Thermochimica Acta, 34 (1979) 29—34
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ENTHALPIC AND ENTROPIC CONTRIBUTIONS TO SUBSTITUENT EFFECTS FOR THE IONIZATION OF *META*- AND *PARA*-NITROBENZOIC ACIDS IN WATER—DIMETHYLSULPHOXIDE MIXTURES AT 25°C

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(Received 11 January 1979)

ABSTRACT

Enthalpic and entropic contributions to substituent effects for the ionization of *m*- and *p*-nitrobenzoic acids are examined, ranging from pure water to 0.8 mole fraction DMSO. The effect of the medium on the substituent and reaction constants is explained in terms of solute—solvent interactions. No structure-breaking effect was found.

INTRODUCTION

The enthalpic and entropic contributions to substituent effects for the dissociation of *m*- and *p*-chlorobenzoic acids in H_2O—DMSO mixtures have previously been examined [1]. The present work examines the influence of the $-NO_2$ (R^- I^-) group on ρ and σ values related to the ionization processes of nitrobenzoic acids at various mole fractions of H_2O—DMSO solutions. Some differences were found in the behaviour of —Cl and $-NO_2$ groups.

According to Hammett [2] and others [3,4], the following equations may be written.

$$(NO_2{-}PhCOOH)_X + (PhCOO^-)_X = (NO_2{-}PhCOO^-)_X + (PhCOOH)_X \tag{1}$$

$$-\delta\ \Delta G^0 = 2.303RT\rho\sigma \tag{2}$$

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

The variation of the solvent composition affects the ρ and σ values in different ways. By using experimental ionization values [5] of benzoic and nitrobenzoic acids, the standard enthalpy change for eqn. (1) is obtained as

$$\delta\ \Delta H^0 = \Delta H^0_{NO_2-PhCOOH} - \Delta H^0_{PhCOOH}$$

In the same way, the $\delta\Delta G^0$ and $\delta\Delta S^0$ values related to process (1) can be obtained.

Equation (2) may be written in the form

$$-\frac{\delta\ \Delta G^\circ}{2.303RT} = \rho_H\sigma_H + \rho_S\sigma_S \tag{3}$$

$\rho_H\sigma_H$ and $\rho_S\sigma_S$ being defined by the relations

$$\rho_H\sigma_H = -\frac{\delta\,\Delta H^0}{2.303RT} \tag{4a}$$

$$\rho_S\sigma_S = \frac{\delta\,\Delta S^0}{2.303R} \tag{4b}$$

The ρ, ρ_H and ρ_S values are assumed to be equal to 1 in water at 25°C and 1 atm.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, the preparation of DMSO—H_2O mixtures and the technique for obtaining values for the ionization of benzoic and nitrobenzoic acids have been described previously [6].

RESULTS AND DISCUSSION

The $\delta\Delta H^0$, $\delta\Delta G^0$ and $\delta\Delta S^0$ values of reaction (1) for *m*- and *p*-nitrobenzoic acids are given by eqns. (2), (4a) and (4b). The $\rho\sigma$, $\rho_H\sigma_H$ and $\rho_S\sigma_S$ values are reported in Table 1. On the other hand, it is possible to calculate the σ_m and σ_p values by using the $\rho_{m,p}$ values [1,7] for the dissociation of benzoic acids at the various DMSO mole fractions (see Table 2). $\rho_{m,p}$, σ_m and σ_p values are plotted against X_{DMSO} in Fig. 1.

As previously reported [1], the variations of the substituent and reaction constants at the various mole fractions can be attributed both to the solvent—solute interactions and to the structural alteration of the medium. As the resonance effect for the —NO_2 group undoubtedly exists, although not

TABLE 1

Results of application of separated enthalpy—entropy and normal Hammett equations to *m*- and *p*-nitrobenzoic acids ionization in H_2O—DMSO mixtures at 25°C

X_{DMSO}	$\rho\sigma$	*m*-NO_2			*p*-NO_2	
		$\rho_H\sigma_H$	$\rho_S\sigma_S$	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.0	0.736	—0.246	0.972	0.755	—0.243	0.998
0.1	0.894	—1.180	2.076	0.931	—0.122	1.052
0.2	1.048	—4.000	5.048	1.055	—0.217	1.270
0.3	1.173	—6.199	7.360	1.180	—3.500	4.680
0.4	1.319	—8.934	10.240	1.268	—3.460	4.730
0.5	1.436	—9.322	10.750	1.326	—2.350	3.660
0.6	1.539	—9.688	11.220	1.436	—3.394	4.820
0.7	1.649	—5.596	7.240	1.546	—4.310	5.850
0.8	1.708	—4.712	6.410	1.678	—7.200	8.730

TABLE 2

σ values calculated by using the Hammett equation for the *m*- and *p*-nitrobenzoic acids in H_2O—DMSO mixtures at 25°C

X_{DMSO}	*m*-NO_2 σ_m	*p*-NO_2 σ_p
0.0	0.736	0.755
0.1	0.737	0.768
0.2	0.774	0.779
0.3	0.757	0.761
0.4	0.805	0.774
0.5	0.821	0.758
0.6	0.815	0.761
0.7	0.799	0.749
0.8	0.746	0.733

to a great extent, one can expect σ values that are independent of solvent [8]. If it is assumed that the inductive and field effects are the same in both the positions, $\sigma_m - \sigma_p$ should be a measure of the resonance effect (see Table 3). In the range $0.0 \leqslant X_{DMSO} \leqslant 0.3$, the resonance is effective (σ_m —

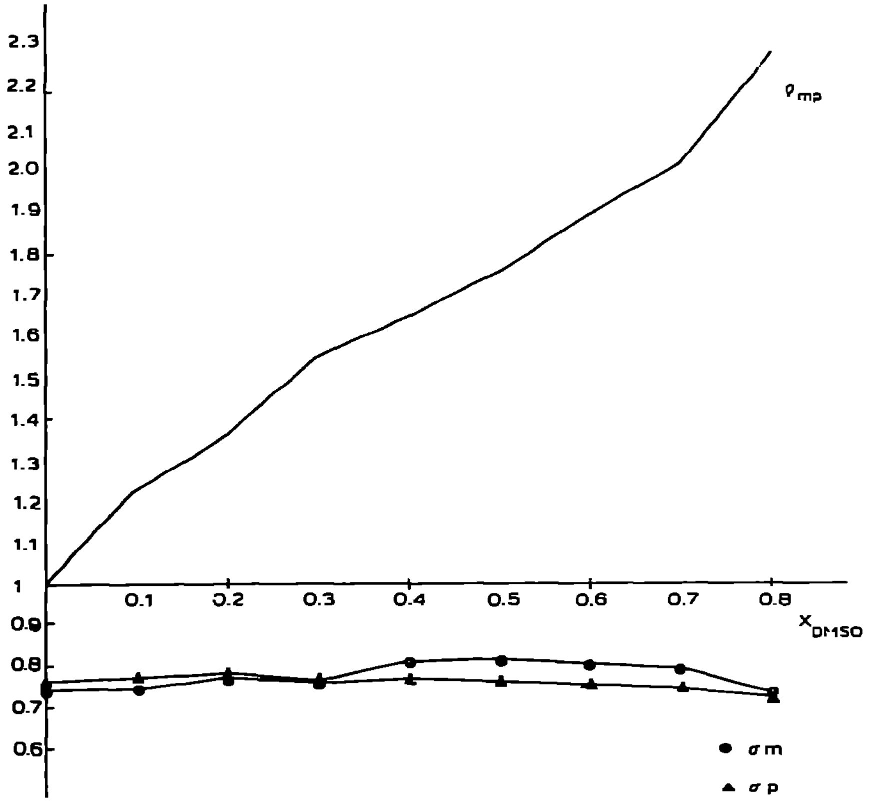

Fig. 1. Variation of the ρ and σ values for the *m*- and *p*-nitrobenzoic acids as a function of the mole fraction at 25°C.

TABLE 3

Variation of the resonance effect $\sigma_m - \sigma_p$ as a function of the mole fraction at 25°C

X_{DMSO}	$\sigma_m - \sigma_p$
0.0	—0.019
0.1	—0.031
0.2	—0.005
0.3	—0.004
0.4	0.031
0.5	0.063
0.6	0.054
0.7	0.050
0.8	0.013

TABLE 4

σ values calculated by using enthalpic and entropic equations for the *m*- and *p*-nitrobenzoic acids in H_2O—DMSO mixtures at 25°C

X_{DMSO}	*m*-NO_2		*p*-NO_2	
	σ_H	σ_S	σ_H	σ_S
0.0	—0.203	0.880	—0.211	0.910
0.1	—0.207	0.887	—0.214	0.921
0.2	—0.216	0.927	—0.217	0.933
0.3	—0.213	0.908	—0.212	0.913
0.4	—0.225	0.962	—0.216	0.927
0.5	—0.230	0.978	—0.211	0.910
0.6	—0.229	0.973	—0.212	0.913
0.7	—0.224	0.955	—0.208	0.900
0.8	—0.207	0.897	—0.204	0.883

TABLE 5

ρ values calculated by using entropic equation for the *m*- and *p*-nitrobenzoic acids in H_2O—DMSO mixtures at 25°C

X_{DMSO}	*m*-NO_2 ρ_S	*p*-NO_2 ρ_S
0.0	1.105	1.100
0.1	2.340	1.142
0.2	5.445	1.361
0.3	8.102	5.124
0.4	10.645	5.100
0.5	10.992	4.024
0.6	11.520	5.279
0.7	7.589	6.500
0.8	7.146	9.888

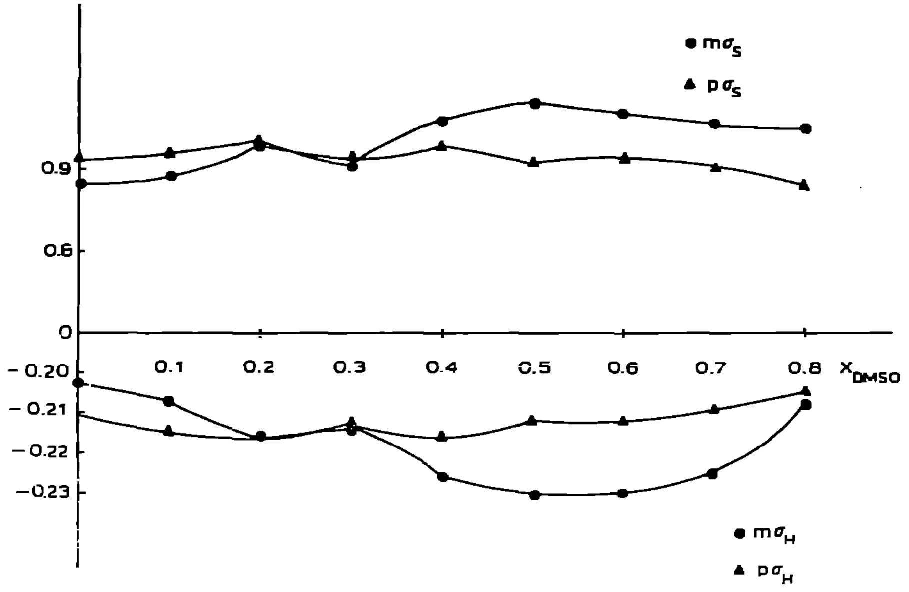

Fig. 2. Variation of the σ_H and σ_S values for the *m*- and *p*-nitrobenzoic acids as a function of the mole fraction at 25°C.

σ_p is negative) and strengthens the inductive effect. Beyond 0.3 mole fraction, the inductive effect prevails over the resonance effect and the order of substituent constants becomes $\sigma_m > \sigma_p$. The explanation of this pattern lies in the fact that at $X_{DMSO} = 0.4$ mole fraction, the *p*-nitrobenzoic acid mole-

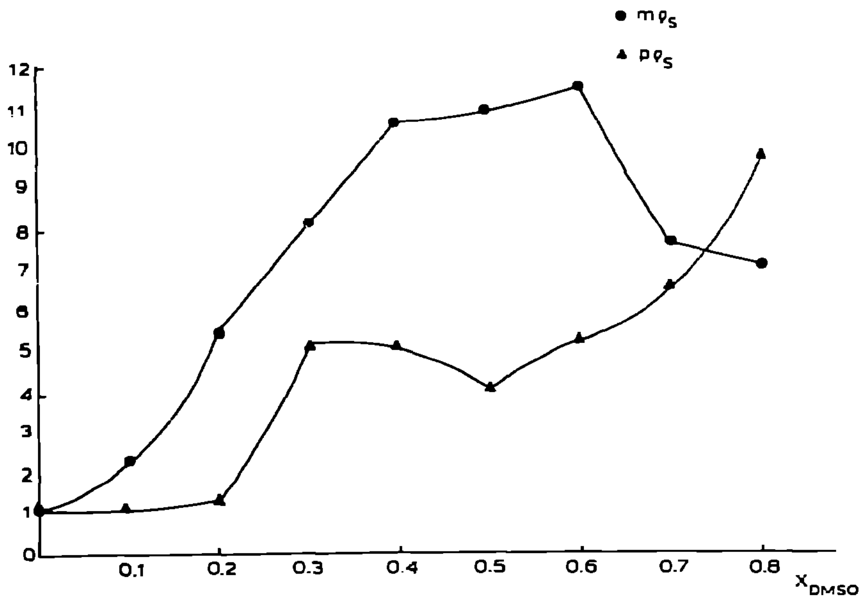

Fig. 3. Variation of the ρ_S values for the *m*- and *p*-nitrobenzoic acids as a function of the mole fraction at 25°C.

cules are completely solvated [7], so that the electron charge density distribution in the solute molecule is altered.

The σ values display a limited dependence on the medium effect so that it seems reasonable to assume that the equations in water [9], $\sigma = 0.91\sigma_S - 0.07$ and $\sigma_S = -3.6\sigma_H + 0.15$, are valid over the whole mole fraction range. With this assumption, σ_H and σ_S values are calculated and tabulated (see Table 4). By using these values, it is possible to calculate ρ_S (see Table 5). σ_H and σ_S are plotted against DMSO mole fraction (Fig. 2), while the ρ_S values are plotted in Fig. 3.

Large negative σ_H values indicate that the undissociated molecules of nitrobenzoic acids strongly interact with the solvent molecules. The fact that the values of σ_S are larger than those of σ_H indicates that the external contributions are mostly entropy controlled [9], so that the solute—solvent interactions are exclusively discussed in terms of ρ_S change.

Unlike the trend of the ρ_S values of the ionization of chlorobenzoic acids, the entropy reaction constants do not show a minimum at $X_{DMSO} = 0.5$. The reaction constants of the *meta* compound are much greater than those of the *para* compound, this being particularly so at $X_{DMSO} = 0.5$. This fact can be related to the drastic *meta*-anion desolvation [7].

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