Revised and Expanded Scale of Gas-Phase Lithium Cation Basicities. An Experimental and Theoretical Study

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The previously reported gas-phase lithium cation basicity (LCB) scale (Taft et al. *Pure Appl. Chem.* **1990**, *62*, 17) was revised on the basis of recent experimental and theoretical (G2 calculations) results. A new anchoring based on the experimental LCA value for H_2O is suggested (all earlier reported values of LCB should be reduced by 2.6 kcal/mol). New LCBs for 28 compounds were measured using FT-ICR, and a revised LCB scale now extended to 205 compounds is given. Correlations between gas-phase basicities toward lithium cation and proton were examined. Though a general trend is discernible, fair correlations are obtained provided that separate lines are drawn for homogeneous families. The differences in slopes are traced back to the different sensitivities to structural effects. Large deviations are explained by either a different attachment center for Li^+ and H^+ or a chelation effect toward Li^+. G2 and G2(MP2) calculations of LCBs for a wide selection of 37 compounds and density functional theory (B3LYP/6-311+G**) calculations of LCBs of 63 compounds of different classes were carried out. In most cases the performed calculations adequately describe the gas-phase lithium cation basicities of a wide variety of bases of different chemical origin and LCB range. The results of the calculations were also used for explaining the largest deviations from correlation lines between gas-phase lithium cation and proton basicities.

Introduction

The interactions of acids and bases are of great importance in chemistry. Quantitative studies in the gas phase provide the intrinsic acidities and basicities free from interference from solvent molecules and counterions. The most widespread study concerns different gas-phase proton-transfer equilibria.[1]

Alkali metal ions were the first metal cations to be studied in the gas phase for their coordination properties. This can be understood by considering their relatively easy production under vacuum. In contrast with transition metal ions, their reactivity toward ligands is quite simple: in general, they form adducts, or clusters, that can be considered as ions "solvated" by one or several ligands. Moreover, the possibility of measuring accurate alkali metal cation affinities with high accuracy, by means of different experimental techniques (equilibrium constant determination by high-pressure mass spectrometry[2] (HPMS) or ion cyclotron resonance[3,4] (ICR), unimolecular dissociation (the Cook's kinetic method),[5] energy-resolved collision-induced dissociation[6] (CID), photodissociation and radiative association kinetics[7]), has stimulated a growing interest in the study of these interactions.[8] Such measurements generate a collection of data that helps the understanding of the fundamental interactions implied in analytical mass spectrometry, organic synthesis, catalysis, lithium battery electrochemistry,[9a] and cation transport in living systems ion channels.[9b] A recent book edited by Sapse and Schleyer[10] presents various aspects of the chemistry of lithium, the most special alkali metal.

The gas-phase lithium cation basicity (LCB) is defined as the Gibbs free energy associated with the thermodynamic equilibrium

$$B + Li^+ \xrightleftharpoons{K_1} [B{-}Li^+] \qquad (1)$$

where $\Delta G_{Li^+} = -RT \ln K_1$ and $LCB = -\Delta G_{Li^+}$. In a similar manner, the gas-phase lithium cation affinity (LCA) is defined as the negative value of the enthalpy change of the reaction 1, $LCA = -\Delta H_{Li^+}$.

The two Lewis acids H^+ and Li^+ present a significant contrast in the nature of the bond formed with the ligand.[11] The proton adds to the base, giving a polar covalent σ bond with a very extensive charge transfer (the positive charge on the hydrogen atom is usually 0.4 or less electronic units whereas the base molecule carries the rest of the positive charge[11]). The large degree of charge transfer results from the fact that H^+ is a bare nucleus, with a very low energy unfilled 1s orbital. On the contrary, the bond formed by Li^+ (with its filled 1s shell) and other alkali metal cations is largely ionic and the alkali metal cation retains 0.8−0.9 units of the positive charge in the complex.[11]

Therefore, one of our goals in this work was to make a general comparison of the gas-phase lithium cation basicities for the widely differing families of Lewis bases—lone pair donors B

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(ethers, alcohols, carbonyl compounds, amines, nitriles, sulfides, mercaptans, sulfuryl and phosphoryl compounds, etc.) with the gas-phase basicities (GB) defined as the Gibbs free energy ΔG_{H^+}, which refers to the thermodynamic equilibrium

$$B + H^+ \overset{K_2}{\rightleftharpoons} [B-H^+] \tag{2}$$

where $\Delta G_{H^+} = -RT \ln K_2$ and $GB = -\Delta G_{H^+}$. A similar attempt was made by some of us almost 10 years ago.[4] In light of new experimental data, the availability of the results of high-level theoretical calculations, and revised scale of the LCB, this problem is now revisited.

The widest consistent scale of gas-phase lithium cation basicities, published by Taft et al.,[4] consists of 110 typical bases and covers a 22.7 kcal/mol (1 kcal/mol = 4.184 kJ/mol) range of relative LCBs. This scale has been widely used for converting relative basicities to absolute ones as well as for obtaining the effective temperature of CID-FT-ICR experiments. The scale of gas-phase lithium cation basicities of simple monofunctional compounds has been further extended by Gal and co-workers[12] to sulfuryl and phosphoryl derivatives.

Rodgers and Armentrout pointed out that there was a flaw in the anchoring process.[6b,c] The relative LCBs determined in Taft's laboratory corresponded to experiments carried out at 373 K but erroneously anchored (reference compound − H_2CO) to the value evaluated by Woodin and Beauchamp[3a,b] at 298 K. Noteworthy, the Woodin and Beauchamp LCBs were obtained using entropies calculated by statistical mechanics procedures involving various simplifying assumptions. Furthermore, Woodin and Beauchamp based their LCB scale on the H_2O/Li^+ bonding energy, which can be traced back to the value of binding energy in H_2O-Li^+ reported by Dzidic and Kebarle.[2a] This bond energy was, however, not directly measured but was extrapolated from measurements made for larger $Li^+-(H_2O)_n$ clusters. Recently, the H_2O-Li^+ bond energy was directly measured by Rodgers and Armentrout,[6a] who report that the H_2O-Li^+ binding energy estimated by Dzidic and Kebarle[2a] was too high. These considerations and other results of Armentrout and co-workers on Me_2O and alcohols[6b,c] prompted us to undertake a systematic revision of all Li^+ cation basicities that have been derived using Taft's LCBs as references.

In the current work, the anchoring of the absolute LCB scale by Taft et al. is reconsidered, taking into account the need for temperature correction, most recent experimental results by other groups as well as those measured by us in the present work, and the results of ab initio calculations at the G2 level. The LCB values for 28 new bases are reported. As already mentioned, the correlation between experimental LCB and the gas-phase basicity (toward proton) is thoroughly examined. The newly developed scale of LCBs is compared with the extensive quantum chemical calculations of LCB up to very high levels of theory (including DFT B3LYP/6-311+G** and G2). Compounds of widely variable chemical origin and LCB ranges are included.

Methodology

Experimental Details. The gas-phase LCB measurements reported in this paper were performed at the Chemistry Department of the University of California, Irvine, with a pulsed Fourier transform (FT) ICR mass spectrometer manufactured by the IonSpec Corp. (Irvine, CA). The major details of the experimental techniques used for the measurements of the equilibrium constants, K_3, of the reversible Li^+-transfer reaction 3 and experimental $LCB = RT \ln K_3$ values (given in Table 1) are mostly the same as those previously described.[3,4] Only significant changes and/or additional procedures will be given here.

TABLE 1: New Absolute LCB (at 373 K, in kcal/mol) Values Obtained from Directly Measured $\Delta\Delta G_{Li^+}$ Values (in kcal/mol) for the Lithium Complexation Equilibria

base BI	absolute LCB	experimental $\delta\Delta G_{Li^+}$
SO_2	18.2	2.1 weaker than $(CF_3)_3COH$
CF_2O	18.4	0.7 weaker than $(CF_3)_2CO$ much stronger than $(CF_3)_2O$ (no signal from $(CF_3)_2OLi^+$)
$(CF_3)_2CO$	19.1	0.7 stronger than F_2CO 0.9 weaker than MeSH 1.7 weaker than $(CF_3)_3COH$
$(CF_3S)_2$	19.2	1.1 weaker than $(CF_3)_3COH$ much weaker than $CH_2(CN)_2$
$(CF_3)_3COH$	20.3	2.1 stronger than SO_2 1.1 stronger than CF_3SSCF_3
CF_3CN	21.3	1.4 weaker than *i*-PrSH 1.8 weaker than Me_2S 0.4 weaker than EtSH 2.5 weaker than $(CF_3)_2CHOH$
CF_3CHO	21.8	0.7 weaker than *n*-PrSH
$[(CF_3)_2CF]_2CO$	21.9	0.5 weaker than *i*-PrSH
C_5F_5N	22.3	0.8 stronger than EtSH 0.1 weaker than *i*-PrSH
$(CF_3)_2CHOH$	23.8	1.4 stronger than *n*-PrSH 2.5 stronger than CF_3CN
$(CF_3)_3CNH_2$	23.8	0.4 stronger than Me_2S 2.6 weaker than CF_3CH_2OH
$(CHF_2)_2CO$	24.6	1.9 weaker than CF_3CH_2OH
$CF_3CO_2CH_2CF_3$	25.7	3.2 weaker than CF_3COOMe
$MeOCH(CF_3)_2$	26.2	0.3 weaker than CF_3CH_2OH
$(CF_3CO)_2CH_2$	27.3	0.8 weaker than CF_3COOMe 0.1 stronger than CF_3CH_2OH
$CHCl_2CN$	27.7	1.2 weaker than CF_3COOMe
$ClCO_2Me$	28.9	equal with CF_3COOMe 1.8 weaker than CF_3COOEt
$(CF_3CH_2)_2O$	29.2	0.5 stronger than CF_3COOMe 2.5 stronger than CF_3CH_2OH
CF_3CH_2OMe	29.6	0.7 stronger than CF_3COOMe
CF_3COSMe	29.9	2.0 stronger than Me_2O 0.7 weaker than CF_3COOEt 0.2 weaker than 1,4-dioxane
CH_3COOH	32.7	0.4 weaker than 2,6-F_2 pyridine 0.8 stronger than MeCHO
2,6-difluoropyridine	33.2	0.8 stronger than HCOOMe 1.2 weaker than 2-methyltetrahydrofuran 0.4 stronger than CH_3COOH
$(CF_3)_3CCO_2Et$	34.5	2.0 stronger than EtCHO 0.1 weaker than 2-methyltetrahydrofuran
Me_3SiOMe	34.6	0.4 weaker than *n*-Pr_2O 0.6 weaker than Me_2CO
$(CF_3CO)_2NH$	35.2	0.06 weaker than Me_2CO 0.3 weaker than *n*-Pr_2O
CF_3COCH_2COMe	35.3	equal with Me_2O
t-$BuCO_2$ Et	38.9	0.1 weaker than Me_2NCN
$MeC(OH){=}CHCOMe$	43.1	1.7 stronger than DMF 0.3 stronger than DMA

All equilibrium measurements were performed at a 1 T uniform magnetic field strength. A 1/8 in. diameter lithium ion source, manufactured by Spectra-Mat Inc., Watsonville, CA, was attached on one of the (2 × 2 × 2 in.) trapping plates of the cell. A trapping voltage of about 1.0 V and a filament current of the Li^+ ion source of ca. 1−1.4 A were applied. The ion source was biased at a slightly negative voltage during the trapping time (no Li^+ emission) and a short (10 ms) pulse of positive voltage was applied to the source to inject Li^+ ions. The typical operating pressures were in the range of 10^{-7} Torr. Isopropyl chloride was used in small amounts (ca. 10^{-7} Torr) to form the monomeric lithium complexes that transfer the Li^+ cation to B_i and B_0.[3a,b] Reaction times in the range of several

TABLE 2: G2 Enthalpies (H, in au), Free Energies (G, in au), Lithium Cation Affinities (LCA, in kcal/mol), and Lithium Cation Basicities (LCB, in kcal/mol), Experimental LCA and LCB Values (Numbers in Parentheses Indicate Experimental Uncertainty), and Differences between Experimental and Calculated LCA or LCB (δLCA or δLCB) Values for Some Reference Compounds

298 K

	H	*G*	LCA	LCB	LCA_{exp}	δLCA
Li^+	−7.23348	−7.24859				
H_2O	−76.32828	−76.34965	32.7	26.4	32.7(3.3)	0.02
H_2O-Li^+	−83.61383	−83.64026				
Me_2O	−154.74133	−154.77213	37.0	30.2	39.9(2.4)	2.9
Me_2O-Li^+	−162.03375	−162.06886				
MeOH	−115.53061	−115.55762	35.9	29.1	37.0(2.1)	1.1
$MeOH-Li^+$	−122.82131	−122.85262				
H_2CO	−114.33511	−114.35988	34.1	28.0		
H_2CO-Li^+	−121.62290	−121.65302				
CH_3CN	−132.51846	−132.54705	42.4	35.5		
CH_3CN-Li^+	−139.81943	−139.85216				
$HCONH_2$	−169.64077	−169.67078	47.7	40.0		
$HCONH_2-Li^+$	−176.95029	−176.98311				

373 K

	H	*G*	LCA	LCB	LCB_{exp}	δLCB
Li^+	−7.23289	−7.25245				
H_2O	−76.32731	−76.35512	32.7	24.8	24.7	−0.1
H_2O-Li^+	−83.61236	−83.64706				
Me_2O	−154.73938	−154.78009	36.9	28.5	29.5	1.0
Me_2O-Li^+	−162.03114	−162.07797				
MeOH	−115.52923	−115.56456	35.9	27.4	28.5	1.1
$MeOH-Li^+$	−122.81932	−122.86071				
H_2CO	−114.33407	−114.36622	34.1	26.4	25.4	−1.0
H_2CO-Li^+	−121.62124	−121.66077				
CH_3CN	−132.51688	−132.55441	42.3	33.7	34	0.3
CH_3CN-Li^+	−139.81722	−139.86062				
$HCONH_2$	−169.63911	−169.67850	47.8	38.1	36.4	−1.7
$HCONH_2-Li^+$	−176.94813	−176.99160				

hundred milliseconds were usually necessary to reach the equilibrium. All experiments reported here were carried out at a cell temperature of 100 °C. While the experiments were being run, the inlet system and the ICR analyzer were warmed to 100 °C with resistance heating tapes. Temperatures were measured with copper−constantan thermocouples attached to the ICR cell and to the walls of the analyzer. Normally, there was a temperature gradient of only a few degrees, and for the purpose of calculating free-energy changes the average of the two temperatures was taken. The mass spectra and the time plots for Li^+-transfer equilibria were acquired and processed in a FT mode. The IonSpec Omega program (version 3.1) was used for these purposes. The equilibrium constants for any Li^+-cation-transfer reaction 3 where K_3 refers to the transfer of Li^+ between

$$B_iLi^+ + B_0 \overset{K_3}{\rightleftarrows} B_i + B_0Li^+ \qquad \delta\Delta G_{Li^+} = -RT \ln K_3 \tag{3}$$

a given (B_i) and a reference base (B_0) were calculated by using the expression

$$K_3 = \frac{I_{B_0Li^+}\, p_{B_i}}{I_{B_iLi^+}\, p_{B_0}} \tag{4}$$

where $I_{B_0Li^+}$ and $I_{B_iLi^+}$ are the equilibrium abundances (mass spectrometric integrated intensities) of Li^+ complexes of B_0 (reference) and B_i (sample) as measured by the FT-ICR technique and p_{B_0} and p_{B_i} are the partial pressures of the neutral bases B_0 and B_i with appropriate correction factors applied to the direct ion gauge readings for the different ionization cross sections of various compounds.[13]

Each experiment was performed at several ratios of partial pressures and at different overall pressures of the reagents. Arithmetic mean values of K_3 were obtained and used to calculate ΔG_{Li^+} values at 373 K. The latter are in most cases characterized by an average uncertainty (standard deviation) that does not exceed ±0.2 kcal/mol. With a few exceptions, multiple overlaps were performed to ensure internal consistency of the data.

In the case of some relatively weak bases B_i (e.g., H_2S, PH_3, CF_3COCl, CS_2, etc.) the signal from the Li^+ complex of these bases was not monitored. Evidently, the LCBs of those molecules are too low to compete with *i*-PrCl and its conversion products[3a] ($MeCH{=}CH_2$ and HCl) for the Li^+ cation. Indeed, the calculated (DFT, B3LYP/6-311+G**) LCB and LCA values (at 298 K) for H_2S are 17.2 and 23.5 kcal/mol, and for PH_3 18.6 and 25.4 kcal/mol, respectively, whereas the corresponding predicted values for $MeCH{=}CH_2$ are 17.8 and 24.5 kcal/mol, and for HCl 10.7 and 16.2 kcal/mol, respectively.

The obtained relative values were converted into absolute values using the absolute LCB of H_2O (24.7 kcal/mol). For justification of such anchoring see the Discussion.

Computational Details. Standard ab initio calculations[14] were carried out at the G2 and G2(MP2) level[15] using the Gaussian 94 and Gaussian 98 program packages.[16] Gibbs free energies and enthalpies at 298 and 373 K were evaluated using the HF/6-31G* frequencies scaled by factor 0.8929.[18]

Density functional theory (DFT) calculations at the B3LYP/6-311+G** level were performed using the Gaussian 98 program package.[16b] Here, the Gibbs free energies and enthalpies at 298 K were evaluated using the unscaled frequencies calculated at the same level of theory.

No corrections for basis set superposition error (BSSE) were made. The magnitude of BSSE was evaluated at the B3LYP/6-311+G** level for a small test set of molecules using counterpoise correction[19] and found to be small (generally 0.5 kcal/mol or less). In the case of G2 results the BSSE should thus be even smaller.

Also, the lower level calculations (HF/6-31G*, HF/6-31+G*, HF/6-311G*) of LCAs for a large number of molecules were performed for comparison. As a rule, the results of these calculations did not lead to LCA values in close quantitative correspondence with the experimentally measured values or with those calculated at G2 and B3LYP/6-311+G** levels of theory.

Results

The directly measured $\delta\Delta G_{Li^+}$ values (at 373 K) are reported in Table 1. The G2 energies, enthalpies and Gibbs free energies, and lithium cation basicities and lithium cation affinities (at 298 and 373 K) for some reference compounds used for anchoring of the absolute LCB scale are given in Table 2. The relative $\delta\Delta G_{Li^+}$ values are converted into absolute LCB values and reported together with values from the other sources in Table 3 simultaneously with proton gas-phase basicities. Results of the regression analysis of the correlation between lithium cation basicity (LCB) and proton basicity are given in Table 4. The G2, G2(MP2), and B3LYP/6-311+G** energies, enthalpies, and Gibbs free energies of calculated bases and their lithium cation complexes (at 298 K) are available in the Supporting Information. Calculated LCBs are given in Table 5.

Discussion

Anchoring of the Absolute LCB Scale. Experiments constituting the relative LCB scale of Taft et al. were carried out at 373 K.[4] Unfortunately, relative $\delta\Delta G_{Li^+}$ values were converted

TABLE 3: Experimental Gas-Phase Lithium Cation Basicities (LCB, in kcal/mol, 373 K) and Proton Basicities (GB, in kcal/mol, 298 K)

base	LCB	GB	base	LCB	GB	base	LCB	GB	base	LCB	GB
CF_3CCH	17.9[a]	150.0[b]	CF_3CH_2OMe	29.6[c]	171.7[d]	1-methylpyrazole	34.3[f]	210.3[d]	imidazole	38.1[f]	217.3[d]
SO_2	18.2[c]	153.8[d]	pyrimidine (1,3)	29.8[f]	204.5[d]	$NCCONMe_2$	34.5[a]	190.5[d]	1,3,5-trimethylpyrazole	38.3[h]	219.3[d]
CF_2O	18.4[c]	152.2[d]	CF_3COSMe	29.9[c]	175.5[d]	$(CF_3)_3CCO_2Et$	34.5[c]	177.2[e]	c-Pr_2CO	38.4[f]	203.3[d]
$(CF_3)_2CO$	19.1[c]	152.9[d]	PhOMe	30.2[a]	192.9[d]	Me_3SiOMe	34.6[c]	194.7[d]	3-(dimethylamino)pyridine	38.6[p]	225.4[d]
$(CF_3S)_2$	19.2[c]	162.6[e]	NH_3	30.2[f]	195.7[d]	$C_6H_{13}CHO$	34.6[a]	187.0[j]	3,4,5-trimethylpyrazole	38.7[f]	218.9[d]
$(CF_3)_3COH$	20.3[c]	154.6[d]	1,4-dioxane	30.3[f]	184.0[d]	Cl_3PO	34.7[a]		*t*-$BuCO_2Et$	38.9[c]	197.1[e]
MeSH	20.3[f]	177.0[d]	CCl_3CH_2OH	30.4[f]	167.0[d]	*n*-Pr_2O	34.8[f]	193.7[d]	tetramethylene sulfone	39.0[i]	189.7[i]
CF_3CN	21.3[c]	157.2[d]	EtOH	30.4[f]	178.0[d]	2,5-dimethyl-tetrahydrofuran	35.0[f]	199.6[d]	Me_2NCN	39.0[f]	196.3[d]
EtSH	21.4[f]	181.3[d]	CF_3CO_2Et	30.6[f]	174.0[d]				1,3,4,5-tetramethylpyrazole	39.0[f]	220.5[m]
CF_3CHO	21.8[c]	156.2[d]	*n*-Bu_2S	30.6[f]	201.3[d]	pyridine	35.0[f]	214.7[d]	$(CH_2)_3OSO$	39.2[i]	198.1[i]
$[(CF_3)_2CF]_2CO$	21.9[c]		*t*-Bu_2S	31.1[f]	206.5[d]	$PhCH_2CN$	35.1[f]	185.2[d]	$PhSO_2(Me)$	39.3[k]	186.5[m]
C_5F_5N	22.3[c]	175.2[d]	$MeNH_2$	31.3[f]	206.6[d]	2-fluoropyridine	35.1[p]	203.8[d]	HCONHMe	39.6[f]	196.1[d]
i-PrSH	22.4[f]	184.6[d]	*n*-PrOH	31.4[f]	180.7[d]	3(5)-methylpyrazole	35.1[h]	208.7[d]	$MeCONH_2$	39.9[o]	199.0[d]
n-PrSH	22.5[f]	182.5[d]	3-chloro-pyridine	31.6[f]	208.3[d]	$MeCO_2Me$	35.2[f]	189.0[d]	CF_3CONMe_2	39.7[a]	195.5[d]
Me_2S	23.4[f]	191.5[d]	MeCHO	31.8[f]	176.0[d]	$(CF_3CO)_2NH$	35.2[c]	172.3[e]	$MeOCONMe_2$	39.9[f]	202.5[d]
i-BuSH	23.7[f]	184.4[d]	Me_3N	32.0[f]	219.4[d]	EtCN	35.3[f]	182.4[d]	4-$MeC_6H_4SO_2(Me)$	40.2[k]	194.5[m]
$(CF_3)_2CHOH$	23.8[c]	156.8[d]	1,2,3-triazole	32.1[a]	202.5[d]	CF_3COCH_2COMe	35.3[c]	186.8[e]	1-methylimidazole	40.2[f]	221.7[d]
$(CF_3)_3CNH_2$	23.8[c]	179.9[d]	Me_2NH	32.1[f]	214.3[d]	Me_2CO	35.3[f]	186.9[d]	Ph_2SO_2	40.6[k]	197.7[m]
t-BuSH	23.8[f]	187.6[d]	*i*-PrOH	32.3[f]	182.3[d]	*n*-PrCN	35.4[f]	183.5[d]	pyridazine (1,2)	41.4[f]	209.6[d]
n-BuSH	24.0[f]	184.2[d]	HCO_2Me	32.4[f]	179.6[d]	*t*-BuOEt	35.4[f]	197.6[d]	MeCONHMe	41.5[o]	205.0[d]
$(CHF_2)_2CO$	24.6[c]	159.9[d]	*i*-BuOH	32.5[f]	182.2[d]	PhCN	35.5[f]	186.6[d]	dimethylformamide	41.5[f]	204.7[d]
H_2O	24.7[g]	157.7[d]	tetrahydrofuran	32.7[f]	189.9[d]	*i*-Pr_2O	35.5[f]	197.9[d]	isophorone	41.5[a]	205.9[d]
EtSMe	25.0[f]	194.9[d]	1,2,4-triazole	32.7[h]	204.6[d]	glycol sulfite	35.6[k]	185.5[l]	dimethyl sulfoxide	41.8[k]	204.0[d]
H_2CO	25.4[f]	163.3[d]	MeCOOH	32.7[c]	179.9[d]	*i*-PrCN	35.7[f]	184.7[d]	1,2-dimethylimidazole	41.8[f]	227.7[d]
$CF_3CO_2CH_2CF_3$	25.7[c]	173.8[e]	$MeOCH_2CN$	32.8[f]	173.9[d]	4-methylpyrazole	35.7[f]	208.7[d]	4-(dimethylamino)pyridine	42.0[f]	232.1[d]
$(CH_2)_4S$	25.8[f]	195.8[d]	EtCHO	32.8[f]	180.2[d]	$PhCH_2OH$	35.8[f]	178.8[d]	tetramehylguanidine	42.4[f]	238.4[d]
HCN	25.9[f]	162.9[d]	*n*-BuOH	32.8[f]	181.4[d]	valeronitrile	35.8[f]	184.4[d]	$(MeO)_2PO(H)$	42.5[r]	206.1[d]
$(CH_2)_5S$	25.9[f]	197.4[d]	isooxazole	32.9[a]	195.2[d]	4-$NO_2C_6H_4SO_2(Me)$	36.0[k]	184.6[l]	$MeOCH_2CH_2OH$	42.6[f]	174.4[d]
$(CF_3)_2CHOMe$	26.2[c]	163.5[e]	glycol sulfate	33.0[i]	177.6[i]	MeCOEt	36.0[f]	190.1[d]	2,4,5-trimethylimidazole	42.6[p]	225.3[m]
CH_2FCN	26.2[a]	169.3[e]	neo-C_5H_9OH	33.1[f]	182.9[d]	$MeCO_2Et$	36.0[f]	192.3[d]	dimethylacetamide	42.8[f]	209.6[d]
$CH_2(CN)_2$	26.3[c]	165.9[d]	2,6-difluoropyridine	33.2[c]	194.0[j]	$MeOSO_2(Me)$	36.3[n]	183.9[n]	PhSO(Me)	42.9[k]	207.1[l]
Et_2S	26.4[f]	197.7[d]	*n*-PrCHO	33.3[f]	181.8[d]	$EtCO_2Me$	36.3[f]	191.0[d]	tetramethylene sulfoxide	43.1[i]	206.5[I]
CF_3CH_2OH	26.5[f]	160.1[d]	*t*-BuOH	33.3[a]	184.6[d]	$(MeS)SO_2(Me)$	36.4[n]	185.6[n]	$MeC(OH){=}CHCOMe$	43.1[c]	200.0[d]
CCl_3CN	26.8[a]	165.5[d]	*s*-BuOH	33.3[f]	187.5[d]	*t*-BuCN	36.4[f]	186.5[d]	1,8-naphthyridine	43.4[f]	219.4[q]
C_6H_6	26.9[f]	173.4[d]	tetrazole	33.3[h]	190.2[m]	*n*-Bu_2O	36.5[f]	195.6[d]	$(MeO)_3PO$	43.7[f]	205.7[d]
CF_3COMe	27.0[f]	165.4[d]	Et_2O	33.3[f]	191.0[d]	3-methylpyridine	36.5[f]	217.9[d]	Ph_2SO	43.9[k]	211.1[l]
CCl_3CHO	27.2[f]	165.0[d]	thiazole	33.4[f]	208.4[d]	$(CH_2)_3OSO_2$	36.7[i]	184.0[I]	$(MeO)_2PO(Me)$	44.0[r]	
$(CF_3CO)_2CH_2$	27.3[c]	173.8[e]	pyrazole	33.6[f]	205.7[d]	Et_2CO	36.7[f]	193.0[d]	(*i*-PrO)$_2$PO(H)	44.1[r]	
$CF_3CH_2OCH{=}CH_2$	27.4[a]	188.6[e]	MeCOSMe	33.8[f]	190.7[d]	*n*-heptyl cyanide	36.8[a]	186.6[j]	$CH_2ClPO(Oet)_2$	44.1[f]	204.0[j]
i-BuSMe	27.4[a]		*n*-BuCHO	33.8[a]	182.8[d]	$(MeO)_2CO$	37.0[f]	191.0[d]	4-$CF_3PhOPO(Ph)_2$	44.3[r]	
$CHCl_2CN$	27.7[c]		CF_3CONH_2	33.9[f]	181.1[e]	1,4-dimethylpyrazole	37.0[f]	214.3[d]	$(CH_2OMe)_2$	44.9[a]	196.0[d]
MeOH	28.5[f]	173.2[d]	HCO_2Et	33.9[f]	183.7[d]	Me_2SO_2	37.1[k]	186.5[l]	$(EtO)_2PO(Me)$	45.0[r]	
pyrazine(1,4)	28.6[f]	202.4[d]	$(MeO)_2SO_2$	34.0[i]	180.1[i]	$CF_3(CH_2)_3NH_2$	37.1[f]	207.8[d]	$(EtO)_3PO$	45.1[r]	210.2[d]
CF_3CO_2Me	28.9[f]	169.6[d]	MeCN	34.0[f]	179.0[d]	c-PrCOMe	37.4[f]	197.0[d]	(MeO)MePO(Ph)	45.1[r]	
n-Pr_2S	28.9[f]	199.5[d]	*t*-BuOMe	34.2[f]	194.2[d]	*n*-octylcyanide	37.5[f]	184.4[j]	$(C_6H_5O)_3PO$	45.2[r]	
i-Pr_2S	28.9[f]	202.3[d]	$MeSCH_2CN$	34.3[f]	180.2[d]	*i*-Pr_2CO	37.5[f]	196.1[d]	$(4\text{-}FC_6H_4O)PO(Ph)_2$	45.6[r]	
$ClCO_2Me$	28.9[c]		c-$C_6H_{11}CH_2OH$	34.3[f]	184.4[d]	$HCONH_2$	37.6[o]	189.1[d]	Me_3PO	45.7[r]	210.3[d]
$(CF_3CH_2)_2O$	29.2[c]	161.3[d]	HCO_2-*n*-Pr	34.3[f]	185.0[d]	1,5-dimethylpyrazole	37.6[f]	215.8[d]	Et_3PO	46.7[r]	216.7[d]
CH_2ClCN	29.4[f]	170.9[d]	HCO_2-*n*-Bu	34.3[f]	185.0[d]	$C_6H_5SO_2(Me)$	37.7[k]	185.9[l]	$C_6H_5OPO(Ph)_2$	46.9[r]	
BrCN	29.4[a]	171.9[d]	$C_5H_{11}CHO$	34.4[a]		PhCHO	37.7[f]	191.7[d]	$(Me_2N)_3PO$	47.5[r]	222.0[d]
Me_2O	29.5[f]	182.7[d]	2-methyl-tetrahydrofuran	34.3[f]	194.0[d]	1-adamantyl cyanide	38.1[f]	192.1[j]	Ph_3PO	47.5[r]	209.5[d]
4-(trifluoromethyl)-pyridine	29.5[f]	206.0[d]				*p*-MeC_6H_4COMe	38.1[f]	201.6[d]			

[a] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from unpublished work of R. W. Taft and F. Anvia. [b] Our G2(MP2) results (to be published). [c] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from this work. [d] From ref 1. [e] Koppel, I. A.; Anvia, F.; Taft, R. W. *J. Phys. Org. Chem.* **1994**, *7*, 717. [f] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from ref 4. [g] Anchor point for absolute LCB scale (see Discussion). [h] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from ref 11f. [i] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from ref 12b. [j] Taft, R. W.; Anvia, F. Unpublished results. [k] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from ref 12a. [l] From ref 12a. [m] From ref 11f. [n] LCB values (reanchored from unpublished data of J.-F. Gal and P.-C. Maria obtained using the kinetic method and the calibration equation of ref 12a): $MeOSO_2(Me)$ more basic than *n*-PrCN by 0.67 kcal/mol, more basic than *i*-PrCN by 0.46 kcal/mol, less basic than MeCOEt by 0.18 kcal/mol; $MeSSO_2(Me)$ more basic than MeCOEt by 0.15 kcal/mol, more basic than *i*-PrCN by 0.92 kcal/mol, less basic than $EtCO_2Me$ by 0.07 kcal/mol. GB values (unpublished data of Gal and Maria; measured by the equilibrium method): $MeOSO_2(Me)$ more basic than *n*-PrCHO by 0.34 kcal/mol, less basic than Me_2O by 0.46 kcal/mol; $MeSSO_2(Me)$ more basic than Me_2O by 1.07 kcal/mol, more basic than HCO_2Et by 0.32 kcal/mol, same basicity as *n*-PrCN. [o] Herreros, M.; Gal, J.-F.; Maria, P.-C.; Decouzon, M. To be published. [p] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from ref 11g. [q] From ref 11g. [r] Values calculated using the absolute LCB value of water (24.7 kcal/mol, this work) and relative LCB values from ref 12c.

into absolute ones using the LCB value (at 298 K), reported for H_2CO by Woodin and Beauchamp.[3c] Furthermore, the value of Woodin and Beauchamp can be traced back to $H_2O{-}Li^+$ bond dissociation energy from Dzidic and Kebarle,[2a] which was estimated from the measurements made for larger $Li^+{-}(H_2O)_n$ clusters. Recent CID measurements by Armentrout[6b] indicate that this value is somewhat overestimated and several alternative possibilities (H_2O, MeOH, and Me_2O) for anchoring of the absolute LCB scale have been put forth.[6]

As no directly measured absolute LCBs are available, one has to start with measured LCA and to convert it into LCB using some approximation to calculate the $T\Delta S$ term. LCA

TABLE 4: Results of the Regression Analysis of the Correlation between Lithium Cation Basicity (LCB) and Gas-Phase Basicity (toward proton, GB) According to Formula LCB = aGB + b (with Uncertainties)[a]

bases	a	$-b$	R^2	N
all	0.258 ± 0.073	15.6 ± 3.6	0.497	191
O-bases	0.374 ± 0.017	35.0 ± 3.2	0.809	114
O-bases[b]	0.380 ± 0.016	36.2 ± 2.9	0.844	87
alcohols	0.348 ± 0.079	29.7 ± 14.0	0.559	17
nonchelating alcohols[c]	0.399 ± 0.021	40.4 ± 3.2	0.860	10
ethers	0.243 ± 0.088	13.0 ± 16.9	0.446	18
ethers[d]	0.420 ± 0.022	46.9 ± 4.2	0.936	9
carbonyl compounds	0.387 ± 0.018	37.6 ± 3.3	0.906	52
carbonyl compounds[e]	0.395 ± 0.016	39.2 ± 2.9	0.930	51
carbonyl compounds[f]	0.396 ± 0.015	39.4 ± 2.7	0.940	49
S═O and P═O compounds	0.395 ± 0.026	37.7 ± 5.0	0.909	25
N-bases	0.185 ± 0.024	2.6 ± 4.9	0.504	57
cyano compounds	0.458 ± 0.023	49.0 ± 4.3	0.951	20
amines (cyclic and acyclic)	0.324 ± 0.034	33.2 ± 7.4	0.711	37
cycles	0.341 ± 0.040	36.1 ± 8.5	0.720	30
monodentate cycles[g]	0.436 ± 0.037	57.4 ± 7.9	0.865	24
monodentate six-member cycles[h]	0.453 ± 0.021	62.9 ± 4.6	0.987	8
monodentate five-member cycles[i]	0.413 ± 0.022	51.6 ± 4.8	0.961	16
S-bases	0.289 ± 0.029	30.0 ± 5.6	0.864	17
S-bases[j]	0.344 ± 0.031	40.8 ± 6.2	0.890	16
thiols	0.361 ± 0.084	43.5 ± 15.5	0.785	7
thioethers[j]	0.563 ± 0.071	84.5 ± 14.3	0.898	9

[a] R^2 is the square of correlation coefficient and N is the number of data points. [b] Without $CH_3OCH_2CH_2OH$. [c] Without F, Cl, Ph, $PhCH_2$, and MeO substituted species and H_2O. [d] Me_2O, Et_2O, n-Pr_2O, i-Pr_2O, n-Bu_2O, t-BuOMe, t-BuOEt, 1,4-dioxane, and tetrahydrofuran. [e] Without $(CF_3CO)_2NH$. [f] Without $(CF_3CO)_2NH$, $(CF_3)_3CCO_2C_2H_5$, and MeC(OH)═CHCOMe. [g] Without 1,8-naphthyridine, 1,2-pyridazine, tetrazole, 2-fluoropyridine, 2,6-difluoropyridine, and C_5F_5N. [h] Without 1,2-pyridazine, 2-fluoropyridine, 2,6-difluoropyridine, and C_5F_5N. [i] Without tetrazole. [j] Without $(CF_3S)_2$.

TABLE 5: Experimental (LCB_{Exp}) and Calculated (at G2, G2(MP2), and B3LYP/6-311+G Levels: LCB_{G2}, $LCB_{G2(MP2)}$, and LCB_{B3Lyp}) Lithium Cation Basicities (in kcal/mol, at 298 K) and the Calculated Difference of LCBs at 373 and 298 K ($\Delta LCB_{373-298}$, in kcal/mol, Calculated Using Scaled 6-31G* Frequencies)**

compound	LCB_{Exp}	LCB_{G2}	$LCB_{G2(MP2)}$	$\Delta LCB_{373-298}$	LCB_{B3LYP}
CF_3CCH	17.9				17.6
$(CF_3S)_2$	19.2				15.8
CF_2O	18.4				20.3
MeSH	20.3	20.8	20.8	−1.4	22.5
$(CF_3)_3COH$	20.3				23.1
CF_3CN	21.3				23.5
$(CF_3)_2CHOH$	23.8				24.8
EtSH	21.4	22.4	22.4	−1.4	24.8
i-PrSH	22.4	23.5	23.5	−1.4	25.8
Me_2S	23.4	24.6	24.6	−1.3	26.5
H_2O	24.7	26.4	26.1	−1.3	29.7
EtSMe	25.0	26.0	26.0	−1.4	27.9
H_2CO	25.4	28.0	28.0	−1.3	30.6
HCN	25.9	25.4	25.5	−2.3	27.7
$CH_2(CN)_2$	26.3				30.0
CCl_3CN	26.8				29.9
C_6H_6	26.9				30.3
$(CF_3CO)_2CH_2$	27.3				30.8
$CF_3CH_2OCH{=}CH_2$	27.4				29.5
MeOH	28.5	29.1	29.0	−1.4	32.4
Me_2O	29.5	30.2	30.1	−1.2	35.6
PhOMe	30.2				34.0
NH_3	30.2	30.2	29.9	−1.3	34.2
EtOH	30.4	30.9	30.8	−1.5	35.0
$MeNH_2$	31.3	32.0	31.8	−1.5	34.8
MeCHO	31.8	33.0	33.0	−1.4	36.5
Me_3N	32.0	32.4	32.2	−1.6	34.1
Me_2NH	32.1	32.5	32.3	−1.5	34.8
i-PrOH	32.3	33.5	33.4	−1.5	36.8
HCO_2Me	32.4	33.2	33.2	−1.4	36.3
tetrahydrofuran	32.7				37.8
$MeCO_2H$	32.8	33.2	33.2	−1.4	37.0
EtCHO	32.8	34.1	34.1	−1.4	37.6
isoxazole	32.9				37.1
Et_2O	33.3				37.5
pyrazole	33.6	35.3	35.2	−1.5	38.5
MeCN	34.0	35.5	35.5	−1.3	39.2
2-methyl-tetrahydrofuran	34.3				39.6
2,2′-dimethyl-tetrahydrofuran	35.0				40.7
$MeCO_2Me$	35.2				41.1
$(CF_3CO)_2NH$	35.2				48.6
Me_2CO	35.3	36.7	36.7	−1.5	40.9
EtCN	35.3	36.7	36.7	−1.5	40.0
n-PrCN	35.4	37.3	37.3	−1.5	40.8
i-PrCN	35.7	37.7	37.7	−1.5	41.0
4-methylpyrazole	35.7	37.5	37.4	−1.4	41.0
$HCONH_2$	36.4	40.0	39.9	−1.6	43.7
MeCOEt	36.0	37.1	37.1	−1.6	41.6
$MeCO_2Et$	36.0	37.6	37.6	−1.3	42.1
$EtCO_2Me$	36.3	37.7	37.6	−1.4	40.9
t-BuCN	36.4	38.6	38.6	−1.5	42.0
PhCHO	37.7				42.6
imidazole	38.1	42.0	41.9	−1.5	45.0
Me_2NCN	39.0				48.1
$MeCONH_2$	39.3	43.5	43.5	−1.7	47.0
HCONHMe	39.6	44.0	44.0	−1.6	47.4
Me_2SO	40.2	47.0	47.1	−1.4	53.6
$HCONMe_2$	41.5	46.0	46.0	−1.5	49.2
$MeCONMe_2$	42.6				50.9
$MeOCH_2CH_2OH$	42.6				54.8
$(MeO)_3PO$	43.7				52.1
$(MeOCH_2)_2$	44.9				55.7
HCl					10.7
$CH_3CH{=}CH_2$					17.8
H_2S					17.2
PH_3					18.6

values are experimentally available for H_2O, MeOH, and Me_2O.[6] We have carried out ab initio calculations at the G2 level to differentiate between these alternatives.

Noteworthy, our calculated LCA and LCB values for H_2O differ somewhat from those calculated by Remko and Šarišsky[20a] at the G2 level and by Siu et al.[20b] at the G2(MP2) level. The G2 enthalpies and free energies reported by Remko and Šarišsky[20a] are exactly the same as ours reported in Table 2, while the LCA and LCB values differ by 0.6 kcal/mol. Apparently they have corrected their LCA (and LCB) values, calculated as differences between enthalpies (or free energies for LCB) of products and reactants (LCA = $H_{Li^+} + H_{ligand} - H_{complex}$), for the work term Δ(pV). However, the work term (pV) is by definition already included in enthalpy and thus should not be corrected.[17] The G2(MP2) energies at 0 K reported by Siu et al.[20b] are the same as ours, while the LCA and LCB values for H_2O differ by up to 1.5 kcal/mol. Unfortunately, Siu et al.[20b] do not provide details on how they calculated thermochemical parameters at different temperatures. Therefore, we were not able to find the source of the differences.

From the Table 2 one can see that the best correspondence between experimental and calculated LCAs is observed for H_2O. It should be noted that also in the other cases the differences between experiment and calculations are in the range of experimental errors. So, in principle, all three LCAs can be used to build the absolute LCB scale. We have used the values for H_2O for anchoring of our absolute LCB scale because it has the smallest discrepancy with calculated (at G2 level) LCA, and because it has traditionally been used as an anchoring point. One can argue that from the three proposed alternatives, H_2O has the largest experimental uncertainty.[6a] However, on the other hand, several indirect comparisons[6a] support the reported value, while no such information is available about the other alternatives.

We have used HF/6-31G* frequencies (scaled by 0.8929[18]) to evaluate the $T\Delta S$ term and adjust the calculated LCB value for experimental temperature (373 K). As a result, we obtain LCB for H_2O at 373 K, which is 24.7 kcal/mol, 2.6 kcal/mol lower than the value used by Taft.[4] This result agrees well with adjustment suggested by Armentrout (1.7−3.2 kcal/mol).[6b,c] Application of the similar procedure to MeOH and Me_2O leads to the increments of 2.3 and 0.9 kcal/mol, respectively. The increment, corresponding to anchoring at the LCB of Me_2O, is apparently too low, while the value corresponding to MeOH is close to that of H_2O. Now an adjusted LCB scale for 205 compounds is presented in Table 3.

Correlation between Gas-Phase Basicity (GB) and LCB. As described in the Introduction, the two Lewis acids H^+ and Li^+ present a significant contrast in the nature of the bond formed with the ligand. The proton adds to the base, giving a polar covalent σ bond with a very extensive charge transfer, while the bonds formed by Li^+ are largely due to ion−dipole (electrostatic) interaction. As a result, the LCBs are much smaller than GBs and cover a much narrower range in the energy scale.[1,4] The widely different bonding types in H^+ and Li^+ adducts should lead to widely varying basicity orders,[3,4,11h] a matter needing clarification and analysis of the effects of molecular structure that are involved.

Earlier comparisons[4] of experimental basicities toward H^+ and Li^+ have led to the conclusion that there is no precise general correlation between LCBs and GBs, especially when diverse families of compounds with different functional groups are included. Our results presented in Figure 1A and in Table 4 agree with such conclusion ($R^2 = 0.497$, R is the correlation coefficient).

However, closer examination of data (Table 4 and Figure 1) reveals that the correlations for the families with the same basicity center are sometimes fairly precise and even more so for subfamilies where the basicity center is the same functional group (i.e., nitrogen in cyano group, oxygen in carbonyl group, etc.).

So, the investigated 108 oxygen bases exhibit fair correlation between GB and LCB with the slope 0.374 ± 0.017 and intercept −35.0 ± 3.2, $R^2 = 0.809$. Exclusion of the strongly deviating point, corresponding to $MeOCH_2CH_2OH$, improves the correlation considerably ($R^2 = 0.844$). Considering data on the basis of functional classes provides even better correlations between LCB and GB.

For all investigated alcohols R^2 is 0.559. Significant deviations (enhanced stabilities of Li^+ complexes) from a linear relationship between LCB and GB values for alkyl-substituted alcohols are evident for methoxy-, fluorine-, chlorine-, and phenyl-subtituted compounds such as $MeOCH_2CH_2OH$ (LCB deviates from the correlation line by 11.7 kcal/mol), CF_3CH_2OH (2.4 kcal/mol), CCl_3CH_2OH (2.1 kcal/mol), and $PhCH_2OH$ (3.4 kcal/mol), which, according to the literature[4,11b] and our DFT calculations, form bidentate ring structures with the Li^+ cation, but not with a proton (no signs of appreciable "coiling effect"[21] were found for those compounds). When one excludes from the regression all methoxy-, halogen-, and phenyl-substituted alcohols, the correlation between LCB and GB is much better with slope 0.399 ± 0.021, intercept −40.4 ± 3.2, and $R^2 = 0.860$.

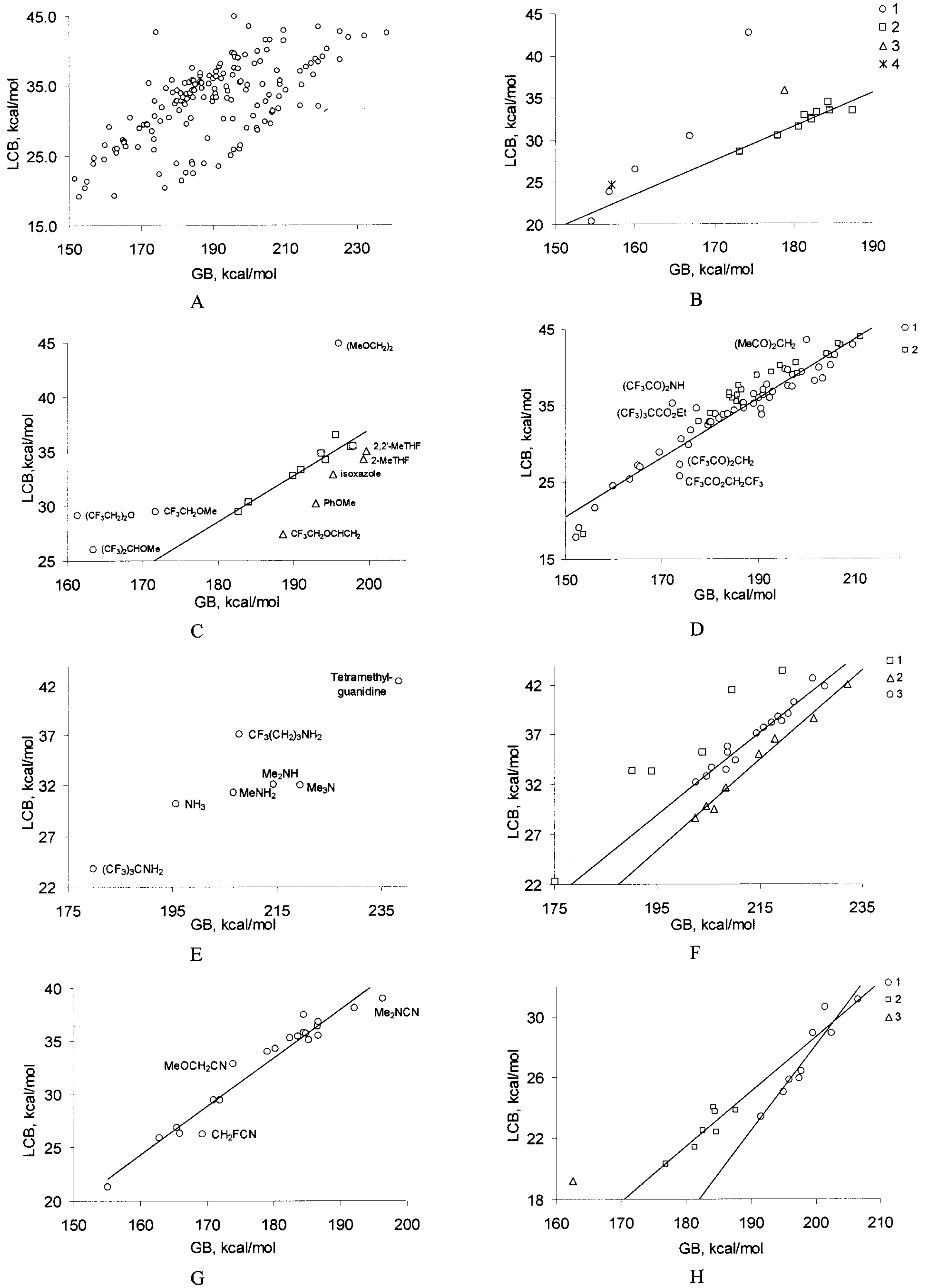
Reasonably satisfactory correlation ($R^2 = 0.906$) is observed for all carbonyl compounds (including aldehydes, ketones, esters, amides, carboxylic acids, etc.). Here one point, corresponding to $(CF_3CO)_2NH$, deviated strongly from the regression line (by 6.2 kcal/mol). As this compound is assumed to exist in the gas phase in enol form (our B3LYP/6-311+G** calculations, to be published), it should be expected to be a nitrogen base toward the proton. However, according to our calculations the lithium cation will bind to the carbonyl group, and the proton will migrate from carbonyl to nitrogen (Figure 2). Exclusion of this point from regression results in some improvement of correlation ($R^2 = 0.930$). Exclusion of the two other strongly deviating points, corresponding to $(CF_3)_3CCO_2C_2H_5$ (deviation from correlation line 3.6 kcal/mol, probably also forming bidentate chelate complex with the lithium cation) and $MeC(OH){=}CHCOMe$ (deviation 3.3 kcal/mol, probably acting as an oxygen base toward the lithium cation and carbon base toward the proton—similar to $(CF_3CO)_2NH$) further improves the correlation ($R^2 = 0.940$). It should be noted that there exist also significant deviations toward decreased stabilities of Li^+ complexes from a linear relationship between LCB and GB values for several other fluorine substituted compounds: $CF_3COOCH_2CF_3$ (3.9 kcal/mol), $(CF_3)_2CO$ (4.0 kcal/mol), and $(CF_3CO)_2CH_2$ (2.4 kcal/mol).

Reasonably good correlation ($R^2 = 0.909$) is observed for the S=O (sulfoxides and sulfones) and P=O bases. Noteworthy, the slope and intercept of the correlation line for those bases is very close to that of carbonyl bases (slopes are 0.395 ± 0.026 and 0.396 ± 0.015, respectively, and intercepts are 37.7 ± 5.0 and 39.4 ± 2.7, respectively, for the S=O and P=O bases and carbonyl bases).

Within the class of oxygen bases the ethers (both acyclic and cyclic) give the worst correlation between basicities toward lithium cation and proton (R^2 is only 0.446 for all 18 ethers considered). There the lithium adducts are much more prone to bidentate chelate formation than in the case of the other oxygen bases, as evidenced by the strong deviations (enhanced stabilities of Li^+ complexes) of methoxy- and fluorine-substituted ethers—their LCBs are greater than predicted from the linear relationship between LCB and GB values for unsubstituted alkyl ethers (for $(MeOCH_2)_2$ by 9.3 kcal/mol, for $(CF_3CH_2)_2O$ by 8.3 kcal/mol, for CF_3CH_2OMe by 4.4 kcal/mol, and for $(CF_3)_2CHOMe$ by 4.3 kcal/mol). Similar to the situation for the carbonyl compounds, in several cases the LCB values are smaller than expected from the linear relationship between LCB and GB values for unsubstituted alkyl ethers (for PhOMe by 3.8 kcal/mol, for $CF_3CH_2OCH{=}CH_2$ by 4.8 kcal/mol, for isoxazole by 2.1 kcal/mol, for 2-methyltetrahydrofuran by 2.4 kcal/mol, and for 2,5-dimethyltetrahydrofuran by 1.8 kcal/mol). If one excludes from the correlation the 9 above-mentioned bases (fluorine-substituted ethers, $(MeOCH_2)_2$, PhOMe, isoxazole, 2-methyl- and 2,5-dimethyltetrahydrofuran), the remaining alkyl ethers have also a reasonable correlation ($R^2 = 0.936$).

The N bases have the worst correlation ($R^2 = 0.504$). This is caused by the fact that we have mixed two very different subfamilies—cyanides with the nitrogen in the sp hybrid state and amines (both acyclic and cyclic) with an sp^2 (or sp^3) nitrogen. Within the subfamilies the correlations between LCB and GB are at least fair. So, the 20 cyanides exhibit good correlation ($R^2 = 0.958$). In the case of amines the correlation is worse ($R^2 = 0.711$ for all amines and 0.720 for cyclic amines). However, when the 6 bidentate bases (1,8-naphthyridine, 2-fluoropyridine, etc.; see ref 11f,g) are excluded, the correlation for cyclic amines improves considerably ($R^2 = 0.865$). Closer inspection of data for the above cyclic amines indicates that we have, in fact, two distinct families of bases: one formed by monodentate six-membered heterocycles and the second formed by monodentate five-membered heterocycles. Both of these families have excellent correlations between LCBs and GBs ($R^2 = 0.987$ and 0.961, respectively).

The sulfur bases (thiols and thioethers) have correlation between GB and LCB with slope 0.289 ± 0.029 and $R^2 = 0.864$.



A B C D E F G H

Figure 1. Correlation between experimental lithium cation basicities (LCB) and gas-phase basicities toward proton (GB): (A) all investigated compounds; (B) alcohols (1, bidentate alchols; 2, alkyl alcohols; 3, $PhCH_2OH$; 4, H_2O); (C) ethers; (D) carbonyl (1) and S=O bases (2); (E) amines; (F) nitrogen heterocycles (1, polydentate bases; 2, pyridines, pyrazines, pyrimidine; 3, pyrazoles, triazoles, imidazoles, thiazole); (G) cyanides; (H) sulfur bases (1, sulfides; 2, thioles; 3, CF_3SSCF_3).

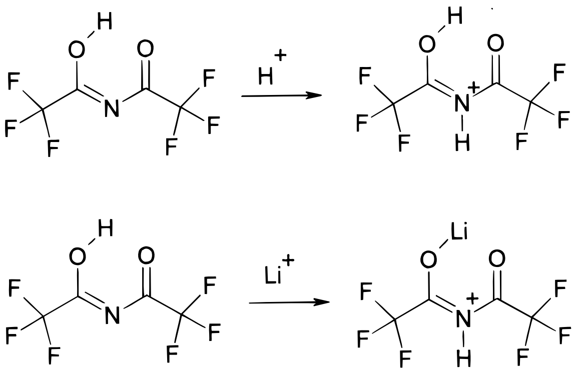


Figure 2. Differences in the mechanism of protonation and lithium cation addition to $(CF_3CO)_2NH$ as seen by our DFT calculations: proton adds directly to the nitrogen atom in the enol form of $(CF_3CO)_2NH$ (a), while Li^+ displaces H^+ at oxygen, and the displaced proton moves to the nitrogen (b).

When one excludes from the correlation $(CF_3S)_2$ (LCB deviating from that expected from the linear relationship between LCB and GB values by 2.2 kcal/mol), which is according to our calculations a strongly chelating in lithium cation complex, the correlation is reinforced ($R^2 = 0.890$).

From the above one can conclude that the existence of different families within correlations between GBs and LCBs is caused by the differences in basicity centers of bases (both differences in electron pair donor atom and donor group), which cause different routes and extents of charge transfer from cation to base. It should also be noted that different subclasses have different sensitivities toward the substituent effects for proton and lithium cation affinity, as attributed by the different slopes in Table 4.

Other causes of the weak correlation between GBs and LCBs are the significant deviation of some particular bases from the family correlations, as some special systems present enhanced Li^+ binding energies with respect to what should be expected from their protonation energies. The origins of such deviations can be classified on the basis of the different types of specific effects, as revealed by our B3LYP/6-311+G** calculations:

•true chelation with the Li^+ cation[4,11g] as in polyfunctional compounds such as $MeOCH_2CH_2OH$ or 1,8-naphthyridine (formation of five, six, etc. membered ring structures; see Figure 3A)

•formation of nonclassical chelates with the Li^+ cation involving fluorine or chlorine atoms in ring formation[4,11g] (see Figure 3B)

•different basicity centers used by the proton and lithium cation to form an adduct ($(CF_3CO)_2NH$; see Figure 2).

Theoretical Calculations of LCB. Numerous theoretical studies[11,20,22] at different levels (ab initio and density functional theory, DFT) have been used to study the structure and thermodynamic properties (including lithium cation affinity) of the interaction between the Li^+ cation and different neutral and anionic bases.

As a rule, such studies have been limited to a fairly small number of similar bases, and limited relationships have been established between experimental and theoretically calculated LCA values.[11h,22d]

However, the major finding is that only the inclusion of electron correlation effects and the use of sufficiently large and flexible polarized diffuse split-valence basis sets can provide the quantitative theoretical reproduction of the experimentally measured LCA values.[22b] Recent papers by Remko[20a,22e,f] and Alcami et al.[11h] indicate that for a limited set of small bases G1, G2(MP2), G2, and CBS-Q methods[15,23] yield LCAs within so-called chemical accuracy (about 2 kcal/mol).

In the present work the gas-phase lithium cation affinities were calculated for 37 compounds at G2 and G2(MP2) levels of theory and for 63 compounds at the DFT B3LYP/6-311+G** level of theory. The results are summarized in Table 5 and in Figure 4.

Comparison of experimentally determined and calculated LCBs (both at 373 K) reveals that G2 and G2(MP2) methods predict LCBs with a reasonable accuracy (average absolute error was in both cases 0.9 kcal/mol). The LCBs, calculated by both of these methods (G2 and G2(MP2)) were within 0.3 kcal/mol (generally within 0.1 kcal/mol), in accordance with earlier results.[11h,20a] So, there is no need to calculate LCBs at more expensive G2 level as the improvement of the results compared to G2(MP2) is negligible.

The correlation analysis of G2 (or G2(MP2)) versus experimental LCB values for all available data (37 compounds) reveals that although the correlation is good ($R^2 = 0.975$), there is some systematic deviation of the calculated LCBs (the slope of the correlation line was 1.14 ± 0.03 and the intercept was −4.58 ± 1.02, instead of regression coefficients 1 and 0 for the ideal

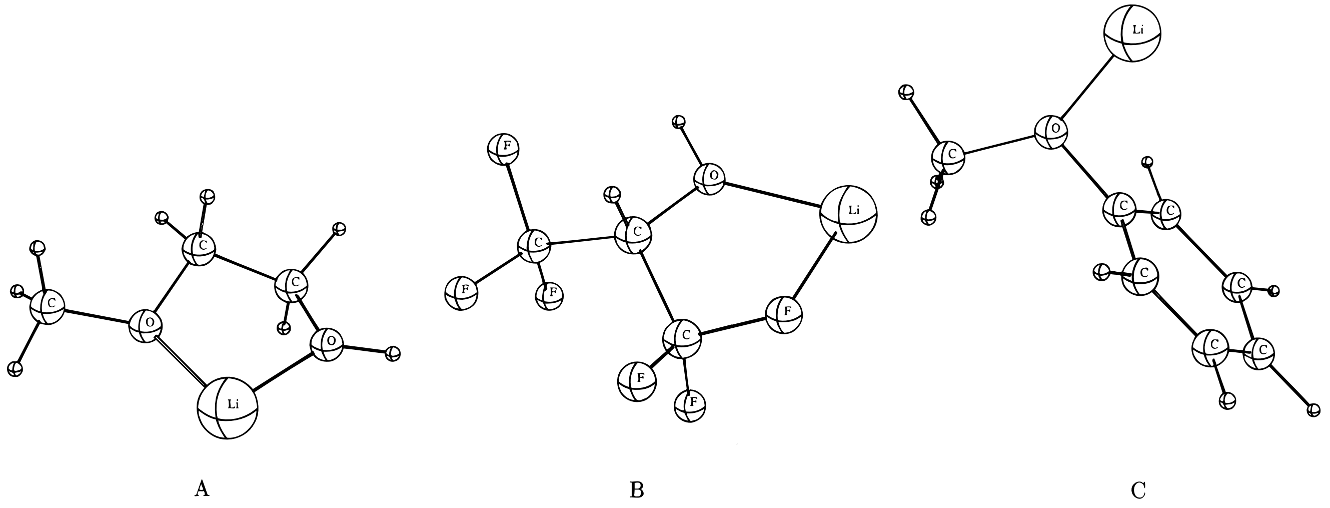


Figure 3. Different types of chelation in Li^+ cation complexes: (A) true chelation with polyfunctional compund ($MeOCH_2CH_2OH-Li^+$); (B) formation of nonclassical chelates involving fluorine or chlorine atoms in ring formation ($(CF_3)_2CHOH-Li^+$); (C) unexpected "chelate structures" ($PhOMe-Li^+$).

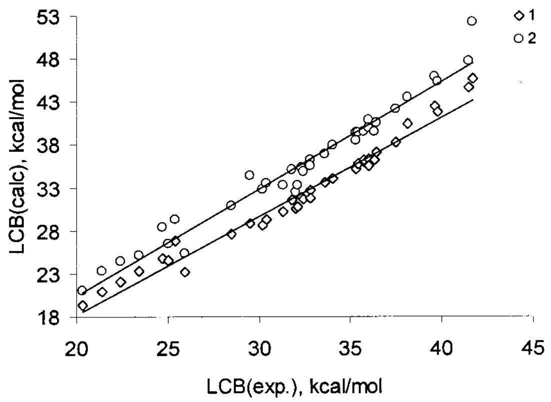


Figure 4. Correlation between experimental lithium cation basicities and lithium cation basicities, calculated at G2 and B3LYP/6-311+G** levels of theory (1, LCBs calculted at G2 level; 2, LCBs calculated at B3LYP/6-311+G** level).

fit of experimental and calculated data) from their experimentally determined counterparts. The standard deviation was 1.05 kcal/mol.

However, one notes that in the region of bases with $\mathrm{LCB}_{\mathrm{exp}}$ < 36 kcal/mol the statistical characteristics of the fit are significantly better: the slope (1.03 ± 0.03) and intercept (−1.43 ± 0.90) are now appreciably closer to their ideal values (1.0 and 0.0). It is currently impossible to say what is the cause of the somewhat nonideal behavior of points with $\mathrm{LCB}_{\mathrm{exp}} > 36$. Absolute measurements of high LCB (>36 kcal/mol) should be useful for deciding if experiments or calculations are at the origin of the "curvature".

LCBs calculated at the B3LYP/6-311+G** level of theory had a larger average unsigned error (3.5 kcal/mol). The systematic error of calculated LCBs was also more significant (the slope of the correlation line was 1.24 ± 0.04, and the intercept was −4.44 ± 1.35) than for the G2 calculated ones. However, the standard deviation of points from the correlation line (calculated versus experimental LCBs, Figure 4) was 1.4 kcal/mol, quite close to that of the G2 results, and the correlation coefficient was only slightly lower than in the previous case ($R^2 = 0.962$). So, one can use the DFT B3LYP/6-311+G** level of theory for quantitative prediction of LCBs, if the above given systematic error is taken into account.

Also, as mentioned above, the extensive lower level calculations (HF/6-31G*, HF/6-31+G*, HF/6-311G*) of LCAs for a large number of molecules were performed for comparison. As a rule, the results of these calculations did not lead to the LCA values, which were in close quantitative correspondence with the experimentally measured values or with those calculated at G2 and B3LYP/6-311+G** levels of theory. However, similar to the aforementioned G2, G2(MP2), and DFT results, in most cases approximate linear relationships between the calculated and experimental LCA values were observed.

Summary

For the first time, the gas-phase lithium cation basicities for 28 compounds were reported.

The anchoring of the absolute scale of lithium cation basicities is revised, and anchoring to the new value based on the experimental LCA value for H_2O[6a] is suggested. As a result, all earlier reported absolute values of LCA should be reduced by 2.6 kcal/mol.

Correlation between gas-phase basicities toward the proton and lithium cation was examined. No general correlation was found for all studied compounds, while satisfactory correlations were found for families with the similar basicity center. The lack of overall correlation is attributed to the widely variable sensitivities in different series to the changes in substituents, as well as to the effects of chelation in some Li^+ adducts and in some cases to the changes in basicity center for different cations.

G2 and G2(MP2) calculations of LCBs for 37 compounds and B3LYP/6-311+G** calculations for LCBs of 63 compounds were carried out. It was found that levels of theory used (G2 and DFT) adequately (but with some systematic error) describe lithium cation binding energies. The results of G2 and G2(MP2) calculations were practically identical, so that there is no need of using a computationally more demanding G2 method for predicting LCBs. Calculated structures reveal the origin of the deviations from the correlation line between gas-phase proton and lithium cation basicities.

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Supporting Information Available: G2, G2(MP2), and B3LYP/6-311+G** energies, enthalpies, and free energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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