

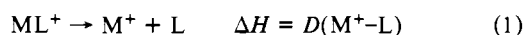
Relative Binding Energies of Organic Molecules to Al⁺ in the Gas Phase

Jack S. Uppal and Ralph H. Staley*¹

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received May 6, 1981

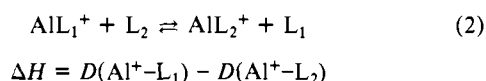
Abstract: Relative ligand binding energies, $\delta D(\text{Al}^+-\text{L})$, for Al⁺ with 30 organic molecules are determined. A pulsed laser ionization source is used to generate Al⁺ which reacts with EtOH to give Al(EtOH)⁺ in a two-step sequence. The equilibrium constant for the ligand exchange reaction $\text{AlL}_1^+ + \text{L}_2 \rightleftharpoons \text{AlL}_2^+ + \text{L}_1$ is measured to give relative free energies for ligand exchange. These are added and converted to enthalpies to give the $\delta D(\text{Al}^+-\text{L})$ scale with the assumption that entropy changes are small and can be neglected. The dependence of $\delta D(\text{Al}^+-\text{L})$ on functional groups and substituent effects is analyzed. The results for Al⁺ are compared with available results for other reference acids: Li⁺, CpNi⁺, and H⁺.

Measurements of binding energies of ligands to metal cations, the enthalpy of reaction 1, provide gas-phase thermochemical data



for a fundamental process in the chemistry of metals with organic molecules. Such data can be used to evaluate the energetics of mechanisms for organometallic reactions and catalytic processes and to develop and evaluate models for bonding. Metal-ligand binding energies, $D(\text{M}^+-\text{L})$, have recently been determined using ion cyclotron resonance (ICR) techniques for $\text{M}^+ = \text{Li}^{+2,3}$ and $\text{M}^+ = \text{CpNi}^+$ (Cp $\equiv \eta^5\text{-C}_5\text{H}_5$, cyclopentadienyl radical).⁴ The approaches taken in those studies have not proven generally applicable, and attempts to apply them to other systems have led to only very limited success.⁵

The advent of a pulsed laser volatilization/ionization source for atomic metal cations makes it possible to conveniently carry out a variety of mechanistic and thermochemical studies of metal cation species using ICR techniques.⁶⁻⁹ Of particular interest is the recent discovery that Al⁺ reacts with alcohols, ROH, to give Al(ligand)⁺ species.⁶ This provides a convenient source of such species for studies of ligand-exchange reaction 2 and determination of relative ligand binding energies.



In the present paper we report the determination of relative metal-ligand binding energies, $D(\text{M}^+-\text{L})$, for Al⁺ with 30 ligands. The dependence of $D(\text{Al}^+-\text{L})$ on functional group and substituent effects is analyzed. $D(\text{Al}^+-\text{L})$ provides a measure of relative basicity with respect to the reference acid Al⁺. The results for Al⁺ are thus compared with available results for other reference acids: Li⁺,^{2,3} CpNi⁺,⁴ and H⁺.¹⁰ The initial reactions of Al⁺ with the organic molecules studied as ligands are described in a separate

paper along with other chemistry of Al⁺ and Mg⁺ with organic molecules.⁶

Experimental Section

The reported work was performed using an ICR spectrometer and techniques which have been previously described.^{6,8} A pulsed YAG laser was used to produce atomic aluminum cations in the ICR cell.⁶ Chemicals were from commercial sources. Experiments were carried out at 25 °C.

Gas mixtures are prepared in the cell and partial pressures measured as follows. A 0.5-in. diameter line connects the cell to three leak valves which are initially closed. Another line, 1.5 in. in diameter, connects the cell to a 30-L/s ion pump. Pressure is measured with a Bayard-Alpert ionization gage which is located about halfway between the cell and the ion pump. A background pressure reading is taken and then one of the leak valves opened to admit gas from a bulb at 1-100 Torr pressure. The leak valve is adjusted to give the desired partial pressure which is determined as the difference between the total pressure and the background. A period of several minutes is typically needed to obtain a stable pressure reading after the leak valve is adjusted. This procedure is repeated to admit up to three gases to the cell, each partial pressure being measured by difference using the previous total pressure as the background value. When the experiment is complete, the procedure is reversed, again taking pressure readings after each leak valve is closed and the pressure has stabilized. The partial pressure values for each gas from before and after the experiment are compared. When agreement is found to within 20%, the before and after values are averaged to give a partial pressure for each gas for that experiment. When a deviation of more than 20% is found for one or more gases, the data from that experiment are rejected and the experiment is repeated.

Results

Ethanol was used as a reagent for the preparation of the ligand-aluminum cation complex Al(EtOH)⁺ which is formed in a rapid two-step sequence as is described separately.⁶ When two ligand molecules are present, one of which may be ethanol, competition for the available ligand site on Al⁺ occurs by reaction 2. Figure 1 shows the variation of Al(HCO₂Et)⁺ and Al(HCO₂-*n*-Pr)⁺ ion abundances with time for a 2.4:1.0:0.7 mixture of HCO₂Et, HCO₂-*n*-Pr, and EtOH at a total pressure of 14×10^{-6} Torr. The ligand exchange reaction 2 of these ions with the HCO₂Et and HCO₂-*n*-Pr neutrals is shown by delayed ejection double resonance experiments to be rapid and approaches equilibrium. The ratio of the Al(HCO₂Et)⁺ and Al(HCO₂-*n*-Pr)⁺ signals becomes constant to within $\pm 10\%$ after about 100 ms. There is a slow decrease in total ion abundance because of loss by diffusion to the walls of the ICR cell, but this does not significantly affect the ratio of ion abundances.¹¹ An equilibrium constant for reaction 2 is calculated from the measured ratio of ion abundances and the partial pressures of the HCO₂Et and

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(11) The diffusional loss rates depend on the magnetic field strength. Since the signal for each ion is recorded at a magnetic field strength proportional to its mass, effective loss rates are different for each ion. This becomes important when the masses of the ions studied are significantly different and the loss rates are high (due to high pressure and/or low magnetic field strengths) but was not a problem in the present work.

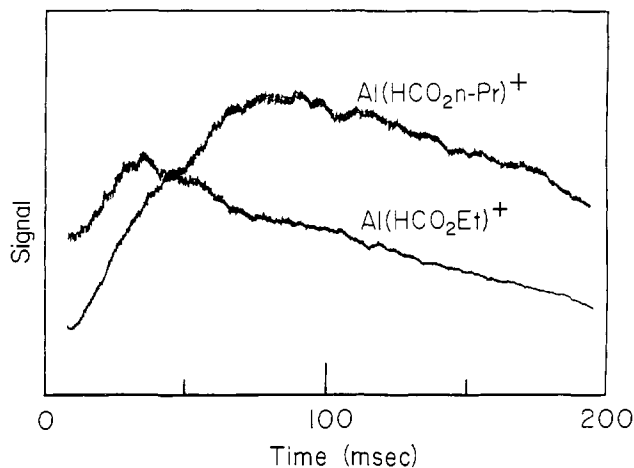


Figure 1. Variation of $\text{Al}(\text{HCO}_2\text{Et})^+$ and $\text{Al}(\text{HCO}_2\text{-}n\text{-Pr})^+$ abundances with time in a 2.41:1.00:0.69 mixture of HCO_2Et , $\text{HCO}_2\text{-}n\text{-Pr}$, and EtOH , respectively, with the Al^+ source. The total pressure is 14.2×10^{-6} Torr. Initial reactions (not shown) during the first 70 ms yield $\text{Al}(\text{HCO}_2\text{Et})^+$ and $\text{Al}(\text{HCO}_2\text{-}n\text{-Pr})^+$ as the predominant ions in this system. The ligand-exchange reaction of these ions with the HCO_2Et and $\text{HCO}_2\text{-}n\text{-Pr}$ neutrals is shown by double resonance to be rapid and approaches equilibrium, giving an equilibrium constant of 4.7. Four determinations give an average of $K = 4.5 \pm 0.5$ for this experiment. The slow decrease in total ion abundance results from ion loss by diffusion to the walls of the ICR cell.

$\text{HCO}_2\text{-}n\text{-Pr}$ neutrals. Four determinations give an average of $K = 4.5 \pm 0.5$ for $L_1 = \text{HCO}_2\text{Et}$ and $L_2 = \text{HCO}_2\text{-}n\text{-Pr}$. This corresponds to a free energy difference $-\Delta G_{\text{exchange}} = 0.89$ kcal/mol calculated from the relation $-\Delta G = RT \ln K$ for the operating temperature of 25 °C.

Equilibria were measured for reaction 2 for various pairwise combinations of 30 different molecules as ligands. Values for $\Delta G_{\text{exchange}}$ from these experiments are given in Table I. Each value represents an average of at least three determinations. The results are combined into a ladder to give a scale of relative free energies for ligand binding $\delta D(\text{Al}^+\text{-}L)$ for each ligand. Redundant determinations in this scale provide an internal consistency check on the results. Agreement is found to within about 0.10 kcal/mol in all cases.

Other molecules were studied as ligands for which quantitative data were not obtained. The ligands benzene, furan, NH_3 , MeNO_2 , MeNCO , MeNCS , Me_2S , $\text{C}_6\text{H}_5\text{OH}$, and HCONH_2 are unreactive with $\text{Al}(\text{EtOH})^+$. The displacement of MeSCN by EtOH is reversible but too slow for quantitative data to be obtained. Cyclopentanol is about 0.4 kcal/mol stronger than *sec*-BuOH, based on one determination. *t*-BuOH lies between *sec*-BuOH and acetone, and *t*-BuCHO is stronger than *sec*-BuOH. $\text{Al}(\text{HCONMe}_2)^+$ is formed in a mixture of EtOH and HCONMe_2 ; however, there is no double resonance evidence for either the displacement of EtOH by HCONMe_2 or the reverse reaction. Efforts to study Me_3N , pyridine, and $\text{C}_2\text{H}_5\text{OCH}_3$ were unsuccessful owing to reaction of $\text{Al}(\text{H}_2\text{O})^+$ with these ligands by proton transfer rather than ligand displacement.⁶

Discussion

Relative enthalpies of binding to Al^+ , $\delta D(\text{Al}^+\text{-}L)$, for the 30 molecules studied are given in Table I. These are given relative to $D(\text{Al}^+\text{-}EtOH) = 0$ which is chosen arbitrarily. The absolute zero of this enthalpy scale cannot be determined from the present work. The enthalpy scale is obtained from the free-energy scale by the assumption that entropy changes are small and tend to cancel so that they may be neglected.

There are two contributions to ΔS for reaction 2 which could be significant: (1) symmetry number changes¹² and (2) changes in moment of inertia.³ Accurate treatment of either of these

Table I. Relative Gas-Phase Ligand Binding Energies to Al^+ for Various Molecules^a

Ligand (L)	Measured $\Delta G_{\text{exchange}}^b$	$\delta D(\text{Al}^+\text{-}L)^c$
<i>n</i> -PrCO ₂ Et		10.60
EtCO ₂ Et	0.72	9.88
MeCO ₂ Et	1.34	8.53
Et ₂ CO	0.21	8.32
EtCO ₂ Me	0.22	8.10
<i>t</i> -BuOMe	1.15	7.13
MeCOEt	0.35	6.99
MeCO ₂ Me	0.21	6.78
THF ^d	1.42	6.21
Me ₂ CO	0.79	5.43
HCO ₂ <i>n</i> -Bu	0.58	4.84
Et ₂ O	0.33	4.67
HCO ₂ <i>n</i> -Pr	0.12	4.52
C ₆ H ₅ CN	0.89	3.99
HCO ₂ Et	0.37	3.62
<i>s</i> -BuOH	1.11	3.36
<i>i</i> -PrCHO	0.85	2.52
<i>n</i> -PrCN	0.01	2.51
<i>i</i> -BuOH	0.19	2.34
<i>i</i> -PrOH	0.76	2.32
<i>n</i> -BuOH	0.93	2.26
HCO ₂ Me	0.67	1.61
EtCN	0.02	1.59
EtCHO	0.20	1.39
Me ₂ O	0.06	1.38
<i>n</i> -PrOH	1.24	1.33
C ₂ H ₃ CN	1.44	0.09
EtOH	0.09	0.00
MeCN	0.17	-0.17
MeCHO	0.62	-0.62

^a All data in kcal/mol. ^b For the reaction $\text{AlL}_2^+ + L_1 + L_2 \rightleftharpoons \text{AlL}_1^+ + L_2$. ^c Values are relative to $D(\text{Al}^+\text{-}EtOH) = 0$. Free-energy differences from the second column are added to give relative free energies which are converted to relative enthalpies, $\delta D(\text{Al}^+\text{-}L)$, by assuming that entropy changes are small and can be neglected (see text). ^d Tetrahydrofuran.

contributions requires knowledge of the geometries of the species involved. Geometries are not available for the $\text{Al}(\text{ligand})^+$ species. However, both effects seem likely to be unimportant in the present work. None of the 30 molecules studied should undergo symmetry number changes on formation of the $\text{Al}(\text{ligand})^+$ species.¹³ Moment of inertia changes in reaction 2 are important when aluminum–ligand bonding distance and ligand mass are significantly different for the two ligands. The ligands studied are similar in mass and can be expected to bond similarly to Al^+ . Neglect of entropy changes thus appears to be an acceptable assumption in the present work.

Ligand binding energies for the 30 molecules studied in this work, arranged by functional group, are plotted in Figure 2. Within each functional group series alkyl substitution is seen to have a systematic effect. The results are consistent with and

(13) The $\text{Al}(\text{ligand})^+$ ions for Me_2O , THF, Et_2O , Me_2CO , and Et_2CO are assumed to have a planar structure with a twofold symmetry axis like the neutrals. While bent structures for these ions cannot be ruled out, theoretical calculations for the $\text{Li}(\text{H}_2\text{O})^+$ species have shown the symmetric planar geometry to be the most stable: Clementi, E.; Popkie, H. *J. Chem. Phys.* **1972**, *57*, 1077. Cyanobenzene is assumed to bind Al^+ on the nitrogen; this assumption is supported by some recent results: Kappes, M. M.; Staley, R. H., *J. Am. Chem. Soc.*, submitted for publication.

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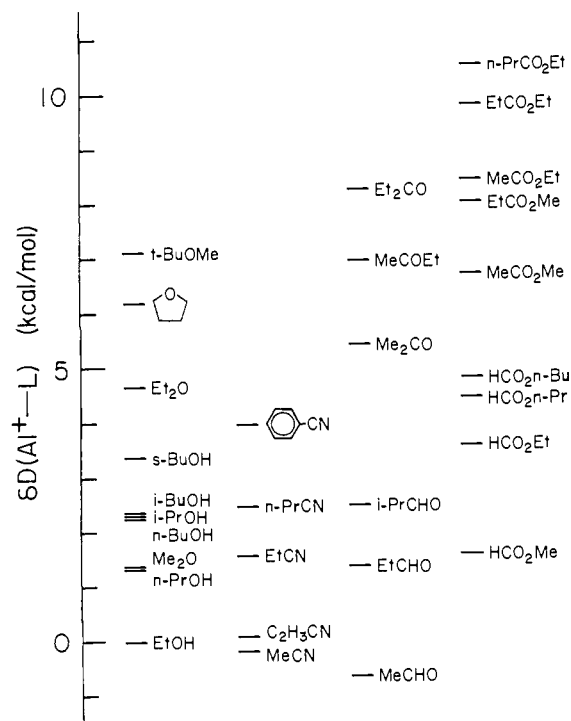


Figure 2. Binding energies of 30 molecules to Al⁺ arranged by functional group relative to $D(\text{Al}^+-\text{EtOH}) = 0$.

illustrate an increase in basicity in the sequence $\text{H} < \text{Me} < \text{Et} < n\text{-Pr} < n\text{-Bu} \sim i\text{-Pr} \sim i\text{-Bu} < \text{sec-Bu} < t\text{-Bu}$. Similar systematic alkyl substituent effects have been observed for proton affinities, $\text{PA}(\text{B}) \equiv D(\text{B}-\text{H}^+)$, of amines,^{10,14} nitriles,¹⁵ and various oxygen compounds.¹⁶ Examples of such effects are also apparent in the results for $D(\text{Li}^+-\text{L})$.²

The nature of the bonding interaction of Al⁺ with ligands can be illuminated by comparison of ligand bonding energies for Al⁺ with available data sets for other reference acids. Al⁺ has a ¹S ground state corresponding to a Ne(3s)² electronic configuration.¹⁷ Ligands are attracted to Al⁺ by interaction of intrinsic and induced ligand dipoles with the charge on Al⁺. Some covalent bonding occurs by delocalization of electrons into the empty 3p_z orbital of Al⁺, for example, for an n-donor base along the z axis. However, repulsion between the donor electrons and the (3s)² electrons on Al⁺ should severely limit this delocalization. Ligand-Al⁺ bonding is therefore expected to be largely ionic in character.

Comparison of relative binding energies of molecules to H⁺ and Al⁺ is shown in Figure 3. Proton affinities, $D(\text{B}-\text{H}^+)$, are available from the literature for 20 of the molecules studied in the present work.¹⁰ The data in Figure 3 show a general linear correlation. A least-squares fit to the data gives $D(\text{B}-\text{H}^+) = 1.43\delta D(\text{Al}^+-\text{L}) + 190.2$ kcal/mol (correlation coefficient = 0.93). This seems a remarkably good correlation considering that bonding to the proton is much stronger and certainly contains a large covalent component compared to bonding to Al⁺, which is expected to be ionic in character. Similar good general correlations to proton affinities were obtained for much of the data for $D(\text{Li}^+-\text{L})$ ² and $D(\text{CpNi}^+-\text{L})$.⁴ An even better correlation of $D(\text{B}-\text{H}^+)$ with $D(\text{Al}^+-\text{L})$ is found if the data set is restricted to molecules having the same functional group. For example, the six esters in Figure 3 fall approximately on the line $D(\text{B}-\text{H}^+) = 1.53\delta D(\text{Al}^+-\text{L}) + 188.3$ kcal/mol (correlation coefficient = 0.997). The slope of

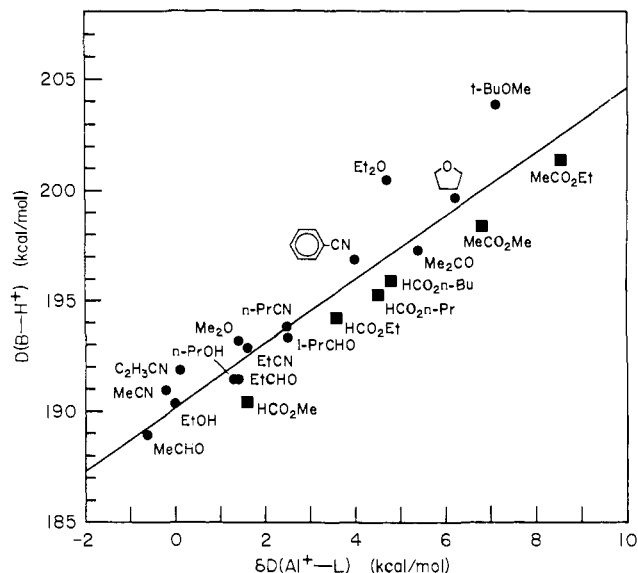


Figure 3. Comparison of relative binding energies of molecules to H⁺ and Al⁺. The solid line is a least-squares fit to the data: $D(\text{B}-\text{H}^+) = 1.43\delta D(\text{Al}^+-\text{L}) + 190.2$ kcal/mol (correlation coefficient = 0.93).

1.53 supports the expectation that the charge center in the protonated esters is closer to the center of the ester molecule than for the Al(ester)⁺ complex so that alkyl substituent effects are larger for the proton affinities. This seems to be the case for the other functional groups studied as well since the slope in the least-squares fit for all the data is 1.43. Overall, the comparison of $D(\text{B}-\text{H}^+)$ to $\delta D(\text{Al}^+-\text{L})$ in Figure 3 supports the expectation that bonding to the base by the proton has a strong covalent component which varies with functional group plus a contribution from polarization of the substituent attached to the functional group, and that ligand bonding to Al⁺ shows smaller substituent effects because the charge center in the Al(ligand)⁺ complex is further from the center of the ligand base. The scatter of the data in Figure 3 about the least-squares fit line suggests that a more detailed comparison, if data were available, would show a more complex dependence of the relative basicities to H⁺ and Al⁺ on functional group and perhaps other factors.

It is possible to construct a plot similar to Figure 3 to compare $\delta D(\text{Al}^+-\text{L})$ with $D(\text{Li}^+-\text{L})$. This comparison should be instructive since bonding to Al⁺ and Li⁺ is expected to be similar and mainly ionic in character. However, the presently available data sets for $\delta D(\text{Al}^+-\text{L})$ and $D(\text{Li}^+-\text{L})$ have only six common points. There is also considerable scatter in the data for a plot of $D(\text{Li}^+-\text{L})$ vs. $\delta D(\text{Al}^+-\text{L})$. The correlation coefficient for a least-squares fit to the data is only 0.67. Further analysis of this comparison will therefore not be given here. Future studies of binding energies to Al⁺ and Li⁺ might usefully focus on obtaining a larger common data set.

The overlap of the Al⁺ data set with the CpNi⁺ data set is better, 11 points, than that with Li⁺. $D(\text{CpNi}^+-\text{L})$ is plotted vs. $\delta D(\text{Al}^+-\text{L})$ in Figure 4. The data points for the oxygen bases are well correlated. A least-squares fit is given by $D(\text{CpNi}^+-\text{L}) = 0.595\delta D(\text{Al}^+-\text{L}) + 47.5$ kcal/mol with a correlation coefficient of 0.93. The relatively flat slope of this line, 0.595, shows that the substituents have a smaller effect on the basicity with respect to CpNi⁺ than with respect to Al⁺. This could result from a shorter metal-ligand bond distance in the Al(ligand)⁺ complexes than for the CpNi(ligand)⁺ species. However, it seems more likely that this smaller substituent effect is due to the presence of a second ligand in the CpNi(ligand)⁺ complexes. Polarization of the CpNi⁺ group produces an internal dipole moment which opposes the dipole moment induced in the ligand in the CpNi(ligand)⁺ complex. This tends to cancel the favorable interaction of the CpNi⁺ charge with the induced ligand dipole. No such cancellation occurs for the Al(ligand)⁺ complex since Al⁺ does not have an internal dipole moment.

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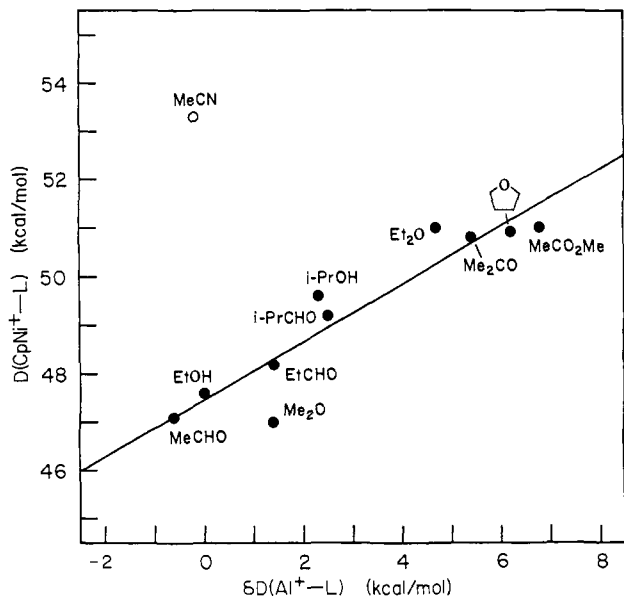


Figure 4. Comparison of relative ligand binding energies for CpNi^+ and Al^+ . The solid line is a least-squares fit to the data: $\delta D(\text{CpNi}^+-\text{L}) = 0.595\delta D(\text{Al}^+-\text{L}) - 4.95$ kcal/mol (correlation coefficient = 0.93) omitting the data point for MeCN.

The data point for MeCN is clearly off the correlation line for the oxygen bases in Figure 4. The binding energy of MeCN to CpNi^+ is 6 kcal/mol stronger than expected from the correlation line for the measured value of $\delta D(\text{Al}^+-\text{MeCN}) = -0.2$ kcal/mol. Enhanced bonding of HCN, MeCN, and MeNC by about 6 kcal/mol to CpNi^+ compared to H^+ was noted by Corderman and Beauchamp and attributed to π back-bonding of Ni 3d electrons into empty π^* CN orbitals.⁴

The zero of the $\delta D(\text{Al}^+-\text{L})$ scale is arbitrarily chosen because the present results do not allow an absolute calibration of the scale. The intercepts in Figures 3 and 4 are therefore not meaningful. Absolute lower limits for $D(\text{Al}^+-\text{L})$ are available in some cases from the observation of certain elimination reactions.⁶ The most useful of these is $D(\text{Al}^+-\text{MeOH}) \geq 38$ kcal/mol from the reaction of Al^+ with MeCO_2Me to give $\text{Al}(\text{MeOH})^+$ eliminating ketene.⁶ This lower limit is the same as the $\text{Li}(\text{MeOH})^+$ binding energy $D(\text{Li}^+-\text{MeOH})^+ = 38$ kcal/mol showing that bonding to Al^+ is at least as strong as to Li^+ , at least for alcohols and probably also for other oxygen bases. Better absolute calibration of the $\delta D(\text{Al}^+-\text{L})$ scale awaits new results by other techniques.

The methods reported in the present work are generally applicable to determinations of relative ligand binding energies for other atomic metal cations. Results of studies of ligand binding energies to Mn^+ are described in a companion paper.¹⁸ Studies are under way in our laboratory to measure relative ligand binding energies for complexes of Cu^+ , Ni^+ , Co^+ , and FeBr^+ with two ligand molecules. The results of these studies along with the present work promise to significantly advance the quantitative understanding of metal-ligand bonding in the gas phase.

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Registry No. Ag^+ , 14701-21-4; *n*-PrCO₂Et, 105-54-4; EtCO₂Et, 105-37-3; MeCO₂Et, 141-78-6; Et₂CO, 96-22-0; EtCO₂Me, 554-12-1; *t*-BuOMe, 1634-04-4; MeCOEt, 78-93-3; MeCO₂Me, 79-20-9; THF, 109-99-9; Me₂CO, 67-64-1; HCO₂*n*-Bu, 592-84-7; Et₂O, 60-29-7; HCO₂*n*-Pr, 110-74-7; C₆H₅CN, 100-47-0; HCO₂Et, 109-94-4; *s*-BuOH, 78-92-2; *i*-PrCHO, 78-84-2; *n*-PrCN, 109-74-0; *i*-BuOH, 78-83-1; *i*-PrOH, 67-63-0; *n*-BuOH, 71-36-3; HCO₂Me, 107-31-3; EtCN, 107-12-0; EtCHO, 123-38-6; Me₂O, 115-10-6; *n*-PrOH, 71-23-8; C₂H₃CN, 107-13-1; EtOH, 64-17-5; MeCN, 75-05-8; MeCHO, 75-07-0.

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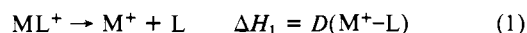
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Gas-phase thermochemical data are useful in evaluating the energetics of reaction processes and in developing models of bonding. Ion cyclotron resonance (ICR) techniques have been used recently to obtain such data for various metal ion species.²⁻¹¹

In particular, relative bond dissociation energies, $D(\text{M}^+-\text{L})$, the enthalpy of reaction 1, have been determined for complexes of



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