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Free energies of cation–molecule complex formation and of cation–solvent transfers (ref. 1)

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Abstract - The effects of molecular structure on gas phase basicity toward Li^+ has been extensively studied. It is shown that both the magnitudes and the basicity orders differ markedly from the corresponding gas phase bacisities toward H^+. An analysis of these results is presented together with some preliminary comparisons of basicity orders observed in other adducts having largely electrostatic bonds, i.e., for Al^+, K^+, Mn^+, and neutral hydrogen-bond donors. Implications to ionic solvation energies of the differing basicity orders are considered.

INTRODUCTION

This work is concerned particularly with the basicities of neutral inorganic and organic ligands toward H^+ and Li^+ in gas phase, free of solvent and counter ion influences. The two Lewis acids H^+ and Li^+ present a marked contrast in the nature of the bond formed with the ligand (ref. 2). The proton adds to the base giving a polar covalent σ bond with a residual positive charge on the hydrogen atom of ca. 0.35 or less electronic units, the base molecule having to accommodate the balance of the charge (ref. 3). The large degree of charge transfer results from the fact that H^+ is a bare nucleus, with a very stable unfilled 1s orbital. A major energetic consideration is the ease of removal of electronic charge to form the shared pair bond. Accordingly, the basicities decrease markedly in the sequence, NH_3>>OH_2>>FH (overall decrease 87 kcal/mol, ref. 4) and in the sequence PH_3>> SH_2>>ClH (overall decrease 54 kcal/mol, ref. 4). In contrast, the bonds formed by Li^+ with its filled 1s shell) are largely ionic and the Li^+ retains 0.8 to 0.9 of the positive charge in its adducts (ref. 3). Ab initio calculations by Jorgensen (ref. 5) agree satisfactorily with the available relative basicities, showing for Li^+ that there is the same basicity order for the hydrides but now differences over-all in the first sequence are only 17 kcal/mol, and in the second only 12. kcal/mol, in accord with the small extent of electron transfer in the Li^+ adducts.

We have made a global study of Li^+ basicities for organic bases for several reasons. First, we wished to establish whether or not there is any reasonably general correlation of basicities toward H^+ and Li^+. In this we were motivated by the notion that the widely different bonding types should lead to widely varying basicity orders, a matter needing clarification and analysis of the effects of molecular structure that are involved. Second, the Li^+ basicities are useful in developing organic synthetic procedures and have relevance to the relative solubilities of Li^+ salts in various solvents. The basicities toward Li^+ and other alkali ions also provide important biomedical and physicological information related to understanding of alkali metal ion channels and medical treatments. Third, a knowledge of the different effects of molecular structure for different bonding types can provide improved understanding of the changes in basicities that are observed in solution. The basicities toward Li^+ have been analyzed by both empirical and ab initio theoretical methods.

In addition to gas phase basicities toward Li^+, we also report some preliminary basicity comparisons for the corresponding K^+, Al^+, Mn^+ and hydrogen-bond donor adducts.

$$-\Delta G_{H^+} \quad \text{vs.} \quad -\Delta G_{Li^+}$$

The standard free energies of H^+ adduct formation in the gas phase ($B{:}+H^+ \rightleftharpoons BH^+$) are given by $-\Delta G_{H^+}$ and those for Li^+ adduct formation ($B{:} + Li^+ \rightleftharpoons BLi^+$) by $-\Delta G_{Li^+}$. These values are obtained from experimental determinations of series of relative basicity ($\delta\Delta G$) measurements (refs. 4a and 6). The $\delta\Delta G$ values have been converted to $-\Delta G_{H^+}$ and $-\Delta G_{Li^+}$ values using for $B = NH_3$ the standard values of 195.6 (ref. 4b) and 32.1 (ref. 7), kcal/mol, respectively.

The first comparison of experimental basicities toward H^+ and Li^+ (ref. 8) involved 29 molecules, generally of small size. Nineteen organic functional groups were represented,

most by only one or two members. A linear correlation of slope ~3 for H^+ vs. Li^+ was obtained for 16 of the bases. The remaining 13 bases all give (in a scattered fashion) enhanced basicities toward the H^+ that were attributed to the greater covalent bonding of the H^+. The conclusion that Li^+ offers an immediate contrast to H^+ in both the magnitude and relative ordering of basicity was supported subsequently by comparisons of experimental and calculated values for 11 bases. (ref. 7).

An ab initio theoretical (HF/3-21G) study followed (ref. 9) including 21 small molecules containing only H, C, N, O and F atoms and it was concluded that the H^+ vs. Li^+ affinities plotted to give a reasonable correlation. Another ab initio (631G*/3-21G) theoretical study (ref. 5) of 20 small base molecules, eight of which involved additions to Cl, S, or P atoms, concluded that H^+ and Li^+ affinities cannot be simply compared to elucidate the general nature of acid-base interactions, since there is considerable scatter in the correlation of these two affinities. The scatter results from the different bonding types (ref. 2). These ab initio studies give the best available gas-phase structures and are in agreement that the different bonding types give different changes in molecular structure for Li^+ than H^+ adduct formation.

Figure 1 is a plot for 110 typical bases of ΔG_{Li^+} values (ref. 10) vs. corresponding $-\Delta G_{H^+}$ (cf. Table 1). There is indeed little general correspondence between the basicities toward Li^+ and H^+, especially between different families of functional groups. Brief summaries of the results of our analysis of the causes of the non-linear basicities of this pair and other adducts follow.

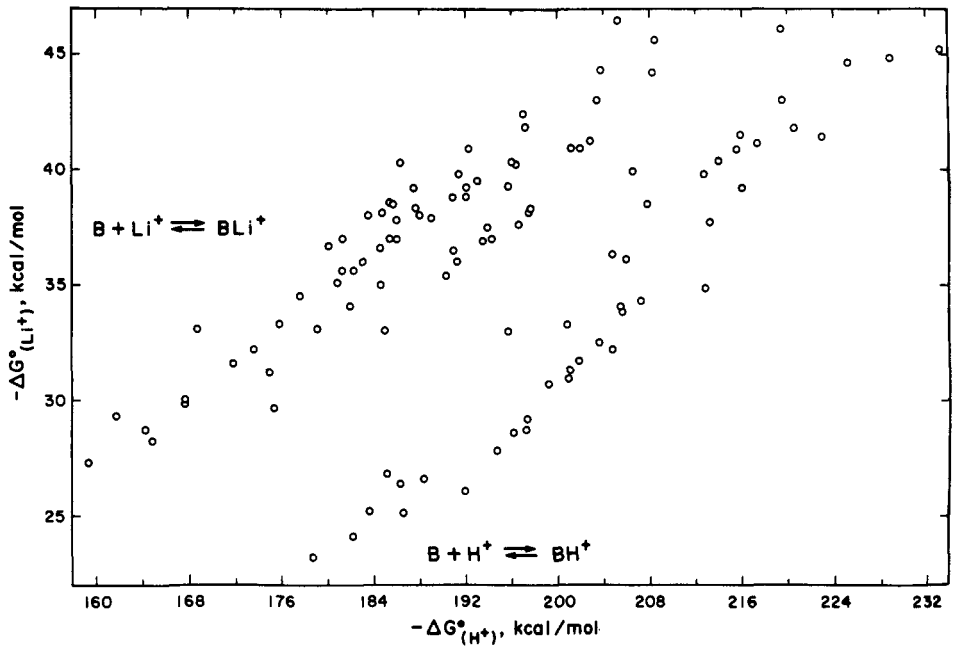

Figure 1.

TABLE 1. Values of $-\Delta G_{H^+}$ and $-\Delta G_{Li^+}$[a] (in kcal/mol, all values uncorrected)

Base[b]	$-\Delta G_{H^+}$	$-\Delta G_{Li^+}$	Base[b]	$-\Delta G_{H^+}$	$-\Delta G_{Li^+}$
MeSH	178.7	23.2	PrOH	182.0	34.1
EtSH	182.2	24.1	$MeNH_2$	205.4	34.1
iPrSH	185.5	25.1	3-Clpyr	207.1	34.3
PrSH	183.6	25.2	MeCHO	177.6	34.5
Me2S	191.9	26.1	Me_2NH	212.7	34.9
iBuSH	185.3	26.4	Me_3N	217.6	34.8
tBuSH	188.3	26.6	iPrOH	184.6	35.0

TABLE 1. (continued)

Base[b]	$-\Delta G_{H^+}$	$-\Delta G_{Li^+}$	Base[b]	$-\Delta G_{H^+}$	$-\Delta G_{Li^+}$
BuSH	185.1	26.8	HCO_2Me	180.9	35.1
H_2O	159.4	27.3	iBuOH		35.2
EtSMe	194.7	27.8	THF	190.4	35.4
H_2CO	164.8	28.2	$MeOCH_2CN$		35.6
$(CH_2)_4S$	196.1	28.6	EtCHO	181.2	35.6
$(CH_2)_5S$	197.3	28.7	BuOH	182.3	35.6
HCN	164.2	28.7	neo-C_5H_9OH		35.8
Et_2S	197.2	29.2	s-BuOH		35.9
CF_3CH_2OH	161.8	29.3	PrCHO	183.0	36.0
CF_3COMe	167.6	29.8	Et_2O	191.3	36.0
C_6H_6	175.3	29.7	thiaz	205.9	36.1
Cl_3CCHO	167.6	30.0	pyz	204.7	36.3
MeOH	174.9	31.2	MeCOSMe	191.0	36.5
pyrazine	201.3	31.3	CF_3CONH_2		36.6
iPr_2S	201.8	31.7	HCO_2Et	184.6	36.6
CF_3CO_2Me	171.8	31.6	2-MeTHF	194.3	37.0
Pr_2S	199.1	31.7	CH_3CN	180.1	36.7
$ClCH_2CN$	173.6	32.2	t-BuOMe	193.5	36.9
Me_2O	183.9	32.3	1-Mepyz	208.8	37.0
3-CF_3pyr	204.7	32.2	HCO_2Pr	185.8	37.0
pyrimd	203.6	32.5	$MeSCH_2CN$	181.4	37.0
dioxane	185.1	33.0	c-$C_6H_{11}CH_2OH$	185.4	37.0
NH_3	195.6	33.0	HCO_2Bu	186.0	37.0
CCl_3CH_2OH	168.8	33.1	Pr_2O	193.9	37.5
EtOH	179.8	33.1	2,2'-diMeTHF	196.6	37.6
CF_3CO_2Et	179.8	33.3	pyr	213.2	37.7
Bu_2S	200.8	33.3	$PhCH_2CN$	186.1	37.8
t-Bu_2S	205.6	33.8	$MeCO_2Me$	186.1	37.8
EtCN	183.5	38.0	PhCHO	192.1	40.7
Me_2CO	187.9	38.0	1-AdamCN	192.3	40.9
PrCN	184.8	38.1	p-MePhCOMe	201.1	40.9
t-BuOEt	197.5	38.1	imid	215.6	40.9
iPr_2O	197.6	38.3	c-Pr_2CO	202.8	41.2
PhCN	187.6	38.3	3,4,5-Me_3pyz	216.8	41.5
4-Mepyz	207.7	38.5	Me_2NCN	197.2	41.8
iPrCN	185.7	38.5	1,3,4,5-Me_4pyz	220.5	41.8
BuCN	185.4	38.6	$MeCONH_2$		42.1
$PhCH_2OH$		38.6	HCONHMe	197.0	42.4
MeCOEt	190.8	38.8	$MeOCONMe_2$	201.9	42.7
$MeCO_2Et$	192.0	38.8	DMSO	203.3	43.0
$HCONH_2$	192.0	39.2	1-Meimid	219.4	43.0
t-BuCN	187.5	39.2	pyrid	208.2	44.2
Bu_2O	195.7	39.3	DMF	203.6	44.3
3-Mepyr	215.9	39.2	1,2-Me_2imid	225.1	44.6
Et_2CO	193.0	39.5	4-NMe_2pyr	228.8	44.8

TABLE 1. (continued)

Base[b]	$-\Delta G_{H^+}$	$-\Delta G_{Li^+}$	Base[b]	$-\Delta G_{H^+}$	$-\Delta G_{Li^+}$
$(MeO)_2CO$	191.4	39.8	TMG	233.2	45.2
1,4-Me_2pyz	212.7	39.8	$MeO(CH_2)_2OH$		45.4
$CF_3(CH_2)_3NH_2$	206.5	39.9	DMA	208.4	45.6
c-PrCOMe	196.3	40.2	1,8-Napht	219.4	46.2
$C_8H_{17}CN$	184.4	40.3	$(MeO)_3PO$	205.2	46.5
iPr_2CO	196.0	40.3	$ClCH_2PO(OEt)_2$	204.0	46.9
1,5-Me_2pyz	214.0	40.4			

(a) Experimental temperature 373K.

(b) Abbreviations are: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Adam, adamantyl; Ph,C_6H_5; imid, imidazole; pyr, C_5H_5N; Pyz, pyrazole; pyrid, pyridazine; Napht, naphthyridine; thiaz, thiazole; DMA, CH_3CONMe_2; DMF, $HCONMe_2$; DMSO, Me_2SO; THF, $(CH_2)_4O$; TMG, $(Me_2N)_2CNH$.

COORDINATION CENTER EFFECTS

The foremost cause of scatter in Figure 1 is the effect of changing the coordination center since this and the adduct regulates (through the bonding types) the various routes and extents of charge flow that occur on complexion. In Table 2 are given the basicities of a number of "parent" bases relative to water for a variety of adducts for which data exists or can be estimated (the values in paranthesis are the only estimated ones). The variation in basicity of the parents is significantly changed for the different "acids" and no general basicity order between any two of the adducts is observed. For most pairs of adducts, the $-\Delta G_{H^+}$ vs. $-\Delta G_{Li^+}$ plots are highly scattered (but the pattern differs from that in Figure 1).

While it is not possible to relate the changes in parent basicities simply with the variation of the coordinating atom, a crude evaluation is possible from Table 2. The parent bases $H_2C{=}O$, $HC{\equiv}N$, pyridine and imidazole, in particular, all involve significant polarizability and resonance effects on their complexing equilibria. The magnitudes of these molecular effects are unknown but appear to be significantly greater for charged adducts. Least affected are the uncharged hydrogen-bonded complexes of CF_3CO_2H in CCl_4. The results in Table 2 seem to indicate that for monodentate atomic centers forming weak dipolar bonds the basicity order is

$\overset{\diagdown}{\underset{\diagup}{S}}: < -F: < =O: < N: < \overset{\diagdown}{\underset{\diagup}{O}}: < =N: < \overset{\diagdown}{\underset{\diagup}{N}}:$. This order changes sharply with the reagent, particularly as it is more polarizing and removes more charge. Changes then occur in lone-pair electronic repulsions, in charge/dipole, and charge/induced dipole interactions, in sigma and pi bond resonances, and in orbital overlaps. Any truly general patten of behavior for parent bases seems unlikely.

TABLE 2. Parent Functional Group (B_o) Basicities Relative to Water (in kcal/mole). Positive values denote increased basicity.

B_o	H^+		Al^+	$Ni^+(B)_2Mn^+$		Li^+		CF_3CO_2H[e]
HF	-48.0		(-13.5)[b]			(-9.6)[a]	(-11.1)[c]	
H_2O	0.0	(0)[a]	(0.0)[b]	(0.)[a]	(0)[a]	0.0	(0.0)[c]	0.0
H_2S	3.9	-	(-)	(6.)[a]	(<-2.)[a]	(-12.)[a]	(-21.)	-2.9
HCN	4.7	(-1.9)[a]	(-2.8)[b]	19.3	1.8	1.4	(-1.6)[c]	-0.2
H_2CO	5.2	-1.0	(1.0)[b]	(4.)	1.6	0.9	1.1[c]	-0.9
H_3N	36.7	-	(8.5)[b]	26.8	5.7	4.8	(5.9)[c]	2.0
C_5H_5N	53.5	16.5	(-)	38.7	-	10.5	(12.2)[d]	2.4
imidazole	56.3	-	(-)	-	-	13.6	-	3.7
ref.	4	12	13	14a	14b	10	5	15

(a) ΔG value estimated from expl. value for CH_3 derivatives
(b) Relative affinities from 6-31G*//3-21G calculations
(c) Relative affinities from 6-31G*//3-21G calculations
(d) Relative affinity from 6-31G//3-21G calculation of reference 3.
(e) Values in dilute CCl_4 solutions, 298K.

CHELATION EFFECTS WITH Li^+

Toward H^+ at 298K, CCl_3CH_2OH is a less basic monodentate than CH_3CH_2OH by 8.1 powers of ten ($-\Delta\Delta G_{H^+}/1.36$). This has been explained quantitatively by the combined field/inductive and polarizability effects of the CCl_3 compared to the CH_3 substituent (ref. 11). Toward Li^+ at 298°, these effects would be expected to reduce the corresponding basicity difference to ca. 3.0 powers of ten if monodentate behavior were involved. Bidentate behavior is implied by the observed equal basicity of these two compounds with Li^+. This result is not unexpected due to the larger size and the greater positive charge of Li^+ in the adduct. For example, a six-membered ring chelate structure can be written in which Li^+ interacts simultaneously with lone-pair electrons at both O and one of the Cl atoms. An alternate structure is one in which Li^+ interacts simultaneously with the oxygen lone-pair and the negative end of CCl_3 group dipole. Similar bidentate basicity toward Li^+ is indicated by our $-\Delta G_{Li^+}$ values for CF_3CH_2OH and $CF_3(CH_2)_3NH_2$.

Staley and Beauchamp (ref. 8) found very significant basicities of cyclohexane and, particularly of benzene toward Li^+. It is therefore not surprising to find that while the basicities of cyclohexyl methanol and benzyl alcohol toward H^+ can be accounted for as monodentates, bidentate behavior is implied toward Li^+. Both have greater basicities than are expected for monodentate substituent field/inductive and polarizability effects (ref. 11), particularly for the C_6H_5 substituent.

The result above for the cyclohexyl substituent suggests that other alkyl groups (even methyl substituents) can also enter into chelate formation with Li^+ by closing a 5 or larger membered ring through a charge induced dipole interaction of sufficient magnitude to overcome the entropy loss of ring formation. Indeed, such a suggestion (ref. 16) has been put forward for cyclization in the H^+ adducts of n-alkylamines giving a small constant gas phase basicity increment of 0.2 kcal/mol per CH_2 increment in chain length. Evidence has also been obtained (ref. 17) for such coiling in gaseous straight chain alkoxides, giving larger (0.5 kcal/mol) methylene increments in gas phase acidities of straight chain alcohols. Our $-\Delta G_{Li^+}$ values for straight chain alcohols, ethers, thiols, thioethers indicate the presence of even larger bidentate basicity effects toward Li^+. A specific example based upon symmetric dialkylethers and thioethers follows.

Short chain non-conjugated alkyl substituents in numerous series of amines, alcohols, ethers, mercaptans and thioethers have gas phase acidities and basicities that increase linearly with the alkyl substituent polarizability parameter, σ_α (ref. 18). The $-\Delta G_{H^+}$ values for R_2O and R_2S, where R = CH_3, C_2H_5, C_3H_7, i-C_3H_7 and t-C_4H_9 are examples: for R_2O: $-\Delta G_{H^+} = 165.8-(51.9)\sigma_\alpha$; sd = 0.2 kcal, R = .9994; for R_2S: $-\Delta G_{H^+} = 180.1-(34.4)\sigma_\alpha$, sd = 0.4, R = .9977 (as noted in ref. 11 for NH_3 compared to NR_3, for example, H_2O or H_2S cannot be included in these families). For $-\Delta G_{Li^+}$ values, the same kind of correlation equations are expected and are observed, except it is found that $(C_3H_7)_2O$, $(C_4H_9)_2O$, $(C_3H_7)_2S$ and $(C_4H_9)_2S$ give enhanced values. That is, restricted to R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, for R_2O: $-\Delta G_{Li^+} = 24.7-(22.3)\sigma_\alpha$, sd = 0.3, R = .9937 and for R_2S: $-\Delta G_{Li^+} = 19.6-(19.3)\sigma_\alpha$, sd = 0.2, R = .9975. The basicity enhancements that we believe to be attributed to bidentate chelation with Li^+ are obtained as the difference between experimental values of $-\Delta G_{Li^+}$ and those calculated by the appropriate equation above: $(C_3H_7)_2O$, 0.8; $(C_4H_9)_2O$, 1.9; $(C_3H_7)_2S$, 1.7; $(C_4H_9)_2S$, 2.8 kcal/mol, respectively. It is to be noted in the above results that the larger S than O atom decreases the coefficients to σ_α (the ρ_α) value in the equations, but it increases the basicity enhancements attributed to bidentate behavior.

The bases pyridazine and 1,8-naphthyridine are known bidentates toward transition metal ions (ref. 19). These bases have very much greater observed basicities toward Li^+ (enhancements of ca. 10. and 6. kcal/mol, resp.) than are expected from a LFER relationship between corresponding $-\Delta G_{Li^+}$ vs. $-\Delta G_{H^+}$ values (slope .49) for monodentate azines. Theoretical 6-31G//3-21G calculations have confirmed that the above two azines are monodentate toward H^+ but form bidentate three-membered ring structures in the gas phase with both Li^+ and Na^+ (ref. 3). Imidazole, pyrazole and their methyl derivatives as well as thiazole and 1,2,4-triazole, give a satisfactory LFER between corresponding $-\Delta G_{Li^+}$ and $-\Delta G_{H^+}$ values (slope .41) that indicates monodentate behavior. However, tetrazole deviates from this LFER, giving a Li^+ basicity 4.2 powers of ten greater than expected from its monodentate H^+ basicity. This result is consistent with Li^+ bridging the 3 and 4 nitrogen positions of tetrazole (ab initio calculations of M. Yanez, private communications).

SUBSTITUENT POLARIZABILITY, FIELD INDUCTIVE, AND RESONANCE EFFECTS

There are three kinds of generalized substituent effects that may make significant contributions to most organic reaction rates and equilibria, either alone (as for the substituent polarizability (P) effects for the ether series discussed above) or in various appropriate combinations. These are (in addition to the P effects) the substituent field/inductive and pi electron delocalization or resonance effects given by the parameters σ_F and σ_R respectively. An empirical theoretical analysis for obtaining quantitative estimates for each of these effects in a given family has been done for the gas phase H^+ basicities for many

equilibria (ref. 4a, 11). For monodentate families of bases with Li^+ and other reagents, the treatment is also successful. This is illustrated by the results given in Table 3 for the formyl family, X-CHO (X is a general substituent). All three kinds of substituents of effects can be significant for this family when X is a heteroatom or unsaturated substituent. Eqn. (1) is utilized to describe the measured substituent effects on basicities, that is, the $-\Delta G$ values relative to the family parent, H_2CO (given as $-\delta\Delta G$).

$$-\delta\Delta G = \sigma_\alpha\rho_\alpha + \sigma_F\rho_F + \sigma_R\rho_R \qquad (1)$$

The substituent parameters for polarizability, field/inductive and resonance effects are σ_α, σ_F, and σ_R, respectively. Tables of the σ parameters are given in refs. 11 and 18. The ρ values denote reaction constants that are characteristic of each family of equilibria. In Table 3, ρ values are given for each reagent. For successful linear regression analysis, the family must consist of a set of substituents for which the three kinds of substituent parameters are mutually non-colinear. This condition was found to be relatively easily fulfilled for proton adducts, (ref. 11), and it has accordingly been utilized here for the other addends (the correlation coefficients between any pair of the independent variables of eqn. (1) are always less than ±0.3 and the residuals in each least squares analysis are zero within their uncertainty estimates).

TABLE 3. Analysis of Substituent Effects on Complex Formation in the Formyl Family, XCHO

Addend	$-\rho_\alpha$	$-\rho_F$	$-\rho_R$	$-\rho_R/\rho_F$	$-\rho_\alpha/\rho_F$	n	R	sd
H^+	24.9±.4	35.5±.6	49.1±.4	1.38±.08	.70±.05	13	.9997	0.4
Al^+	16.5±.7	26.3±.8	36.1±.5	1.37±.03	.63±.03	9	.9996	0.3
Li^+	11.6±.6	16.7±.8	21.0±.6	1.26±.07	.69±.05	13	.9974	0.5
CF_3CO_2H	1.1±.2	8.9±.7	6.4±.3	0.72±.07	.12±.03	5	.9969	0.1

The values of ρ indicate that all three kinds of substituent effects increase in the order of electron withdrawal by the "acid": CF_3CO_2H (hydrogen-bond complex CCl_4) < $Li^+(g)$ < $Al^+(g)$ < $H^+(g)$. The degree of linearity of observed effects between all four sets of equilibria depends upon the composition of the contributions to the observed values. This is given by the ratios, ρ_R/ρ_F and ρ_α/ρ_F. Interestingly, these ratios are precisely the same for H^+ and Al^+, even though each of the ρ values are distinctly less for Al^+. The result is a very precise LFER for these two sets of equilibria. For Li^+ and CF_3CO_2H complexes these rho ratios become increasingly dissimilar to those for H^+ and Al^+. It will be noted in particular that ρ_α/ρ_F is essentially the same for all of the cation complexes but it has a very much smaller value, as expected, for the neutral hydrogen-bonded complex. Thus, even if ρ_R/ρ_F is similar for two equilibria, a significantly different value of the ρ_α/ρ_F ratio will lead to a scatter pattern in the $-\Delta G_{Li^+}$ vs. $-\Delta G_{H^+}$ plot. This is similar but not precisely the situation that prevails, for a plot of $-\Delta G°_{Li^+}$ vs. $-\Delta G°_{CF_3CO_2H}$ (or more generally, the latter may be replaced by the β_2 values, for scaled hydrogen-bonded basicities, cf. ref. 15). Many additional examples of results like those in Table 3 are available and these will be discussed elsewhere. Eqn. (1) provides a quantitative basis for assessing how the strength of a given coordination agent and basicity site is modified by substituents.

ALKALI ION TRANSFER, $\Delta_{tr}G_{(w\to s)}$, VS. $-\Delta G$ FOR THE CORRESPONDING GAS PHASE ADDUCTS

The free energies of ion transfer between pure solvents, obtained with the aid of the TATB assumption, have recently been treated by applying scales of solvent hydrogen-bond acidities to anions and hydrogen-bond basicities to cations (ref. 20). The poor correlation between gas phase $-\Delta G_{Li^+}$ and corresponding values of $-\Delta G_{CF_3CO_2H}$ (or, the equivalent, of the β_2 scale of ref. 15) raises questions regarding limitations of this treatment of ion transfer free energies. Many ion/solvent interactions involve electrostatic type interactions that do have a similarity to those involved in hydrogen-bonding. An important difference between these ion solvent interactions is that the polarization of individual solvent molecules is less extreme than it is in the formation of 1:1 molecular complexes in the gas phase. It is in the latter and not the former case that, for example, Table 3 shows a major difference in the ρ_α/ρ_F ratio for formation of Li^+ compared to corresponding CF_3CO_2H hydrogen-bonded complexes. If ρ_R/ρ_F ratios in the solution electrostatic interactions are rather similar, then our gas phase $-\Delta G$ values for alkali metals and corresponding $\Delta_{tr}G_{(w\to s)}$ values may correlate fairly well for a certain class of solvents. Correlations have been carried out using the data of ref. 20 (and our unpublished $-\Delta G_{K^+}$ values) and found to be best obeyed by weakly self-associated solvents. Considering the limited available data and the relatively large experimental errors for the transfer energies, the correlations are reasonably satisfactory, especially if accompanied by a term involving the solvent dipolarity/polarizability (as represented, for example, by the π^* parameters used

in ref. 20). The precision of the two parameter correlations for both Li^+ and K^+ are then essentially equivalent in quality whether one uses π^* and β_2 or π^* and gas phase $-\Delta G_{Li^+}$ or K^+. The ratio (2.5) of the coefficients of the basicity parameters for Li^+ compared to K^+ is the same as reported in ref. 20.

A final point to be made can be illustrated using proton transfer basicities in solution. These are composite equilibria involving not only the underlying proton transfer between largely covalently bonded acids and bases, but frequently there are numerous competing equilibria involving electrostatic solvent interactions with each of the acid/base pairs of the proton transfer equilibria. In general, the composites are complex and plots of $\Delta G_{H^+}(g)$ vs. either corresponding $\delta\Delta G_{H^+}$ (aqueous) or $\delta\Delta G_{H^+}(Me_2SO)$ are highly scattered (ref. 21). However, within appropriate families of bases excellent linear correlations are found. The family LFER's and their limitations that we have noted in the gas phase between H^+ and corresponding metal ion adducts (of very different bonding types) offers encouragement in obtaining an improved understanding of solution equilibria, both "physical" and "chemical".

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