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THE EFFECTS OF SOLVATION UPON THE ACIDITIES OF NITROAROMATICS

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Abstract. Specific solvation of nitrated phenoxide, anilide and benzyl anions is shown to decrease in that order, with concomitant increases in substituent solvation assisted resonance effects - the nitrobenzyl anions are suggested to be essentially charge-delocalized.

The increased availability of free energy data for gas phase ion-molecule reactions [1,2] has allowed more searching studies of solvation effects upon proton transfer reactions to be made in recent years. In particular, Taft and his co-workers have proposed an extensive, generalized scheme to take account of both the nature of the solvation of the ion and the neutral molecule, and the influence of solvation of substituents, upon the position of equilibrium.[3] Their studies have shown that, in the case of the ionization of phenols in the gas phase, water and DMSO for which extensive data on substituent effects are available, specific solvation of the phenoxide oxygen is ca. twice as effective by water than DMSO.[3,4] However, as expected, no specific solvation of highly charge-delocalized carbanions (by DMSO) is observable (e.g. fluorenyl, diphenylmethyl).[3] (Because of their insolubility in water, no reliable data for the ionization of hydrocarbons to yield delocalized anions in this medium are available).

As the electronegativity of the ionizing centre decreases (i.e. O > N > C), specific solvation of this atom should decrease. In the limit of a totally charge-delocalized system, no differential specific solvation effect between water and DMSO should be observed, but (specific) substituent solvation assisted resonance (SSAR) effects should become dominant for +R conjugated substituents. Those predictions could be conveniently tested by comparisons of data for phenols, anilines and toluenes, but gas phase data are unavailable for many of the derivatives of interest. However, polysubstitution of these compounds by nitro groups leads to derivatives generally amenable to pKa studies in water and DMSO solutions, and our recent measurements on the acidities of 4-nitro, 2,4-dinitro- and 2,4,6-trinitro-toluene[5] allow comparisons of the solvent effects upon these charge- localized → charge delocalized series of ions to be made.

pKa values in water and in DMSO are shown in the Table for phenol, aniline, diphenylamine and toluene together with data for their 4-, 2,4- and 2,4,6-tri-nitro derivatives. Except for the estimated value for toluene, pKa's in DMSO are higher than those in water for the parent compounds in accord with the far better solvation of mainly charge-localized

TABLE

pKa Values in Water and DMSO for Some Para- and Ortho, Para- Substituted Nitroaromatics.

	Phenols[a]		Anilines		Toluenes		Diphenylamines	
	H_2O	DMSO	H_2O	DMSO	H_2O	DMSO	H_2O	DMSO
Unsubstituted	10	16.4	27.3[c]	30.7[f]	∿42[h]	42[f]	22.4[c]	∿23[d]
4-NO_2	7.15	11.0	19.5[d]	>21[g]	∿23.5[i]	∿22.5[i]	∿15.7[c]	17[g]
2,4-$(NO_2)_2$	4.1	5.2	14.7[d]	16[g]	16[i]	15[i]	14.3[d]	13[g]
2,4,6-$(NO_2)_3$	0.3	-1[b]	13.6[e]	13.5[h]	13.6[i]	∿10.5[i]	10.6[c]	8[g]

a. Values taken from M.K. Chantooni Jr. and I.M. Kolthoff, J. Phys. Chem., 80, 1306 (1976).
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h. Estimated value.
i. Ref. 5.

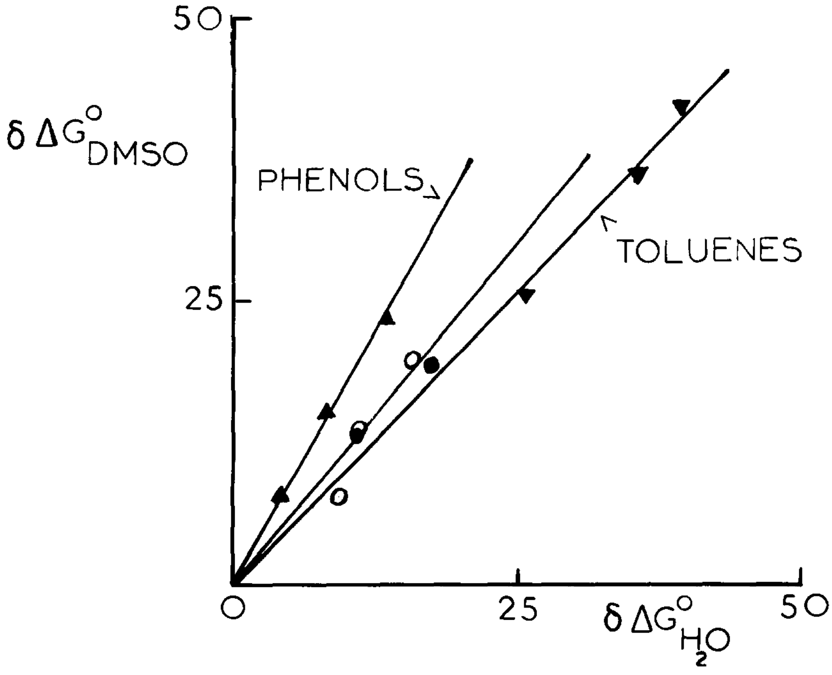
anions by the latter solvent. The pKa differences between DMSO and water tend to decrease with increasing acidity for phenols and anilines.

The introduction of a 4-nitro substituent decreases the pKa values for all compounds in both solvents, the effect being greatest upon the weakest acid, toluene. Also, the pKa differences between DMSO and water are generally less than those for the parent compounds. Successive nitration in the ortho-positions of the 4-nitro-derivatives further reduces the pKa values in both solvents and a somewhat greater substituent effect in DMSO is maintained, leading to lower pKa's in DMSO than in water for all the 2,4,6-trinitro-derivatives studied (see Table). Whereas the introduction of the second and third nitro groups into 4-nitrophenol has virtually the same effect upon pKa's, identical to that upon introduction of the 4-nitro group into phenol itself, nitration of aniline and toluene derivatives has progressively smaller effects upon their pKa's. For mono- and di-nitration, this order of substituent effects is thus exactly that anticipated from a consideration of the electronegativity of the ionizing centre, from which the magnitude of the effect of a +R group should be greatest upon toluene. Similar behaviour is observed in the gas phase, where enhanced resonance stabilization of charge is found for the 4-nitro-derivatives in the order C > N > O.[1-3,6]

In the Figure the acidity data of the Table are plotted for each class of compounds, relative to the unsubstituted parent, from which decreasing values of the slope $\frac{\Delta(\delta\Delta G)DMSO}{\Delta(\delta\Delta G)H_2O}$ in the order phenols (1.9), amines (1.2), toluenes (1.1) are obtained. The slope of 1.1 for the toluenes implies that specific solvation of the exocyclic carbon atom by water is only marginally greater than that by DMSO, and therefore that the charge in these substituted toluenes is essentially fully delocalized (cf. a slope of 1.0 for charge-delocalized anions). This conclusion is supported by the lower pKa of 4-nitrotoluene in DMSO than in water. The slope of 1.2 found for the amine derivatives confirms, as expected, that these ions are only weakly specifically solvated, the large influences of substituents arising from SSAR effects of these +R groups conjugated to the formally electron-rich centre. The value of 1.9 for the phenols is lower than the value (2.3) obtained from a study of a range of meta- and para-substituted derivatives,[4] but covers a much wider span of energies. The differential SSAR effects for the phenol derivatives thus increase considerably with increasing nitration (measured with reference to the literature data)[4] as expected for increasingly substituent-charge-localized anions.

That the introduction of ortho-nitro groups does not greatly interfere with any solvation of the ionized centre is indicated by the good linear plots obtained, deviations of the trinitro-derivatives towards the line of unit slope being anticipated if steric hindrance to approach of solvent molecules were important.

FIGURE : Relative acidities of ortho- and ortho, para-nitrated aromatics in aqueous and DMSO solutions. ▲ Phenols ; ▼ Toluenes ; ● Anilines ; ○ Diphenylamines.



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