobenzene; its acid–base interactions are determined by the cyano group. Deviation of C_6H_5CN from the oxygen base correlation line therefore implies that NO^+ is a relatively harder acid than Ni^+.

Comparison of the results for Li^+[13] with the Ni^+ data is similar to the Al^+, Mn^+, and NO^+ comparisons to the Ni^+ data. Six oxygen bases fall on or around a line given by $D(Li^+–L) = 0.491\delta D(Ni^+–2L) + 38.5$ kcal/mol ($r = 0.790$). Various soft bases such as nitriles, amines, and sulfides fall off the line for oxygen bases bonding relatively more strongly to Ni^+. This is as expected for the comparison between a hard acid such as Li^+ and a soft acid such as Ni^+.

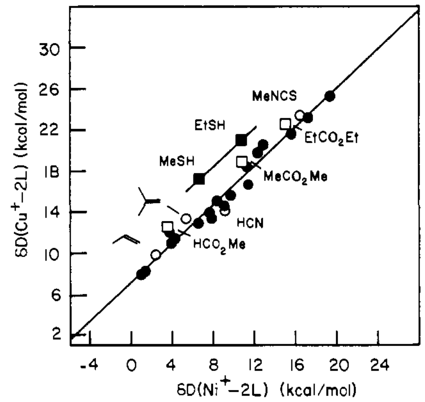

Figure 6. Comparison of relative two-ligand dissociation enthalpies for Cu^+ to relative two-ligand dissociation enthalpies for Ni^+. Two mercaptans define the upper solid line (■): $\delta D(Cu^+–2L) = 0.922\delta D(Ni^+–2L) + 11.2$ kcal/mol. The lower solid line is a least-squares fit for 18 oxygen bases (●): $\delta D(Cu^+–2L) = 0.940\delta D(Ni^+–2L) + 7.1$ kcal/mol ($r = 0.974$). Three ester data points (□) are omitted from the regression analysis for the oxygen base line because they appear to fall on their own separate correlation line (which is not drawn).

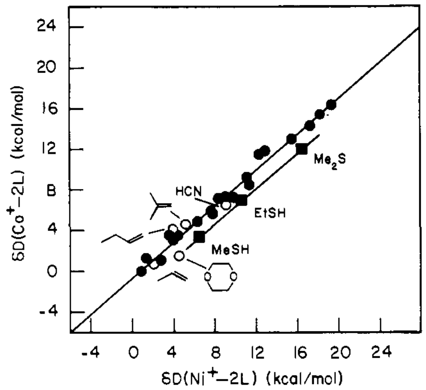

Figure 7. Comparison of relative two-ligand dissociation enthalpies for Co^+ and Ni^+. A least-squares fit to the data for 20 oxygen bases (●) results in the upper solid line: $\delta D(Co^+–2L) = 0.869\delta D(Ni^+–2L) - 0.50$ kcal/mol ($r = 0.979$). The lower solid line is a least-squares fit for the three sulfur bases (■): $\delta D(Co^+–2L) = 0.861\delta D(Ni^+–2L) - 2.3$ kcal/mol ($r = 1.000$).

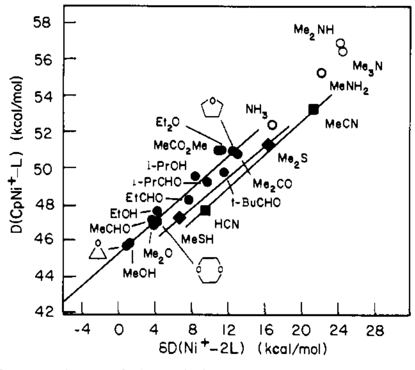

Figure 8. Comparison of ligand-dissociation enthalpies for $CpNi^+$ to relative two-ligand dissociation enthalpies for Ni^+. The upper solid line is a least-squares fit for 14 oxygen bases (●): $D(CpNi^+–L) = 0.446\delta D(Ni^+–2L) - 7.1$ kcal/mol ($r = 0.938$). Two mercaptans define the middle solid line: $D(CpNi^+–L) = 0.405\delta D(Ni^+–2L) + 44.5$ kcal/mol (♦). The lower solid line is drawn through the data points for the two nitriles (■): $D(CpNi^+–L) = 0.466\delta D(Ni^+–2L) + 43.4$ kcal/mol.

The relative acid hardness/softness of Ni^+, Cu^+, and Co^+ is clearly demonstrated by comparisons among their data sets. Comparison of the Cu^+ and Co^+ data sets has shown that Cu^+ is softer than Co^+.[5] In the Cu^+[4] vs. Ni^+ comparison (Figure 6), 18 oxygen bases which include alcohols, ethers, ketones, and aldehydes are seen to fall around a line given by $\delta D(Cu^+–2L) = 0.940\delta D(Ni^+–2L) + 7.1$ kcal/mol ($r = 0.974$). The two mercaptans define a line of similar slope but offset by -4.0 kcal/mol on the $D(Ni^+–2L)$ axis: $\delta D(Cu^+–2L) = 0.922\delta D(Ni^+–2L) + 11.2$ kcal/mol. This result shows that Cu^+ is a slightly softer acid than Ni^+. The three ester data points appear to fall on a line separate from the other oxygen bases, but this line is not drawn. A comparison of the Co^+[5] and Ni^+ basicity scales (Figure 7) shows that Co^+ is slightly harder than Ni^+. Twenty oxygen bases fall on a line given by $\delta D(Co^+–2L) = 0.869\delta D(Ni^+–2L) - 0.50$ kcal/mol ($r = 0.979$). Data points for HCN and alkenes fall approximately on this line. The three sulfur bases define a line with a similar slope but offset by 2.1 kcal/mol on the $D(Ni^+–2L)$ axis: $\delta D(Co^+–2L) = 0.861\delta D(Ni^+–2L) - 2.3$ kcal/mol ($r = 1.000$). This indicates that the sulfur bases bond slightly more strongly to Ni^+. Therefore Ni^+ is the softer acid. Figures 6 and 7 together demonstrate the expected periodic trend in acid softness: Co^+ is a harder acid than Ni^+, which in turn is harder than Cu^+. This effect results from an increase in d-electron density through the series Co^+, Ni^+, and Cu^+.

Figure 8 presents a comparison of ligand binding energies to $CpNi^+$,[16] $D(CpNi^+–L)$ vs. the results for Ni^+, $\delta D(Ni^+–2L)$.

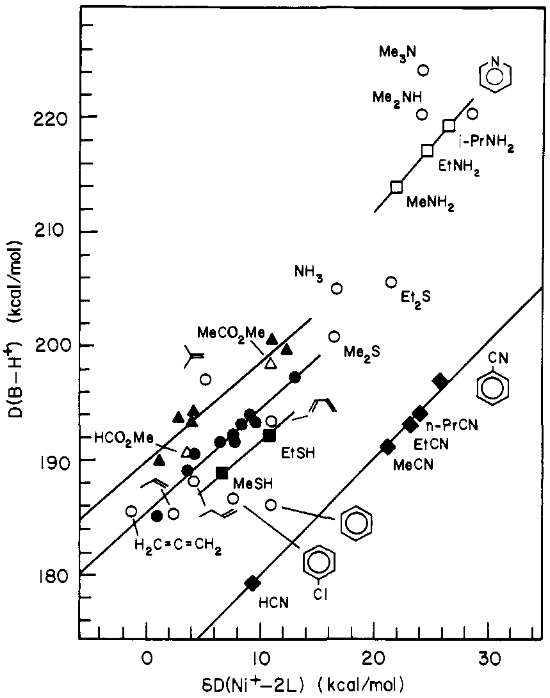

Figure 9. Comparison of proton affinities PA(B) = $D(B-H^+)$ to relative two-ligand dissociation enthalpies for Ni^+. Least-squares fit lines are drawn for 3 primary amines (□), PA = $1.18\delta D(Ni^+-2L) + 187.9$ kcal/mol ($r = 1.000$), 6 ethers (▲), PA = $0.872\delta D(Ni^+-2L) + 189.8$ kcal/mol ($r = 0.945$), 10 other oxygen bases (●), PA = $0.917\delta D(Ni^+-2L) + 185.1$ kcal/mol ($r = 0.949$), 2 mercaptans (■), PA = $0.825\delta D(Ni^+-2L) + 183.1$ kcal/mol, and 5 nitriles (◆), PA = $1.04\delta D(Ni^+-2L) + 169.1$ kcal/mol ($r = 0.994$).

Fourteen oxygen bases fall on a line given by $D(CpNi^+-L) = 0.446\delta D(Ni^+-2L) - 7.1$ kcal/mol ($r = 0.938$). Lines with similar slopes, but offset toward stronger bonding to Ni^+, are seen for sulfur compounds: $D(CpNi^+-L) = 0.405\delta D(Ni^+-2L) + 44.5$ kcal/mol and nitriles: $D(CpNi^+-L) = 0.466\delta D(Ni^+-2L) + 43.4$ kcal/mol, respectively. These results indicate that Ni^+ is a slightly softer acid than $CpNi^+$. This is expected since Co^+ and $CpNi^+$, which are both d^9 systems, have been previously seen to be similar in softness,[5] and Co^+ was found above to be a harder acid than Ni^+.

A comparison of the Ni^+ results to proton affinities,[12,18] PA(B) = $D(B-H^+)$ is presented in Figure 9. Two separate lines are seen for oxygen bases. Ten oxygen bases fall on a line given by PA = $0.917\delta D(Ni^+-2L) + 185.1$ kcal/mol ($r = 0.949$). These bases include alkyl alcohols, aldehydes, and ketones. Six ethers define a separate line with a similar slope but offset from the first oxygen base line by −5 kcal/mol on the $D(Ni^+-2L)$ axis: PA = $0.872\delta D(Ni^+-2L) + 189.8$ kcal/mol ($r = 0.943$). A third line for oxygen bases could be drawn through the two ester data points but is omitted here. Five nitriles fall along a line which is offset from the main oxygen base line by 14 kcal/mol on the $D(Ni^+-2L)$ axis: PA = $1.04\delta D(Ni^+-2L) + 169.1$ kcal/mol ($r = 0.994$). Two mercaptans define a line given by PA = $0.825\delta D(Ni^+-2L) + 183.1$ kcal/mol and offset from the oxygen lines toward stronger binding to Ni^+ by 4 kcal/mol on the $D(Ni^+-2L)$ axis. These results are consistent with the expectation that Ni^+ is a softer acid than H^+. Three primary amines define a line given by PA = $1.18\delta D(Ni^+-2L) + 187.9$ kcal/mol ($r = 1.000$). This correlation line is offset by −6 kcal/mol from the oxygen lines and indicates that amines bond relatively more strongly to H^+ than to Ni^+. It is interesting to note that secondary and tertiary amines do not fall on this line, just as ethers are not located on the same correlation line as alcohols or sulfides on the same line as mercaptans. The reason for this is related to increased stabilization of protonated species having multiple indistinguishable hydrogens.[19]

It is interesting to note that the slopes of all correlation lines that can be drawn through the data in Figure 6 are quite similar, ranging from 0.83 to 1.18. It is a general observation for all correlation diagrams presented in this work that the slopes of the lines in any one figure are similar. While slopes of correlation lines within a specific correlation diagram are generally similar, systematic variations become apparent when comparing the slopes of correlation lines for a specific functionality among different correlation diagrams. The slopes of the correlation plots of those reference acids which bind one ligand, vs. Ni^+, for oxygen bases vary in the order H^+ (0.917), NO^+ (0.655), Al^+ (0.641), Mn^+ (0.491), and Li^+ (0.491). Similarly one obtains for nitrile correlation lines H^+ (1.037), Al^+ (0.915), and Mn^+ (0.607). This same order has been seen for correlation plots for these reference acids with one another. It likely reflects the relative metal–ligand bond distance, H^+ having the shortest bond distance and Li^+ the longest. With a shorter bond distance the effect of a larger alkyl substituent is greater, since it is closer to the charge center. The slope of the line thus favors the metal with the shorter bond distance as basicity increases with increasing alkyl substitution. When the $\delta D(Ni^+-2L)$ scale is divided by two to give the relative dissociation enthalpy per ligand for Ni^+, the slopes for the oxygen lines become H^+ (1.84), NO^+ (1.31), Al^+ (1.28), Mn^+ (0.98), and Li^+ (0.98). For the nitriles these slopes are H^+ (2.07), Al^+ (1.84), and Mn^+ (1.22). In the case of oxygen compounds the ligand bonding distance to Ni^+ this appears to be shorter than that to Li^+ and Mn^+, since the slope for Ni^+ vs. itself is 1.00. This is not the case for nitriles where the ligand-bonding distance to Ni^+ appears to be longer than that to Mn^+. Actually, the one-ligand dissociation enthalpies are not known from the *average* dissociation energy available from the present work and may well be higher, as discussed above. This would give a higher effective slope for comparisons of Ni^+ to H^+, NO^+, Al^+, Mn^+, and Li^+. As a result it is not entirely clear whether bonding distance of oxygen bases to Ni^+ may be shorter than that to Al^+, NO^+, or even H^+ as well as Li^+ and Mn^+ or not. The significance of the slope in the correlation of $CpNi^+$ to Ni^+ is also not clear since two-ligand effects are present in both data sets in this comparison in different ways. For Cu^+ and Co^+ vs. Ni^+, the slopes should be meaningful, however, since two-ligand dissociation enthalpies are available in all cases. The slopes for oxygen bases are 0.940 and 0.869 for Cu^+ and Co^+ comparisons to Ni^+, respectively. These numbers indicate that Co^+ and Cu^+ *both* have slightly longer average bond distances toward oxygen bases than does Ni^+. This nonperiodic effect contrasts with the observed periodic behaviors of acid softness.

In conclusion, the relative gas-phase two-ligand dissociation enthalpies for Ni^+, $\delta D(Ni^+-2L)$, measured in this work show that Ni^+ is a soft acid similar to Co^+ and Cu^+. It is slightly softer than Co^+ but harder than Cu^+. Because of the extensive Ni^+ data set, correlation diagrams *clearly* show systematic differences in bonding among compounds with different functional groups. These differences in bonding are particularly noticeable between oxygen compounds and alkenes, nitriles, sulfur bases, and other ligands capable of π-back-bonding. Previous studies of other metal ions have provided some indication of these bonding effects, but the evidence was generally not adequate to demonstrate them clearly. The relative slopes of the correlation plots indicate that the average metal–ligand bonding distance for $Ni(ligand)_2^+$ complexes is shorter than that for both Co^+ and Cu^+.

Acknowledgment is made to the National Science Foundation for support of this work by Grant CHE-76-17304.

Registry No. $Ni(pyridine)_2^+$, 80697-80-9; $Ni(i\text{-}PrNH_2)_2^+$, 80697-81-0; $Ni(C_6H_5CN)_2^+$, 80697-82-1; $Ni(EtNH_2)_2^+$, 80697-83-2; $Ni(Me_3N)_2^+$, 80697-84-3; $Ni(Me_2NH)_2^+$, 80697-85-4; $Ni(n\text{-}PrCN)_2^+$, 80697-86-5; $Ni(EtCN)_2^+$, 80697-87-6; $Ni(MeNH_2)_2^+$, 80697-88-7; $Ni(Et_2S)_2^+$, 80697-89-8; $Ni(MeCN)_2^+$, 80719-31-9; $Ni(i\text{-}Pr_2CO)_2^+$, 80719-32-0;

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Ni(*t*-BuCOMe)$_2^+$, 80719-33-1; Ni(Et$_2$CO)$_2^+$, 80719-34-2; Ni(NH$_3$)$_2^+$, 80719-35-3; Ni(MeNCS)$_2^+$, 80719-36-4; Ni(Me$_2$S)$_2^+$, 80719-37-5; Ni(MeCOEt)$_2^+$, 80737-27-5; Ni(EtCO$_2$Et)$_2^+$, 80737-28-6; Ni(EtCO$_2$Me)$_2^+$, 80719-38-6; Ni7Me$_2$CO)$_2^+$, 80719-39-7; Ni(THF)$_2^+$, 80719-40-0; Ni(1,3-butadiene)$_2^+$, 80719-41-1; Ni(benzene)$_2^+$, 80719-42-2; Ni(*t*-BuCHO)$_2^+$, 80719-43-3; Ni(Et$_2$O)$_2^+$, 80719-44-4; Ni(MeCO$_2$Me)$_2^+$, 80719-45-5; Ni(EtSH)$_2^+$, 80719-46-6; Ni(C$_6$H$_5$Cl)$_2^+$, 80719-47-7; Ni(*i*-PrCHO)$_2^+$, 80719-48-8; Ni(HCN)$_2^+$, 80719-49-9; Ni(*n*-PrCHO)$_2^+$, 80719-50-2; Ni(*i*-PrOH)$_2^+$, 80719-51-3; Ni(EtCHO)$_2^+$, 80719-52-4; Ni(*n*-BuOH)$_2^+$, 80719-53-5; Ni(MeSH)$_2^+$, 80719-54-6; Ni(*n*-PrOH)$_2^+$, 80737-29-7; Ni(Me$_2$C=CH$_2$)$_2^+$, 80719-55-7; Ni(1,4-dioxane)$_2^+$, 80719-56-8; Ni(EtOH)$_2^+$, 80719-57-9; Ni(EtCH=CH$_2$)$_2^+$, 80719-58-0; Ni(Me$_2$O)$_2^+$, 80719-59-1; Ni(MeCHO)$_2^+$, 80719-60-4; Ni(HCO$_2$Me)$_2^+$, 80719-61-5; Ni(furan)$_2^+$, 80719-62-6; Ni(oxirane)$_2^+$, 80719-63-7; Ni(MeOH)$_2^+$, 80737-14-0; Ni(allene)$_2^+$, 80719-64-8; Ni(C$_2$H$_2$)$_2^+$, 80719-65-9; Ni(MeCH=CH$_2$)$_2^+$, 80719-66-0.

Relative Bond Dissociation Energies for Two-Ligand Complexes of FeBr$^+$ with Organic Molecules in the Gas Phase

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Abstract: Relative two-ligand dissociation enthalpies, $\delta D(\mathrm{FeBr^+{-}2L})$, for FeBr$^+$ with 24 organic molecules are determined. A pulsed laser volatilization–ionization source is used to generate Fe$^+$ which reacts with MeBr to give FeBr$^+$. With various organic molecules present, FeBr$^+$ reacts to give FeBr(ligand)$_2^+$ complexes. Equilibrium constants are measured for the ligand-exchange reactions which occur when pairs of ligand molecules are present. Free energies for two-ligand exchange are obtained from the equilibrium constants for the reaction $\mathrm{FeBr(A)_2^+ + 2B \rightleftarrows FeBr(B)_2^+ + 2A}$. The free-energy differences are added to give a scale of relative free energies for ligand exchange. These are converted to enthalpies to give $\delta D(\mathrm{FeBr^+{-}2L})$. The results are compared to available results for other reference acids: H$^+$, Al$^+$, Mn$^+$, Co$^+$, Cu$^+$, Ni$^+$, and CpNi$^+$. These comparisons show that FeBr$^+$ is a moderately soft acid. It is harder than Co$^+$, Ni$^+$, Cu$^+$, and CpNi$^+$, slightly softer than Mn$^+$, and much softer than Al$^+$ or H$^+$. Comparison of the FeBr$^+$ and Mn$^+$ scales shows that the bonding interactions in FeBr(L)$_2^+$ and Mn(L)$^+$ complexes are similar. This is expected because the iron in FeBr$^+$ is formally isoelectronic with Mn$^+$. FeBr$^+$–ligand bonding interactions are influenced by steric effects which result from the presence of the bulky Br atom on the iron.

Relative gas-phase ligand-binding energies for various metal cations have recently been obtained by using a combination of ion cyclotron resonance (ICR) spectroscopy and a pulsed laser volatilization–ionization source of atomic metal cations. One-ligand binding energies, $D(\mathrm{M^+{-}L})$, were measured for Al$^+$ and Mn$^+$,[2,3] while two-ligand binding energies have been determined for Cu$^+$, Co$^+$, and Ni$^+$.[4-6] Comparisons between different scales can be quite informative and have revealed some interesting aspects of metal–ligand interactions. Recent work in our laboratory has shown that complexes of FeBr$^+$ with two ligands can be readily produced and do not react further except by ligand-exchange reactions. Determinations of relative binding energies in two-ligand complexes of FeBr$^+$ are therefore possible. These two-ligand binding energies should reveal effects due to the presence of the large bromine atom on the metal atom when compared to two-ligand binding energies for bare metal cations. Formally, the iron atom in FeBr$^+$ is a dipositive Fe(II) species. Different bonding effects might be observed for such an ion when compared to unipositive metal ions. Comparison of Mn$^+$ and FeBr$^+$ results is also of interest since they are formally isoelectronic systems. In the present paper we report relative dissociation energies of 24 organic molecules in two-ligand complexes of FeBr$^+$. The results are compared to available gas-phase basicity scales for other reference acids: H$^+$, Al$^+$, Mn$^+$, Co$^+$, Ni$^+$, CpNi$^+$, and Cu$^+$.

Experimental Section

Experiments were carried out by using ICR instrumentation and techniques which have been previously described.[7,8] The output of a pulsed YAG laser is focused onto a stainless steel target mounted on the end plate of the ICR cell. The mass spectrum for this source with no added gases shows ions of mass 52 (18), 53 (2), 54 (4), 56 (74), and 57 (2), with ion abundances (in percent) given in parentheses. This corresponds to the isotope distribution expected for a target consisting of 80% Fe and 20% Cr. The small amounts of Cr$^+$ produced were not found to be a problem because Cr$^+$ does not react with MeBr. Cr$^+$ reaction products with various ligand species were only formed in small quantities and in all cases could be easily distinguished from FeBr$^+$ complexes. Chemicals used were from commercial sources and were degassed by repeated freeze–pump–thaw cycles before use. All experiments were carried out at an ambient temperature of 25 °C. Gas mixtures were prepared in the cell and partial pressures measured by difference as has been previously described. Accuracy of pressure ratios is limited to about ±30% because the ion gauge used for pressure measurements is not individually calibrated for each gas.

Results

Formation of FeBr$^+$. Reaction of Fe$^+$ with MeBr results in rapid formation of FeBr$^+$,[9] reaction 1 ($k = 4.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). In the presence of only MeBr, FeBr$^+$ does not react further except to undergo bromine isotope exchange (reaction

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