Levelling of Substituent Effects on Acidities in the Gas Phase compared with those in Solution

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Substituent effects on a series of ionization reactions of neutral and positively charged acids have been studied in different media (gas phase, water and dimethyl sulphoxide) through linear plots of relative free energies ($\delta_X\Delta G$) using the ionization of benzoic acids in the same medium as a reference. While the absolute magnitudes of $\delta_X\Delta G$ values in solution are lower than in the gas phase (this effect being well known as 'solvent attenuation'), we show that ρ values in the gas phase are levelled to values close to unity for all reactions considered, while in solution they are spread over a range of values. Therefore, if substituent effects in a given system are calculated by making reference to an equilibrium in the same system, structural effects on reactivities are actually better differentiated in solution than in the gas phase.

The quantitative study of substituent effects, which began with the familiar Hammett equation, continues to be a valuable tool of physical organic chemistry, as it provides a simple method for predicting reactivities and gives indications about the nature of the interactions between the substituent and the reaction site.[1] By far the largest body of data suitable for such analysis consists of equilibrium constants for acid–base ionization reactions in water.[1] The scope was considerably broadened when substituent effects on gas-phase ionization reactions became available. These studies, combined with those in solvents other than water, have provided a more complete picture in which the often complex interplay between structural and solvent effects in determining reactivities is appropriately taken into account.[2] Substituent effects have been thoroughly analysed by Taft *et al.*, by dissecting them into field-inductive, resonance and polarizability contributions.[2–7]

The usual procedure for studying gas-phase substituent effects is to employ σ values derived from solution data [1,8] and thus calculate ρ values for gas-phase equilibria.[4–6,9–11] With this approach, a large attenuation of substituent effects from gas phase to water ($\rho_g > \rho_{aq}$) is observed for the ionization of benzoic acids,[12] phenols,[6,12b] pyridinium [5,9] and anilinium [5] ions. The attenuation factor can be 2–10 (possibily not constant for all substituents).[5] When σ values for the gas phase were derived, they came from a dissection of relative free energies,[7] as seen before, or by extracting an inherent contribution for solution σ_m,[5] so that values similar to those in solution are obtained.

Despite the success of this approach (which also has the merit of maintaining consistency among the various σ scales), we think that a detailed analysis of substituent effects in any given system would profit from a direct comparison of relative free energies in that system, because in this way 'intrinsic' ρ values for each system can be obtained and eventually compared.

While this has of course been done for aqueous solutions, to which all σ values refer, to our knowledge gas-phase substituent effects have never been directly derived from gas-phase equilibria. This circumstance prompted us to pursue an investigation of substituent effects using the ionization of benzoic acids in the appropriate phase as reference.

Results

In this paper, consistent with common usage, we will denote substituent effects as $\delta_X\Delta G = \Delta G - \Delta G_0$, where ΔG_0 is the free-energy change for the reaction of the unsubstituted compound. Likewise, $\delta_X\Delta G^* = \Delta G^* - \Delta G_0^*$ will denote the substituent effect on the reference reaction. If a linear free energy relationship (LFER) exists, the Hammett equation [$\delta_X\Delta G = \rho\delta_X\Delta G^*$, or $\log (K/K_0) = \rho \log (K^*/K_0^*)$] holds and ρ can be calculated. We have determined ρ values simply by plotting $\delta_X\Delta G_i$ *vs.* $\delta_X\Delta G^*_i$ in the same phase *i*, thus obtaining ρ_i as in eqn. (1).

$$\delta_X\Delta G_i = \rho_i\delta_X\Delta G^*_i \qquad (1)$$

We have deliberately avoided using σ instead of $\delta_X\Delta G^*$ because another σ scale might generate confusion and, more importantly, because the correct definition of a σ scale requires different criteria for the selection of substituents,[2b] which is not the object of this study.

Thus we plotted data for $\delta_X\Delta G$ for a variety of equilibria *vs.* the same for benzoic acids, in the same system. Only *meta* and *para* substituents were selected, and treated together.[5] Substituents which lead to a different site of ionization in anilinium ions [13] (*m*-NH_2 and *m*-OCH_3) were excluded *a priori.*

Suitable gas-phase data were available for the ionization of neutral (phenols, anilines, arylacetonitriles and toluenes) and positively charged acids (anilinium, *N,N*-dimethylanilinium and pyridinium ions, protonated benzaldehydes, acetophenones, methyl benzoates, benzamides and α-methylstyrenes) (Table 1). Wherever possible, corresponding data in water and DMSO were similarly treated; these are reported in Tables 2 and 3.

$\delta_X\Delta G^*_{aq}$ values were calculated from σ values.[8] Owing to the limited data available, a ρ value could be obtained in all systems only for phenols, anilines and anilinium ions. The correlation line for the deprotonation of toluenes in DMSO is based on two points only, one of which (for toluene itself) is a calculated value.

From the first columns in Tables 1–3 ($ArCO_2H$, $\delta_X\Delta G^*$) the well known attenuation between gas phase and solution is readily apparent; σ values for the gas phase (though with the above precautions) might be obtained as $\sigma_g = -10^3\delta_X\Delta G_g/2.303RT$. ρ Values for all reaction families in each system were obtained as the slopes of the linear plots of eqn. (1) and are collected in Table 4. Figs. 1–3 show the data for each system.

There is a noticeable scatter in many of the plots, with standard deviations between 0.05 and 1 in the slopes. In fact, these plots would qualify only as 'limited linear free-energy

Table 1 Ionization ($\delta_X\Delta G$, in kcal mol^{-1} at 298 K) of *m*- and *p*-substituted acids in the gas phase[a]

X	$ArCO_2H$	ArOH	$ArNH_2$	$ArCH_2CN$	ArMe	$ArNH_3^{+}$[b]	pyH^+
m-NH_2	1.6	0.5					
m-OCH_3	-0.5	-1.9	-1.2*	-1.4*			3.1
m-F	-3.8	-6.2	-4.4	-0.6	-4.8	-3.4	-6.9
m-Cl	-4.8	-8.1	-6.7	-7.0	-6.2	-2.8	-6.1
m-CH_3	0.7	0.2	0.6	0.0*	0.7	3.1	3.0
H	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
m-CF_3	-6.4	-11.0	-8.6	-9.2	-11.0		-8.5
m-CN	-9.6	-14.5	-13.7	-12.3	-11.0		-11.9
m-NO_2	-9.1	-15.9	-14.5	-13.7	-17.4		-13.5
3,5-di-CF_3	-14.3	-20.5	-18.6		-18.9		
p-NH_2	2.5	3.1	3.9*				11.4
p-OCH_3	0.4*	0.4	0.8	0.4	13.3*	4.0	6.5
p-F	-2.9	-3.1	-1.7	-2.0	-0.7	-2.3	-4.2
p-Cl	-4.5	-6.9	-5.7	-6.1	-6.2	-1.8	-3.4
p-CH_3	1.0	0.6	1.2	0.4	1.7	3.2	3.5
p-CF_3	-6.4	-13.4	-12.2	-11.6	-13.4		-8.2
p-CN	-10.3	-17.9	-17.8	-16.6	-19.6		-11.1
p-COMe	-4.5	-7.9	-15.4		-18.2		-3.6
p-CHO	-5.9	-17.4	-17.1		-20.5		
p-NO_2	-11.7*	-22.5	-23.1	-21.9	-27.5	-3.3	-12.6

X	$ArNMe_2H^+$	$ArCHOH^+$	$ArCMe_2^+$	$ArC(OH)Me^+$	$ArC(OH)OMe^+$	$ArC(OH)NMe_2^+$
m-NH_2						
m-OCH_3		2.7	2.1	2.4	1.5	1.2
m-F		-4.0	-5.1	-3.7	-4.1	-3.0
m-Cl		-3.3	-4.7	-3.4	-3.6	-3.8
m-CH_3		2.8	1.8	1.7	1.4	1.0
H	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
m-CF_3	-5.9	-5.6	-6.2	-5.5	-5.5	-5.9
m-CN	-8.8	-7.6	-9.0	-8.1	-7.9	-7.8
m-NO_2	-8.9	-8.4	-11.1	-8.8	-8.4	-8.3
3,5-di-CF_3	-10.9		-12.4	-10.8		
p-NH_2	4.6		15.2		8.0	5.1
p-OCH_3	3.3	10.2	10.5	8.1	4.8	3.1
p-F	-2.2	-0.6	-0.1	-0.6	-2.2	-1.9
p-Cl	-2.6	-0.7	-0.5	-0.7	-2.0	-2.8
p-CH_3	2.1	4.5	4.1	3.9	2.3	1.6
p-CF_3	-6.9	-5.9	-7.0	-5.8	-5.7	-6.2
p-CN	-10.0	-7.9	-9.8	-8.2	-8.1	-8.2
p-COMe				-1.8		
p-CHO						
p-NO_2		-8.7	-11.5	-8.8	-8.9	-9.2

[a] All data for the ionization of neutrals from: S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, suppl, 1, except for those marked with an asterisk [ref 2(*b*)]. [b] Ref. 5, except *p*-NO_2 (S. G. Lias, J. F. Liebman and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695) and *m*-Me (R. W. Taft, quoted in 1987 in an informal update of the preceding reference). All other data from ref. 2(*b*).

relationships';[6] these correlations have therefore a very limited predictive value. This is probably due to the fact that no strict selection was made on the substituents with regard to the various possible interactions with the backbone (or with the solvent, where applicable); these have been discussed elsewhere.[2]

Discussion

It is not the purpose of this paper to discuss the relative merits of the various σ scales available, or the applicability of each to the reaction family and substituents selected here. Despite the good correlations and the numerous insights it gives, we also have not used Taft's approach[2] involving the dissection of relative free energies into field, resonance and polarizability ($\delta_X\Delta G = \rho_F\sigma_F + \rho_R\sigma_R + \rho_\alpha\sigma_\alpha$) contributions,[2b] because this involves to some extent processing the data according to various assumptions.

We would rather like to draw attention to the fact that the range of ρ values spanned by gas-phase ionizations is much smaller than that for ionizations in solution, for wide variations in substrate type. Thus, the ionization of pyridinium and anilinium ions in water has rather large ρ values, *i.e.* a three- to six-fold increased sensitivity to structural changes compared with benzoic acids (Table 4). However, in the gas phase, despite the intrinsically larger $\delta_X\Delta G$, all ρ values are close to unity. In DMSO, the deprotonation of phenols and anilines leads to the same conclusions, while the values of ρ in the solution phases (water and DMSO) are similar, at least in the few cases in which a comparison was possible.

These results are not due to the particular reference reaction chosen. In fact, the attenuation of substituent effects from the gas phase to water is known to be largest for benzoic acids.[12,14] Changing the reference to another reaction (denoted with **) implies that $\delta_X\Delta G^{**} = \rho^{**}\delta_X\Delta G^{*}$ and $\delta_X\Delta G = \rho'\delta_X\Delta G^{**}$; thus $\rho' = \rho/\rho^{**}$. Therefore, switching to a reference reaction for which the attenuation is lower (*e.g.* pyridinium ions),[14] leads only to lower absolute ρ values with the same percentage differences.

The present data indicate that two major effects take place upon solvation: (*a*) the overall scale of relative acidities ($\delta_X\Delta G$) is compressed to smaller values; (*b*) the reduced $\delta_X\Delta G$ values correlate with $\delta_X\Delta G^*$ in a way characteristic for each reaction, thus differentiating reactivities much better than in the gas phase, where all the reactions studied hardly differ in behaviour from those of benzoic acids.

Table 2 Ionization ($\delta_X\Delta G$, in kcal mol^{-1} at 298 K) of *m*- and *p*-substituted acids in water

X	$ArCO_2H$[a]	ArOH[b]	ArCOMe[c]	ArCONHOH[d]	$ArNH_2$[e]	$ArNH_3^+$[f]
H	(0.000)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
m-NH_2	0.219	−0.15				0.11
m-CH_3	0.0942	0.12				0.18
m-OCH_3	−0.157	−0.48				−0.53
m-F	−0.460	−1.08				−1.43
m-Cl	−0.509	−1.19			−2.32	−1.47
m-CN	−0.765	−1.88			−4.24	−2.51
m-NO_2	−0.970	−2.21				−2.91
p-NH_2	0.902	0.44		0.70		1.72
p-OCH_3	0.366	0.29	0.79	0.33		1.03
p-CH_3	0.232	0.35		0.19		0.65
p-F	−0.0847	−0.12	0.11	−0.14		0.07
p-Cl	−0.310	−0.79	−0.46	−0.29		−0.85
p-CN	−0.902	−2.76		−0.89	−6.42	−3.94
p-NO_2	−1.063	−3.89	−2.36	−1.08		−4.88

X	pyH^+[f]	$ArNMe_2H^+$[g]	$ArCHOH^+$[h]	$ArC(OH)Me^+$[i]	$ArC(OH)_2^+$[j]	$ArC(OH)NH_2^+$[k]
H	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
m-NH_2	1.13					
m-CH_3	0.63			−0.30	!	
m-OCH_3	−0.59					
m-F	−3.00					
m-Cl	−3.27	−1.73	−0.78		−0.93	
m-CN	−5.27					
m-NO_2	−6.03	−3.33				−0.67
p-NH_2	5.33					
p-OCH_3	1.87			0.95		0.50
p-CH_3	1.12	0.23		0.27	0.56	
p-F					0.18	
p-Cl	−1.88	−0.31	−0.30		−0.44	
p-CN	−4.57					
pNO_2	−5.43	−6.02		−1.55		−0.81

[a] Ref. 8. [b] Ref. 6. [c] J. P. Guthrie, J. Cossar and A. Klym, *Can. J. Chem.*, 1987, **65**, 2154. [d] Y. K. Agrawal and J. P. Shkula, *Aust. J. Chem.*, 1973, **26**, 913. [e] R. A. Cox and R. Stewart, *J. Am. Chem. Soc.*, 1976, **98**, 488. [f] Ref. 5. [g] R. Stewart, *The Proton: Applications to Organic Chemistry*, Academic Press, Orlando, 1985. [h] M. R. Sharif and R. I. Zalewski, *Bull. Acad. Polonaise Sci.*, 1981, **XXIX**, 385. [i] R. A. Cox, R. A. Smith and K. Yates, *Can. J. Chem.*, 1979, **57**, 2952 (*m*-Me, *p*-Me, *p*-NO_2); A. Bagno, V. Lucchini and G. Scorrano, *J. Phys. Chem.*, 1991, **95**, 345 (H, *p*-OMe). [j] Z. Geltz, H. Kokocinska, R. I. Zalewski and T. M. Krygowski, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1069. p*K* Values were determined using the H_0 acidity function and therefore are not reliable in themselves; included because p*K* differences are likely to be correct. [k] J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, 1966, **44**, 1899 (*m*-NO_2, *p*-OMe); R. A. Cox, L. M. Druet, A. E. Klausner, T. A. Modro, P. Wan and K. Yates, *Can. J. Chem.*, 1981, **59**, 1568 (H); J. T. Edward and S. C. Wong, *J. Am. Chem. Soc.*, 1977, **99**, 4229 (*p*-NO_2).

Table 3 Ionization ($\delta_X\Delta G$, in kcal mol^{-1} at 298 K) of *m*- and *p*-substituted acids in DMSO

X	$ArCO_2H$[a]	ArOH[b]	$ArNH_2$[c]	$ArCOCH_3$[d]	$ArCONH_2$[e]	ArCONHOH[e]	$ArNHSO_2Ph$[f]	ArMe[g]	$ArNH_3^+$[h]
H	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0)	(0.0)
m-Me	0.0	0.3	0.4	0.4					
m-Cl	−1.6	−3.0		−2.0	−1.4	−1.2	−1.2		
p-Cl	−1.2	−1.8	−1.8	−1.2	−0.9	−0.9	−1.2		−1.2
m-Br	−1.6		−3.1	−2.0					
p-Br	−1.1		−2.2	−1.2					
m-NO_2	−2.6	−4.9							−2.6
p-NO_2	−3.0	−9.9	−13.4				−4.6	−31	−3.0

[a] C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, 1968, **90**, 2821 (H, *m*-Me, *p*-Cl); V. S. Pilyugin, L. Ya. Khrustaleva, S. L. Smimova and M. E. Ginzburg, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1983, **53**, 1250 (*m*-Cl, *m*-NO_2, *p*-NO_2); V. S. Pilyugin, S. L. Kuznetsova and N. A. Shkunova, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1986, **56**, 373 (*p*-Br, *m*-I). [b] F. G. Bordwell, R. J. McCallum and W. N. Olmstead, *J. Org. Chem.*, 1984, **49**, 1424 except *p*-NO_2 (F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456). [c] F. G. Bordwell and D. J. Algrim, *J. Am. Chem. Soc.*, 1988, **110**, 2964. [d] F. G. Bordwell and F. J. Cornforth, *J. Org. Chem.*, 1978, **43**, 1763. [e] F. G. Bordwell, H. E. Fried, D. L. Hughes, T-Y. Lynch, A. V. Satish and Y. E. Whang, *J. Org. Chem.*, 1990, **55**, 3330. [f] D. N. Kravtsov, A. S. Peregudov, E. S. Petrov, M. I. Terekhova and A. I. Shatenshtein, *Bull. Acad. Sci. USSR* (*Engl. Transl.*), 1981, **30**, 993. [g] F. G. Bordwell, D. Algrim and N. R. Vanier, *J. Org. Chem.*, 1977, **42**, 1817 (*p*-NO_2); value for unsubstituted compound estimated in: F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456. [h] A. G. Cook and G. W. Mason, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2579 (*p*-Cl, *m*-NO_2, *p*-NO_2); B. A. Korolev, T. V. Levandovskaya and M. V. Gorelik, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1978, **48**, 135 (H).

The first effect, commonly called solvent attenuation of substituent effects, is readily apparent from Tables 1–3 and has been well recognized. It might be expected, therefore, that substituent effects in solution contain less information than those in the gas phase, which must depend only on intrinsic molecular properties.[15] On the contrary, the above results show that substituent effects in solution (which depend on molecular properties and on interactions with the solvent) are more sensitive to the nature of the reaction being considered, despite the narrower range they span. The spread of ρ values is rather

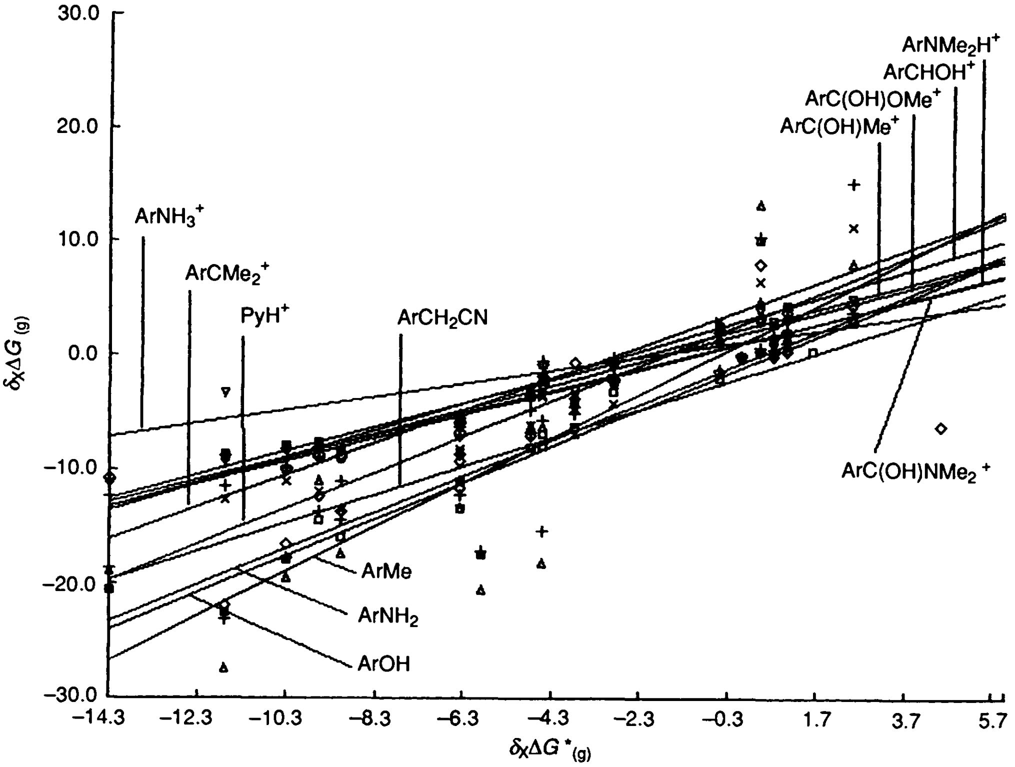

Fig. 1 Substituent effect ($\delta_X\Delta G$ *vs.* $\delta_X\Delta G^*$) on ionization reactions in the gas phase

Table 4 Values of ρ in water, DMSO and in the gas phase[a]

Species undergoing ionization	ρ_{aq}	ρ_{DMSO}	ρ_g
$ArCO_2H$	(1.0)	(1.0)	(1.0)
$ArOH$	2.1 (0.3)	2.8 (0.5)	1.6 (0.1)
$ArNH_2$	6.6 (1.2)	4.2 (0.8)	1.6 (0.2)
$ArCH_2CN$			1.2 (0.2)
$ArCOCH_3$	2.2 (0.2)	1.3 (0.1)	
$ArCONH_2$		0.8 (0.1)	
$ArCONHOH$	0.92 (0.03)	0.80 (0.05)	
$ArNHSO_2Ph$		1.5 (0.3)	
$ArCH_3$		(10)[b]	1.9 (0.3)
$ArNH_3^+$	3.2 (0.3)	1.8 (0.4)	0.6 (0.2)
pyH^+	5.7 (0.2)		1.6 (0.1)
$ArNMe_2H^+$	4.5 (0.8)		1.0 (0.1)
$ArCHOH^+$	1.5 (0.4)		1.2 (0.1)
$ArC(OH)CH_3^+$	1.5 (0.3)		1.0 (0.1)
$ArC(OH)_2^+$	2.0 (0.2)		
$ArC(OH)OCH_3^+$			1.1 (0.1)
$ArC(OH)NMe_2^+$			0.97 (0.05)
$ArC(OH)NH_2^+$	0.8 (0.1)		
$ArC(CH_3)_2^+$			1.4 (0.2)

[a] Standard deviations in brackets. [b] Two points, one of which is calculated (see the text).

similar in water and DMSO, despite the small solvent compression claimed for the latter medium.[15]

This behaviour is not entirely unexpected, considering that in the gas phase ionic stabilization is achieved mainly through the polarization of the whole molecular framework, while in solution, and particularly in water, it is mostly due to dipolar and hydrogen bonding interactions. In the present study we have considered only substituted benzene derivatives, *i.e.* molecules with a similar size and for which the substituent is indeed a perturbation (as opposed to a major skeletal change). It is reasonable, then, that the relative free energies, in a situation where stabilization is due to the molecule itself (which remains the same, with a variable perturbation), behave similarly, irrespective of the nature of the reaction centre. In water, stabilizing interactions are largely dependent on local molecular features, so that specific (reaction centre–solvent and substituent–solvent) interactions may dominate $\delta_X\Delta G$ values and lead to different ρ values.

Relationship between ρ_g *and* ρ_{aq}.—As an appendix to this work, we have also derived expressions which relate the values of ρ_g and ρ_{aq} in order to give a mathematical explanation of the origin of their different relative magnitudes.

Like free energies, the values of ρ for the same reaction in two systems are mutually related through a thermodynamic cycle; the notation used below refers to the ionization equilibrium $BH^+ \rightleftharpoons B + H^+$ in water and the gas phase, but the same arguments apply to $AH \rightleftharpoons A^- + H^+$ and to any pair of phases.

The free-energy changes (ΔG_g and ΔG_{aq}) are related by a Born–Haber cycle as given in eqn. (2) where $\Delta G_{aq}(i)$ denotes the free

$$\Delta G_{aq} = \Delta G_{aq}(BH^+) + \Delta G_g - \Delta G_{aq}(B) - \Delta G_{aq}(H^+) \quad (2)$$

energy of hydration of species *i*. We define as usual[16] the solvent effect on the reaction as shown in eqn. (3). Introducing the

$$\delta_{aq}\Delta G = \Delta G_g - \Delta G_{aq} = \Delta G_{aq}(B) - \Delta G_{aq}(BH^+) + \Delta G_{aq}(H^+) \quad (3)$$

expression for the substituent effect, we obtain eqn. (4). An

$$\delta_X\Delta G_{aq} = \delta_X\Delta G_g - (\delta_{aq}\Delta G - \delta_{aq}\Delta G_0) \quad (4)$$

analogous expression holds for the reference reaction. The quantity $D = \delta_{aq}\Delta G - \delta_{aq}\Delta G_0$ can be easily calculated from the data at hand recalling that, by simple rearrangement, eqn.

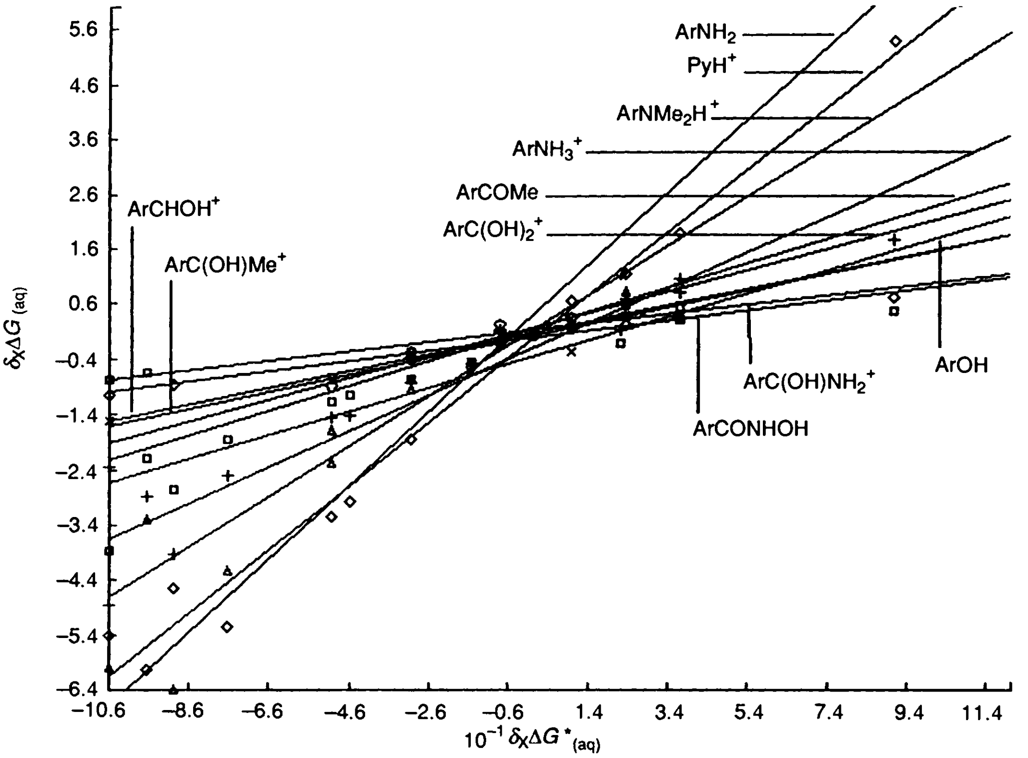

Fig. 2 Substituent effect on ionization reactions in water

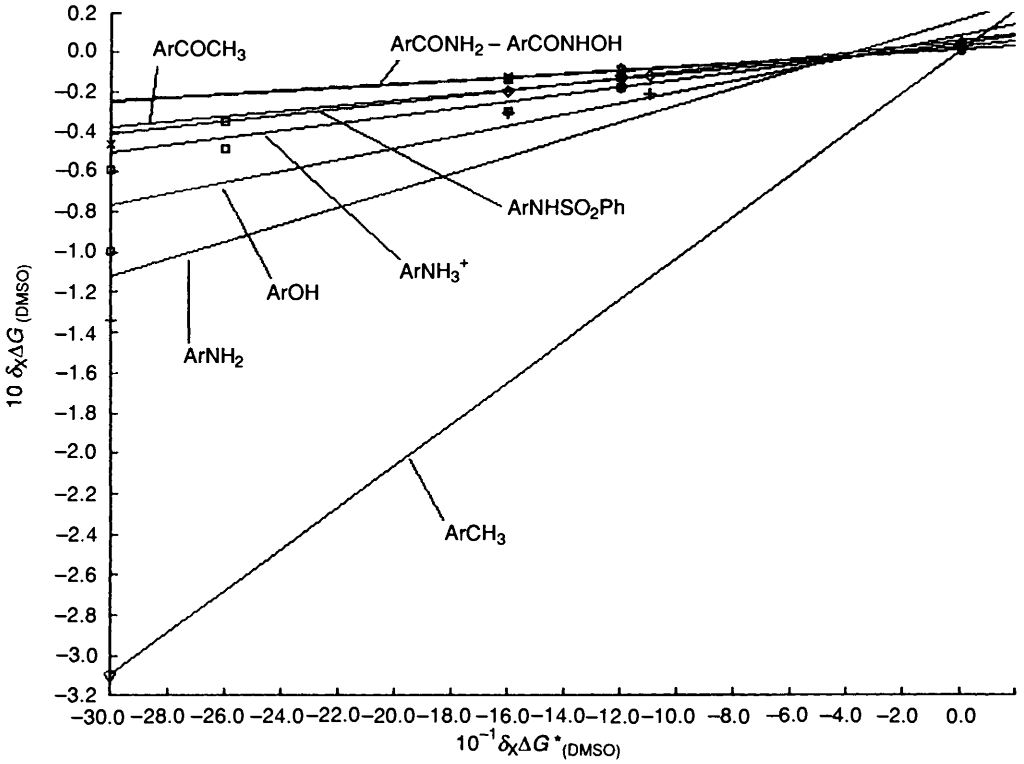

Fig. 3 Substituent effect on ionization reactions in dimethyl sulphoxide

(5) results. Therefore, by substitution, we obtain the two

$$D = \delta_{aq}\Delta G - \delta_{aq}\Delta G_0 = \delta_X\Delta G_g - \delta_X\Delta G_{aq} \quad (5)$$

equivalent expressions, eqn. (6a) and (6b).

$$\rho_g = (\delta_X\Delta G_{aq} + D)/(\delta_X\Delta G_{aq}{}^* + D^*) \quad (6a)$$

$$\rho_{aq} = (\delta_X\Delta G_g - D)/(\delta_X\Delta G_g{}^* - D^*) \quad (6b)$$

Eqns. (6*a*) and (6*b*) show the relationship between gas-phase and solution substituent effects, and are valid for a single substituent. If a LFER exists, a constant ρ value will be obtained. Thus ρ_g is given by the substituent effect in water plus the difference between the solvent effect on the reaction and that on the unsubstituted compound, divided by the same quantity for the reference reaction. An analogous relationship holds for ρ_{aq}, with gas phase in place of water and changed signs of *D* and *D**.

The relative contributions of the various terms are best shown by pyridinium ions, which exhibit a very large difference between ρ_g and ρ_{aq}. As an example we take the *m*-NO_2 substituent, for which $\delta_X\Delta G$ is largest in both systems (-6.03 and -13.5 in water and gas phase, respectively; see Tables 1 and 2). Substituting the values of *D* (-7.47) and D^* (-8.1), we have $\rho_g = (-6.03-7.47)/(-0.97-8.1) = 13.49/9.07 = 1.5$ and $\rho_{aq} = (-13.5 + 7.47)/(-9.1 + 9.83) = 6.04/1.0 = 6.0$. Thus, the main factor determining the size of ρ_{aq} is that the denominator is small compared with the numerator, because $\delta_X\Delta G_g^* \approx D^* = \delta_{aq}\Delta G^* - \delta_{aq}\Delta G_0^*$, while in the expression for ρ_g the denominator is similar to the numerator. For ρ_g to be higher, it should be that $\delta_X\Delta G_{aq}^* \approx -D^*$. These conditions are mutually exclusive, because otherwise $\delta_X\Delta G_g^* \approx -\delta_X\Delta G_{aq}^*$, *i.e.* the substituent effect in the gas phase for the reference reaction would be equal and opposite to that in solution. This is not true, because substituent effects in the gas phase (*i.e.* $\delta_X\Delta G_g$) are intrinsically higher than in solution, and generally follow the same qualitative trend. Moreover, these results do not depend on the choice of $ArCO_2H$ as reference compounds, and thus should be general.

We can also explicitly show that gas-phase substituent effects are higher compared with those in solution, defining ρ' as given in eqn. (7). Given the magnitudes of these quantities (*D* and $\delta_X\Delta G_{aq}^*$ have the same sign) it follows that normally $\rho_g' > \rho_{aq}$, as is generally found.

$$\rho_g' = \delta_X\Delta G_g/\delta_X\Delta G_{aq}^* = (\delta_X\Delta G_{aq} + D)/\delta_X\Delta G_{aq}^* = \rho_{aq} + D/\delta_X\Delta G_{aq}^* \quad (7)$$

Conclusions

It has long been known that structural effects on acidities in the gas phase are much more marked than in solution, as shown by the large $\delta_X\Delta G$ and ρ values (if obtained using solution σ values). We have shown that, if substituent effects in a given system are calculated by making reference to an equilibrium in the same system, structural effects in solution are spread over a wide range of ρ values, while in the gas phase they level off to values close to unity for a large number of reactions.

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