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Lithium-Cation and Proton Affinities of Sulfoxides and Sulfones: A Fourier Transform Ion Cyclotron Resonance Study*

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The kinetic method was used for the quantitative determination of lithium-cation affinities by Fourier transform ion cyclotron resonance. This method was applied to a series of XYSO and XYSO$_2$ compounds. Proton basicities of the SO and SO$_2$ compounds were also determined. When comparison is made between Li$^+$ basicities and proton basicities, a linear regression encompassing XYSO and XYSO$_2$ families suggests that Li$^+$ may be bonded in a similar way to the SO and SO$_2$ moieties, that is, to only one oxygen on the latter. PM3 calculations support this hypothesis. © 1997 American Society for Mass Spectrometry (J Am Soc Mass Spectrom 1997, 8, 262–269)

The interaction between organic compounds or biologically active molecules and alkali-metal cations in the gas phase has attracted much attention. Such interactions are important in chemical and biological processes occurring in solution [1]: for example, ion solvation [1a], catalysis [1b], transport through membranes [1c], affinity of active compounds toward receptors, and antibiotic activity [1d]. Furthermore, the corresponding complexes have useful applications in analytical mass spectrometry [2].

Understanding these phenomena necessitates a knowledge of the energetics of the corresponding interactions. Alkali-metal ion affinity scales are a good basis for an analysis and a modeling of such interactions in complex systems. They are also reference data to test the validity of ab initio and semiempirical quantum calculations. Many experimental bonding energies can be found in the exhaustive review by Keesee and Castleman [3]. Most of the reported data were obtained by high-performance mass spectrometry (HPMS) [4], by ion cyclotron resonance (ICR) [5], and later by Fourier transform ion cyclotron resonance (FT-ICR) [6]. There is at present a paucity of quantitative data concerning the interaction in the gas phase of the

lithium cation with molecules relevant to biological processes [7]. In particular, lithium cation bonding to P=O- and S=O-containing compounds has hardly been investigated so far. It is the purpose of the presently initiated studies including this work to fill these gaps and to undertake experimental investigations in this area by using FT-ICR in parallel with molecular orbital calculations.

Data obtained by ICR are based on the equilibrium constant determination of the alkali-metal ion M$^+$ transfer reaction

$$B_1M^+ + B_2 \rightleftharpoons B_1 + B_2M^+ \qquad (1)$$
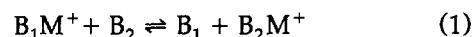
between two neutral bases B$_1$ and B$_2$. Equilibrium constants are derived by measuring ion intensities and neutral partial pressures. As is the case for proton transfer, the application of this method is restricted to sufficiently pure, stable, and volatile compounds. Furthermore, the equilibrium must not be disturbed by secondary reactions, such as the formation of ion-bonded clusters. This problem may be severe when studying alkali-metal ion transfer, as was experienced during an exploratory study of Na$^+$ affinity determinations [8].

Taking advantage of the formation of such ion-bound clusters, Cooks et al. [9] developed a method based on their unimolecular dissociation, referred to as

the kinetic method. This method has been largely used for the study of the thermodynamics of proton transfer, and we have recently discussed its applicability to the determination of gas-phase basicities (GBs) by FT-ICR mass spectrometry [10]. Affinities for various charged species other than the proton and, in particular, affinities for alkali-metal cations, have also been investigated by means of the Cooks method [9].

In the present work we report the determination by the kinetic method of lithium-cation basicity (LCB) and affinity (LCA), corresponding, respectively, to Gibbs energy and enthalpy changes of the reaction

$$BLi^+ \rightarrow B + Li^+ \qquad (2)$$
$$LCB = \Delta_2 G^\circ; \qquad LCA = \Delta_2 H^\circ$$
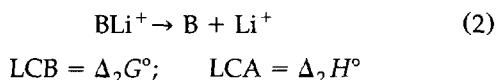
for compounds with the S=O or SO_2 functional group, mainly sulfoxides and sulfones.

Knowledge of the simple interaction of the bare alkali-metal cation with the isolated substrate is important for the understanding of alkali-metal ion effects on mechanisms of nucleophilic reactions on sulfur-based esters in solution [1b]. In this regard, it is interesting to pay attention to the mode of bonding of alkali-metal ions to the $XYSO_2$ derivatives, which can be considered as a possible bidentate ligand. Compounds bearing two basic sites appropriately oriented may exhibit a relatively stronger interaction with Li^+, Na^+, or K^+ than with H^+ [6, 11], as seen, for example, on plots of LCB versus GB. However, our recent PM3 calculations [12] favor the "linear" adduct 1 in Scheme I relative to the bidentate form 2 by about 20 kJ mol^{-1}.

With the aim of identifying a possible bidentate bonding in the $XYSO_2$–Li^+ adducts, we intended to compare the bonding behavior of the $XYSO_2$ and XYSO families toward Li^+ and H^+. Surprisingly, within these series only the proton basicity of dimethyl sulfoxide (DMSO) is known [13]. Therefore, we have also measured, by using the equilibrium method, the GBs of the 10 compounds for which the LCBs have been determined by the kinetic method. Previous PM3 calculations [12] have been extended and compared with the experimental data obtained during the present work.

Experimental

Most of the chemicals were obtained commercially (Sigma-Aldrich-Fluka, St. Quentin Fallavier, France, or Strem, Bischheim, France) and were used without further purification other than degassing reactants by
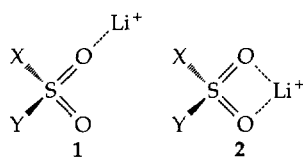
Scheme I

freeze–pump–thaw cycles in the spectrometer inlet system.(p-MePh)MeSO$_2$ and (p-NO$_2$Ph)MeSO$_2$ were supplied by Professor Otto Exner (Prague).
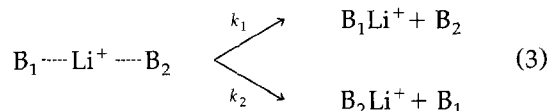
The FT-ICR spectrometer, based on an electromagnet (1.6 T) and a Bruker (Fällanden, Switzerland) CMS 47 console [14], and its use for proton-transfer equilibrium-constant determinations [15] have been described elsewhere.

Li$^+$ Ion Generation

Li$^+$ ions were generated by means of an N$_2$ laser (Laser Science Inc., Cambridge, MA, model VSL 337 ND) desorption–ionization system [16] implemented to our spectrometer. Whereas the handling of pure alkali metals may pose some technical problems, we tried a commercially available 5% Li/95% Al alloy, which is stable to air. A small piece of the alloy was machined and installed as a usual metal target. Because our data system does not handle masses below 12 u, the generation of Li$^+$ was monitored by adding a complexing molecule such as n-PrCN. It should be noted that we have not observed significant signals for Al$^+$ or its adducts. Whereas ionization is necessarily a two-photon event for both metals, Al$^+$ should be produced simultaneously with Li$^+$ ($h\nu = 3.699$ eV; ionization energies of Al and Li are, respectively, 5.986 and 5.392 eV). The enthalpy of vaporization of Li is half that of Al, favoring the lithium desorption–ionization process. If some Al$^+$ ions are produced, they are probably scavenged by charge exchange with the neutral Li atoms.

Collision-Induced Dissociation Experiments

Relative LCBs (ΔLCBs) can be estimated by considering the rates of the unimolecular dissociation of a collisionally activated Li$^+$-bonded dimer,

$$B_1 \cdots Li^+ \cdots B_2 \quad \begin{array}{c} k_1 \nearrow \\ \\ k_2 \searrow \end{array} \quad \begin{array}{c} B_1 Li^+ + B_2 \\ \\ B_2 Li^+ + B_1 \end{array} \qquad (3)$$

and by using the equation

$$\ln(k_1/k_2) = \ln[I(B_1 Li^+)/I(B_2 Li^+)] \approx \Delta LCB/RT \quad (4)$$

This kind of equation, which relies on the assumption of negligible reverse activation energies, was first derived for the proton by using the proton affinity (an enthalpy) as the thermodynamic quantity. It was shown later that it was the Gibbs energy rather than the enthalpy that is in fact linked to the branching ratio [17, 18], provided the reverse entropy barrier is also negligible. The practical use of this equation necessitates knowledge of the temperature T, which is in fact a calibration factor obtained from a plot of the Napierian logarithm of branching ratios versus thermodynamic data. This calibration factor corresponds to

an effective temperature of the dissociating clusters assumed to be constant under controlled experimental conditions. The kinetic method has been largely applied to affinity measurements for ions other than proton [9] and recently, Rice–Ramsperger–Kassel–Marcus calculations have demonstrated the generality of this approach [19]. Therefore, the application of eq 4 to Gibbs energies of Li^+ cation attachment is justified. Li^+-bonded dimers are obtained by allowing the Li^+-generated ions to react with the two neutrals at $1–3 \times 10^{-5} Pa$ partial pressures in the presence of argon for a total pressure of about $1–2 \times 10^{-4}$ Pa. Reaction delays for heterodimer formation are in the range of 1–2 s at these pressures. Selection of the Li^+-bonded dimer was performed in such a way as to minimize uncontrolled excitation of $B_1 \cdots Li^+ \cdots B_2$. Ions of mass close to that of $B_1 \cdots Li^+ \cdots B_2$ were first ejected by using a long and low-amplitude pulse with the aim of avoiding excitation of $B_1 \cdots Li^+ \cdots B_2$. A second ejection step was then carried out in the low mass range of the spectrum by using a short and intense pulse. After isolation, the dimer was accelerated by resonant excitation at a kinetic energy in the range of 3–30 eV.

The maximum kinetic energy imparted to ions is calculated [20] according to

$$E_{k,lab} = q^2 E_0^2 t^2 / 8m \qquad (5)$$

in which q is the elementary charge, t is the rf resonant excitation duration for collisional activation, and m is the ion mass.

The radiofrequency electric field magnitude, E_0, is calculated according to

$$E_0 = V_{0(p-p)} S_{E1}^1 / d \qquad (6)$$

where $V_{0(p-p)}$ is the peak-to-peak voltage amplitude applied between the two excitation plates, d is the diameter of the cylindrical cell, and S_{E1}^1 is a first order correction factor for the effective electric field taking into account the specific geometry of the system [21]. The value $S_{E1}^1 = 0.808593$, applicable in our case, is reported in ref 21b.

The center-of-mass collision energy, $E_{k,cm}$, is calculated according to

$$E_{k,cm} = E_{k,lab}(M_{cg}/M_{cg} + M_{ion}) \qquad (7)$$

where M_{cg} is the mass of the collision gas (argon, in our case) and M_{ion} is the mass of the Li^+-bonded dimer.

After translational excitation, the duration allowed for collision with argon was chosen in the range 5–10 ms to avoid ion–molecule reactions. The dissociation of the Li^+-bonded dimers, according to reaction 3, was monitored as a function of $E_{k,cm}$. Owing to the difficulty of studying all dissociations at the same energy, we decided to extrapolate the quantity $\ln[I(B_1Li^+)/I(B_2Li^+)]$ to zero collision energy for all experiments

by using a linear least-square regression treatment. The low values obtained for the slopes indicate that $\ln[I(B_1Li^+)/I(B_2Li^+)]$ is very weakly sensitive to $E_{k,cm}$ variations, as previously observed for proton-bonded dimers [10].

Results and Discussion

Values extrapolated to zero center-of-mass kinetic energy of the Napierian logarithm of the intensity ratio obtained for 29 Li^+-bonded dimers are reported in the third column of Table 1. These individual measurements, carried out by means of the kinetic method, were combined to form a ladder of uncalibrated relative Li^+ basicities, referenced to n-PrCN (fourth column). Then the data were calibrated, according to eq 4, by using a least-square regression against relative Li^+ basicity data (ΔLCBs in column 5) extracted from the scale of Taft and co-workers [6] that reported Gibbs energies of Li^+ attachment determined by the equilibrium method at 373 K. This treatment leads to the equation

$$\ln[I(B_1Li^+)/I(n\text{-PrCNLi}^+)]$$
$$= (-0.051 \pm 0.355) + (0.302 \pm 0.017)\Delta LCB \qquad (8)$$

where the number of data points $n = 12$, reference data point $(0,0)$ included and DMSO excluded; correlation coefficient $r = 0.9849$; standard deviation sd $= 0.77$. If the regression is forced to a zero intercept ($y = bx$, $n = 11$), an almost identical slope of 0.300 is obtained. When DMSO, for which a LCB value is given in ref 6c, is included in the regression analysis, it deviates significantly. It was therefore excluded from our calculations. Equilibrium measurements on this compound [6c] have probably been hampered by fast dimer formation, leading to an underestimated value (see subsequent text).

Equation 4 is therefore fulfilled and our scale is validated. The slope of eq 8 corresponds to an effective temperature of 398 ± 23 K for the Li^+-bonded dimers, a value not significantly different from that obtained for the proton-bonded dimers under the same FT-ICR conditions [10]. The standard deviation on $\ln[I(B_1Li^+)/I(n\text{-PrCNLi}^+)]$ can be converted into energy units and leads to an uncertainty of about 2.6 kJ mol^{-1}. In the case where several measurements for the same base against different reference compounds were carried out, we observed an overlap error ranging from 0.6 to 2.9 kJ mol^{-1}. Therefore, the general precision of the two methods—kinetic (this work) and equilibrium [6]—appears to be similar.

ΔLCBs of sulfur compounds have been calculated from $\ln[I(B_1Li^+)/I(n\text{-PrCNLi}^+)]$ data in Table 1 through the use of eq 8 and anchored to the absolute LCB of n-PrCN given by Taft et al. The LCB values for sulfur compounds are therefore scaled to the available Li^+ scale [6c] and are reported in the last column of

Table 1. Relative lithium-cation basicities $\ln[I(B_1Li^+)/I(B_2Li^+)]$ obtained by the kinetic method

B_1	B_2	$\ln[I(B_1Li^+)/I(B_2Li^+)]^a$	$\ln[I(B_1Li^+)/I(n\text{-PrCNLi}^+)]^b$	$\Delta LCB(B_1)^c$
n-PrCN			0	0
glycol sulfite	n-PrCN	0.14 ± 0.11	0.14	
i-PrCN	Glycol sulfite	0.47 ± 0.15	0.61	1.67
(p-NO$_2$Ph)MeSO$_2$	n-PrCN	0.24 ± 0.06		
	i-PrCN	0.17 ± 0.10	0.51 ± 0.48	
n-BuCN	Glycol sulfite	0.33 ± 0.08	0.47	2.09
t-BuCN	Glycol sulfite	1.28 ± 0.28		
	i-PrCN	0.35 ± 0.14		
	(p-NO$_2$Ph)MeSO$_2$	0.47 ± 0.10	1.12 ± 0.27	4.60
Me$_2$SO$_2$	t-BuCN	0.84 ± 0.08	1.96	
c-PrCOMe	Me$_2$SO$_2$	0.38 ± 0.12	2.34	8.79
(PhO)MeSO$_2$	t-BuCN	1.32 ± 0.10		
	c-PrCOMe	0.69 ± 0.19	2.74 ± 0.52	
(c-Pr)$_2$CO	(PhO)MeSO$_2$	1.28 ± 0.05	4.02	12.97
(Ph)MeSO$_2$	(c-Pr)$_2$CO	0.86 ± 0.10	4.88	
MeCONH$_2$	(Ph)MeSO$_2$	0.44 ± 0.09	5.32	16.74
(p-MePh)MeSO$_2$	c-PrCOMe	3.58 ± 1.11	5.92	
HCONHMe	(p-MePh)MeSO$_2$	-0.93 ± 0.18	4.99	17.99
Ph$_2$SO$_2$	HCONHMe	1.44 ± 0.22	6.43	
Me$_2$SO (DMSO)	HCONHMe	3.81 ± 0.72		
	(p-MePh)MeSO$_2$	1.42 ± 0.23		
	Ph$_2$SO$_2$	1.20 ± 0.38	7.92 ± 0.86	$(20.5)^d$
HCONMe$_2$	Me$_2$SO	-0.29 ± 0.10	7.63	25.94
(Ph)MeSO	HCONMe$_2$	1.70 ± 0.13	9.33	
MeCONMe$_2$	HCONMe$_2$	2.24 ± 0.07		
	Me$_2$SO	1.66 ± 0.11		
	(Ph)MeSO	0.27 ± 0.07	9.68 ± 0.17	31.38
Ph$_2$SO	MeCONMe$_2$	0.90 ± 0.10	10.58	
(CH$_2$OMe)$_2$	Ph$_2$SO	-0.07 ± 0.15	10.51	40.17
(MeO)$_3$PO	Ph$_2$SO	1.72 ± 0.09	12.30	35.15

[a] Reported uncertainties correspond to the standard deviation on the intercept of the regression $\ln[I(B_1Li^+)/I(B_2Li^-)]$ versus the center-of-mass kinetic energy $E_{k,cm}$.

[b] Values relative to n-PrCN are obtained from individual measurements in column 3. Reported uncertainties correspond to the standard deviation estimated from the range of values obtained from different reference bases.

[c] Lithium-cation basicities, in kilojoules per mole, obtained by the equilibrium method in Professor Taft's Laboratory [ref 6c, except (CH$_2$OMe)$_2$, LCB = 199.58 kJ/mol; unpublished datum, personal communication]. For the sake of consistency with data in column 4, ΔLCBs are referenced to n-PrCN.

[d] Not included in eq 8; see text.

Table 2. For DMSO, the kinetic method leads to a LCB value about 6 kJ mol^{-1} larger than the equilibrium value previously reported by Taft et al.

With the exception of DMSO, no proton gas-phase basicity was known for the sulfur–oxygen-containing compounds studied here. Our proton-transfer equilibrium measurements are given in Table 2, column 3, and are converted to absolute GBs by using literature data at 298 K for the reference compounds [13].

A perusal of the data shows that the replacement of a methyl by a phenyl increases the basicity and that the basicity tends to decrease as the number of oxygen atoms linked to the sulfur increases. The general trend in basicity toward Li$^+$ and H$^+$ is very similar within the series and can be expressed through the regression

equation

$$LCB = (-62.0 \pm 18.6) + (0.292 \pm 0.023)GB$$
$$n = 10, r = 0.9766, sd = 2.7 \text{ kJ mol}^{-1} \quad (9)$$

Comparatively, slightly larger slopes were obtained for carbonyls (0.4) [22] and for nitrogen-containing heterocycles (0.4–0.5) [6a, b]. The correlation coefficient and the standard deviation reveal some scatter. In fact, a plot of these data (Figure 1) shows that all the data points for XYSO$_2$ compounds lie slightly above a line drawn through the data points for the S=O derivatives ($r = 0.9980$, sd = 1.2 kJ mol^{-1}). This enhancement of Li$^+$ bonding energy (XYSO$_2$ compared to XYSO) ranges from 2.1 kJ mol^{-1} for (p-NO$_2$Ph)MeSO$_2$ to 7.6 kJ

Table 2. Gas-phase basicities in kilojoules per mole from proton-transfer equilibrium measurements and lithium basicities obtained by using the kinetic method

B$_1$	B$_2$	$\Delta_1 G^\circ$ (338 K)[a]	GB(B$_1$)[b]	LCB(B$_1$)[c]
Glycol sulfite	n-PrCHO	8.20 ± 0.21		
	n-BuCHO	2.05 ± 0.21		
	n-BuCN	−3.26 ± 0.17	776.0 ± 1.0	160.0
(p-NO$_2$Ph)MeSO$_2$	n-PrCHO	5.06 ± 0.08		
	n-PrSH	0.42 ± 0.29		
	Me$_2$O	2.38 ± 0.08	772.4 ± 2.5	161.3
Me$_2$SO$_2$	i-PrCHO	5.86 ± 0.42		
	n-PrCN	5.02 ± 0.42		
	t-BuCN	−6.02 ± 0.42	780.3 ± 1.7	166.1
(PhO)MeSO$_2$	i-PrCHO	3.93 ± 0.14		
	HCO$_2$Et	2.38 ± 0.24		
	n-PrCN	2.09 ± 0.03		
	i-PrCN	−1.67 ± 0.13	778.0 ± 1.0	168.7
(Ph)MeSO$_2$	MeCOEt	4.24 ± 0.01		
	Et$_2$O	−0.17 ± 0.25		
	MeCO$_2$Et	−1.13 ± 0.04	806.1 ± 1.6	175.7
(p-MePh)MeSO$_2$	Et$_2$O	9.81		
	Et$_2$CO	5.08 ± 0.12		
	Cyclohexanone	0.90 ± 0.50		
	t-BuCOMe	1.38 ± 0.11	813.6 ± 1.2	179.2
Ph$_2$SO$_2$	(i-Pr)$_2$CO	1.59 ± 0.42		
	c-PrCOMe	0.69 ± 0.08		
	(i-Pr)$_2$O	−1.76 ± 0.17	827.2 ± 1.2	180.9
Me$_2$SO (DMSO)	2-Fluoropyridine	0.84 ± 0.20		
	Pyrimidine	−3.77 ± 0.27		
	HCONMe$_2$	−1.34 ± 0.18	849.4 ± 1.5 (851.4)[d]	185.8 (179.9)[e]
(Ph)MeSO	2-Chloropyridine	2.72 ± 0.10		
	2-Bromopyridine	−0.84 ± 0.14		
	MeCONMe$_2$	−4.60 ± 0.27	866.6 ± 1.0	190.5
Ph$_2$SO	n-PrNH$_2$	5.44 ± 0.09		
	n-BuNH$_2$	1.67 ± 0.23		
	n-C$_6$H$_{13}$NH$_2$	−1.26 ± 0.39	883.1 ± 1.5	194.6

[a]Gibbs energy for reaction 1. Reported uncertainties correspond to standard deviation on three to five determinations of K.
[b]From GB(B$_2$) at 298 K in ref 13; no temperature correction. Reported uncertainties correspond to the standard deviation estimated from the range of values obtained from different reference bases.
[c]Lithium-cation basicities, in kilojoules per mole, inferred from the calibration equation 8. Anchor value for the scale in ref 6c: LCB(n-PrCN) = 159.4 kJ/mol.
[d]Value in parentheses, ref 13.
[e]Value in parentheses, from equilibrium measurements, ref 6c; see text.

mol^{-1} for (PhO)MeSO$_2$, with a mean value of about 5 kJ mol^{-1}. Chelation effects reported for nitrogen heterocycles are in the range of about 20–40 kJ mol^{-1}. Oxygen ligands exhibit a similar behavior. For example, 2,4-pentanedione exhibits a Li$^+$ basicity enhancement of about 17 kJ mol^{-1} [6d]. It is worth noting that the structure of this compound offers a favorable geometry for the chelation of H$^+$ as well as of Li$^+$. Therefore, the Li$^+$-bonding energy enhancement of about 5 kJ mol^{-1} observed for XYSO$_2$ compounds seems to be too small to be attributed to a chelating effect. This observation is in line with our previous PM3 calculations [12], which led to the conclusion that

the chelate structure 2 is energetically unfavorable by about 20 kJ mol^{-1}.

A comparison between calculated and experimental LCAs for the whole series of compounds studied here is in order. Experimental LCAs may be inferred from LCBs (373 K) in Table 2, by estimating the $T \Delta S$ term for reaction 2:

$$\Delta_2 S = S(B) - S(BLi^+) + S(Li^+) \qquad (10)$$

The entropy of the lithium cation is calculated from the Sackur–Tetrode equation:

$$S\left({}_3^7Li^+, 373 \text{ K}, 10^5 \text{ Pa}\right) = 137.81 \text{ J K}^{-1} \text{ mol}^{-1} \qquad (11)$$
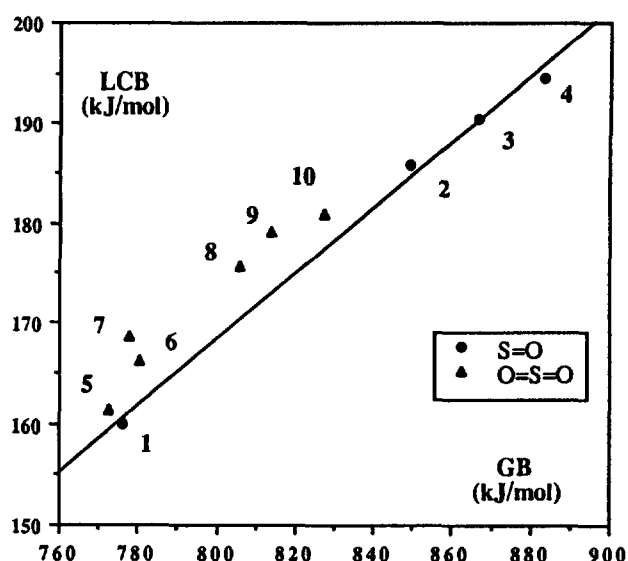
Figure 1. Plot of lithium-cation basicities obtained by the kinetic method versus gas-phase basicities obtained by the equilibrium method, with the line drawn through the points for the S=O derivatives [1, glycol sulfite; 2, Me$_2$SO; 3, (Ph)MeSO; 4, Ph$_2$SO]. The points for the O=S=O compounds lie above [5, (p-NO$_2$Ph)MeSO$_2$; 6, Me$_2$SO$_2$; 7, (PhO)MeSO$_2$; 8, (Ph)MeSO$_2$; 9, (p-MePh)MeSO$_2$; 10, Ph$_2$SO$_2$].

The $S(B) - S(BLi^+)$ term may be dissected into its translational, vibrational, and rotational components. In the case of bases having masses much larger than Li$^+$, the translational term may be neglected (for example, this term is equal to -1.1 J K^{-1} mol^{-1} for DMSO). As proposed by Woodin and Beauchamp [5c], the vibrational term is considered as constant within the series. The value used here (-32.8 J K^{-1} mol^{-1}) is obtained from the calculated frequencies (MP2/6-31 + G*) of More et al. [23] for dimethyl ether and its Li$^+$

adduct and by using tabulated vibration entropies for harmonic oscillators [24]. The rotational component involves changes of both symmetry numbers and moments of inertia. Considering the large masses of the sulfur compounds studied, the latter term may be neglected. Here, the problem of symmetry change upon Li$^+$ addition is relevant only for the XYSO$_2$ derivatives when structure 1, which was found to be the most stable by PM3 calculations, is considered. Therefore, for XYSO$_2$ compounds, a gain of local symmetry of order 2 upon dissociation of the adduct is taken into account: $S_{rot}(B) - S_{rot}(BLi^+) = -R \ln 2$. Uncertainty in entropy is estimated to be less than 10 J K^{-1} mol^{-1}, or less than 4 kJ mol^{-1} in the correction term.

LCBs at 373 K are transformed into LCAs at 373 K by adding a $T \Delta S$ term equal to 39.2 and 37.0 kJ mol^{-1} for XYSO and XYSO$_2$, respectively. These "experimental" LCAs at 373 K are listed in Table 3 together with the corresponding PM3-calculated values at 298 K. At this point, we think it is not useful to correct further the experimental LCAs to 298 K. This would necessitate a temperature correction of the reference LCB scale [6c] to 298 K, which is outside the scope of the present work.

Experimental and PM3 calculated PAs (at 298 K) are also reported in Table 3. Experimental PAs are derived from GB values in Table 2 by adding a $T \Delta S$ term equal to 32.5 kJ mol^{-1}, which corresponds to the translation of the proton. All other terms are neglected except a symmetry correction of $-R \ln 2$ for the XYSO$_2$ derivatives. If experimental LCAs and PAs are compared, we obtain the regression equation

$$LCA_{exp} = (-43.9 \pm 15.3) + (0.305 \pm 0.018)PA_{exp}$$
$$n = 10, \ r = 0.9862, \ sd = 2.2 \ kJ \ mol^{-1} \quad (12)$$

SO$_2$ has been excluded from the set of compounds

Table 3. Experimental and theoretical proton affinities and lithium-cation affinities

| B$_1$ | Pa[a] | | Error in calc. PA | LCA[a] | | Error in calc. LCA |
	Exp.	Calc. (PM3)		Exp.	Calc. (PM3)	
SO$_2$	636.4[b]	758.1[c]	121.7	129.9[d]	145.6[c]	15.7
Me$_2$SO (DMSO)	881.9	883.7[c]	1.8	225.0	208.4[c]	−16.6
	884.1[b]			219.1[e]		
(Ph)MeSO	899.1	921.3	22.2	229.7	211.3	−18.4
Ph$_2$SO	915.6	934.7	19.1	233.8	212.1	−21.7
Glycol sulfite	808.5	823.4	14.9	199.2	168.6	−30.6
Me$_2$SO$_2$	811.1	866.9[c]	55.8	203.1	182.0[c]	−21.1
(p-NO$_2$Ph)MeSO$_2$	803.2	854.4	51.2	198.3	162.3[c]	−36.0
(p-NO$_2$Ph)MeSO$_2$		(738.9)[f]			(98.7)[f]	
(Ph)MeSO$_2$	836.9	896.2[c]	59.3	212.7	191.2[c]	−21.5
(p-MePh)MeSO$_2$	844.4	902.5[c]	58.1	216.2	195.0[c]	−21.2
Ph$_2$SO$_2$	858.0	922.6[c]	64.6	217.9	203.3[c]	−14.6
(PhO)MeSO$_2$	808.8	852.7[c]	43.9	205.7	161.9[c]	−43.8

[a]This work, unless otherwise stated.
[b]Ref 13.
[c]Ref 12. Calculated LCAs correspond to structure 1, Scheme 1, in the case of XYSO$_2$Li$^+$ adducts.
[d]Unpublished value from R. W. Taft.
[e]From LCB in ref 6c.
[f]This work, corresponding to protonation or lithium-cation attachment to the NO$_2$ group.

used for the establishment of this equation. Its LCA, which is back-calculated from eq 12 (150 kJ mol^{-1}), exceeds the reported experimental value by about 20 kJ mol^{-1}. This discrepancy may indicate a different behavior from that of the sulfones, or a specific experimental problem [6d].

PM3-calculated LCAs reported in Table 3 correspond to structure 1 in Scheme I for the XYSO$_2$ compounds (smaller affinities were obtained when structure 2 in Scheme I was considered). When compared with experimental LCAs, the theoretical data appear to be underestimated, with the exception of SO$_2$. The largest deviations are observed for the weakest bases: (PhO)MeSO$_2$, (p-NO$_2$Ph)MeSO$_2$, and glycol sulfite. For the seven remaining compounds, the following regression equation, which exhibits a slope fairly close to 1, is obtained:

$$LCA_{PM3} = (-30.2 \pm 25.8) + (1.05 \pm 0.12)LCA_{exp}$$

$$n = 7, r = 0.9701, sd = 3.0 \text{ kJ mol}^{-1} \quad (13)$$

The precision of this regression, similar to that obtained for proton affinities within families of homologous compounds by using PM3 [25] or AM1 [26] calculated values, supports the hypothesis of a similar mode of bonding between Li$^+$ and XYSO and XYSO$_2$ derivatives. PM3 PAs appear to be overestimated. This kind of systematic deviations is not unusual when semiempirical methods are used [27]. The deviations are significantly larger for the XYSO$_2$ compounds (> 43 kJ mol^{-1}) than for the XYSO derivatives (< 23 kJ mol^{-1}).

Note that the nitro group in (p-NO$_2$Ph)MeSO$_2$ is calculated to be significantly less basic toward H$^+$ and Li$^+$ than is the SO$_2$ moiety, and it was not considered as the effective basic site in this study. For proton affinity, it is possible to confirm the preferred site of protonation by taking into account PM3-calculated substituent effects and experimental data. This is equivalent to correcting the systematic error of the semiempirical results, as was done in an FT-ICR/AM1 study of substituted anilines [28]. The estimated PAs for the two potential basic sites in (p-NO$_2$Ph)MeSO$_2$ are obtained by adding the difference in PM3 PAs, PA[(p-NO$_2$Ph)MeSO$_2$] − PA[(Ph)MeSO$_2$] and PA[(p-MeSO$_2$)PhNO2] − PA[PhNO$_2$], to the experimental PAs for (Ph)MeSO$_2$ and PhNO$_2$, respectively. This leads to an estimated PA for the protonation on the SO$_2$ site (795.1 kJ mol^{-1}) much closer to the experimental value (803.2 kJ mol^{-1}) than is the PA estimated for protonation on the NO$_2$ site (773.6 kJ mol^{-1}). For lithium-cation affinity, the same empirical correction applied to the LCA calculated for the sulfonyl site leads to a value of 183.8 kJ mol^{-1}, which is in fair agreement with the experimental value (198.3 kJ mol^{-1}). The experimental LCA for nitrobenzene is lacking and it is not possible to make a similar correction for Li$^+$ attachment to the NO$_2$ group. However,

the $\sim$ 100-kJ mol^{-1} correction needed to bring the PM3-calculated value close to the experimental determination is very unlikely.

Concluding Remarks

So far, the kinetic method applied to FT-ICR has been used quantitatively for the determination of proton affinities [29] or gas-phase basicities [10], but qualitatively only for the determination of metal ion affinities [30]. This quantitative approach was applied to a series of XYSO and XYSO$_2$ compounds to which the equilibrium method cannot be applied due to the rapid formation of clusters. This phenomenon is much more frequently encountered for alkali-metal ions than for proton. In fact, for the compounds studied here, it was possible to determine the gas-phase basicities by the equilibrium method. When LCBs are plotted against GBs, all the SO$_2$-containing compounds are found to exhibit a small positive deviation from a line drawn solely through the points for the S=O derivatives, but the magnitude ($\sim$ 5 kJ mol^{-1}) of this deviation is appreciably smaller than would be expected on the basis of bidentate binding (structure 2 in Scheme I). Our tentative conclusion is that the two series of XYSO and XYSO$_2$ derivatives behave effectively as a single family when proton and lithium-cation basicities (or affinities) are compared, Li$^+$ probably being bonded to only one oxygen of the SO$_2$ moiety. PM3 calculations also favor structure 1 in Scheme I as the lowest energy form [12]. In an endeavor to reproduce more accurately the Li$^+$ affinities, ab initio calculations are underway on compounds of reasonable size and flexibility.

Acknowledgments

References

1. (a) Castleman, A. W.; Keesee, R. G. Acc. Chem. Res. 1986, 19, 413–419; Gal, J.-F.; Maria, P.-C. Prog. Phys. Org. Chem. 1990, 17, 159–238; (b) Nagelkerke, R.; Pregel, M. J.; Dunn, E. J.; Thatcher, G. R. J.; Buncel, E. Org. React. (Tartu) 1995, 24, 11–18; Pregel, M. J.; Dunn, E. J.; Nagelkerke, R.; Thatcher, G. R. J.; Buncel, E. Chem. Soc. Rev. 1995, 24, 449–455; (c) Kumpf, R. A.; Dougherty, D. A. Science 1993, 261, 1708–1710; (d) Cox, B. G.; Schneider, H. Coordination and Transport Properties of Macrocyclic Compounds in Solution; Elsevier: New York, 1992.

2. Bombick, D.; Pinkston, J. D.; Allison, J. Anal. Chem. 1984, 56, 396–402; Bombick, D.; Allison, J. Anal. Chem. 1987, 59, 458–466; Fujii, T. Anal. Chem. 1992, 64, 775–778; Teesch,

L. M.; Adams, J. *Org. Mass Spectrom.* **1992**, *27*, 931–943; Teesch, L. M.; Adams, J. In *Experimental Mass Spectrometry*; Russel, D. H., Eds.; Plenum: New York, 1994; Summerfield, S. G.; Dale, V. C. M.; Despeyroux, D.; Jennings, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 10093–10097.

3. Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011–1071.

4. Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445–476; Magnera, T. F.; Caldwell, G.; Sunner, J.; Ikuta, S.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 6140–6146; Guo, B. C.; Conklin, B. J.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6506–6510, and references therein.

5. (a) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920–5921; (b) Hodges, R. V.; Beauchamp, J. L. *Anal. Chem.* **1976**, *48*, 825–829; (c) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501–508; (d) Woodin, R. L.; Beauchamp, J. L. *Chem. Phys.* **1979**, *41*, 1–9.

6. (a) Anvia, F.; Walsh, S.; Capon, M.; Koppel, I. A.; Taft, R. W.; de Paz, J. L. G.; Catalan, J. *J. Am. Chem. Soc.* **1990**, *112*, 5095–5097; (b) Alcami, M.; Mo, O.; Yañez, M.; Anvia, F.; Taft, R. W. *J. Phys. Chem.* **1990**, *94*, 4796–4804; (c) Taft, R. W.; Anvia, F.; Gal, J.-F.; Walsh, S.; Capon, M.; Holmes, M. C.; Hosn, K.; Oloumi, G.; Vasanwala, R.; Yazdani, S. *Pure Appl. Chem.* **1990**, *62*, 17–23; (d) unpublished data from Pr. R. W. Taft Laboratory.

7. Liou, C.-C.; Brodbelt, S. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 543–548; Bojesen, G.; Breindahl, T.; Andersen, U. N. *Org. Mass Spectrom.* **1993**, *28*, 1448–1452; Chen, Q.; Cannel, K.; Nicoll, J.; Dearden, D. V. *J. Am. Chem. Soc.* **1996**, *118*, 6335–6344.

8. Maria, P.-C.; Anvia, F.; Taft, R. W. Presented at Techniques et Mécanismes de Formation des Ions, Soc. Fr. Chim., Soc. Fr. Spectrom. Masse, Paris, 22–24 November 1992.

9. Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287–339.

10. Decouzon, M.; Gal, J.-F.; Herreros, M.; Maria, P.-C.; Murrel, J.; Todd, J. F. J. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 242–245.

11. (a) Alcami, M.; Mo. O.; Yañez, M. *J. Phys. Chem.* **1989**, *93*, 3929–3936; (b) Mo, O.; Yañez, M. *Trends Phys. Chem.* **1992**, *3*, 81–105.

12. Gal, J.-F.; Koppel, I.; Kurg, R.; Maria, P.-C. *Int. J. Quantum Chem.* **1996**, *59*, 409–420.

13. Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–806; Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1; NIST Positive Ion Energetics Database, Version 1.1, NIST Standard Reference Database 19A, Gaithersburg, MD, 1990.

14. Decouzon, M.; Gal, J.-F.; Géribaldi, S.; Maria, P.-C.; Rouillard, M. *Spectra 2000* **1989**, *17*, 51–57.

15. Berthelot, M.; Decouzon, M.; Gal, J.-F.; Laurence, C.; Le Questel, J.-Y.; Maria, P.-C.; Tortajada, J. *J. Org. Chem.* **1991**, *56*, 4490–4494.

16. Decouzon, M.; Gal, J.-F.; Géribaldi, S.; Rouillard, M.; Sturla, J.-M. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 298–299; Breton, S. Thesis, University of Nice-Sophia Antipolis, 1995.

17. Majumdar, T. K.; Clairet, F.; Tabet, J.-C.; Cooks, G. *J. Am. Chem. Soc.* **1992**, *114*, 2897–2903.

18. Wu, Z.; Fenselau, C. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 777–780.

19. Craig, S. L.; Zhong, M.; Choo, B.; Brauman, J., unpublished.

20. (a) Comisarow, M. B. *J. Chem. Phys.* **1978**, *69*, 4097–4104; (b) Marshall, A. G.; Roe, D. C. *J. Chem. Phys.* **1980**, *73*, 1581–1590.

21. (a) Kofel, P.; Alleman, M.; Kellerhals, H. P.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 1–12; (b) Kofel, P. Thesis, University of Bremen, 1987.

22. Gal, J.-F.; Taft, R. W.; McIver, R. T., Jr. *Spectrosc. Int. J.* **1984**, *3*, 96–104.

23. More, M. B.; Glendening, E. D.; Ray, D.; Feller, D.; Armentrout, P. B. *J. Phys. Chem.* **1996**, *100*, 1605–1614.

24. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

25. Notario, R.; Herreros, M.; Ballesteros, E.; Essefar, M.; Abboud, J.-L. M.; Sadekov, I. D.; Minkin, V. L.; Elguero, J. *J. Chem. Soc. Perkin Trans. 2* **1994**, 2341–2344.

26. Gal, J.-F.; Leito, I.; Maria, P.-C.; Raczynska, E. D.; Taft, R. W.; Anvia, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1995**, *92*, 22–36.

27. Dewar, M. J.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075–8086.

28. Maria, P.-C.; Leito, I.; Gal, J.-F.; Exner, O.; Decouzon, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 394–401.

29. Campbell, S.; Marzluff, E. M.; Rodgers, M. T.; Beauchamp, J. L.; Rempe, M. E.; Schwinck, K. F.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1994**, *116*, 5257–5264.

30. (a) Operti, L.; Tews, E. C.; Freiser, B. *J. Am. Chem. Soc.* **1988**, *110*, 3847–3853; (b) Operti, L.; Vaglio, G. A.; Gord, J. R.; Freiser, B. S. *Organometallics* **1991**, *10*, 104–111.