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ORTHO EFFECTS OF CHLORO- AND NITROBENZOIC ACIDS IN WATER—DIMETHYLSULPHOXIDE MIXTURES AT 25°C

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ABSTRACT

The dissociation of *ortho*-chloro- and nitro-benzoic acids in water—DMSO mixtures (0.0 + 0.8 DMSO mole fraction) was studied by means of a linear combination of the ordinary polar, proximity polar, and steric effects. Enthalpic and entropic contributions to substituent effects for the *ortho*-derivatives were also examined. The dissociation of the *ortho*-chloro-derivatives appears to be mostly anion-controlled. However, for the *ortho*-nitro-derivatives, the steric inhibition of solvation on the undissociated molecules may also be involved in controlling the course of the reaction.

INTRODUCTION

The enthalpic and entropic contributions to substituent effects on the ionization of *meta*- and *para*-chlorobenzoic and nitrobenzoic acids, in water—dimethylsulphoxide mixtures, have previously been examined [1,2]. The following equations have been used to illustrate the substituent effects

$$(\mathrm{X{-}PhCOOH})_s + (\mathrm{PhCOO^-})_X = (\mathrm{X{-}PhCOO^-})_X + (\mathrm{PhCOOH})_X \quad (1)$$

$$-\delta\Delta G^0 = 2.303RT\rho\sigma \quad (2)$$

$$\rho_H\sigma_H = -\frac{\delta\Delta H^0}{2.303RT} \quad (3a)$$

$$\rho_S\sigma_S = \frac{\delta\Delta S^0}{2.303R} \quad (3b)$$

The variation of ρ, σ, σ_S, σ_H, and ρ_S values as functions of the solvent composition has been determined. In order to obtain a more complete picture, the behaviour of the *ortho*-compounds undergoing the same processes has been assessed. Fujita and Nishiota [3] assume that the total *ortho*-substituent effect can be expressed in terms of the ordinary polar, proximity polar, and steric effects, according to the following equation

$$\log\left(\frac{K_{ortho}}{K_H}\right) = \rho_o\sigma_o + fF_o + \delta E_s^0 \quad (4)$$

The ordinary polar effect would be imaginary from *ortho* substituents without the steric and proximity polar effects. The primary polar effect is defined equal to that of *para*-substituents, so that $\sigma_o \cong \sigma_p$ [3]. The proximity polar effect, F, would account for the inductive and field effects. The steric effect would include the space-filling factor of the *ortho*-substituent (primary steric effect) with a consequent steric hindrance to solvation for the functional group (E_s). The latter effect also includes a steric inhibition of the resonance in the substituent or in the functional group (secondary steric effect). Equation (4) may be written as

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_o\sigma_o + fF_o + \delta E_s^0 \tag{5}$$

Equation (5), in turn, may be written as [1,2]

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_H\sigma_H + \rho_S\sigma_S + fF_o + \delta E_s^0 \tag{6}$$

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

$$-\frac{\delta\Delta H^0}{2.303RT} = \rho_H\sigma_H + \delta E_s^0 \tag{7a}$$

$$\frac{\delta\Delta S^0}{2.303R} = \rho_S\sigma_S + fF_o \tag{7b}$$

Because the external contributions for the nitro- and chlorobenzoic acids are chiefly inductive in character [1,2] and entropy-controlled, it seems reasonable to place an inductive term in eqn. (7b). Since the secondary steric effect influences the resonance effect [3] and the latter affects the enthalpic term [4], the steric term is included in eqn. (7a).

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, the preparation of the DMSO—water mixtures and the technique for obtaining the thermodynamic values for the chloro- and nitro-*ortho*-derivatives, have been described previously [5,6].

RESULTS AND DISCUSSION

Using experimental ionization values for benzoic [7], chlorobenzoic [5] and nitrobenzoic [6] acids, the standard free energy for reaction (5) is obtained as

$$S\Delta G^0 = \Delta G^0_{\text{O-X-PhCOOH}^-} - \Delta G^0_{\text{PhCOOH}}$$

In the same way, the $\delta\Delta H^0$ and $\delta\Delta S^0$ values related to eqns. (7a and b), respectively, can be obtained.

The ρ_0, fF_o and δE_s^0 values for the dissociation of the substituted benzoic acids in H_2O—DMSO mixtures have been reported in the literature [3]. For the E_s^0 values, the reference substituent is $H(E^0_{s(H)} = 0)$. For the nitro-compound the E_s^0 value for the minimum dimension has been used [3], corresponding to the perpendicular position of the —NO_2 group with respect to the reaction site.

If the above-mentioned values are included in eqn (5), σ_o values are found on the same scale as σ_m and σ_p.

σ_o values at the various mole fraction are reported in Table 1. The values of σ_o and ρ_o for nitro- and chloro-benzoic acids are plotted against X_{DMSO} in Fig. 1.

The order of the substituent constant is NO_2-σ_o > Cl-σ_o throughout the molar fraction range. Indeed, the —NO_2 group is a more powerful electron acceptor than the —Cl group

In pure water no resonance interaction is to be expected for *o*-nitrobenzoic acid, because the —NO_2 and —COOH groups are not in the plane of the benzene ring [3]. When DMSO is added to water, the mixture displays maximum structure [8] at $X_{DMSO} = 0.15$, so that the extent of the interaction of nitrobenzoic acid molecules with the organic solvent is reduced For this reason the coplanarity of the nitro- and carboxyl-groups may be only marginally reduced, this, in turn, allowing the resonance to be recovered. Thus, the resonance overlaps the inductive effect, so that at $X_{DMSO} = 0.2$ the NO_2-σ_o term displays a maximum.

For the chloro-derivatives the σ values decrease according to the sequence [1] $\sigma_o \geqslant \sigma_m > \sigma_p$ in the range of mole fraction 0 1 + 0.8 because the inductive effect prevails. The order [2] for the nitro-compounds is $\sigma_o \geqslant \sigma_m > \sigma_p$, except in the mole fraction range $0.1 \leqslant X_{DMSO} \leqslant 0.3$, where the order is $\sigma_o > \sigma_p > \sigma_m$. In pure water, the order is $\sigma_p > \sigma_m > \sigma_o$, for the nitro-derivatives, while for the chloroderivatives the following order is observed $\sigma_m > \sigma_o > \sigma_p$.

The steric effect seems to be strongly dependent on the nature of the solvent, so that in pure water δE_s^0 has a significant value, whereas in DMSO—H_2O mixtures it is negligible [3].

The $\delta\Delta H^0$, $\delta\Delta S^0$, δE_s^0 and fF_o values are included in eqns. (7a and b) and the $\rho_H\sigma_H$ and $\rho_S\sigma_S$ values are reported in Table 2. The σ_o values lie on the

TABLE 1

σ_o values calculated using eqn. (5) for the *o*-chlorobenzoic and *o*-nitrobenzoic acids in water—DMSO mixtures at 25°C

X_{DMSO}	σ_o	
	o-Chlorobenzoic acid	*o*-Nitrobenzoic acid
0.0	0.292	0.650
0.1	0.426	0.785
0.2	0.388	0.869
0.3	0.344	0.780
0.4	0.384	0.799
0.5	0 501	0.814
0.6	0.421	0.807
0 7	0.406	0.807
0.8	0.365	0.781

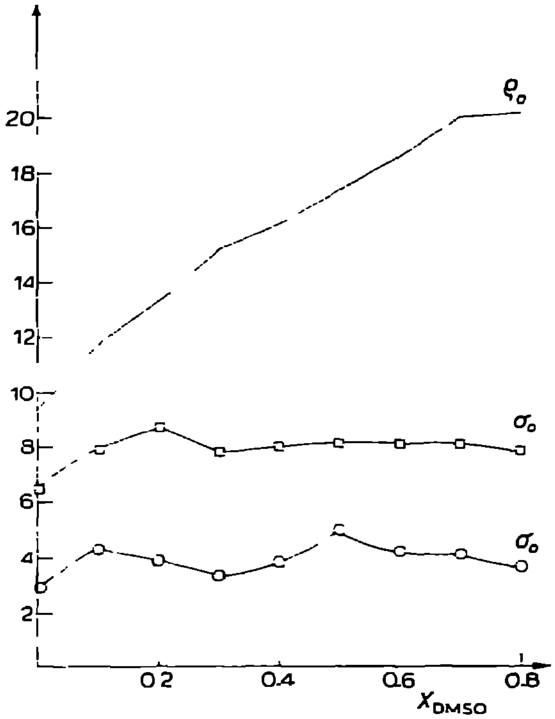


Fig 1. Variation of the ρ and σ values for *o*-chlorobenzoic and *o*-nitrobenzoic acids as a function of the mole fraction of DMSO at 25°C. □, *o*-NO_2, ○, *o*-Cl.

same scale as σ_m and σ_p and display a limited dependence on the medium effect (see Fig. 1). Thus, it seems reasonable to assume that the equations tested in water [4], viz. $\sigma = 0.91\ \sigma_S - 0.07$ and $\sigma_S = -3.6\ \sigma_H + 0.15$, which were also used [1,2] for σ_m and σ_p values over the whole mole fraction range, are also valid for the σ_o values. The values of *o*-σ_S and *o*-σ_H have been calculated and are reported in Table 3.

TABLE 2

Results of application of separate enthalpy—entropy equations to ionization of *o*-chlorobenzoic and *o*-nitrobenzoic acids in water—DMSO mixtures at 25°C

x_{DMSO}	*o*-Chlorobenzoic acid		*o*-Nitrobenzoic acid	
	$\rho_H\sigma_H$	$\rho_S\sigma_S$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.0	1.525	−1.240	0.249	0.400
0.1	1.277	−0.771	0.177	0.753
0.2	−1.278	1.791	0.246	0.903
0.3	−0.611	1.134	−1.513	2.700
0.4	−0.509	1.127	−2.235	3.519
0 5	−0.566	1.429	−5.199	6.597
0.6	−3.239	3.920	−3.123	4.619
0.7	−6.169	6.984	−2.358	3.969
0.8	−4.307	5.091	−2.499	4.185

TABLE 3

σ Values calculated using enthalpic and entropic equations for the *o*-chlorobenzoic and *o*-nitrobenzoic acids in water—DMSO mixtures at 25°C

x_{DMSO}	*o*-Chlorobenzoic acid		*o*-Nitrobenzoic acid	
	σ_H	σ_S	σ_H	σ_S
0.0	−0.068	0.398	−0.178	0.791
0.1	−0.110	0.545	−0.219	0.939
0.2	−0.098	0.504	−0.245	1.032
0.3	−0.084	0.454	−0.218	0.934
0.4	−0.097	0.499	−0.223	0.954
0.5	−0.132	0.627	−0.228	0.971
0.6	−0.108	0.539	−0.226	0.963
0.7	−0.104	0.523	−0.226	0.964
0 8	−0.091	0.478	−0.218	0.935

Using the values from Table 2, it is possible to calculate the *o*-ρ_S values (see Table 4). *o*-σ_S and *o*-σ_H values are plotted against DMSO mole fraction in Fig. 2, while the *o*-ρ_S values are plotted in Fig. 3.

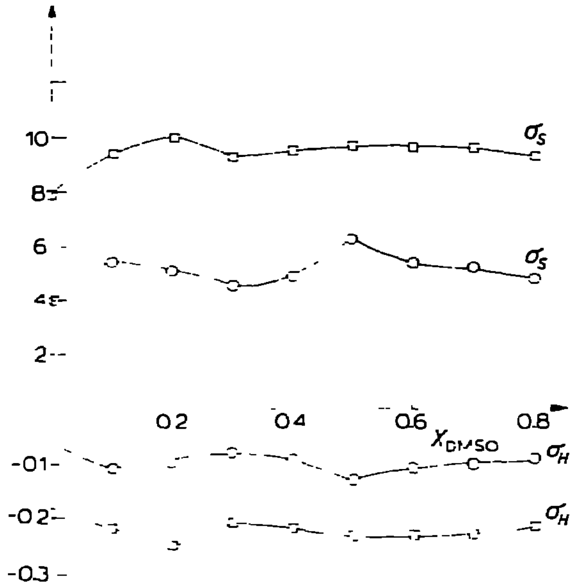
For the chlorobenzoic acids the values of *o*-ρ_S are negative in the mole fraction range 0.0—0.15. This fact can be ascribed to the drastic desolvation, in water-rich solutions, of the *o*-chlorobenzoic anion [5] with respect to the unsubstituted anion. On the other hand, beyond 0.15 mole fraction, both the anions are desolvated and the *o*-ρ_S values become positive. This behaviour is in agreement with the hypothesis that, for the chloro-derivatives, the solvation of the anions rather than that of the undissociated molecules is involved in the control of the course of the reaction.

However, for the nitro-compounds it seems reasonable to assume that both the undissociated molecules and their anions exhibit a steric inhibition of solvation on the carboxyl and carboxylate groups, respectively.

TABLE 4

σ_S values calculated using the entropic equation for *o*-chlorobenzoic and *o*-nitrobenzoic acids in water—DMSO mixtures at 25°C

x_{DMSO}	ρ_S	
	o-Chlorobenzoic acid	*o*-Nitrobenzoic acid
0.0	−3.117	0.505
0.1	−1.415	0.802
0.2	3.555	0.875
0 3	2 495	2.891
0.4	2.258	3.689
0.5	2.277	6.795
0.6	7.266	4.796
0.7	13.338	4.117
0.8	10.655	4.476



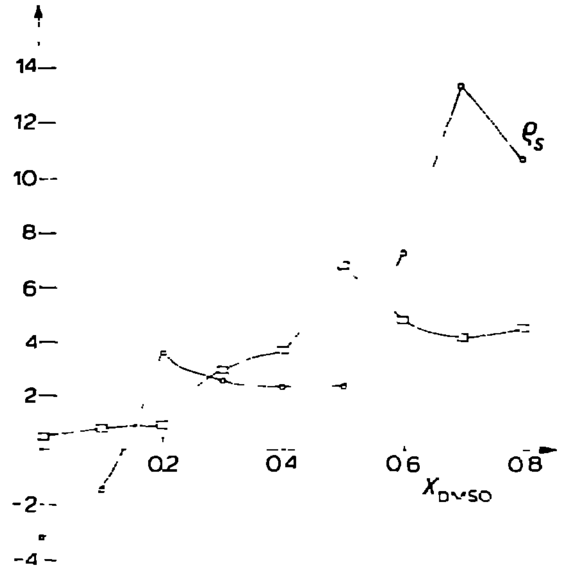


Fig. 2. Variation of the σ_H and σ_S values of *o*-chlorobenzoic and *o*-nitrobenzoic acids as a function of the mole fraction of DMSO at 25°C. □, *o*-NO_2 ; ○, *o*-Cl.

Fig 3. Variation of the ρ_S values for the *o*-chlorobenzoic and *o*-nitrobenzoic acids as a function of the mole fraction of DMSO at 25°C. □, *o*-NO_2; ○, *o*-Cl.

The primary steric effect on the solvated carboxyl group and the resulting congestion accelerate the dissociation of the neutral molecules. The steric inhibition of solvation for the anions counteracts the steric acceleration effect on the undissociated molecules and tends to reduce the dissociation rate of the compound. This fact explains the very low values of *o*-ρ_S with respect to those of the chloro-derivatives beyond 0.5 mole fraction.

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