

DISSOCIATION OF PHENOLS, AZOPHENOLS AND AZONAPHTHOLS IN ANHYDROUS DIMETHYL SULPHOXIDE*

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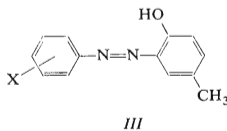
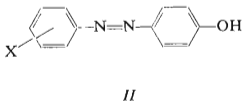
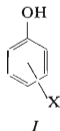
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Dissociation constants of substituted phenols, phenylazophenols and phenylazonaphthols have been determined in anhydrous dimethyl sulphoxide. The Hammett substituent constants σ and σ^- fit the correlation of the substituted phenols and azophenols, whereas σ^o fit that of azonaphthols. The sensitivity increase of the reaction centre towards the substituent in this solvent as compared to that in 50% aqueous ethanol has been found to be especially marked with the phenols. The ρ values have been calculated for the individual series. The transmission coefficient $\pi' = 0.16$ has been obtained for azophenols.

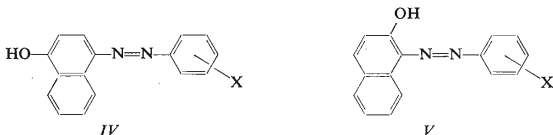
In previous papers¹⁻⁴ dissociation constants of the compounds types II-V in 50% aqueous ethanol were studied and correlated with the structure. Mixed solvents are much-sought-for for dissociation constants determination because of the increased solubility of substances. However, the complex process of dissociation is further complicated and the interpretation of results more difficult. The dissociation constants of phenols change irregularly with solvent composition⁵⁻⁹. Both the dissociation constants and the Hammett ρ constants are very close for water and low ethanol concentrations⁷, however, they increase considerably with increasing ethanol content¹⁰. The dependence of the dissociation constant on the dielectric constant of solvent defined by Born¹¹ does not fully reflect the relation between solvent and dissociation.

That was why for our dissociation constants determination dimethyl sulphoxide (DMSO, ϵ 46.7, ref.¹³) was chosen as solvent, its dielectric constant being close to that of 50% aqueous ethanol (ϵ 49, ref.¹²). As the dielectric constant of the both solvents are practically identical, the changes in macroscopic dissociation constants could be well compared.



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The dissociation equilibria of the substituted phenols *I*–*V* have been studied in this work by a potentiometric method developed by us for dissociation constants determination of benzoic acids in DMSO (ref.¹⁴).



EXPERIMENTAL

The substances used. The substituted phenols (*I*) were obtained by purification of commercial samples until the melting point agreed with that given in literature, or they were prepared by known procedures. The substituted 4-hydroxyazobenzenes (*II*), 5-methyl-2-hydroxyazobenzenes (*III*), 4-phenylazo-1-naphthols (*IV*) and 1-phenylazo-2-naphthols (*V*) were the same as those in the previous reports^{1–3}.

Dimethyl sulphoxide was dried with calcium oxide, poured through Nalsit and distilled in vacuum (b.p. 56°C/5 Torr). It was stored in dark bottles over Nalsit under nitrogen.

The dissociation constants were determined by the potentiometric titration method described in the previous report¹⁴.

RESULTS AND DISCUSSION

Table I summarizes the dissociation equilibrium constants of the compound types *I*–*V* determined by potentiometric titration in DMSO at 25°C. The solutions used for titration had the concentration of $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ M to prevent the ionic pair formation, homoconjugation and heteroconjugation.

These effects were observed by Kolthoff¹⁵ in the case of dissociation of acids in acetonitrile, they were, however, not observed in the more polar DMSO at such low concentrations. DMSO is more basic and stronger acceptor of hydrogen bond than acetonitrile, so that the undissociated acids are more solvated and have a lower tendency to form a hydrogen bond with the anion. Among our results there are three phenols the dissociation constants of which were measured by other authors^{16–18}, too, which makes it possible to verify the correctness of our measurements. We suppose that some values published by Kreškov and coworkers¹⁹ for phenol and *p*-nitrophenol (pK_a 13.7 and 10.1 resp.) and the Hammett reaction constant of dissociation of phenols in anhydrous DMSO (ρ 2.66 and 3.46 with the use of σ^- and σ resp.) do not fully agree with both the literature mentioned and our results.

TABLE I

pK_a Values of Compound Types *I–V* Determined in Anhydrous Dimethyl Sulphoxide at $25 \pm 0.01^\circ\text{C}$

X	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	σ
4-OCH ₃	17.58	13.82	14.07	11.46	15.05	-0.27
4-CH ₃	16.96	13.68	14.24	11.46	14.61	-0.17
3-CH ₃	16.86 ^a	13.66	14.21	11.01	14.90	-0.07
H	16.47 ^b	13.62	14.22	11.05	14.79	0.00
3-OCH ₃	15.72	13.52	14.06	10.77	14.62	0.12
4-Cl	16.10	13.45	—	—	—	0.23
4-Br	15.24	13.43	13.96	11.21	14.12	0.23
3-Cl	—	13.28	13.96	10.44	13.84	0.37
3-COCH ₃	15.14	13.28	13.80	—	14.18	0.38
4-SO ₂ CH ₃	—	13.16	—	10.61	13.51	0.49 ^c
4-COCH ₃	13.68	13.01	13.64	10.71	14.04	0.50 ^d
3-SO ₂ CH ₃	13.56	—	—	10.26	13.28	0.60
4-CN	13.01	13.15	13.50	10.74	13.44	0.66 ^e
3-NO ₂	13.91	13.07	13.41	10.10	13.31	0.70
4-NO ₂	11.27 ^f	12.83	13.27	10.49	13.00	0.80 ^g

^a pK_a 17.0 (ref.¹²); ^b pK_a 16.9 (ref.¹²); ^c $\Delta\sigma_p^- = 0.56$; ^d $\Delta\sigma_p^- = 0.37$; ^e $\Delta\sigma_p^- = 0.24$; ^f pK_a 10.4 (ref.¹³) and 11.0 (ref.¹⁴); ^g $\Delta\sigma_p^- = 0.44$.

TABLE II

Comparison of Dissociation Constants of Unsubstituted and *m*-Nitro-Substituted Compounds of Types *I–V* in 50% (by vol.) Aqueous Ethanol and Anhydrous Dimethyl Sulphoxide

Series	X	pK_a		ΔpK_a
		50% EtOH	DMSO	
<i>I</i>	H	11.16	16.47	5.31
	<i>p</i> -NO ₂	7.89	11.27	3.38
<i>II</i>	H	9.49	13.62	4.13
	<i>m</i> -NO ₂	8.95	13.07	4.12
<i>III</i>	H	11.24	14.22	2.98
	<i>m</i> -NO ₂	10.36	13.41	3.05
<i>IV</i>	H	9.18	11.05	1.87
	<i>m</i> -NO ₂	8.55	10.10	1.55
<i>V</i>	H	12.53	14.79	2.26
	<i>m</i> -NO ₂	11.55	13.31	1.76

The dissociation constants determined in anhydrous DMSO are substantially higher than those determined in 50% aqueous ethanol (Table II). This increase is caused by electrostatic effects, by that the phenolate anion cannot be stabilized through a hydrogen bond, and by the DMSO basicity itself. As the dielectric constants of the both solvents used are very close, the pK_a changes caused by electrostatic effects are very small and can be neglected. The main reason of the pK_a difference is ascribed to the enhanced stabilization of the phenolate anion in aqueous solvent by hydrogen bonds which are not present in DMSO. From Table II it can be seen that the acidity change is not the same for the individual compound types. In the case of the more acidic azophenols these differences are decreasing, which suggests that the solvation of anion is not so significant in alcohol and the anions are weaker bases with a markedly lower solvation.

The equation $\log(K/K_0) = \rho(\sigma + R \Delta\sigma_p^-)$ published by Yoshioka²⁰ was used for correlation of the values measured, and the relations obtained are presented in Table III. The highest value of the reaction constant was found with the substituted phenols of the type *I*. Again the increased influence of substituents on the reaction centre is caused by a decrease of the phenolate anion stabilization, the anions of weaker acids (with less delocalized charge) being more strongly hydrated in ethanol whereby the acidity of the whole series is smoothed out *i.e.* the ρ constant is lowered. This effect does not operate in DMSO, and, therefore, the influence of substituents on the overall dissociation constant is greater. The lower reaction constants of the compounds *II-V* stand in accord with the greater distance between the reaction centre and substituent.

By comparison of the reaction constants of the substituted azophenols (*II*) and azocresols (*III*) calculated for the dissociation in 50% aqueous ethanol ($\rho_{II} = -0.734$, $\rho_{III} = -1.233$) with those calculated for DMSO (-0.695 and -0.947 , respectively) it can be seen that the reaction constants of the series *II* are the same in aqueous ethanol and DMSO. Therefrom it follows that in the series *II* the substituent effects are transmitted through the phenylazo group in the both cases. The same transmission of the substituent effects exists in the series *III*, but here the reaction constant is lowered due probably to the increase of transmission by the hydrogen bond in aqueous ethanol.

The interpretation of substituent effects on the dissociation of phenylazonaphthols *IV* and *V* is made difficult by the azo-hydrazone tautomerism existing in the both series. For the time being it is impossible to determine the precise value of tautomeric equilibrium constant and hence separate the individual effects. It can be stated that the compound type *IV* behave similarly in DMSO and in 50% aqueous ethanol, which means that the correlation of the whole set is not homogeneous; it is possible to correlate quite well separately the series of 3'- and 4'-substituted phenylazonaphthols. In the case of the series *V*, where the σ^o values were used for correlation as for 50% aqueous ethanol, an increase of sensitivity of the reaction

TABLE III

Correlation Characteristics of Series *I–III* and *IV–V* according to Yoshioka²⁰ and Hammett Equations, Respectively

s Standard deviation, *R* resonance contribution in the Yoshioka equation (p. 278), *r* regression coefficient.

Compound	pK_0, s	q, s	<i>R</i>	<i>r</i>	Note
<i>I</i>	16.551 (1.875)	-4.090 (0.042)	0.804	0.978	—
	11.251 (1.461)	-2.914 (0.014)	0.802	0.989	<i>a</i>
<i>II</i>	13.595 (0.290)	-0.695 (0.002)	0.436	0.963	—
	9.473 (0.036)	-0.734 (0.027)	0.487	0.992	<i>b</i>
<i>III</i>	14.170 (0.344)	-0.947 (0.002)	0.248	0.976	—
	11.296 (0.054)	-1.223 (0.035)	0.286	0.996	<i>b</i>
<i>IV</i>	10.940 (0.050)	-1.16 (0.120)		0.980	<i>c</i>
	9.18 (0.020)	-0.87 (0.030)		0.997	<i>d</i>
	11.34 (0.060)	-1.01 (0.110)		0.97	<i>e</i>
<i>V</i>	14.69 (0.060)	-1.87 (0.130)		0.986	—
	12.53 —	-1.44 —		0.99	<i>f</i>

^a For values of the *p*-substituted derivatives in 50% EtOH see ref.²²; ^b see ref.²; ^c correlation in DMSO according to the Hammett equation using σ_m constants; ^d correlation in 50% EtOH according to the Hammett equation using σ_m constants (ref.²³); ^e correlation in DMSO according to the Hammett equation using σ_p constants; ^f correlation in 50% EtOH according to the Hammett equation using σ^0 constants (ref.¹).

centre towards the substituent effect was observed. This sensitivity increase can be ascribed to the resonance stabilization caused by quinonehydrazone tautomeric form.

In the series of compounds *I–III* the resonance factor (*R*) of the Yoshioka equation was computed, too. From Table III it follows, that the differences between the resonance factors in 50% aqueous ethanol and DMSO are so small that they can be considered identical with respect to experimental error. It means that both in 50% aqueous ethanol and DMSO the charge is dispersed and the resonance stabilization is the same in the both solvents.

From the dependence of the dissociation constants of equally substituted phenols *I* and 4-hydroxyazobenzenes *II* the transmission coefficient (π') of the *p*-phenylazo group was calculated by the least squares method. The value $\pi' 0.16$ was calculated for anhydrous DMSO; it is lower than that for 50% aqueous ethanol (0.257) (ref.²), and 20% aqueous ethanol (0.22), but it approaches to that calculated by Jaffé²¹ using MO method (0.136). The transmission coefficient of the compounds *III* was computed in the same way, and the value found (0.17) agreed with that of the compounds *II* within experimental error. This agreement of the transmission coefficients

confirms that the substituent effects on the reaction centre are transmitted by the phenylazo group in the both series (*II* and *III*), and the hydrogen bond is insignificant in DMSO.

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