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ORTHO EFFECTS OF HYDROXYBENZOIC ACID IN WATER—DIMETHYLSULFOXIDE MIXTURES AT 25°C

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ABSTRACT

The *ortho* effect in the ionization of hydroxybenzoic acid in water—DMSO mixtures (0.0—0.8 mole fraction) was studied by means of a linear combination of the ordinary polar, proximity polar and steric effects. A measure of the internal hydrogen bond was found as $\sigma_o^1 - \sigma_p$. This difference was included in the linear combination as an additional term for the field effect so that a better approximation for substituent constant values σ_o^2 was found. The dielectric constant of the medium and the field effect created by the internal hydrogen bond seem to be related to each other in a regular fashion.

INTRODUCTION

The dissociation of *ortho*-chloro and nitrobenzoic acids in water—DMSO mixtures has been studied by means of a linear combination of the ordinary polar, proximity polar and sterics effects [1]. Enthalpic and entropic contributions to substituent effects for the *ortho*-derivatives have also been examined. In this way the substituent and reaction constants for the *ortho*-chloro and nitrobenzoic acids have been calculated.

The dissociation of the chloro derivatives was found mostly anion-controlled [1]. For the nitro derivatives, the steric inhibition of solvation of the undissociated molecules plays a major role in controlling the course of the reaction [1]. The *ortho*-hydroxybenzoic acid shows a strong intramolecular and intermolecular hydrogen bond.

It is interesting to ascertain if the equation used [1] for the nitro and chloro *ortho*-isomers also holds true for the *ortho*-hydroxy compound in the same mole fraction.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, the preparation of the DMSO—water mixtures and the technique for obtaining the thermodynamic values for the *ortho*-hydroxy and benzoic acids have been previously described [2,3].

The total *ortho*-substituent effect can be expressed [4] in terms of the ordinary polar, proximity polar and steric effects, according the following equations

$$(\mathrm{HO{-}PhCOOH})_x + (\mathrm{PhCOO^-})_x = (\mathrm{HO{-}PhCOO^-})_x + (\mathrm{PhCOOH})_x \tag{1}$$

$$-\frac{\delta\,\Delta G^0}{2.303RT} = \rho_0\sigma_0 + \mathrm{f}F^0 + \delta E^0_{\mathrm{s}} \tag{2}$$

were x (ranging from 0.0 to 0.8) represents the mole fraction of the solvent.

The ordinary polar effect would be imaginary [4] from *ortho*-substituents without the proximity polar and steric effects. The ordinary polar effect is equal, by definition, to that of *para*-substituents, so that $\sigma_o \cong \sigma_p$.

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^0_{s}). The latter effect also includes a steric inhibition of the resonance in the substituent or in the functional group (secondary steric effect).

Equation (2) may also be written as [1]

$$-\frac{\delta\,\Delta G^0}{2.303RT} = \rho_{\mathrm{H}}\sigma_{\mathrm{H}} + \rho_{\mathrm{s}}\sigma_{\mathrm{s}} + \mathrm{f}F^0 + \delta E^0_{\mathrm{s}} \tag{3}$$

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

$$-\frac{\delta\,\Delta H^0}{2.303RT} = \rho_{\mathrm{H}}\sigma_{\mathrm{H}} + \delta E^0_{\mathrm{s}} \tag{3a}$$

$$\frac{\delta\,\Delta S^0}{2.303R} = \rho_{\mathrm{s}}\sigma_{\mathrm{s}} + \mathrm{f}F^0 \tag{3b}$$

The ρ, ρ_{s} and ρ_{H} values are assumed equal to 1 in water at 25°C and 1 atm.

The external contributions for the ionization of the *meta*- and *para*-hydroxybenzoic acids are chiefly inductive in character and entropy-controlled, as seen in a previous work [5], so that an inductive term may be reasonably put in eqn. (3b). Since the secondary steric effect influences the reasonance effect [4] and the latter affects the enthalpic term [6], the steric term is included in eqn. (3a).

Using experimental ionization values for benzoic [3] and *ortho*-hydroxybenzoic acid [2], the standard free energy for reaction (2) is obtained as

$$\delta\,\Delta G^0 = \Delta G^0_{o\text{-}\mathrm{OH{-}PhCOOH}} - \Delta G^0_{\mathrm{PhCOOH}}$$

In the same way, the $\delta\Delta H^0$ and $\delta\Delta S^0$ values related to eqns. (3a) and (3b) can be obtained.

The ρ_o, f, F^0, δ and E^0_{s} values for the dissociation of the *ortho*-benzoic acids in water—DMSO mixtures are reported in the literature [4]. For the E^0_{s} value the reference substituent is H : $E^0_{\mathrm{s(H)}} = 0$. If the above values are included in eqn. (2), σ^1_o values are found on the same scale as σ_m and σ_p.

RESULTS AND DISCUSSION

σ_o^1 values at the various mole fractions are reported in Table 1 and plotted against X_{DMSO} in Fig. 1. For the substituent constants of the three hydroxy-isomers, the following orders were observed throughout the mole fraction range: $o\text{-}\sigma_o > m\text{-}\sigma_m > p\text{-}\sigma_p$.

Considering also the σ_o values [1] of the *o*-chloro and *o*-nitrobenzoic acids, the order of the substituent constants is $o\text{-}\sigma_{\mathrm{NO_2}} > o\text{-}\sigma_{\mathrm{OH}} > o\text{-}\sigma_{\mathrm{Cl}}$ in the range $0 < X_{\mathrm{DMSO}} < 0.1$, while in the range $0.1 < X_{\mathrm{DMSO}} < 0.8$ the order observed is $o\text{-}\sigma_{\mathrm{OH}} > o\text{-}\sigma_{\mathrm{NO_2}} > o\text{-}\sigma_{\mathrm{Cl}}$.

This behaviour can be related mostly to the field effect created by the strong intramolecular hydrogen bond, which shows a nonlinear dependence on the composition of the medium. Indeed, the dielectric constant [7] of the medium decreases linearly, while the σ_o^1 values increase with different slopes (Fig. 1).

The *ortho*-hydroxybenzoic molecule is poorly solvated [2] with respect to the *meta*- and *para*-hydroxy derivatives throughout the mole range. This means that the intramolecular hydrogen bond is present even when X_{DMSO} approaches unity. Therefore the steric hindrance to solvation for the functional group (E_s^0) should be significant throughout the mole range fraction.

It has to be remarked that for the chloro and nitro-derivatives the σ_o values [1] are very close to the respective σ_p values [1,8,9]. Thus for these derivatives, the hypothesis that [4] the ordinary polar effect is equal to the *para* effect ($\sigma_o \cong \sigma_p$), may be considered as valid. On the contrary, for the *o*-hydroxy derivatives, the σ_o^1 values differ from the σ_p values [5]. This difference can be assumed as a measure of the internal hydrogen bond (Table 1).

At high DMSO mole fractions the decreasing $\sigma_o^1 - \sigma_p$ seems to be attributable to the congestion of the *o*-hydroxybenzoic acid solvated with strong proton accepting solvent molecules (see Fig. 2). Thus the coplanarity of —COOH and —OH groups and, in turn, the field effect of the internal hydrogen bond, can be reduced, while the dielectric constant shows the smallest values.

TABLE 1

σ_0^1 Values calculated using eqn. (2) for the *o*-hydroxybenzoic acid and $\sigma_0^1 - \sigma_p$ values in water—DMSO mixtures at 25°C

X_{DMSO}	σ_0^1	$\sigma_0^1 - \sigma_p$
0.0	0.586	0.967
0.1	0.685	1.035
0.2	0.990	1.353
0.3	1.064	1.502
0 4	1.228	1.559
0.5	1.311	2.002
0.6	1.363	1.739
0.7	1.379	1.752
0.8	1.336	1.635

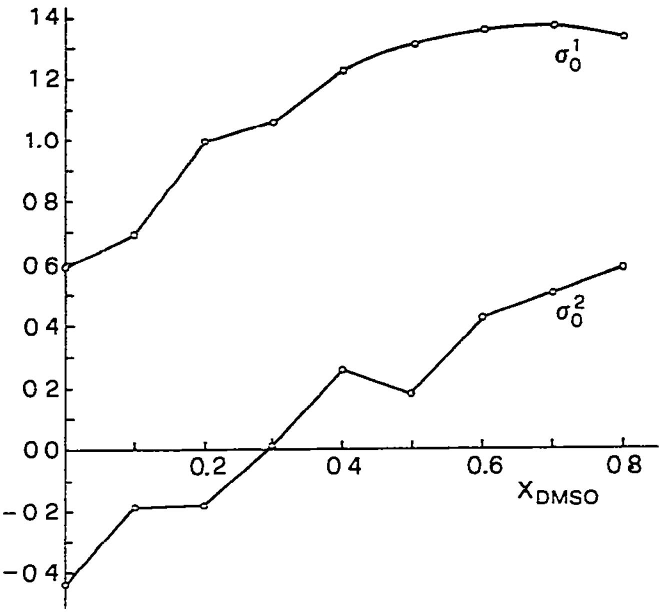

Fig. 1. Variation of the σ_o^1 and σ_o^2 values for the *o*-hydroxybenzoic acid as a function of the mole fraction of DMSO at 25°C.

The $\sigma_o^1 - \sigma_p$ values are included in eqn. (2) as an additional term for the field effect. Thus a better approximation for the substituent constant values (σ_o^2) is found (Table 2) using eqn. (4)

$$-\frac{\delta\,\Delta G^0}{2.203RT} = \rho_0\sigma_0^2 + fF^0 + \sigma_0^1 - \sigma_p + \delta E_s^0 \qquad (4)$$

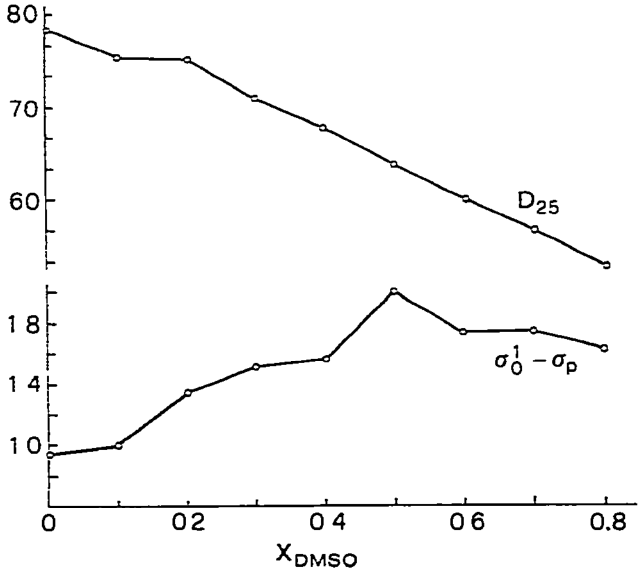

Fig. 2. Variation of the dielectric constant and of the difference $\sigma_o^1 - \sigma_p$ values as a function of the mole fraction of DMSO at 25°C.

TABLE 2

σ_0^2 Values calculated using eqn. (4) for the *o*-hydroxybenzoic acid in water—DMSO mixtures at 25°C

x_{DMSO}	σ_0^2
0.0	−0.434
0.1	−0.186
0.2	−0.031
0.3	0.08
0.4	0.265
0.5	0.148
0.6	0.430
0.7	0.543
0.8	0.581

TABLE 3

Results of application of separate enthalpy—entropy equations to ionization of *o*-hydroxybenzoic acid in water—DMSO mixtures at 25°C

x_{DMSO}	$\rho_H\sigma_H$	$\rho_s\sigma_s$
0.0	−0.678	−1.807
0.1	−0.443	−2.222
0.2	−0.752	−2.350
0.3	−1.230	−2.231
0.4	−4.411	0.635
0.5	−3.786	−0.637
0.6	−3.991	−0.391
0.7	−5.558	0.988
0.8	−3.067	0.715

TABLE 4

σ_s and ρ_s values calculated using entropic equations for the *o*-hydroxybenzoic acid in water—DMSO mixtures at 25°C

x_{DMSO}	σ_s	ρ_s
0.0	−1.807	1.000
0.1	−0.127	17.480
0.2	0.043	−54.651
0.3	0.165	−13.521
0.4	0.368	1.726
0.5	0.240	−2.654
0.6	0.549	−0.717
0.7	0.674	1.466
0.8	0.715	−2.108

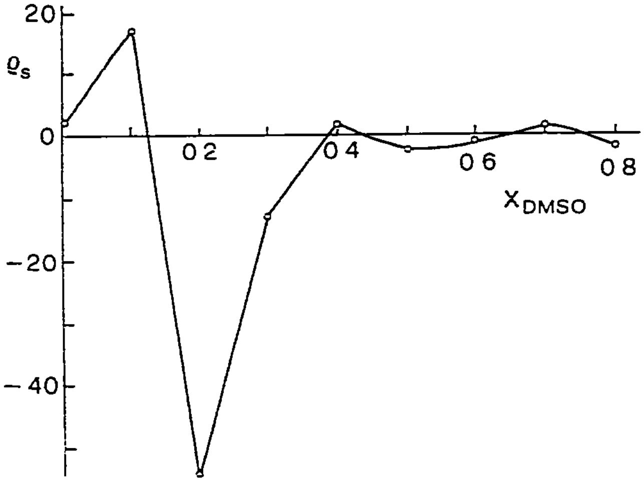

Fig. 3. Variation of the ρ_s values for the *o*-hydroxybenzoic acid as a function of the mole fraction of DMSO at 25°C.

These new values display a limited dependence on the medium effect, so it is possible to calculate the σ_s values for the *ortho*-hydroxy compound by means of the equation [6] $\sigma = 0.91\sigma_s - 0.07$. This equation was also used to calculate σ_s values of *m*- and *p*-hydroxy isomers over the whole mole fraction range [5].

It is also possible to modify eqn. (3b) by including the $\sigma_o^1 - \sigma_p$ term. Thus eqn. (4b) was obtained

$$\frac{\delta\ \Delta S^0}{2.303RT} = \rho_s\sigma_s + fF^0 + \sigma_0^1 - \sigma_p \tag{4b}$$

The $\delta\Delta H^0$, $\delta\Delta S^0$, δE_s^0, fF^0 and $\sigma_o^1 - \sigma_p$ values are included in eqns. (3a) and (4b) and the $\rho_H\sigma_H$ and $\rho_s\sigma_s$ values are reported in Table 3. Using these last values and the σ_s values it is also possible to calculate the ρ_s values. σ_s and ρ_s values are reported in Table 4 and ρ_s values are plotted against X_{DMSO} in Fig. 3.

For the hydroxybenzoic acid the values of ρ_s are negative with the exception of the 0.0—0.133 mole fraction range. This can be ascribed to the drastic desolvation of the *ortho*-anion with respect to the unsubstituted anion. This behaviour shows that for the hydroxybenzoic acid the solvation of the anions is the main factor controlling the course of the reaction.

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