Gas-Phase Lithium Cation Basicities of Acetophenones: A Linear Relationship between Lithium Cation and Proton Basicities

Hideaki Maeda,[1] **Maki Irie,**[2] **Soe Than,**[1] **Kiyoshi Kikukawa,**[2] **and Masaaki Mishima***[1,3]

[1]Department of Chemistry and Physics of Condensed Matter, Graduate School of Sciences, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581

[2]Department of Biological and Environmental Chemistry, Kinki University, Iizuka 820-0055

[3]Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581

Received July 13, 2006; E-mail: mishima@ms.ifoc.kyushu-u.ac.jp

The free energy changes (ΔG) for the reaction $B_2Li^+ = Li^+ + 2B$ were obtained in the gas phase for *m*- and *p*-substituted acetophenones based on the measurement of ligand-exchange equilibria of the type $LiA_2{}^+ + 2B = LiB_2{}^+ + 2A$ using a FT-ICR spectrometer. A plot of ΔG (relative lithium cation basicity, $\Delta LCB[B_2Li^+]$) values against the ΔGB (proton basicity) showed a limited linear correlation for *meta* substituents and *para* electron-withdrawing groups with a slope of 1.06. Negative deviations observed for strong π-donor susbstituents suggested that the resonance effect of these substituents is reduced in the Li^+ complex compared to that in the protonated ion. Based on the correlation analysis using the Yukawa–Tsuno equation, $\Delta LCB = \rho(\sigma^o + r^+\Delta\bar{\sigma}_R^+)$, the substituent effect on $\Delta LCB[B_2Li^+]$ of acetophenone was characterized by a ρ value of -12.5 and an r^+ value of 0.49. A ρ value of -8.3 was determined for $\Delta LCB[BLi^+]$ based on the reaction $LiB^+ = Li^+ + B$ from a ρ value for $\Delta LCB[B_2Li^+]$ by using a factor of 1.5 that was obtained from a linear relationship between calculated $\Delta LCB[B_2Li^+]$ and $\Delta LCB[BLi^+]$. In comparison with the corresponding results for other Lewis cation basicities, it was shown that the ρ value decreases in the order of H^+ (-11.6) > Me_3Si^+ (-11.0) > Me_3Ge^+ (-9.7) > Li^+ (-8.3). The decrease in the ρ value indicates that the positive charges at the Lewis cation moiety of the adduct ion increases in this order. The small ρ value for the Li^+ basicity is consistent with largely ionic (ion–dipole interaction) nature of the bonding interaction between Li^+ and the carbonyl oxygen atom. The r^+ value that indicates the degree of charge-delocalization into the aromatic π-system also decreases in the same order. In spite of a small charge transfer from Li^+ to acetophenone ligand, the moderate r^+ value of 0.49 observed for the Li^+ complex is interpreted to be due to the redistribution of the induced positive charge in the acetophenone moiety by binding with Li^+.

Quantitative determination of the affinity and/or basicity of alkali metal cation binding small model ligands in the gas phase that are free from interference from solvent molecules and counter ions, provides fundamental information necessary for better understanding of the intrinsic interactions between organic compounds and alkali metal cations. Among the alkali metal cations, lithium ion has been studied most extensively. In particular, the structural aspects of the Li^+/base interaction were investigated in detail from both the experimental and theoretical points of view.[1–5] Quantitative structure–property relationships (QSPR) were also studied from a practical point of view to predict lithium cation basicity.[6,7]

Gas-phase lithium cation basicity (LCB) is defined as the Gibbs free energy associated with the thermodynamic equilibrium (Eq. 1),

$$B\text{–}Li^+ = B + Li^+, \tag{1}$$

where $\Delta G_1 = -RT\ln K_1$ and $LCB = \Delta G_1$. In a similar manner the gas-phase lithium cation affinity (LCA) is defined as the enthalpy change of the reaction (Eq. 1), $LCA = \Delta H_1$. Such thermodynamic quantities have been determined for a variety of organic compounds by using different experimental techniques, such as equilibrium constant determination by pulsed high-pressure mass spectrometry[8–10] and ion cyclotron resonance spectrometry,[11] unimolecular dissociation,[12] energy-resolved collision-induced dissociation,[13] photodissociation, and radiative association.[14] Pioneering studies involving a comparison between experimental LCBs and the corresponding gas-phase basicities (GB) toward protons were reported by Taft and co-workers.[1] GB is defined as the Gibbs free energy ΔG_2, which refers to the thermodynamic equilibrium (Eq. 2),

$$B\text{–}H^+ = B + H^+, \tag{2}$$

where $\Delta G_2 = -RT\ln K_2$ and $GB = \Delta G_2$. More extensive comparisons have recently been carried out by Burk et al.[2] based on a revised, re-anchored, and widened LCB scale containing 205 compounds. These comparisons showed that, although there is no precise general correlation between LCBs and GBs, the correlations for the families with the same basicity center are fairly precise. For example, oxygen, nitrogen, and sulfur bases exhibit linear correlations with slopes of 0.37, 0.32, and 0.34, respectively. Other correlations were observed for subfamilies, in which the basicity center has the same functional group, such as ethers, alcohols, and carbonyl compounds. Such a family-dependent linear relationship between LCB and GB with a smaller slope than unity arises from the widely different bonding types in H^+ and Li^+ complexes. That is, the bond formed by Li^+ and other alkali metal cations is largely ionic, and the alkali metal ions retains 0.8–0.9 units

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of the positive charge in the complex, while the protonation of the base gives a polar covalent σ bond with an extensive charge transfer.[15,16] In addition, significant deviations (showing enhanced stabilities of the Li-complexes) from a linear relationship between LCB and GB were observed for compounds having polyfunctional groups. These deviations are mostly attributed to formation of cyclic structures in the Li^+ adducts,[2,17] indicating that Li^+ can form more than one bond compared to a proton. Thus, the two Lewis acids H^+ and Li^+ present a significant contrast in the nature of the bond formed with the ligand.

In order to understand further the nature of the bond formed by Li^+, it is necessary to separate quantitatively the overall binding energy into respective interaction terms. First of all, it is important to elucidate the electronic effect of ligands having a single binding site under constant geometrical environment at that site. For this purpose, one particularly interesting subset of ligands is aromatic compounds with a single basic site where the electronic properties can be varied by changing remote ring-substituents. Recently, we applied this approach to the study of the binding interaction of Lewis cations, such as Me_3Si^+ and Me_3Ge^+, with neutral organic molecules.[18,19] The same approach will be applied to the interaction between Li^+ and organic ligands. In this study, we therefore determined the lithium cation basicity for *m*- and *p*-substituted acetophenones where thermodynamic data, such as gas-phase basicities and Lewis cation basicities, are available for comparison.[18–20]

Results

Measurements of Gas-Phase Lithium Cation Basicity. LCBs were determined by measuring the equilibrium constants of the reversible ligand-transfer reactions on a Fouier transform ion cyclotron resonance (ICR) mass spectrometer.

$$A + Li^+ = ALi^+, \tag{3}$$

$$B + Li^+ = BLi^+, \tag{4}$$

$$ALi^+ + B = BLi^+ + A. \tag{5}$$

When two acetophenone derivatives A and B are present in the ICR cell, initial reactions forming ALi^+ (Eq. 3) and BLi^+ (Eq. 4) can be followed by ligand-exchange reactions (Eq. 5). From the equilibrium constant (K_5) the relative LCB is obtained. However, initial products ALi^+ and BLi^+ decreased gradually after several hundred milliseconds, and then the dimeric adducts ALi^+A, ALi^+B, and BLi^+B formed. This is in contrast to the reaction of Li^+ with the relatively low basic compounds, such as methanol and benzene, that did not give dimer complexes under the conditions used for the present work. The reactions forming the dimer complexes stopped without further addition of ligands. These reactions were also followed by ligand-exchange reaction (Eqs. 6 and 7).

$$ALi^+A + B = ALi^+B + A, \tag{6}$$

$$ALi^+B + B = BLi^+B + A, \tag{7}$$

$$ALi^+A + 2B = BLi^+B + 2A. \tag{8}$$

When the neutral compounds were present in the ICR cell at low pressures, e.g., 0.8 to 1.5×10^{-7} Torr (1 Torr = 133.322 Pa), the relative abundances of two adduct ions (ALi^+ and BLi^+) appeared to be constant after several hundred milliseconds. Thus, K_5 for the ligand-exchange reaction (Eq. 5) could be calculated. However, the accuracy of such data must be low due to the formation of dimeric adduct ions. Therefore, we determined the free energy change for the formation of dimer complexes instead of monomer complexes.

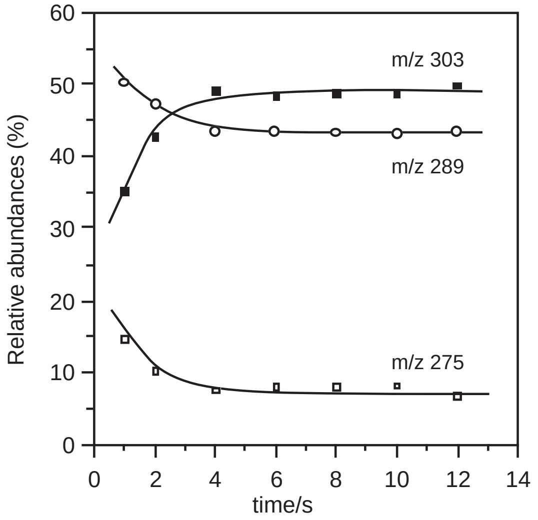


Fig. 1. Time profile of lithium adducts formed from a binary mixture of *m*-methylacetophenone and 3,5-dimethylacetophenone. Partial pressures, *m*-Me: 1.60×10^{-7} Torr, 3′,5′-Me_2: 1.70×10^{-7} Torr. Open squares; $[m\text{-Me}]_2Li^+$, closed squares; $[3',5'\text{-Me}_2]_2Li^+$, open circles; $[m\text{-Me}]Li^+[3',5'\text{-Me}_2]$. $K_6 = 1.54$ and $K_7 = 7.18$ give $\Delta G_8 = 1.73\,\text{kcal mol}^{-1}$ (1 cal = 4.184 J).

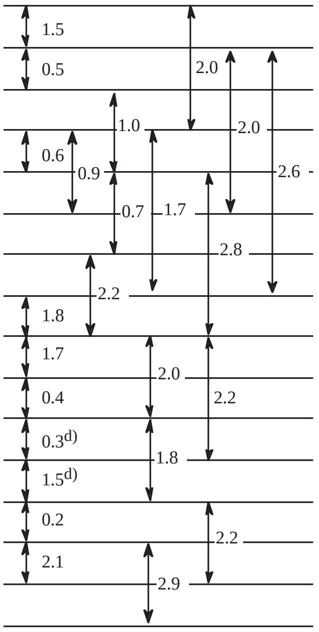
Figure 1 shows a typical time profile for dimeric adduct ions of acetophenones with Li^+. On the basis of ligand-exchange equilibria measurements, the free energy changes (ΔG_8) for reaction (Eq. 8) were obtained.

$$\Delta G_8 = \Delta G_6 + \Delta G_7. \tag{9}$$

From these results, a ladder of $LCB[B_2Li^+]$ was constructed as shown in Table 1. Generally, such relative scales can be converted to absolute values for LCB by calibrating to the known value for one given ligand, when such a value is available in the literature due to determinations by some other method. Unfortunately, since such an absolute value was not available for the present range of dimeric complexes, the value calculated at the DFT-B3LYP/6-311+G** level of theory for an unsubstituted derivative was used as an anchor to convert absolute values. However, the calculated LCBs at this level tend to overestimate the LCBs of monomeric complexes by several kilocalories, e.g., the calculated LCB of benzaldehyde is 42.7 kcal mol^{-1}, while the experimental value is $37.0\,\text{kcal mol}^{-1}$.[2] This is not serious problem for the present study because we need only the relative values for the discussion. The ΔG values measured for respective ligand-transfer equilibria (Eq. 8) and $\Delta LCB[B_2Li^+]$ relative to the unsubstituted derivative are summarized in Table 1 along with the corresponding ΔGB determined previously in our laboratory.[20]

Computations of Relative Gas-Phase Lithium Cation Basicity. The geometries of the neutral acetophenones and those of their complexes with Li^+ have been optimized at the B3LYP/6-311G and B3LYP/6-311+G** levels of theory.

Table 1. Measured ΔG for Ligand-Exchange Equilibira ($A_2Li^+ + 2B = B_2Li^+ + 2A$), ΔLCB-[B_2Li^+], and the Corresponding ΔGB[a)]

Acetophenones	Measured ΔG	LCB	ΔLCB[B_2Li^+]	ΔGB[b)]
p-MeO		78.0	5.8	8.1
3′,4′-Me_2		76.6	4.4	5.1
p-SMe		76.1	3.9	6.5
3′,5′-Me_2		65.7	3.5	3.9
p-Me		75.1	2.9	4.0
3′-Cl-4′-MeO		74.6	2.4	5.4
m-MeO		74.4	2.2	2.7
m-Me		74.0	1.8	1.7
H		72.2[c)]	0.0	0.0
p-F		70.5	−1.7	−0.6
p-Cl		70.2	−2.0	−0.6
p-COMe		69.9	−2.3	−1.7
m-F		68.4	−3.8	−3.7
m-Cl		68.2	−4.0	−3.3
m-CF_3		66.2	−6.0	−5.3
p-CF_3		65.3	−6.9	−5.8

a) All values in kcal mol^{-1} (1 cal = 4.184 J). b) Ref. 20. c) Calculated value at B3LYP/6-311+G**, used as an anchor to convert relative values to absolute scales. d) Statistical correction was applied.

The harmonic vibrational frequencies were also evaluated at the same level of theory to ensure that each optimized structure was a true minimum on the potential energy surface and to calculate thermochemical quantities.

The optimized geometric structures of the BLi^+ and B_2Li^+ complexes are shown in Fig. 2 along with values for selected bond distances. The two phenyl planes in the B_2Li^+ complexes are orthogonal with a small deviation from a perpendicular conformation. Although the deviations of the *m*-CF_3 and *p*-CF_3 complexes are somewhat larger than others (Table S2), the magnitude of these deviations is not related to the calculated binding energies and the LiO8 distances, suggesting that the potential surface is nearly flat. The LiO8 distance in the monomeric complex is slightly shorter, 1.726 Å, than that for the dimeric complex, 1.785 Å, and the C7O8 distance in the former is longer (1.251 Å) than the latter (1.242 Å), which is similar to the results for $Li(OMe_2)_n$ system.[21] The C1C7 bond in the monomeric complex is also slightly shorter than in the dimeric complex. These differences in bond distance between monomeric and dimeric complexes are consistent with the fact that the binding energy with the first ligand is stronger than with the second one.[22]

The calculated ΔLCBs and ΔLCAs at 298 K for B_2Li^+ and BLi^+ are summarized in Table 2 along with the corresponding ΔGB values calculated at the same level of theory. Selected bond distances and the group natural charges of the complexes derived using the natural population analysis (NPA) scheme are summarized in Table 3. Detailed results of the calculated species are available in Tables S1 and S2 in Supporting Information.

Discussion

The ΔLCB[B_2Li^+] values of acetophenones are plotted against the ΔGB values in Fig. 3. When the correlation is limited to *meta* substituents and *para* electron-withdrawing groups, there is an excellent linear correlation with a slope of 1.06 ($R^2 = 0.998$).

Since the ΔLCB[B_2Li^+] values indicate the effect of two acetophenone molecules on the stability of the Li^+ complexes, the slope of a linear relationship between ΔLCB for the monomeric complex (BLi^+) and ΔGB may be assumed to be 0.53 (=1.06/2) as the first approximation. This will be discussed later in more detail. The assumed slope of 0.50 indicates that the substituent effect is significantly reduced in the Li^+ complex compared to that in the protonated system. This is also qualitatively consistent with the values observed for many families of organic compounds; however, the slope of 0.5 is somewhat larger than the reported values.[2]

More importantly, Fig. 3 shows that strong π-donor substituents in the *para* position have smaller stabilization effects in the Li^+ complex compared to the expected values from the line obtained for *meta* substituents and *para* electron-withdrawing groups. Closer examination of these deviations implies that the stronger π-donor substituent has a larger negative deviation and vice versa. Such behavior of π-donor substituents has been observed whenever there is difference in the contribution of the resonance effect of π-donor substituent between two systems of interest.[20] Accordingly, these negative deviations suggest that the resonance effect of π-donor substituent is also reduced in the Li^+ complex compared to that

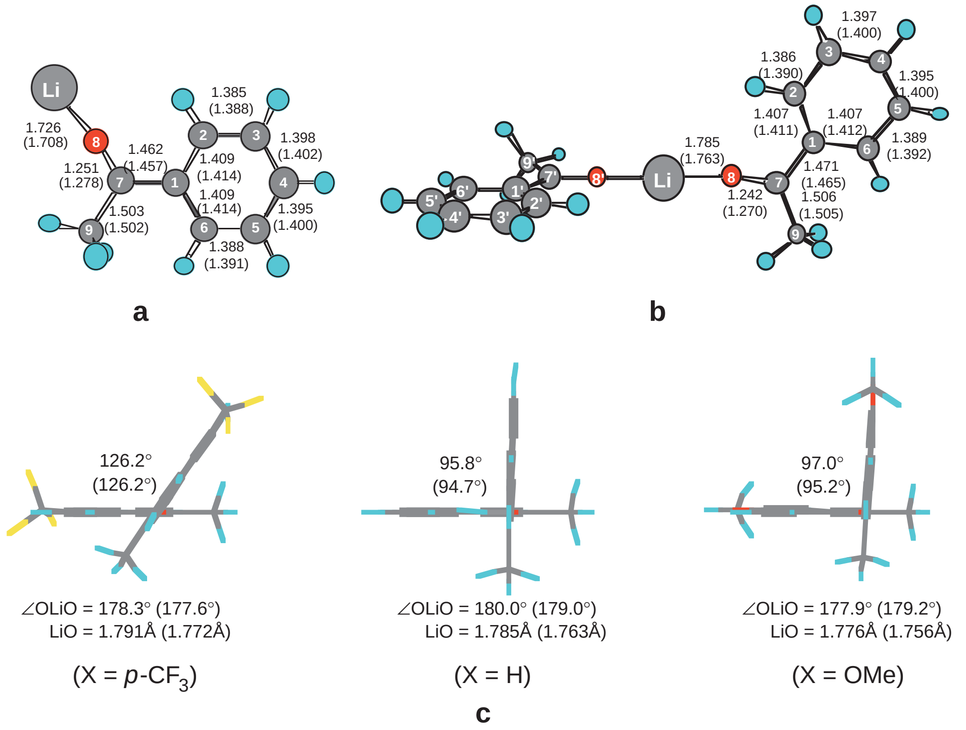


Fig. 2. The optimized geometries of (a) $(C_6H_5COCH_3)Li^+$, (b) $(C_6H_5COCH_3)_2Li^+$, and (c) the side view of the dimeric complexes of substituted acetophenones. Values given in (a) and (b) are bond distances in Å, and values in c are dihedral angles (C2C1C1′C2′) and angles (O8LiO8′) in degree and bond distance (LiO8) in Å. Values in parentheses are optimized at B3LYP/6-311G.

Table 2. Relative Thermochemical Quantities[a)] (ΔLCB, ΔLCA, and ΔGB) of Subsitituted Acetophenones Calculated at the B3LYP/6-311+G** Level of Theory

Subst. in	B_2Li^+ [b)]		BLi^+ [c)]		BH^+ [d)]	
acetophenones	ΔLCB	ΔLCA	ΔLCB	ΔLCA	ΔGB	ΔPA
p-NMe_2	14.6	14.6	10.5	10.2	19.7	19.3
p-MeO	6.1	6.4	4.1	4.2	9.1	9.0
p-MeS	5.2	5.3	3.3	3.7	8.5	8.9
3′-Cl-4′-MeO	1.8	1.7	1.6	1.6	5.3	5.3
p-Me	2.8	3.1	2.1	2.2	3.7	4.2
m-Me	2.0	1.9	0.7	1.3	1.4	2.3
H	0.0	0.0	0.0	0.0	0.0	0.0
	(72.2)[e)]	(88.0)[e)]	(44.2)[e)]	(51.3)[e)]	(200.5)[e),f)]	(207.7)[e),g)]
p-F	−2.9	−3.1	−1.7	−1.8	−1.6	−1.8
p-Cl	−3.0	−3.2	−1.7	−1.8	−1.2	−1.4
m-F	−4.6	−5.0	−3.2	−3.1	−4.4	−4.6
m-Cl	−4.1	−5.0	−3.1	−3.0	−3.6	−4.2
m-CF_3	−8.2	−8.6	−5.0	−5.1	−7.0	−7.2
p-CF_3	−9.3	−8.9	−5.0	−5.4	−7.7	−7.8

a) All values in kcal mol^{-1}. b) For $2A + B_2Li^+ = 2B + A_2Li^+$, where A and B are unsubstituted acetophenone and substituted one, respectively. c) For $A + BLi^+ = B + ALi^+$. d) For $A + BH^+ = B + AH^+$. e) Values in parentheses are the calculated absolute values. f) Experimental value; 198.2 kcal mol^{-1}, Ref. 23. g) Experimental value; 205.8 kcal mol^{-1}, Ref. 23.

in the protonated ion. This is not unexpected because charge transfer from lithium cation to acetophenone should be small.[15,16]

It is interesting to examine whether theoretical calculations reproduce the unique behavior of π-donor substituents on the stability of the Li^+ complex in addition to elucidation of their geometrical features. There are many calculations at different levels to study the structure and thermodynamic properties of the interaction between the Li^+ and neutral molecules.[16c,22,24–31] Very high level calculations, such as G2(MP2), G2, and CBS-Q methods, are required to reproduce quantitatively the experimentally measured LCB values within so-called chemical accuracy (2 kcal mol^{-1}) in absolute scale. However, for the present discussion on the substituent effects,

Table 3. Selected Bond Distances (Å) and Group Natural Charges of Lewis Acid–Acetophenone Complexes at B3LYP/6-311+G**

Lewis acids	M^+C7	C1C7	C7O8	$\Sigma q(Ph)$[a]	$\Sigma q(M^+)$[b]
H^+	0.970	1.422	1.303	0.327	0.518
Me_3Si^+	1.809	1.444	1.274	0.243	0.737
Me_3Ge^+	1.988	1.453	1.264	0.202	0.751
Li^+ [c]	1.726	1.462	1.251	0.155	0.984
Li^+ [d]	1.788	1.471	1.242	0.119	0.956
None	—	1.502	1.217	−0.002	—

a) Summed natural charge of the phenyl moiety. b) Summed natural charge of the Lewis acid moiety. c) Monomeric complex, $(C_6H_5COCH_3)Li^+$. d) Dimeric complex, $(C_6H_5COCH_3)_2Li^+$.

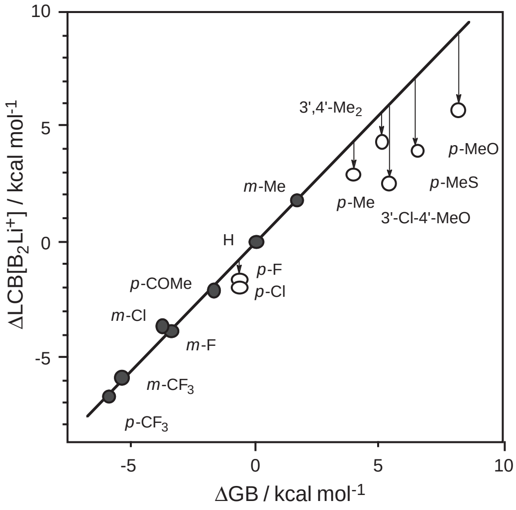


Fig. 3. Correlation between experimental $\Delta LCB[B_2Li^+]$ and ΔGB for acetophenones.

the absolute values are not needed, and the relative values are enough. In addition to this, Burk et al.[2] reported that the DFT B3LYP/6-311+G** level of theory can be used for quantitative prediction of LCB, although there is systematic error somewhat larger than that based on the G2 calculations. Therefore, we used the B3LYP/6-311+G** level of theory for the calculations of B_2Li^+ and BLi^+.

Figure 4 shows a plot of calculated $\Delta LCB[B_2Li^+]$ against experimental values. There is a satisfactory correlation with small systematic error, i.e., the slope of the correlation line is 1.21 instead of 1 for the ideal fit of experimental and calculated data; $\Delta LCB[B_2Li^+]_{calc} = 1.21(\Delta LCB[B_2Li^+]_{exp}) - 0.4$ ($R = 0.992$). This systematic error is similar to the value (1.24) obtained for the monomeric adducts BLi^+ from a large variety of organic compounds (57 compounds).[2]

These results allow us a direct comparison of the calculated ΔLCBs between B_2Li^+ and BLi^+ without any corrections. Indeed, there is an excellent linear relationship between $\Delta LCB[B_2Li^+]_{calc}$ and $\Delta LCB[BLi^+]_{calc}$; $\Delta LCB[B_2Li^+]_{calc} = 1.50(\Delta LCA[BLi^+]_{calc}) - 0.3$ ($R = 0.993$). Naturally, a similar linear relationship was found for the calculated ΔLCA; $\Delta LCA[B_2Li^+]_{calc} = 1.52(\Delta LCA[BLi^+]_{calc}) - 0.4$ ($R = 0.999$). The magnitude of the slope (1.5) for both correlations indicates that the each ligand in the dimeric complex has a smaller effect than that in the monomer complex. That is, a simple additive rule does not hold for the dimeric complex. This seems to be consistent with the fact that the binding energy of the second ligand with Li^+ is smaller than the first one.[22,32] Indeed, a similar attenuation factor is obtained for experimental LCBs of several substituted benzenes;[33] $\Delta LCB[B_2Li^+]_{exp} = 1.52(\Delta LCB[BLi^+]_{exp}) - 0.4$ ($R = 0.999$), although these adducts are considered to be π-bonded complexes.[32,33] In addition, the linearity of the correlation reveals that the effects of all the substituents are consistently reduced in the dimeric adduct ion system. Accordingly, it is possible to apply a factor of 1.5 to experimental data for the estimation of ΔLCB of the monomeric complexes, giving a slope of 0.70 for the linear relationship between $\Delta LCB[BLi^+]$ and ΔGB. This value is significantly larger than 0.39 reported for the carbonyl compounds, which contain much wider variation in structure.[2] When the carbonyl compounds are further divided into subfamilies, more precise correlations are obtained with different slopes, 0.187 ($R = 0.988$), 0.343 ($R = 0.981$), and 0.410 ($R = 0.990$) for ketones, esters, and aldehydes, respectively. Thus, the slope of the linear relationship between LCB and GB significantly depends on the structure of the subfamily, suggesting that the factors governing the slope are not so simple even within a family that has a similar binding site, and therefore, the magnitude of the slope must be interpreted with caution. In this sense, our present approach will provide a new insight into the meaning of the slope between the LCBs and GBs because the substituent on the acetophenones causes only a change in the electronic properties of the carbonyl group that binds with Li^+ and proton without any changes in geometrical structure at the binding site.

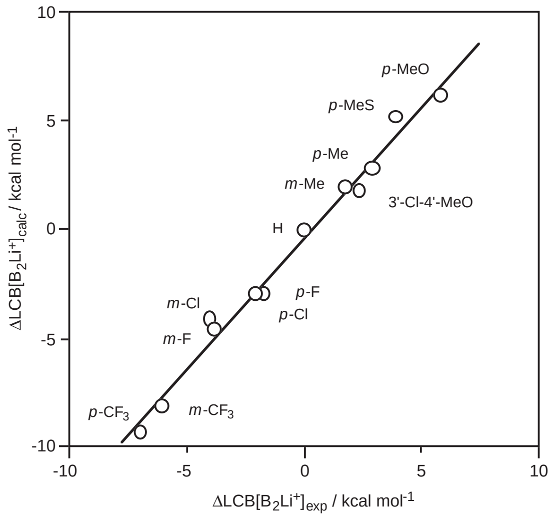


Fig. 4. Correlation between experimental and calculated $\Delta LCB[B_2Li^+]$.

Since the theoretical calculations of ΔGBs at the present level of theory also reproduce the experimental values with a small systematic error, i.e., $\Delta GB_{calc} = 1.15(\Delta GB_{exp}) - 0.4$ ($R = 0.996$), it is possible to compare $\Delta LCB[B_2Li^+]_{calc}$ with ΔGB_{calc}. Figure 5 shows a plot of the calculated $\Delta LCB[B_2Li^+]$ values against the corresponding ΔGB_{calc} covering a wide variation of substituents.

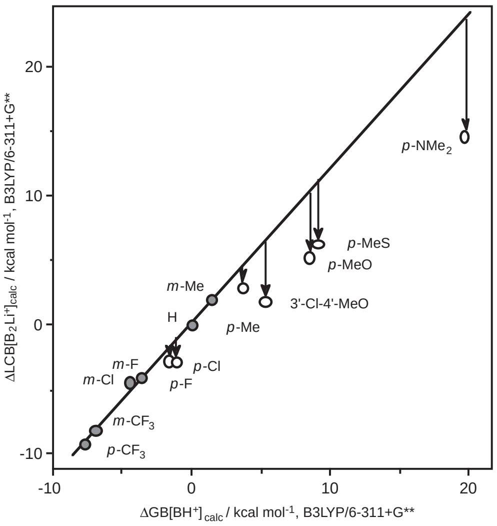


Fig. 5. Correlation between $\Delta LCB[B_2Li^+]_{calc}$ and ΔGB_{calc}.

It was found that non-conjugating substituents give a linear relationship with a slope of 1.20 and *para* strong π-donor substituents clearly show negative deviations from this line depending on the π-donating ability. This trend is in complete agreement with the experimental observation seen in Fig. 3. These negative deviations for strong π-donors is attributed to a reduced resonance effect in the Li^+ complex.

To describe quantitatively the contribution of the resonance effect involved in the stability of the Li^+ complex, a correlation analysis using the Yukawa–Tsuno (Y–T) equation (Eq. 10)[34] is useful.

$$\Delta G = \rho(\sigma^o + r^+ \Delta\bar{\sigma}_R^+), \tag{10}$$

where σ^o and $\Delta\bar{\sigma}_R^+$ are the normal substituent constant and the resonance substituent constant, respectively, and r^+ is the resonance demand parameter representing the degree of the π-delocalization of the positive charge into the aryl π-system. Application of the Y–T equation to $\Delta LCB[B_2Li^+]$ gives a ρ value of -12.5 and an r^+ value of 0.49 with satisfactory precision (R = 0.995, SD = ±0.4) as shown in Fig. 6. The results of the Y–T analysis for Li^+, H^+, Me_3Si^+, and Me_3Ge^+ basicities of acetophenones are summarized in Table 4.

The ρ of -8.3 can be assumed for the $\Delta LCB[BLi^+]$ from a ρ of -12.4 for $\Delta LCB[B_2Li^+]$ by using an attenuation factor of 1.5 as discussed above. The ρ value decreases in the order of $H^+ > Me_3Si^+ > Me_3Ge^+ > Li^+$. Since the ρ value is generally considered a measure of the magnitude of the charge developed at the benzylic carbon and/or of distance between the substituent and the reaction (charge) center, a decreasing ρ value indicates that the charge at the benzylic carbon decreases along this series, i.e., more positive charge is localized at the Lewis acid moiety of the adduct ions compared with that for protonation. The small ρ value for the Li^+ complex results from the highly ionic nature of the bond formed with Li^+. Similarly, the r^+ value decreases in the same order. Since the r^+ value represents the degree of charge-delocalization into the aromatic π-system, the moderate r^+ value of 0.49 for the ΔLCB shows the existence of the π-delocalization of the positive charge into the aryl group, although charge transfer from lithium cation to acetophenone is much smaller than that in the protonated acetophenone. The group natural charges derived from natural population analysis summarized in Table 3 show that the summed charge of the phenyl moiety in the Li^+ complex is only 0.119 and 0.155 unit for monomeric and dimeric complexes, respectively, while that of the protonated ion is 0.327 unit. Supporting the change in the charge, the C1C7 bond distance shortens by 0.040 Å in the monomeric complex and 0.031 Å in the dimeric complex on formation of the Li^+ complex and by 0.080 Å on protonation (numbering of atoms is given in Fig. 2). On the other hand, the C7O8 bond lengthens by 0.034 Å in the monomeric complex and 0.025 Å in the dimeric complex on formation of the Li^+ complex and by 0.086 Å on protonation. Including the other Lewis acid adducts and neutral acetophenone, there is a good linear relationship between the natural charge of the phenyl moiety and the C1C7 bond distance as shown in Fig. 7. A similar relationship is also observed between the C7O8 bond distance and the natural charge of the phenyl moiety (Eq. 12). In addition, it was found that the natural charge of the phenyl moiety decreases linearly with an increase in the natural charge of the Lewis acid moiety (Eq. 13).

$$\Sigma q_{Ph} = -4.15R_{C1C7} + 6.230 \quad (R = 0.999). \tag{11}$$

$$\Sigma q_{Ph} = 3.85R_{C7O8} - 4.671 \quad (R = 0.993). \tag{12}$$

$$\Sigma q_{Ph} = -0.37\Sigma q_{M^+} + 0.505 \quad (R = 0.967). \tag{13}$$

These changes in bond distance and in the group natural charg-

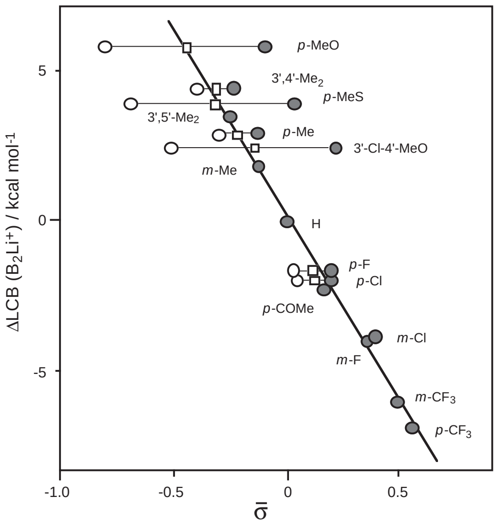


Fig. 6. The Y–T plot for $\Delta LCB[B_2Li^+]$. Closed circles; σ^o, open circles; σ^+, squares: apparent $\bar{\sigma}$ at $r^+ = 0.49$. Substituent constants were taken from Ref. 20.

Table 4. Correlation Results of Y–T Analysis for Lewis Cation Basicities of Acetophenones

Lewis cation	$-\rho$	r^+
H^+ a)	11.6	0.82
Me_3Si^+ b)	11.0	0.75
Me_3Ge^+ c)	9.7	0.71
Li^+	12.5 (8.3)d)	0.49

a) Ref. 20. b) Ref. 18. c) Ref. 19. d) The estimated value for $\Delta LCB[BLi^+]$, see text.

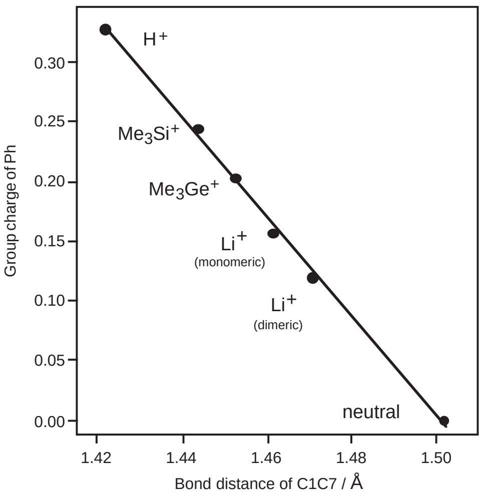


Fig. 7. Correlation between the group natural charge of the phenyl moiety and the bond distance (C1C7) of the Lewis cation bound acetophenone.

es with the variation of the Lewis acid are consistent with the change of the π-delocalization of the positive charge described by the r^+ value.

It should be noted that the moderate π-delocalization ($r^+ = 0.49$) is present in the Li^+ adduct, despite retaining the positive charge at Li^+ (natural charge of Li^+ of 0.9). The apparent π-delocalization in the Li^+ complex would result from the polarization of the carbonyl bond caused by ionic interaction between Li^+ and O=C. Since the π-orbitals of the double bond of the carbonyl group and the π-orbital of the benzene ring lie on the same plane, the positive charge induced at the carbonyl carbon atom can be stabilized by charge transfer to the benzene ring through π-interaction. In other words, the apparent π-delocalization in the Li^+ adduct results from the redistribution of the positive charge in the acetophenone moiety. Thus, the r^+ value reflects the charge-redistribution in the ligand molecule as well as charge transfer from a Lewis acid to a ligand.

Accordingly, the smaller ρ value for the LCB than that for the GB reflects the intrinsic nature of the ionic bond formed with Li^+. The magnitude of the ρ value, rather than an apparent slope of a linear relationship between LCBs and GBs, shows the effects of the substituent more clearly, suggesting that the degree of the decreasing ρ value is a good measure of the increasing ionic strength of the bond formed by a Lewis cation. This is consistent with our previous results in which a constant ρ value of -12 was observed for GBs of a series of benzoyl compounds, ArCOR, although the r^+ value as well as the GB value of the parent compounds varies significantly with the polar effect of the R group. In other words, the r^+ value decreases from 1.29 for α,α,α-trifluoroacetophenone (GB = 183.4 kcal mol^{-1}),[35] to 0.50 for methyl benzoate (195.9)[20] and to 0.23 for *N*,*N*-dimethylbenzamide (215.5).[36] That is, the ρ value is less sensitive to the change in thermodynamic stability of the adduct ion where a covalent bond is formed with extensive charge transfer. In conclusion, the present analysis suggests that the use of the slope of a linear relationship between LCBs and GBs for the characterization of the nature of the bond formed by Lewis acid must be limited to compounds having a similar framework. For example, a very small slope of 0.19 obtained for simple alkanones, RCOR′ where R and R′ = Me, Et, *i*-Pr, *cyclo*-Pr may arise not only from the differences in the nature of the bond formed with Li^+ but also from the different steric environment at the binding site.

Conclusion

Relative LCB[B_2Li^+] were obtained for *m*- and *p*-substituted acetophenones in the gas phase by the measurement of ligand-exchange equilibria of the type $LiA_2^+ + 2B = LiB_2^+ + 2A$ using a FT-ICR spectrometer. The substituent effects on LCB[B_2Li^+] of acetopheone are characterized by a ρ value of -12.5 and an r^+ value of 0.49 based on an analysis using the Yukawa–Tsuno equation. A ρ value of -8.3 for monomeric adduct [BLi^+] was determined by dividing the ρ value for B_2Li^+ by a factor of 1.5, which was obtained from a comparison of the calculated LCBs between B_2Li^+ and BLi^+. In comparison with the corresponding results for other Lewis cation basicities, it was shown that the ρ value decreases in the order of H^+ (-11.6) > Me_3Si^+ (-11.0) > Me_3Ge^+ (-9.7) > Li^+ (-8.3). The decrease in the ρ value indicates that the amount of positive charge localized at the Lewis cation moiety of the adduct ion increases in this order. The small ρ value for the Li^+ basicity is consistent with the largely ionic (ion–dipole interaction) nature of the bonding interaction between Li^+ and the carbonyl oxygen atom. The r^+ value also decreases in the same order. The moderate r^+ value of 0.49 observed for the Li^+ adduct ions in spite of a small charge transfer from Li^+ to a ligand is due to the redistribution of the positive charge in the acetophenone moiety.

Experimental

ICR Measurements. Equilibrium-constant measurements were performed on an Extrel FTMS 2001 spectrometer. Although the apparatus is equipped with a dual cell system, a single cell was used for the ionization, ion-molecular reactions, excitation, and detection. All measurements were performed in the temperature range of 50–70 °C at a constant magnetic field strength of 3.0 T. The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.[37] The overall pressures of the reagents were maintained between 2 and 4×10^{-7} Torr by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the reaction cell in the vacuum chamber. Li^+ was generated by laser irradiation with an Nd:YAG (Continuum, Minilite II) at 532 nm (10 mJ) of pure metal pieces mounted at the end-face of a solid probe rod. A small amount of 2-chloropropane ($<10^{-7}$ Torr) was added to the system to generate the propene/Li^+ adduct, which in turn transfers Li^+ to ligands of larger LCB. After an appropriate reaction period of 6 to 20 s, depending upon the reactant and pressures, equilibrium was attained and the relative abundances of $ALiA^+$, $ALiB^+$, and $BLiB^+$ were measured based on the signal intensities in the ICR spectra. For cooling excited metal ions helium or argon gas was added by using a pulsed valve; however, significant differences were not observed in the ligand-transfer equilibrium. Therefore, most of measurements were carried out without buffer gas. Each experiment was performed at several ratios of partial pressures and at different overall pressures. The arithmetic-mean values of equilibrium constants were used to calculate ΔG^o at 343 K with an average uncertainty of $\pm 0.3\,\mathrm{kcal\,mol^{-1}}$ in most of these cases. The occurrence of the ligand-transfer reaction was examined by an ion-eject experiment using the SWIFT technique.[38]

Chemicals. Acetophenone derivatives used in this study were available from our previous studies.[17] All the materials were degassed prior to use by several freeze–pump–thaw cycles on the sample-inlet system of the ICR. Their purities were checked using an FT-ICR mass spectrometer.

DFT Calculations. Conformational searches were carried out using Spartan '04 program (Wavefunction Inc.) and several conformers, which have the lowest-energy, were further optimized at RHF/3-21G* level of theory to determine the lowest energy conformer (global minimum). Finally, the geometries were fully optimized at the B3LYP/6-311G and B3LYP/6-311+G** levels of theory using the Gaussian 03 program[39] suite. Vibrational normal mode analyses were also performed at the same level. Relative thermochemical values (ΔLCB, ΔLCA, and ΔGB) were obtained from isodesmic reactions of each ligand-transfer reaction with the reference compound for monomeric and dimeric Li^+ complexes. No corrections for the basis set superposition error (BSSE)[40] were made because the magnitude of BSSE evaluated at the present level for a small test set of molecules using counterpoise correction was found to be small.[2]

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Supporting Information

Detailed results of the calculated species are available in Tables S1 and S2 in Supporting Information (Tables S1 and S2). This material is available free of charge on the Web at: http://www.csj.jp/journal/bcsj/.

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