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STUDY OF THE EFFECT OF THE MEDIUM ON THE ENTROPIC AND ENTHALPIC REACTION CONSTANTS FOR THE DISSOCIATION OF NITRO-PHENOLS IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

The effect of the medium on the reaction constants of the dissociation of nitro-phenols in water–dimethylsulfoxide mixtures ranging from 0.0 to 0.8 mole fraction of DMSO was further investigated. Some more correct reaction constants together with the entropic (ρ_S) and enthalpic (ρ_H) reaction constants give a more complete picture of the effect of the medium.

INTRODUCTION

The effect of the medium on the reaction constants of the dissociation of nitro-phenols in water–dimethylsulfoxide (DMSO) mixtures has been examined previously [1]. The ionization processes of nitro-benzoic acids at the same mole fractions were used as standard reactions. In this research some linear free energy relationships were used

$$(NO_2PhOH)_X + (PhO^-)_X = (NO_2PhO^-)_X + (PhOH)_X \quad (1)$$

$$(NO_2PhCOOH)_X + (PhCOO^-)_X = (NO_2PhCOO^-)_X + (PhCOOH)_X \quad (2)$$

$$-\delta\Delta G^0 = 2.303RT\rho\sigma \quad (3)$$

$$-\delta\Delta G^0 = 2.303RT\rho(\sigma + R\Delta\sigma_p^-) \qquad \Delta\sigma_p^- = \sigma_p^- - \sigma_p \quad (4)$$

$$-\delta\Delta G^0 = \rho_0\sigma_0 + fF + \delta E_S + rR \quad (5)$$

where X (ranging from 0.0 to 0.8) represents the mole fraction of the solvent.

Some different equations were used for the *meta*, *para* and *ortho* derivatives. Indeed the nitro group in the *para* position exerts a much greater influence on the substituent constant of phenol than it does on that of benzoic acid because the reaction center involves an atom with unshared electron pairs and it is directly conjugated with the strong withdrawing group NO_2.

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Furthermore, *ortho*-nitro-phenol has been shown to take part in a strong internal hydrogen bond. It could be concluded that such equations represent the reaction constants of the three isomers. quite well, but in order to calculate the $pK_{a/1}$ values of phenol at 25°C the ΔH_1^0 values of *m*-nitro-phenol were used in the equation

$$pK_{25^\circ C} = pK_{20^\circ C} - \frac{\Delta H^0_{\text{ion}} \Delta T}{1.987 \times 2.303 T_1 T_2}$$

because no ΔH^0_{ion} values for the ionization of phenol in the various water–DMSO mixtures at 25°C were found [1]. For this reason neither enthalpic nor entropic contributions of the substituent effect on the reaction constants have been calculated.

Since the ΔH^0 and ΔS^0 values of the ionization of phenol have recently been obtained in this laboratory [2], a more complete picture of the ionization of the isomers of nitro-phenol can be supplied. This is possible by separating the substituent effects into enthalpic and entropic contributions

$$-\frac{\delta \Delta G^0}{2.303RT} = \rho_{\mathrm{H}}\sigma_{\mathrm{H}} + \rho_{\mathrm{S}}\sigma_{\mathrm{S}} \tag{6}$$

$\rho_{\mathrm{H}}\sigma_{\mathrm{H}}$ and $\rho_{\mathrm{S}}\sigma_{\mathrm{S}}$ being defined by the relations

$$\rho_{\mathrm{H}}\sigma_{\mathrm{H}} = -\frac{\delta \Delta H^0}{2.303RT} \tag{6a}$$

$$\rho_{\mathrm{S}}\sigma_{\mathrm{S}} = \frac{\delta \Delta S^0}{2.303R} \tag{6b}$$

It is clear that some different relations must be used to account for the different behavior of the nitro group in the three isomers. For the *meta* isomers eqns. (6a) and (6b) are satisfactory, while the *para* isomers need the relations

$$-\frac{\Delta H^0}{2.303RT} = \rho_{\mathrm{H}}\sigma_{\mathrm{H}} + \rho R \Delta \sigma_p^- \tag{6c}$$

and

$$\frac{\Delta S^0}{2.303R} = \rho_{\mathrm{S}}\sigma_{\mathrm{S}} \tag{6b}$$

because the resonance effect influences the enthalpic term. Finally, the *ortho* isomers require the relations

$$-\frac{\Delta H^0}{2.303RT} = rR + \delta E_{\mathrm{S}} + \rho_{\mathrm{H}}\sigma_{\mathrm{H}} \tag{6d}$$

$$\frac{\Delta S^0}{2.303R} = \rho_S \sigma_S + fF \tag{6e}$$

because the inductive effects are entropy controlled, and the secondary steric effect influences the resonance effect which, in turn, affects the enthalpic term [1].

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO–water solutions and the technique for obtaining the thermodynamic values for nitro-phenols and phenol have been described previously [2,3].

RESULTS AND DISCUSSION

Using the experimental ionization values of phenol and nitro-phenols, the standard free energy change for eqns. (3), (4) and (5) is obtained as

$$\delta\Delta G^0 = \Delta G^0_{\mathrm{NO_2PhOH}} - \Delta G^0_{\mathrm{PhOH}}$$

In the same way, $\delta\Delta H^0$ and $\delta\Delta S^0$ can be calculated.

The σ_m, σ_p and σ_o values for nitro-benzoic acids have been calculated previously in the various mole fractions [4,5]. The σ_{H} and σ_{S} values for the three isomers are also available [4,5]. The f, F, R, r, δ and E_{S} values in the same mole fractions have been reported previously [1,4,5] These values and the new $\delta\Delta G^0$ values for the three nitro isomers are included in eqns. (3), (4) and (5). Thus, some more correct values for the reaction constants of the above-mentioned compounds, in the whole mole fraction range, are obtained and reported in Table 1.

TABLE 1

ρ Values calculated using eqns. (3)–(5) for *m*-, *p*-, and *o*-nitro-phenols in water–DMSO mixtures at 25°C

X_{DMSO}	ρ		
	m-Nitrophenol	*p*-Nitrophenol	*o*-Nitrophenol
0.0	2.17	2.28	1.91
0.1	3.01	2.54	2.40
0.2	3.11	2.80	2.70
0.3	3.67	3.19	3.07
0.4	3.74	3.59	3.53
0.5	4.47	4.16	4.31
0.6	4.77	4.42	5.12
0.7	4.67	4.51	5.08
0.8	4.49	4.41	5.30

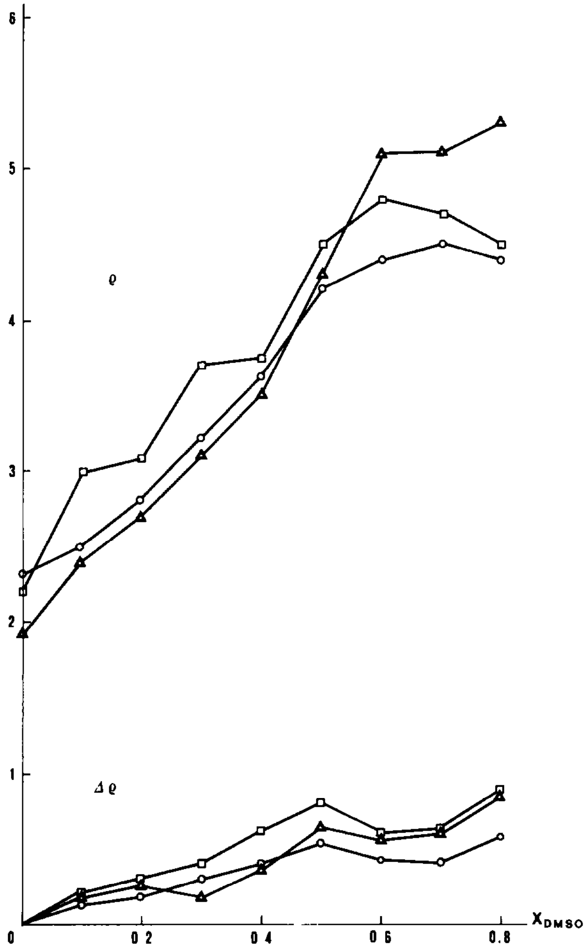

Fig. 1. Variation of the ρ and $\Delta\rho$ values for *m*- (□), *p*- (○) and *o*-nitro-phenols (△) as a function of the mole fraction of DMSO at 25°C.

The values of the reaction constants, ρ, and the variations, $\Delta\rho$, with respect to their previous values [1] are plotted in Fig. 1. The trend of the three reaction constants remains similar to that previously found [1] for $X_{\mathrm{DMSO}} \leqslant 0.6$. Beyond this mole fraction, the $\Delta\rho$ values start to modify the shapes of the curves.

Equations (6a), (6b), (6c), (6d) and (6e) give the $\rho_H\sigma_H$ and $\rho_S\sigma_S$ values for *m*-, *p*- and *o*-nitro-phenol, respectively. From these values, it is also possible to calculate the enthalpic (ρ_H) and entropic (ρ_S) reaction constants for the three isomers (Tables 2–4).

The values of the enthalpic reaction constants, ρ_H (see Fig. 2), are larger (mostly for the *ortho* and *para* derivatives) than those of the entropic reaction constants, ρ_S (see Fig. 3). This indicates that for the reaction

TABLE 2

ρ Values calculated using enthalpic [eqn. (6d)] and entropic [eqn. (6e)] equations for *o*-nitro-phenol in water + DMSO mixtures at 25°C

X_{DMSO}	ρ_H	ρ_S
0.0	−6.18	0.61
0.1	−10.10	−0.46
0.2	−19.14	−2.26
0.3	−16.69	−1.10
0.4	−24.65	−2.64
0.5	−58.43	−6.35
0.6	−5.37	3.08
0.7	8.86	6.21
0.8	5.08	5.56

TABLE 3

ρ Values calculated using enthalpic [eqn. (6a)] and entropic [eqn. (6b)] equations for *m*-nitro-phenol in water–DMSO mixtures at 25°C

X_{DMSO}	ρ_H	ρ_S
0.0	−2.09	1.33
0.1	−7.08	0.86
0.2	−22.36	−2.61
0.3	2.54	3.65
0.4	−3.34	2.34
0.5	−5.69	2.41
0.6	11.73	6.76
0.7	20.51	8.71
0.8	35.51	11.93

TABLE 4

ρ Values calculated using enthalpic [eqn. (6c)] and entropic [eqn. (6b)] equations for *p*-nitro-phenol in water–DMSO mixtures at 25°C

X_{DMSO}	ρ_H	ρ_S
0.0	2.36	2.44
0.1	−2.43	1.53
0.2	−7.20	0.66
0.3	−0.30	2.21
0.4	−29.02	8.41
0.5	−2.17	4.36
0.6	10.97	6.10
0.7	53.36	13.35
0.8	27.17	8.80

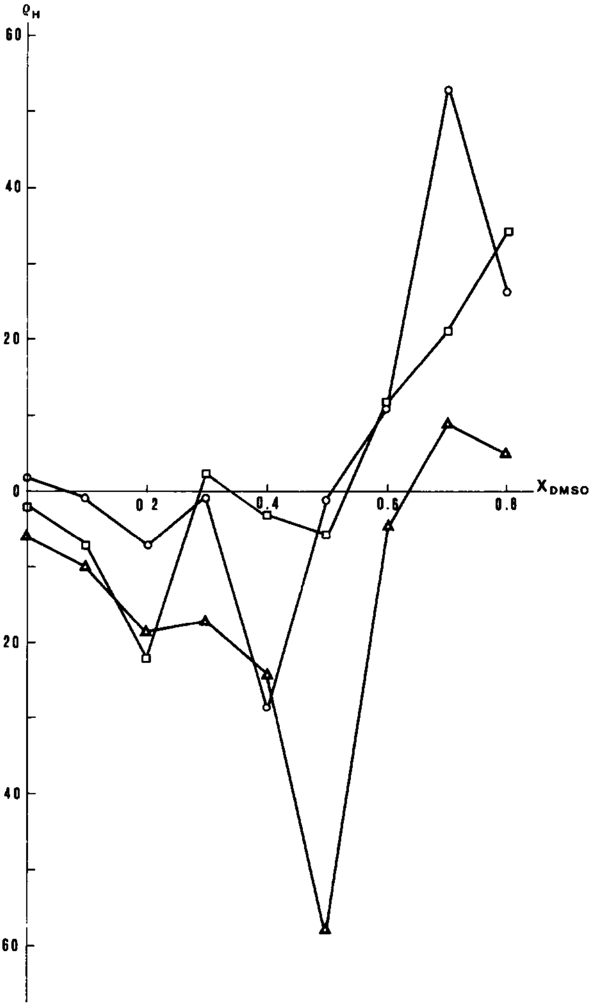

Fig. 2. Variation of the ρ_H values for the *o*- (△), *m*- (□) and *p*-nitro-phenols (○) as a function of the mole fraction of DMSO at 25°C.

constants the enthalpic contribution prevails over the entropic contribution, as could be expected by virtue of the greater delocalization shown by the nitro group in the phenate ion [1].

Furthermore, it is noteworthy that the ρ_S values for the *ortho* derivatives are negative in the mole fraction range 0.0–0.6 and show a maximum at $X_{DMSO} = 0.5$. This pattern can be explained bearing in mind that the solute–solvent interactions are expressed by means of the entropic reaction constants, ρ_S. Thus the greater desolvation of the phenol anions with respect to the benzoic anions influences the shape of ρ_S curves. The differences [2,6] in the solvation enthalpy among the nitro-benzoic and nitro-phenol anions,

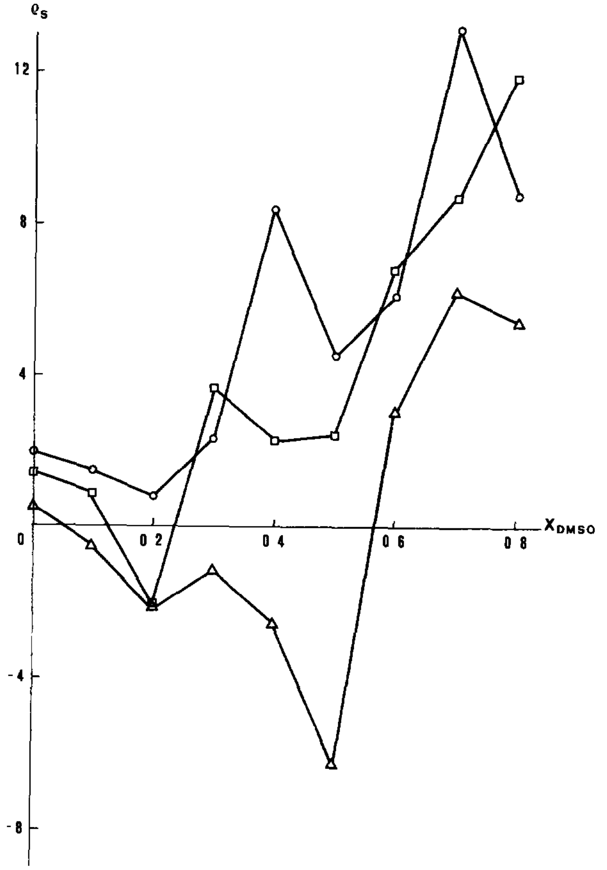

Fig. 3. Variation of the ρ_S values for the *o*- (△), *m*- (□) and *p*-nitro-phenols (○) as a function of the mole fraction of DMSO at 25°C.

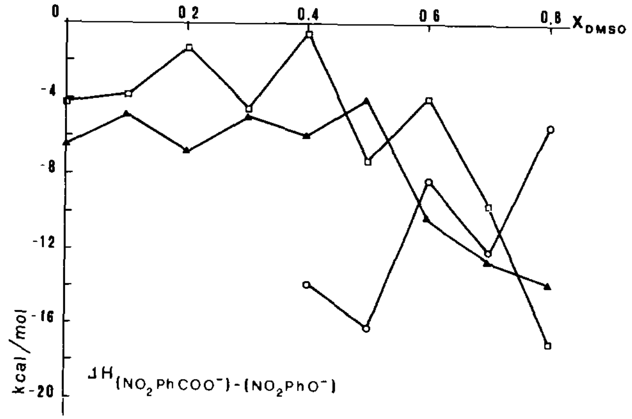

Fig. 4. Differences in the solvation enthalpies between nitro-benzoic and nitro-phenol anions in various DMSO–water mixtures at 25°C. (▲) *o*-, (□) *m*-, and (○) *p*- nitro-phenol.

$\Delta H^0_{(NO_2PhCOO^-)_X-(NO_2PhO^-)_X}$, are plotted in Fig. 4.

As previously shown [1], the ρ values measure the sensitivity of the phenol derivatives to the electron withdrawing effect of the nitro group with respect to the benzoic derivatives in the same solvent. It is also known [1] that the solvent interferes to a minor extent with the interactions between the reaction site and the substituent group of the nitro-phenols.

The ρ_H and ρ_S curves give a more complete picture of the effect of the medium on the reaction constants. At $X_{DMSO} = 0.5$, where the charge delocalization of the *ortho* phenol anion is maximum, its solvation is maximum [1].

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