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STUDY OF SOLVENT AND SUBSTITUENT EFFECTS ON ORGANIC ACIDS. PART III. CONSISTENCY OF A THERMODYNAMIC AND AN ELECTROSTATIC MODEL WITH EXPERIMENTAL RESULTS OF *ORTHO*-BENZOIC ACID DERIVATIVES

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ABSTRACT

The experimental models of the transfer proton process of *ortho*-benzoic acid derivatives in DMSO–water solutions were used to check an electrostatic and a thermodynamic model.

As in the case of the *meta* and *para* derivatives, the electrostatic model was found to be consistent with experimental results.

INTRODUCTION

The consistency of a thermodynamic and an electrostatic theory, related to substituent and solvent effects on organic acids, with the experimental results of the proton transfer reactions in DMSO–water solutions of *meta*- and *para*-benzoic acid derivatives, has formed the subject of extended research in parts I and II of this work [1,2]. These two models were checked by means of the following equations [1,2]

$$\text{R–PhCOOH}_{(s)} + \text{PhCOO}^-_{(s)} = \text{R–PhCOO}^-_{(s)} + \text{PhCOOH}_{(s)} \tag{1}$$

$$\delta\Delta G^0 = \delta\Delta H_{\text{in}}(1+\gamma) \tag{2}$$

$$\gamma = B\epsilon_i/\epsilon_s(1-B) \tag{3}$$

$$\frac{\rho_x}{\rho_{x'}} = \frac{1 - B(\epsilon_x - \epsilon_i)/\epsilon_x}{1 - B(\epsilon_{x'} - \epsilon_i)/\epsilon_{x'}} \tag{4}$$

$$\beta_i = \beta_e - \frac{1+\gamma}{\partial\gamma/\partial T} = T - \frac{1+\gamma}{\partial\gamma/\partial T} \tag{5}$$

The meaning of the terms γ, B, ϵ_i, and ϵ_s has been discussed previously [1,2].

Both the models were found to be consistent with the experimental results

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for the *meta* derivatives, while in the case of the *para* derivatives this is true only for the electrostatic model. The latter feature has been ascribed to the resonance effect, even though the greatest disagreement with the experimental values is shown by the chloro derivative in which the resonance effect is absent.

In order to obtain a more complete picture, the behaviour of *o*-chloro, *o*-nitro and *o*-hydroxy compounds, undergoing the same processes in the same solutions, has been assessed.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO–water solutions, and the technique for obtaining the thermodynamic values for the benzoic [3] and substituted benzoic acids [4–6] have been described previously.

RESULTS AND DISCUSSION

As shown in parts I and II of this work [1,2], the γ values of the *ortho* derivatives in the whole mole fraction range can be calculated by means of eqn. (2). These values are reported in Table 1 and are plotted against DMSO mole fraction in Fig. 1.

Unlike the γ values found for the *meta* and *para* derivatives [1,2], the γ values of the chloro and nitro derivatives are very dissimilar. Moreover,

TABLE 1

Values of $-\gamma$ for the dissociation of *o*-chloro, *o*-nitro and *o*-hydrobenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	*o*-Cl	*o*-NO_2	*o*-OH
0.0	0.55	0.69	0.88
0.1	0.63	0.72	0.86
0.2	0.69	0.74	0.82
0.3	0.70	0.73	0.79
0.4	0.66	0.72	0.75
0.5	0.57	0.70	0.72
0.6	0.63	0.68	0.69
0.7	0.58	0.66	0.67
0.8	0.59	0.65	0.65

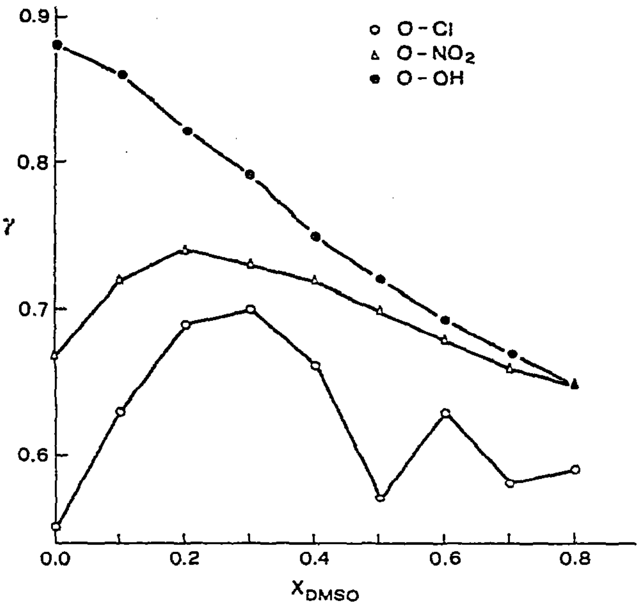

Fig. 1. Variation of $-\gamma$ for *o*-chloro (○), *o*-nitro (△) and *o*-hydroxybenzoic acid (●) as a function of the mole fraction of DMSO at 25°C.

those of the chloro derivative show a dramatic increase in the 0.0–0.3 mole fraction range. The solvent hinders the proton transfer process as could have been expected from the drastic desolvation in water-rich solutions of the *o*-chlorobenzoic anion with respect to the unsubstituted anion [4,7]. Beyond 0.3 mole fraction, both the anions are desolvated and the γ values decrease. This behaviour is in keeping with the assumption that, for the chloro derivatives, the solvation of the anions rather than that of the undissociated molecules controls the course of the reaction.

It is also worth noting that the γ values of the hydroxy derivative decrease almost linearly. This can be explained bearing in mind that both the anion and the undissociated molecule of the hydroxy derivative are poorly solvated by virtue of the internal hydrogen bond [6,8]. The hindrance of the solvent decreases as the content of DMSO increases.

For the nitro compound it is known that the undissociated molecules and their anions undergo a steric inhibition of solvation on the carboxyl and carboxylate groups, respectively [7]. The primary steric effect on the solvated carboxyl group and the resulting congestion accelerate the dissociation of the neutral molecules, while the steric inhibition of the anions tends to reduce the dissociation of the compound. Indeed the trend of the γ values shows that the solvent hinders the proton transfer process just at $X_{DMSO} = 0.2$, while beyond this mole fraction the process is favoured.

Thus it can be concluded that the information obtained from the γ

TABLE 2

Values of $-\rho/\gamma$ for the ionization of *o*-chloro, *o*-nitro and *o*-hydroxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	*o*-Cl	*o*-NO_2	*o*-OH
0.0	1.73	1.38	1.08
0.1	1.89	1.65	1.38
0.2	1.91	1.65	1.61
0.3	2.17	2.08	1.92
0.4	2.44	2.24	2.15
0.5	3.02	2.46	2.39
0.6	2.95	2.73	2.69
0.7	3.46	3.03	2.98
0.8	3.66	3.32	3.32

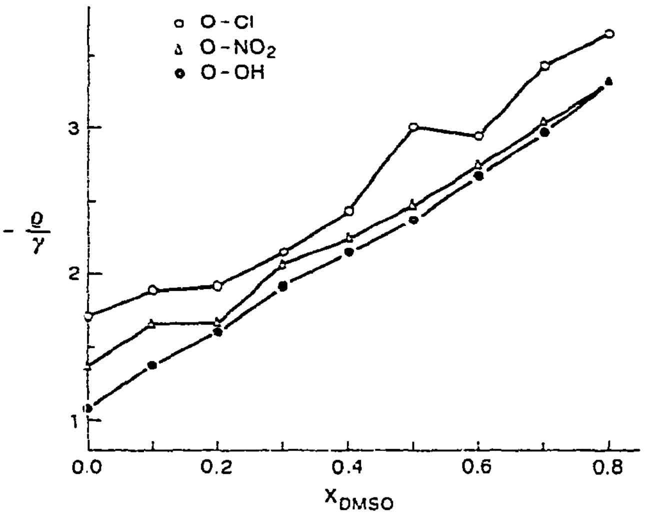

Fig. 2. Variation of $-\rho/\gamma$ for *o*-chloro (○), *o*-nitro (△) and *o*-hydroxybenzoic acid (●) as a function of the mole fraction of DMSO at 25°C.

parameter is very useful and contributes, along with those from ρ_g and $T\delta\Delta\rho^{g\to\rho}$ [1,2], to picture the solute–solvent interactions related to the proton transfer process of the benzoic acid derivatives in water–DMSO solutions.

The ρ/γ ratio (Table 2, Fig. 2) varies differently from that of the *meta* and *para* derivatives: in this case the same correlation between the ρ and γ parameters can be assumed for the nitro and hydroxy derivatives.

As previously shown [1,2], by writing eqn. (2) as

$$\rho_0\sigma_0 = [C(1+\gamma)/2.303RT][-\delta\Delta H_{in}/C] \tag{6}$$

TABLE 3

Values of σ_0 calculated using the equation $\sigma_0 = -\delta\Delta H_{in}/C$ in water–DMSO mixtures at 25°C

X_{DMSO}	*o*-Cl	*o*-NO_2	*o*-OH
0.0	0.295	0.650	−0.436
0.1	0.427	0.786	−0.571
0.2	0.388	0.868	−0.031
0.3	0.344	0.777	0.080
0.4	0.384	0.796	0.270
0.5	0.502	0.816	0.148
0.6	0.368	0.808	0.430
0.7	0.411	0.808	0.503
0.8	0.363	0.780	0.580

(where ρ_0 was identified with $[C(1+\gamma)/2.303RT]$ and σ_0 with $[-\delta\Delta H_{in}/C]$), the C values and thus the σ_0 values can be calculated. Yet, to calculate these values the terms related to inductive, field, steric and internal hydrogen bond effects have to be introduced [1].

The σ_0 values are identical to those previously calculated using the 'modified' Hammett equation [8] (Table 3). By using eqn. (3) it is possible to calculate the values of the B parameter. This has been made for $\epsilon_i = 2.5$ and $\epsilon_i = 6$.

Figure 3 shows that for $\epsilon_i = 2.5$ the B values are identical for the nitro and hydroxy derivatives and nearly constant in various solutions. The B values for the chloro derivative are different from those of other derivatives mostly in the 0.5–0.7 mole fraction range. Furthermore, the $\rho_x/\rho_{x'}$ ratio in the whole mole fraction range (Table 4, Fig. 4) and the difference $|(\rho_x/\rho_{x'})_{cal} - (\rho_x/\rho_{x'})_{exp}|$ between the calculated [1,2] and the experimental ratios can be obtained by means of eqn. (4).

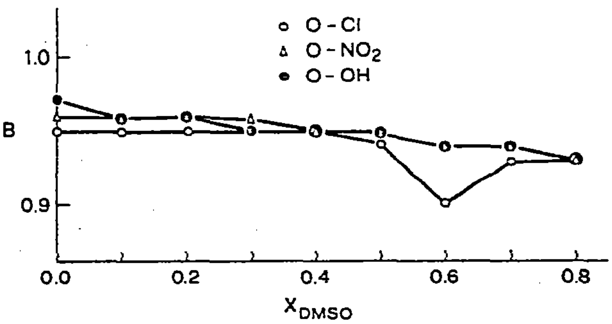

Fig. 3. Variation of the B parameter for *o*-chloro (○), *o*-nitro (△) and *o*-hydroxybenzoic acid (●) as a function of the mole fraction of DMSO at 25°C.

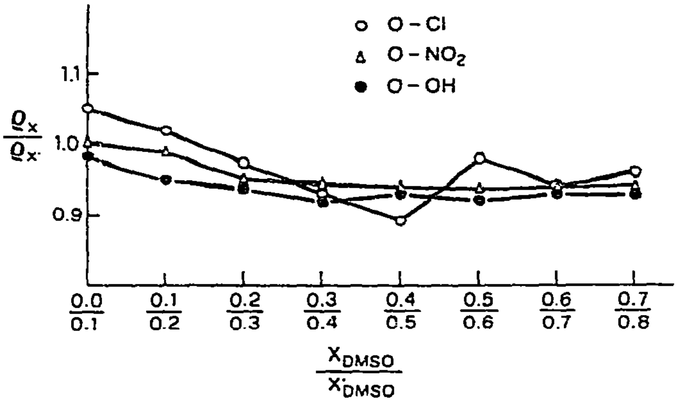

Fig. 4. Variation of $\rho_x/\rho_{x'}$ values for *o*-chloro (○), *o*-nitro (△) and *o*-hydroxybenzoic acid (●) as a function of the ratio X_{DMSO}/X'_{DMSO} of the mole fraction of DMSO at 25°C.

TABLE 4

Values of $\rho_x/\rho_{x'}$ calculated using eqn. (4) for the dissociation of *o*-chloro, *o*-nitro and *o*-hydroxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}/X_{DMSO}	*o*-Cl		*o*-NO$_2$		*o*-OH	
	$\epsilon_i=2.5$	$\epsilon_i=6$	$\epsilon_i=2.5$	$\epsilon_i=6$	$\epsilon_i=2.5$	$\epsilon_i=6$
0.0/0.1	1.000	1.049	1.005	1.003	0.976	0.973
0.1/0.2	1.024	1.024	0.986	0.986	0.945	0.951
0.2/0.3	0.959	0.967	0.946	0.956	0.943	0.944
0.3/0.4	0.925	0.928	0.944	0.944	0.918	0.928
0.4/0.5	0.875	0.886	0.935	0.941	0.933	0.936
0.5/0.6	0.942	0.978	0.925	0.934	0.915	0.929
0.6/0.7	0.906	0.927	0.931	0.938	0.932	0.934
0.7/0.8	0.945	0.959	0.941	0.939	0.932	0.932

The standard deviations of the differences have been calculated for every derivative. For the chloro, nitro and hydroxy derivatives the standard deviations are 0.08, 0.07 and 0.06, respectively. If the largest difference (the first) is eliminated, the standard deviations reduce to 0.04, 0.04 and 0.03, respectively. This indicates that the *meta* and *para* derivatives approach the experimental values better than the *ortho* derivatives. It is also worth noting that in this case the *ortho*-chloro derivative has the largest scattering. Thus it can be noted that the inductive effect of the chlorine atom plays a very important role in the so-called '*ortho* effect'.

Finally, eqn. (5) can provide the isoequilibrium temperature parameter β_i [1,2]. These values are given in Table 5 and plotted in Fig. 5. Figure 5 shows

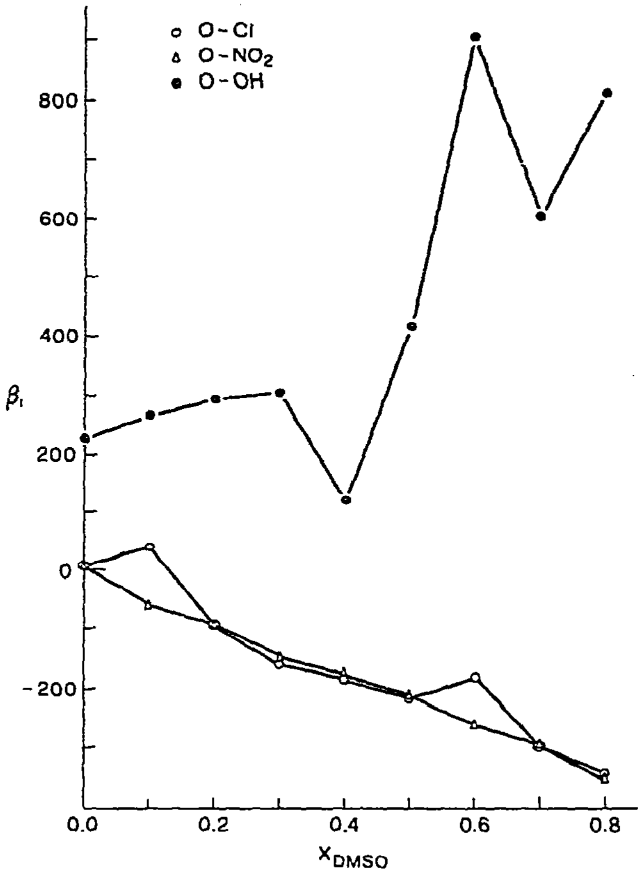

Fig. 5. Variation of the β_i parameter for *o*-chloro (○), *o*-nitro (△) and *o*-hydroxybenzoic acid (●) as a function of the mole fraction of DMSO at 25°C.

TABLE 5

Values of the β_i parameter for the ionization of *o*-chloro, *o*-nitro and *o*-hydroxybenzoic acid in water–DMSO mixtures at 25°C

X_{DMSO}	*o*-Cl	*o*-NO_2	*o*-OH
0.0	11.26	1.66	228.99
0.1	41.26	−57.03	268.16
0.2	−95.41	−95.64	292.90
0.3	−160.37	−150.64	314.31
0.4	−184.44	−175.64	97.23
0.5	−219.84	−220.81	418.15
0.6	−183.84	−256.6	907.69
0.7	−303.84	−299.44	607.04
0.8	−342.84	−347.14	822.53

that none of the three *ortho*-isomers shows any agreement between experimental results and the thermodynamic model. This could have been expected from the occurrence of the resonance, field and steric effects. Indeed these effects hinder a simple isoequilibrium relationship, from which eqn. (5) is derived.

Finally it can be concluded that while the electrostatic model is consistent with the experimental values of all the isomers considered (with the exception of the *ortho*-chloro derivative), for the thermodynamic model this is true for the *meta* derivatives only. This confirms the fact that the requirements for an isoequilibrium relationship to occur are more stringent than those for a free energy relationship [9,10].

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