

Binding of Li⁺ to Lewis Bases in the Gas Phase. Reversals in Methyl Substituent Effects for Different Reference Acids

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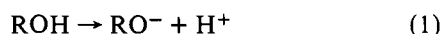
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Abstract: Gas-phase binding energies of Li⁺ to ten simple Lewis bases have been determined by ion cyclotron resonance spectroscopy. Species studied include water, methanol, dimethyl ether, formaldehyde, ammonia, the methylamines, hydrogen cyanide, and benzene. Equilibrium constants for reactions involving Li⁺ transfer between different base pairs are determined and converted to free energies. Enthalpies are calculated from the measured free energies and calculated entropies. The results are compared to data for systems with H⁺, K⁺, CH₃⁺, CpNi⁺, and (Me₃)B as the reference acid. Reversals in methyl substituent effects are noted and discussed for different reference acids. The data also allow detailed evaluation of recent theoretical work on Li⁺ affinities.

Introduction

Recently it has become possible to measure acidity and basicity in the gas phase by ion cyclotron resonance spectroscopy (ICR)¹ and by high-pressure mass spectroscopy.² The majority of these studies have been directed toward determining proton affinities.³ In addition, however, these techniques have been applied to determine alkali cation affinities,^{2,4,5} (η⁵-C₅H₅)Ni⁺ (CpNi⁺) affinities,⁶ halide affinities,⁷ and hydride affinities.⁸ Thus data on various acid-base systems, free of solvent effects, are rapidly accumulating. It is now possible to compare solution and gas-phase results for selected systems in an attempt to better understand apparent anomalous effects. An example of this is the anomalous ordering of proton affinities of amines in solution (NH₃ < MeNH₂ < Me₂NH > Me₃N) and their ordering in the gas phase (NH₃ < MeNH₂ < Me₂NH < Me₃N).⁹

One of the simplest and most commonly used concepts to arise from the growing legion of gas-phase acid-base studies is that of a regular alkyl substituent effect. The presence of alkyl groups at the basic site of a molecule is thought to stabilize charge at that site.¹⁰ This conclusion has largely been drawn from gas-phase studies of base strengths toward the proton as a reference acid (proton affinity). Thus it is inferred from the decrease in base strength of RO⁻ (defined by the enthalpy change for process 1)



with increasing size of the alkyl group R (Me < Et < *i*-Pr < *t*-Bu) that RO⁻ is concomitantly stabilized.¹¹ Similarly, for the process



(where R represents either an alkyl group or a hydrogen), substituting an alkyl group for a hydrogen or substituting a larger alkyl group for a smaller one at the heteroatom site increases the base strength. This is the case not only for the amines, but also for oxygen, sulfur, phosphorus, and halogen bases.³

This concept depends on specific characteristics of the acid-base interaction and for certain series of bases often fails with reference acids other than the proton. A natural choice as an acid that would be similar to a proton yet sufficiently different to be interesting is Li⁺, the principal difference being the 1s electrons on the alkali metal ion. This difference causes Li⁺ binding energies to be smaller than the corresponding proton affinities by approximately a factor of 5.⁴

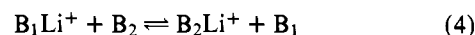
In addition to the experimental studies of lithium cation binding energies, a number of theoretical papers have been addressed to the subject. Some of the topics covered in these theoretical papers are concerned with biological aspects of Li⁺ affinities,¹² chelate effects,¹³ solvation effects,¹⁴ methyl substituent effects,¹⁵ correlation effects,¹⁶ and a detailed comparison of Li⁺ binding in H₂O and NH₃.¹⁷

At the present time, the only accurate absolute Li⁺ affinities are available from H₂O clustering experiments of Kerbarle² and theoretical calculations of Diercksen,¹⁶ Clementi,¹⁴ Goddard et al.,¹⁷ and Hinchliffe and Dobson.¹⁸ These studies have found that the binding energy of Li⁺ to H₂O is 34.0 kcal/mol¹⁶ and that of Li⁺ to NH₃ is 40.8 kcal/mol.¹⁷ Calculated relative Li⁺ affinities of H₂O and NH₃ are in agreement with this and previous work.⁴ Pullman and Brochen¹⁵ have used minimum basis set calculations to predict that the ordering of Li⁺ affinities of methyl-substituted amines should be NH₃ > MeNH₂ > Me₂NH > Me₃N. As experimental evidence they cited solution-phase data of Regis and Corset¹⁹ which indicated a similar trend. This is now seen to be incorrect since the measured gas-phase Li⁺ affinities of NH₃ and NMe₃ show $D(\text{NH}_3\text{-Li}^+) < D(\text{NMe}_3\text{-Li}^+)$.⁴

In this work trapped ion cyclotron resonance techniques have been used to determine the Li⁺ affinities



of ten Lewis bases: H₂O, MeOH, Me₂O, HCN, H₂CO, C₆H₆, NH₃, MeNH₂, Me₂NH, and Me₃N. Relative Li⁺ affinities are found from equilibrium studies



and the results then combined with a known absolute Li⁺ affinity to give absolute Li⁺ binding energies for all ten bases. The relative Li⁺ affinities are accurate to ±0.1 kcal/mol. In addition, several Li⁺ transfer rates are also measured.

This work is a continuation of a study made by Staley and Beauchamp⁴ but dealing with more specific aspects. In particular, the present work represents a more precise study of Li⁺ binding to a smaller number of bases in order to more accurately gauge entropy effects and to investigate methyl substituent effects in oxygen and nitrogen n-donor bases. These effects are contrasted to similar effects observed with the proton as the reference acid. The more accurate measurements also allow a more precise evaluation of theoretical calculations on these systems.

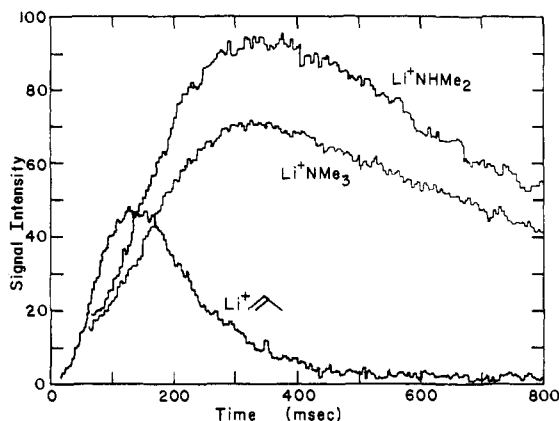


Figure 1. Trapped ion ICR spectrum of intensity as a function of trapping time for the equilibrium $\text{Me}_3\text{NLi}^+ + \text{Me}_2\text{HN} = \text{Me}_2\text{HNLi}^+ + \text{Me}_3\text{N}$. $(\text{C}_3\text{H}_6)\text{Li}^+$ results from reaction of Li^+ with $(\text{CH}_3)_2\text{CHCl}$ (process 5) and rapidly transfers Li^+ to Me_3N or Me_2HN . The ratio of $\text{Me}_3\text{N}:\text{Me}_2\text{NH}:(\text{CH}_3)_2\text{CHCl} = 3:1:1$, total pressure is 7×10^{-7} Torr.

Experimental Section

All chemicals used in this work were available from previous studies, and had been obtained originally from commercial sources. HCN was prepared in this laboratory from KCN and acid and distilled under vacuum. Formaldehyde was prepared fresh before each experiment from thermal decomposition of paraformaldehyde. All samples were degassed by several freeze-pump-thaw cycles before use. Impurities were negligible as discerned by mass spectrometric analysis.

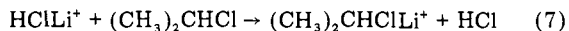
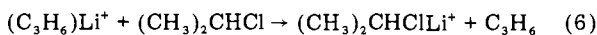
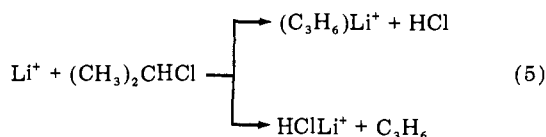
The ICR spectrometer used for this study was built in our laboratory, and incorporates at 15-in. electromagnet capable of 23.4 kG. The detection system utilizes a standard marginal oscillator and a boxcar integrator to process the signal. Experiments are performed using a "flat" ICR cell in the trapping mode,²⁰ with trapping times up to 1 s. Measurements are made at a fixed frequency except when there are large mass differences between ions, in which case a fixed magnetic field is used.

All experiments were carried out in the range of 10^{-7} – 10^{-5} Torr using diffusion pumping. Pressures are measured with a Schulz-Phelps type ionization gauge calibrated against an MKS Instruments Baratron Model 90H1-E capacitance manometer.⁷ It is expected that absolute pressure determinations are within $\pm 20\%$ using this method, with pressure ratios being somewhat more accurate. Sample mixtures are prepared directly in the instrument with three sample inlets and the Schulz-Phelps gauge.

Lithium cations are generated by a glass bead filament made according to the procedure described by Hodges and Beauchamp.²¹ This produces a glass bead of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (1:1:2) composition on 7-mil rhenium wire. Adequate Li^+ emission is achieved with filament currents of 1–2 A. The filament is approximately 1 mm in diameter and is located inside the cell several millimeters from one of the trapping plates. Minor changes in cell potentials are necessary to obtain good ion trapping with the filament in place. To store Li^+ at the beginning of a trapping sequence, an appropriate bias pulse is applied to the filament for 5–10 ms.

The effect of the Li^+ filament on cell temperature is minimal. A thermistor mounted in the cell shows less than a 5°C temperature rise after several hours of use. Further, no differences are noted between equilibrium constants measured immediately after the filament is turned on and those measured after an extended period of operation.

In order to minimize Li^+ bound dimer formation and ion loss, low total pressures are required. Low pressures necessitate the use of bimolecular reactions to form Li^+ complexes as shown by the equations⁴



If $(\text{CH}_3)_2\text{CHCl}$ is the only reagent present the final product is $(\text{CH}_3)_2\text{CHCLi}^+$. It is expected that Li^+ complexes formed will be thermalized by collisions in the initial stages of the trapping sequence. At pressures used in these experiments (up to 10^{-6} Torr) approximately 20 collisions are available for thermalization.

Direct clustering of Li^+ with Lewis bases is observed



(where B indicates a Lewis base) only at higher pressures or for more complex molecules.²² The rate of disappearance of Li^+ in eq 5 is measured to be $1.7 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the rate of Li^+ disappearance to form H_2COLi^+ in reaction 8 is about $5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²²

In these experiments two bases are added to the system in addition to a small amount of $(\text{CH}_3)_2\text{CHCl}$. Li^+ is observed to transfer rapidly from $(\text{C}_3\text{H}_6)\text{Li}^+$ and $(\text{CH}_3)_2\text{CHCLi}^+$ to the other bases. It was found that the Li^+ binding energies of propene and $(\text{CH}_3)_2\text{CHCl}$ are respectively 11 and 14 kcal/mol lower than the Li^+ binding energy of H_2O ,⁴ which is the weakest base used in this study. A typical trapped ion spectrum of the mixture of two bases is shown in Figure 1 for Me_3N and Me_2NH in the ratio 3.0:1.0. From the observed equilibrium the free energy change can be employed to calculate ΔG for reaction 4 using

$$\Delta G = -RT \ln K_{\text{eq}} \quad (9)$$

The equilibrium constant for reaction 4 can be written as either the ratio of concentrations or forward and reverse rate constants:

$$K_{\text{eq}} = \frac{[\text{B}_2\text{Li}^+][\text{B}_1]}{[\text{B}_1\text{Li}^+][\text{B}_2]} = \frac{k_f}{k_r} \quad (10)$$

The method used for the most of these experiments is to find the ratio of ion intensities. Since neutral concentrations are at least a factor of 10^5 larger than ion concentrations, neutral concentrations are taken to be proportional to their pressures. Ion concentrations are proportional to their signal intensity divided by the mass of the ion;¹ hence eq 10 can be rewritten as

$$K_{\text{eq}} = \frac{I(\text{B}_2\text{Li}^+)M(\text{B}_1\text{Li}^+)P(\text{B}_1)}{I(\text{B}_1\text{Li}^+)M(\text{B}_2\text{Li}^+)P(\text{B}_2)} \quad (11)$$

with $M(\text{BLi}^+)$ the mass of the BLi^+ complex, $I(\text{BLi}^+)$ the observed intensity of the complex, and $P(\text{B})$ the partial pressure of the neutral. Equilibrium constants are calculated at three different pressure ratios for each pair of bases and the resulting ΔG 's then averaged together.

As seen in Figure 1, the curves for Me_2HNLi^+ and Me_3NLi^+ decay somewhat at longer trapping times. This may be due either to ion losses or dimer formation. Under the low-pressure conditions in which these experiments are performed, dimer formation is not observed. Ratios of ion intensity are taken at several points on a spectrum and an average value is taken for the intensity ratio.

In addition to checking for equilibrium by varying the pressure ratio of the neutrals, true equilibrium is checked by double resonance. If equilibrium has been reached, then ejection of one complex should cause the signal from the second complex to go to zero. Using this technique it is found that equilibrium conditions are observed after approximately 20 collisions.

The second method for finding equilibrium constants is to determine forward and reverse rates. To measure these rates one of the complexes is ejected (in a time shorter than the time between collisions) after equilibrium has been reached, which results in an exponential decay of the other complex. With ejection of B_2Li^+ ($[\text{B}_2\text{Li}^+] = 0$, and $[\text{B}_1\text{Li}^+]_0$ the initial concentration of B_1Li^+ when ejection starts) the decay of B_1Li^+ is described by pseudo-first-order kinetics:

$$\frac{d[\text{B}_1\text{Li}^+]}{dt} = -k_r[\text{B}_1\text{Li}^+][\text{B}_2] \quad (12)$$

$$[\text{B}_1\text{Li}^+] = [\text{B}_1\text{Li}^+]_0 \exp(-k_r[\text{B}_2]t) \quad (13)$$

An identical scheme can be written down for ejection of B_1Li^+ and observation of the decay of B_2Li^+ . Rates can be determined from the slopes of semilog plots.

A typical delay ejection experiment is shown in Figure 2 for the pair of bases Me_2NH and Me_3N . The ion being monitored in this experiment is Me_2HNLi^+ , with the Me_3NLi^+ being ejected after 760 ms. This yields k_r , the reverse rate constant. A similar treatment of the Me_3NLi^+ signal when Me_2HNLi^+ is ejected at the same delay time

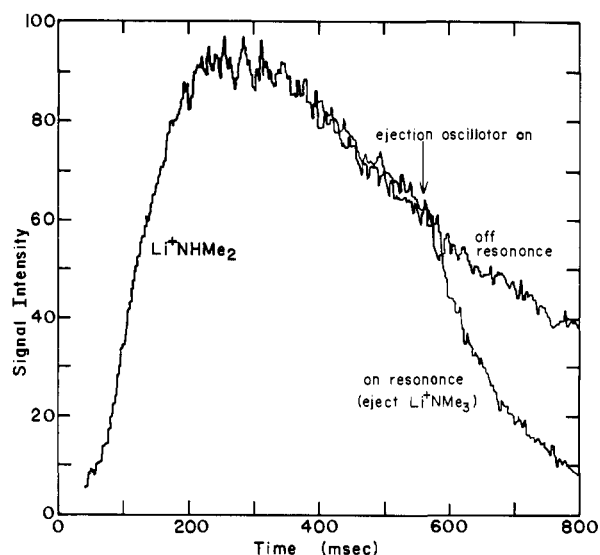


Figure 2. Trapped ion spectrum of intensity as a function of time with delayed ion ejection. This experiment monitors Me₂HNLi⁺ while ejecting Me₃NLi⁺ beginning at 760 ms. The ratio of Me₃N:Me₂NH:(CH₃)₂CHCl = 3.7:0.7:1, total pressure is 8.5 × 10⁻⁷ Torr.

yields k_f , the forward rate. The plots of $\ln(I/I_0)$ vs. t are shown in Figure 3. By taking the ratio I/I_0 at each point, and assuming that the rate of ion loss is the same for the experiment whether the double resonance oscillator is on or off, the effect of ion loss is canceled out. The equilibrium constant is then calculated from the ratio of forward and reverse rate constants.

An indication of the consistency of the measured ΔG values is given in Table I where it is seen that the free energies are independent of path (i.e., B₁ → B₃ is the same as B₁ → B₂ → B₃). Agreement between various pairs of paths is 0.2 kcal/mol or better and leads to an estimated precision of ±0.1 kcal/mol for each measurement.

Entropy Calculations. Since the spectrometer used in this study does not allow changes in temperature, entropies must be calculated from statistical mechanics. Searles and Kebarle²³ have derived expressions for the entropy of alkali-ion clustering for reactions such as 8. These expressions are reproduced here

$$\Delta S = \Delta S_{tr} + \Delta S_v + \Delta S_r + \Delta S_e \quad (14)$$

$$\Delta S_{tr} = \frac{3}{2} R \ln \frac{M'}{M_1 M_2} - \frac{5}{2} R \ln T + 2.313 \quad (15)$$

$$\Delta S_r = R \ln \left\{ \frac{\sigma}{\sigma'} \left[\frac{I'_A I'_B I'_C}{I_A I_B I_C} \right]^{1/2} \right\} \quad (16)$$

$$\Delta S_v = R \sum_{i=1}^3 \left\{ \frac{\theta_i}{e^{\theta_i} - 1} - \ln(1 - e^{-\theta_i}) \right\} \quad (17)$$

$$\Delta S_e = \ln \frac{\omega'_{el}}{\omega_{el}} \quad (18)$$

$$\Delta S_{tr} = \Delta S \text{ translational}$$

$$\Delta S_v = \Delta S \text{ vibrational}$$

$$\Delta S_r = \Delta S \text{ rotational}$$

$$\Delta S_e = \Delta S \text{ electronic}$$

$$M' = \text{mass of the complex in amu}$$

$$M_1 = \text{mass of Li}^+ \text{ in amu}$$

$$M_2 = \text{mass of B in amu}$$

$$\sigma = \text{rotational symmetry number of B}$$

$$\sigma' = \text{rotational symmetry number of the complex}^{24}$$

$$I_A, I_B, I_C = \text{moments of inertia of B}$$

$$I'_A, I'_B, I'_C = \text{moments of inertia of the complex}$$

$$\theta_i = h\nu_i/kT \text{ for the } i\text{th new vibrational mode of the complex}$$

$$\omega_{el} = \text{degeneracy of ground electronic state of B}$$

$$\omega'_{el} = \text{degeneracy of ground electronic state of the complex}$$

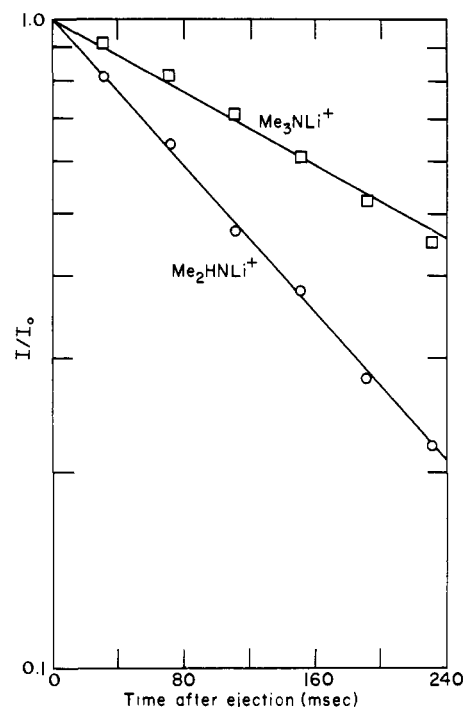


Figure 3. Plots of $\ln(I/I_0)$ vs. time after ejection for delayed ejection experiment in Figure 2. The decay plot for Me₃NLi⁺ while ejecting Me₂HNLi⁺ is shown by squares; the corresponding plot for Me₂HNLi⁺ while ejecting Me₃NLi⁺ is indicated by the circles. The slopes of these lines along with the neutral pressures give k_f (squares) and k_r (circles) (eq 13).

Table I. Experimentally Determined ΔG°_{298} for Li⁺ Transfer, and Thermodynamic Quantities for Li⁺ Clustering^a

Base	Directly measured		Li ⁺ + B → BLi ⁺		
	ΔG°_{298} ^b		ΔG°_{298} ^c	$T\Delta S^{\circ}$ ^d	ΔH°_{298}
Me ₂ NH	↓0.46	↑0.65	-34.1	-8.1	-42.2
Me ₃ N	↓0.34	↑	-33.7	-8.4	-42.1
MeNH ₂	↓1.19	↑1.95	-33.3	-7.8	-41.1
NH ₃	↓0.72	↑1.63	-32.1	-7.0	-39.1
Me ₂ O	↓1.03	↑1.78	-31.3	-8.2	-39.5
MeOH	↓0.67	↑	-30.3	-7.8	-38.1
C ₆ H ₆	↓1.00	↑1.56	-29.7	-8.2	-37.9
HCN	↓0.52	↑2.13	-28.7	-7.7	-36.4
H ₂ CO	↓0.95	↑1.29	-28.2	-7.8	-36.0
H ₂ O	↓	↑	-27.3	-6.7	-34.0

^a All values in kcal/mol. ^b Measured in this work. ^c Calculated from this work and data in ref 2. ^d At standard state 1 atm and 298 K calculated using eq 14.

because of errors in the original article. In using this treatment several assumptions must be made. First, it is assumed that $\omega_{el} = \omega'_{el}$ since all species are in their closed shell ground electronic states. Second, since the B-Li⁺ bond is relatively weak it is assumed that the only contribution to ΔS_v for reaction 8 is from the new B-Li⁺ bond. Because of the similarity in the bonding of Li⁺ to these bases it is assumed that changes in ΔS_v will be small between different systems. Thus for this work the vibrational frequencies for H₂OLi⁺ found by Dierksen¹⁶ are used for all bases, and yield a value of $\Delta S_v = 2.34$ eu. The third

Table II. Forward and Reverse Rates for the Equilibrium

$$B_1Li^+ + B_2 \xrightleftharpoons[k_r]{k_f} B_2Li^+ + B_1^a$$

B ₁	B ₂	k _f	k _r	k _f /k _r	K _{eq}
Me ₃ N	Me ₂ NH	8.26 × 10 ⁻¹⁰	3.62 × 10 ⁻¹⁰	2.28	2.17
MeNH ₂	Me ₂ NH	1.09 × 10 ⁻⁹	3.46 × 10 ⁻¹⁰	3.15	3.00

^a Rate constants are in units of cm³ molecule⁻¹ s⁻¹.

Table III. Calculated Entropy Values for the Reaction Li⁺ + B → BLi⁺ from Equations 14–18 at 298 K^a

B	ΔS _r ^b	ΔS _v ^c	ΔS _{tr}	ΔS ^d
H ₂ O	5.84	2.34	-30.8	-22.6
MeOH	2.61	2.34	-31.2	-26.3
Me ₂ O	1.78	2.34	-31.4	-27.3
NH ₃	5.00	2.34	-30.8	-23.5
MeNH ₂	2.55	2.34	-31.2	-26.3
Me ₂ NH	1.58	2.34	-31.4	-27.5
Me ₃ N	0.91	2.34	-31.5	-28.3
H ₂ CO	2.45	2.34	-31.2	-26.4
HCN	2.78	2.34	-31.1	-26.0
C ₆ H ₆	1.68	2.34	-31.5	-27.5

^a All entropies are in eu, 1 eu = 1 cal mol⁻¹ deg⁻¹. ^b Moments of inertia for neutral bases from ref 36 and 37. Moments of inertia for Li⁺ complexes calculated from assumed geometries. ^c Vibrational frequencies assumed similar for these systems. The frequencies used are from ref 16: ν₁ = 1.66 × 10¹³ s⁻¹; ν₂ = 1.17 × 10¹³ s⁻¹; ν₃ = 1.35 × 10¹³ s⁻¹. ^d ΔS_e = 0, ΔS = ΔS_r + ΔS_v + ΔS_{tr}.

assumption is that variations in the B–Li⁺ bond length for the various bases are small and can be held constant for oxygen or nitrogen bases. For all oxygen-containing bases an O–Li⁺ bond distance of 1.84 Å, the optimum found by Clementi¹⁴ for H₂OLi⁺, was used. Similarly, for all nitrogen-containing bases an n–Li⁺ bond distance of 1.90 Å was used, this being the optimum distance found by Goddard¹⁷ for H₃NLi⁺. For benzene Li⁺ was placed on the C₆ axis 1.50 Å from the center of the ring.

The fourth assumption is that the presence of the Li⁺ does not appreciably change the geometry of the base. This is supported by ab initio calculations for H₃NLi⁺.¹⁷ The geometry of the BLi⁺ complex is assumed to be that of the neutral species B with the Li⁺ placed at the appropriate distance. For the amines the cation is placed on the C₃ axis of NH₃ and methyl groups are then substituted for hydrogens at the appropriate nitrogen–carbon bond distance. Similarly for H₂O, MeOH, and Me₂O the Li⁺ is placed on the C₂ axis of H₂O and methyl groups are substituted for hydrogens at the appropriate oxygen–carbon bond distance. In HCNLi⁺ the geometry is assumed linear with Li⁺ bound to the nitrogen, while in H₂COLi⁺ the Li⁺ is assumed bound to the oxygen on the molecular C₂ axis.

Where it is possible to compare values of ΔS calculated from eq 14 with experimental values, the agreement is good. Searles and Kebarle found agreement of 2% for the H₂O–K⁺ system²³ and similar agreement for the other alkali ion hydration reactions.² It is difficult to check the experimental value of ΔS

for the Li⁺ complex in ref 2 because of a lack of agreement of quoted ΔG, ΔH, and ΔS values.

Results

Experimentally determined free energies of Li⁺ transfer are presented in the “ladder” diagram in Table I. The averaged free energies of Li⁺ transfer are combined with the free energy for process 19 (ΔG^o₂₉₈ = -27.3 kcal/mol²)



to give the free energies found in column 3 of Table I. Calculated entropies and resultant enthalpies are also found in Table I.

In Table II data for the forward and reverse rate constants are presented. These are expected to be accurate to 20%, and it should be noted that the ratio of forward and reverse rate constants for the systems yield equilibrium constants which agree with K_{eq} determined by the ratio method to better than 10%. It is of interest to compare Li⁺ transfer rates to proton transfer rates determined by ICR.¹ Proton transfer rates are of a comparable magnitude, generally between 3 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and 1.2 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹. The rapid rate of Li⁺ transfer facilitates rapid establishment of a true equilibrium.

Discussion

Entropy Effects. Table III summarizes the various entropy terms for the Li⁺ clustering reactions studied. Two features should be noted: translational entropy changes are small but nonnegligible and rotational entropy changes are quite large. Table IV illustrates this further for the bases H₂O, NH₃, and Me₃N by breaking down the contributions and comparing the values with Li⁺ as the acid to the values with H⁺ as the acid. It is seen in column 1 of Table IV that differences in ΔS_{tr} between protonated bases are negligible while the differences between Li⁺ complexes can be significant (0.7 eu = 0.21 kcal/mol at 298 K).

ΔS_r (eq 16) involves changes of both symmetry numbers and moments of inertia. As is expected, moments of inertia change only slightly with addition of a proton while much larger changes are seen with addition of Li⁺ (Table IV, column 2). In contrast, large changes in symmetry number accompany protonation and not addition of Li⁺. It is apparent why ΔS_r calculated from symmetry numbers alone gives radically different results from the values calculated from eq 16. For a small acid such as H⁺ symmetry number corrections are adequate. However, for the more massive Li⁺ use of symmetry numbers alone results in no corrections (except for C₆H₆) while changes in moments of inertia create sizable effects. The entropy terms are in fact large enough to cause the enthalpies and clustering to be reversed from the free energies of clustering for NH₃ and Me₂O.

Relative Li⁺ Affinities. The Li⁺ affinities measured in this work as well as data for five other Lewis acids are presented in Table V. Absolute Li⁺ affinities are estimated to the accuracy to ± 2 kcal/mol while relative Li⁺ affinities are accurate to ± 0.1 kcal/mol. It is evident from Table V that a regular methyl substituent effect for amine basicity is not seen. This is the first such trend to be noted in the gas phase for atomic

Table IV. Comparison between ΔS_{tr} and ΔS_r for Proton Complexing and Li⁺ Complexing for the Reaction M⁺ + B → BM⁺^a

	ΔS _{tr}		Π(I' _i)/Π(I _i) ^b		σ/σ'		ΔS _r (σ) ^c		ΔS _r ^d	
	M = H	M = Li	M = H	M = Li	M = H	M = Li	M = H	M = Li	M = H	M = Li
H ₂ O	-25.8	-30.8	4.25	359.99	0.33	1.00	-2.18	0.00	-0.75	5.84
NH ₃	-25.8	-30.8	2.75	153.75	0.25	1.00	-2.75	0.00	-1.75	5.00
Me ₃ N	-25.9	-31.5	1.07	2.49	1.00	1.00	0.00	0.00	0.07	0.91

^a All entropies are in eu. ^b For protonated species, geometries reflect proper bond angles and bond lengths, e.g., ∠HOH = 120° in H₃O⁺. ^c ΔS_r(σ) = R ln(σ/σ'). ^d ΔS_r = R ln{σ/σ' [(I'_AI'_BI'_C)/(I_AI_BI_C)]^{1/2}.

Table V. Binding Energies (Relative to NH₃) of Various Lewis Acids to the Bases Used in the Present Study^a

B	Li ⁺ (exptl) ^b	Li ⁺ (calcd) ^c	r _e ^d	H ⁺ ^e	K ⁺ ^f	CH ₃ ⁺ ^g	C _p N _i ⁺ ^h	BMe ₃ ⁱ
H ₂ O	-5.1	-5.1	1.86	-32.0	-0.9	-33.4	-9.9	NA
H ₂ CO	-3.1	NC	NC	-27.7	NA	-22.3	-8.5	NA
HCN	-2.7	NC	NC	-27.8	NA	-3.8	-4.7	NA
C ₆ H ₆	-1.2	NC	NC	-20.9	NA	NA	NA	NA
MeOH	-1.0	-1.2	1.91	-20.1	NA	-19.7	-6.7	NA
Me ₂ O	0.4	-0.4	1.95	-12.2	3.0	NA	-5.4	NA
NH ₃	0.0	0.0	1.90	0.0	0.0	0.0	0.0	0.0
MeNH ₂	2.0	1.9	1.96	9.0	1.2	11.0	2.9	3.9
Me ₃ N	3.0	3.0	2.05	19.8	2.1	NA	4.1	5.5
Me ₂ NH	3.1	3.6	2.00	15.6	1.6	17.6	4.5	3.9
NH ₃ ^j	39.1	39.1		202.0	17.9	99.3	53.0	13.8

^a All values in kcal/mol; NA means data not available; NC means data not calculated. ^b Present work. ^c Calculation discussed in text. ^d Base-Li⁺ distance in angstroms for electrostatic calculations. ^e Reference 3. ^f Reference 5. ^g Calculated from data in ref 3 and 38. The proton affinity of CH₃NC used for calculating the CH₃⁺ affinity of HCN is 205.3 kcal/mol; J. F. Vogt and J. L. Beauchamp, unpublished results. ^h Reference 6. ⁱ Reference 39. ^j Absolute binding energies of NH₃ to the different reference acids. All other data in table are relative to NH₃.

Table VI. Dipole Moments and Polarizabilities of Bases Used in This Study^a

Base	μ ^b	α ^c
NH ₃	1.47	2.16
MeNH ₂	1.27	3.92
Me ₂ NH	1.03	5.68 ^d
Me ₃ N	0.63	7.44 ^d
H ₂ O	1.84	1.45
MeOH	1.70	3.25
Me ₂ O	1.30	5.24
HCN	2.95	2.59
H ₂ CO	2.31	2.81
C ₆ H ₆		6.35

^a Dipole moments in D, polarizabilities are in Å³. ^b Reference 25. ^c Reference 26. ^d Estimated.

ion Lewis acids. While a complete reversal (predicted in ref 15) is not verified, our observation of a partial inversion lends support to the physical arguments presented in ref 15. The methylamines are somewhat unique in that decreasing dipole moments (NH₃ > MeNH₂ > Me₂NH > Me₃N)²⁵ accompany the increasing polarizabilities (NH₃ < MeNH₂ < Me₂NH < Me₃N)²⁶ usually associated with increasing base strength. This is directly reflected in the bonding to Li⁺, which Goddard¹⁷ and others¹⁴ have shown to be primarily electrostatic.

In order to better characterize the origin of the partial inversion, simple electrostatic calculations for Li⁺ binding to NH₃, MeNH₂, Me₂NH, Me₃N, H₂O, MeOH, and Me₂O were carried out. The basic method is described by Spears^{27,28} and includes contributions due to ion-permanent dipole, ion-induced dipole, polarization, dispersion, and repulsive interactions (eq 20 in cgs units).

$$E_{\text{binding}} = -\frac{\mu_D e}{R^2} - \frac{\alpha_B e^2}{2R^4} - \frac{3eh}{4\pi m_e^{1/2} R^6} \\ \times \frac{\alpha_i \alpha_B}{\left(\frac{\alpha_i}{N_i}\right)^{1/2} + \left(\frac{\alpha_B}{N_B}\right)^{1/2}} + \sum A_i e^{-B_i/r_i} \quad (20)$$

μ_D is the dipole moment of the base, α_B is the polarizability of the base, α_i is the polarizability of Li⁺, e is the elementary charge, m_e is the electron rest mass, h is Planck's constant, N_B is the number of polarizable electrons on the base, N_i is the number of polarizable electrons on Li⁺, R is the distance from the heteroatom to Li⁺, r_i is the distance from Li⁺ to an atom or group of the base, and A_i and B_i are constants in the repulsive terms between atom or groups of atoms. The Li⁺ polarizability is taken to be 0.029 Å³.²⁹

Table VII. Repulsive Parameters Used in Electrostatic Calculations

Group	A ^a	B ^b
Nitrogen bases		
NH _n	337 577.8	5.20
CH ₃	42 698.0	3.94
Oxygen bases		
OH _n	16 148.8	3.51
CH ₃	22 727.2	3.47

^a Values are in kcal/mol. ^b Values are in Å⁻¹.

Not having enough data to calculate atom-atom repulsive parameters, the amines are treated as having NH_n groups (n = 1, 2, 3) and CH₃ groups. From D(H₃N-Li⁺) and R(H₃N-Li⁺)¹⁷ the A and B for the NH_n groups are calculated since all the attractive terms in eq 20 are known. (The repulsive constants for NH_n are assumed the same for n = 1, 2, 3.) Similarly, using D[Me₃N-Li⁺] and an assumed R[Me₃N-Li⁺] along with the A and B determined from NH₃ for the NH_n group, the A and B factor for CH₃ groups are calculated. Knowing A and B for NH_n and CH₃ groups then allows D(B-Li⁺) to be calculated for MeNH₂ and Me₂NH using eq 20. The oxygen bases H₂O, MeOH, and Me₂O are treated in an analogous manner. R(H₂O-Li⁺) used is from ref 16 and R[Me₂O] is assumed to be 1.95 Å. Calculated binding energies and equilibrium base-cation distances are presented in Table V, with the dipole moments and polarizability used being summarized in Table VI. A and B factors are in Table VII. An assumed N-Li⁺ bond length of 2.05 Å is used for Me₃NLi⁺; varying this distance from 1.85 Å to 2.05 Å has no effect on the ordering of the calculated Li⁺ affinities. The model calculations reproduce the amine inversion as well as the proper ordering of the oxygen bases (Table V). As can be seen in Figure 4, the polarizability interaction is the dominant attractive term. The irregular ordering is most likely due to large repulsions between Li⁺ and the methyl groups of Me₃N, which forces the base-cation distance at the potential minimum to be lengthened enough to result in surprisingly low permanent and induced dipole attractions (Figure 4). For the oxygen bases the trend is similar but attenuated and hence a regular ordering is observed.

Another difference between nitrogen and oxygen bases is seen in the HCN and H₂CO data. The larger dipole moment and polarizability of H₂CO compared to H₂O appears to be reflected in the higher Li⁺ binding energy of the former (Table V). It is particularly surprising to observe that for NH₃ and HCN the Li⁺ binding energy is larger for the former (Table V)! Ab initio calculations on H₂CO³¹ have shown that the

Table VIII. Comparison between Ab Initio Calculation of Li⁺ Affinities and Present Work^a

Base	MBS ^b HF ^b	DZ ^b HF ^b	DZd ^b		Exptl ^c
			HF ^b	Correlated	
H ₂ O		47.9 ^d	37.3 ^e	37.6 ^e	36.0 ± 2 ^f
			35.3 ^g		
			34.4 ^g		
			35.2 ^g		
			36.1 ^h		
			37.0 ⁱ		
H ₂ CO		47.3 ^d	43.5 ^j	34.9 ^h	38.0 ± 2 ^k
			44.0 ^j		
NH ₃	75.5 ^e	45.1 ^e	40.2 ^e	40.4 ^e	41.1 ± 2 ^k
	50.0 ^l	50.7 ^d	40.3 ^m	40.4 ^e	
	54.7 ⁿ	49.4 ^d		40.8 ^e	
MeNH ₂	52.7 ⁿ	50.2 ^d			43.1 ± 2 ^k
Me ₂ NH	51.0 ⁿ	50.0 ^d			44.4 ± 2 ^k
Me ₃ N	48.1 ⁿ	49.2 ^d			44.1 ± 2 ^k

^a Values in kcal/mol. ^b MBS means minimum basis set calculation. DZ means double ζ basis calculation. DZd means double ζ basis with d polarization functions. HF means Hartree-Fock. More extended bases are included under DZ. ^c A zero point correction of 2 kcal/mol (ref 16) has been added to the experimental D_0 values to obtain D_e . ^d Reference 40. The 50.7 kcal/mol NH₃Li⁺ affinity utilizes the experimental NH₃ geometry. The 49.4 kcal/mol value assumes tetrahedral H-N-H angles. The latter value should be used in comparison with values for the methylamines from this reference since tetrahedral angles were assumed for the methylamines. ^e Reference 17. ^f Reference 2. ^g Reference 14. ^h Reference 16. ⁱ Reference 41. ^j Reference 32. ^k Calculated from present work and $D(\text{H}_2\text{O}-\text{Li}^+)$ from ref 2. ^l Reference 42. ^m Reference 18. ⁿ Reference 15.

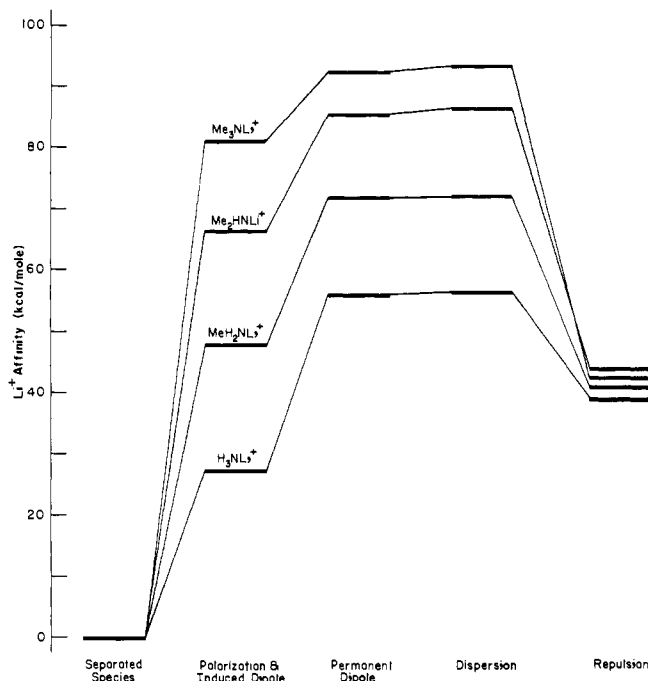


Figure 4. Components of Li⁺ electrostatic binding energies to methylamines. Successive steps represent inclusion of additional components of the binding energy. The polarization and induced dipole terms have an r^{-4} dependence, the permanent dipole term has an r^{-2} dependence, the dispersion term has an r^{-6} dependence, and the repulsive terms have the form Ae^{-Br} . Of particular interest is the inversion of ordering caused by addition of repulsive terms.

oxygen π lone pair experiences a repulsion due to the in-plane C-H bonds. The presence of Li⁺ tends to stabilize the π lone pair orbital of H₂CO leading to a stronger bond than in H₂OLi⁺, even though the oxygen σ lone pair is more s-like in H₂CO than in H₂O. Calculations³² comparing Li⁺ binding to H₂O and H₂CO do in fact show significantly more electron delocalization onto Li⁺ from H₂CO than H₂O. The increased covalent character of the bond in H₂COLi⁺ in addition to the stronger electrostatic interaction leads to a stronger O-Li⁺ bond than in H₂OLi⁺.

Since the Li⁺ affinity of HCN is not what would be expected on the basis of electrostatic arguments, other factors must be involved. These most likely are related to the more s-like character of the HCN lone pair orbital compared to the lone pair orbital of NH₃.

For C₆H₆Li⁺ ab initio calculations indicate that Li⁺ binds along the C₆ axis of benzene to maximize attractive interactions with the π system.³³

Relative Lewis Acid Affinities. Table V compares and contrasts Li⁺ as a reference acid to several other reference acids. It is seen in Table V that Li⁺ offers an immediate contrast to H⁺ in both the magnitude and relative ordering of basicity. Since H⁺ does not have any core electrons the large repulsions associated with the Li⁺ core are not present in protonated complexes. The more intimate interaction which results is much stronger than for Li⁺ because of the largely covalent nature of the base-H⁺ bond. A regular methyl substituent effect is then observed in addition to much larger bond strengths.

The reduced magnitude of binding energy of K⁺ to the methylamines when compared to Li⁺ binding (Table V) evidences effects of a larger electronic core. Since K⁺ binding should closely resemble Li⁺ binding it is interesting to observe a normal methyl substituent effect. K⁺ transfer experiments (analogous to process 4) would be useful to more accurately determine relative K⁺ affinities. As noted in footnote 30 of ref 5, the K⁺ results are within experimental error (2 kcal/mol) and hence it is possible that the K⁺ relative binding energies follow the Li⁺ relative binding energies.

A Lewis acid which demonstrates bonding characteristics intermediate between Li⁺ and H⁺ is CH₃⁺ (Table V). The p-type bonding orbital of CH₃⁺ allows a larger covalent interaction than Li⁺ but not as large as H⁺. CH₃⁺ also has core electrons which have a repulsive effect analogous to Li⁺, lowering the bond strength compared to H⁺. Methyl substituent effects (Table V) involving H⁺ and CH₃⁺ are comparable, however.

The cyclopentadienyl nickel cation (CpNi⁺) affords a further comparison to Li⁺ (Table V). The parallel ordering of basicities of methylamines to CpNi⁺ and Li⁺ is not fully understood at this time; recent theoretical work by Hoffmann³⁴ and Goddard³⁵ may help to elucidate the nature of CpNi⁺ binding. CpNi⁺ serves to illustrate further that acid-base in-

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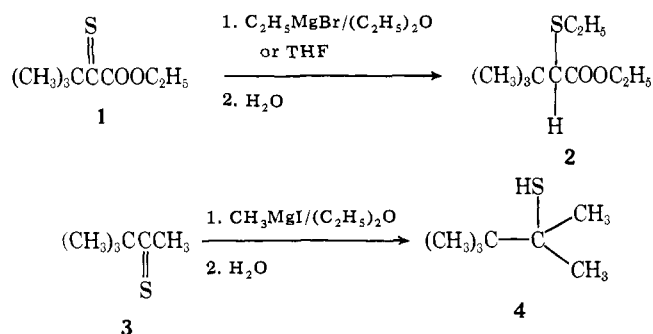
Synthesis of Fulvenes by Reaction of Thiobenzophenones with Cyclopentadienylmetal Carbonyl Anions under Anhydrous or Phase Transfer Catalyzed Conditions

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Abstract: Thiobenzophenones react with the cyclopentadienyliron dicarbonyl anion and the cyclopentadienylmolybdenum or -tungsten tricarbonyl anion at room temperature to give fulvenes as the major product. Disulfides were also formed in some instances, along with the cyclopentadienylmetal carbonyl dimer. These reactions were effected under anhydrous (NaK or Na/Hg in tetrahydrofuran) or phase transfer catalyzed conditions [50% aqueous NaOH/C₆H₆/C₁₆H₃₃N(CH₃)₃⁺Br⁻ or 18-crown-6 as the catalyst], the highest yields being realized by the latter method. The reactivity of the anions toward the thioketones is C₅H₅Fe(CO)₂⁻ >> C₅H₅Mo(CO)₃⁻ ≈ C₅H₅W(CO)₃³⁻. Reaction of a given thiobenzophenone with the methylcyclopentadienyliron or -molybdenum carbonyl anions gave the same ratio of isomeric fulvenes. An electron transfer mechanism is proposed for this novel desulfurization and coupling reaction.

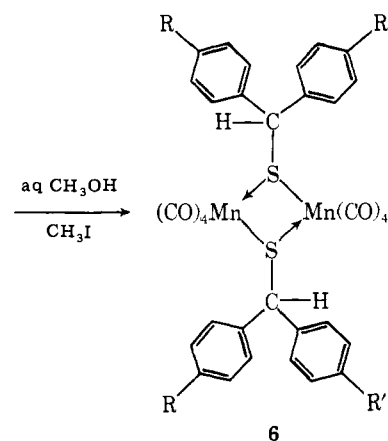
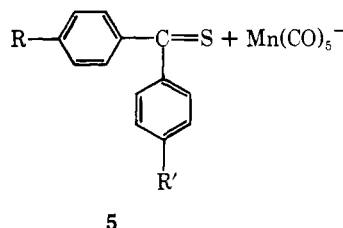
The reactions of thioketones with nucleophiles is a subject of considerable current interest.¹ Both thiophilic and carbo-philic additions have been reported in the literature. For example, ethylmagnesium bromide undergoes thiophilic addition to the α-thioketo ester, **1**, to give **2**,² while the thione **3** reacts with methylmagnesium iodide in ether to form the mercaptan, **4**.^{1b} Reaction solvents and the nature of the groups attached



to the thiocarbonyl carbon have an important influence in some, but not in all, of these reactions.

A systematic investigation of the reactions of thioketones with metal carbonyl anions was recently undertaken in our laboratories. Manganese pentacarbonyl anion undergoes formal thiophilic addition to thiobenzophenones (**5**) to give complexes of structural type **6**.³ A question arises as to what effect metal carbonyl nucleophilicity has on the reaction course.

This paper describes the interesting reaction of thiobenzophenones (**5**) with the cyclopentadienylmetal carbonyl anions, C₅H₅M(CO)_n⁻ [(a) M = Fe; n = 2; (b) M = Mo, W; n = 3], and with several methylcyclopentadienylmetal carbonyl anion derivatives.⁴ Previous studies have indicated the following order of nucleophilicity of the cyclopentadienylmetal carbonyl an-



ions: C₅H₅Fe(CO)₂⁻ >> C₅H₅W(CO)₃⁻ > C₅H₅Mo(CO)₃⁻.^{5,6} The base strength of the cyclopentadienylmolybdenum tricarbonyl anion is approximately the same as that of the manganese pentacarbonyl anion.

Results and Discussion

Reaction of a thiobenzophenone (**5**, R = R¹ = H, CH₃, OCH₃; R = OCH₃, R¹ = H) with the cyclopentadienyliron dicarbonyl anion (**7**, M = Fe, n = 2) in dry tetrahydrofuran (THF), at room temperature, affords fulvenes (**8**) via a novel desulfurization and coupling reaction. By-products of some