Thermochimica Acta, 43 (1981) 199—205
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

ENTHALPIC AND ENTROPIC CONTRIBUTIONS TO SUBSTITUENT EFFECTS FOR THE IONIZATION OF *META*- AND *PARA*-HYDROXYBENZOIC ACIDS IN WATER—DIMETHYLSULFOXIDE MIXTURES AT 25°C

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(Received 25 June 1980)

ABSTRACT

Separate enthalpic and entropic contributions to substituent effects on the dissociation of *m*-hydroxybenzoic acid in water—dimethylsulfoxide mixtures ranging from 0.0 to 0.57 mole fraction of DMSO are presented. The effect of the medium on the reaction constant is explained in terms of solute—solvent interactions. The entropy reaction constant values ρ_s of the *meta*-hydroxy compound are much greater than those of the *meta*-chloro and nitro compounds in the examined mole fraction range.

For the *para*-hydroxy isomer only a trend of σ_s and ρ_s values can be calculated. This fact is due to the electron-releasing resonance effect which overlaps and prevails over the inductive effect.

INTRODUCTION

The enthalpic and entropic contributions to substituent effects for the dissociation of *meta*- and *para*-nitro and chlorobenzoic acids have been examined previously [1,2]. The effect of the medium on the substituent and reaction constants was explained in terms of solute—solvent interactions and a structure-breaking effect.

The σ values of both the chloro and nitro compounds show a limited dependence on the medium effect, so it is possible to assume that the equations in water [1,2]

$$\sigma = 0.91\ \sigma_s - 0.07 \tag{1}$$

$$\sigma_s = -3.6\ \sigma_H + 0.15 \tag{2}$$

are valid throughout the mole fraction range. With this assumption, σ_H and σ_s values are calculated. Using these values, it is possible to calculate the ρ_s values which represent solute—solvent interactions chiefly taking into account the inductive effects.

We thought it interesting to study the behaviour of the *meta*- and *para*-hydroxybenzoic acids. Indeed, for the $\sigma_{p'}$ values of the *para*-hydroxy compound a strong solvent dependence and an electron-releasing resonance effect were observed [3,4].

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO—water mixtures and the technique for obtaining the thermodynamic values for the benzoic and hydroxybenzoic acids have been described [5—9].

According to Hammett [10] and others [4,11] the following equations may be written

$$(\mathrm{OH{-}PhCOOH})_X + (\mathrm{PhCOO^-})_X = (\mathrm{OH{-}PhCOO^-})_X + (\mathrm{PhCOOH})_X \qquad (3)$$

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

where X (ranging from 0.0 to 0.8) is the mole fraction of the solvent. The ρ and σ values are affected in different ways by the variation of the solvent composition.

Using experimental ionization values of benzoic [9] and hydroxybenzoic [8] acids, the standard enthalpy change for eqn. (3) is obtained as

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

In the same way, the $\delta\Delta G^0$ and $\delta\Delta S^0$ values related to process (3) can be obtained.

By separating substituent effects into enthalpic and entropic contributions [12], eqn. (3) may be written in the form

$$-\frac{\delta\Delta G^0}{2.303RT} = \rho_\mathrm{H}\sigma_\mathrm{H} + \rho_\mathrm{s}\sigma_\mathrm{s} \qquad (5)$$

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

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

$$\rho_\mathrm{s}\sigma_\mathrm{s} = \frac{\delta\Delta S^0}{2.303R} \qquad (6b)$$

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

RESULTS AND DISCUSSION

The $\delta\Delta H^0$, $\delta\Delta G^0$ and $\delta\Delta S^0$ values of reaction (3) for the two hydroxy isomers are included in eqns. (4), (6a) and (6b) and the values of $\rho\sigma$, $\rho_\mathrm{H}\sigma_\mathrm{H}$ and $\rho_\mathrm{s}\sigma_\mathrm{s}$ are reported in Table 1. It is possible to calculate the σ_m and σ_p values using the ρ_mp values [13] for the dissociation of benzoic acids at various mole fractions (see Table 2). The σ_m and σ_p values are plotted against X_DMSO in Fig. 1.

It is to be remarked that the σ_m values decrease from 0.0 to 0.1 mole fraction, remain constant in the range $0.1 \leqslant X_\mathrm{DMSO} \leqslant 0.57$ and change sign beyond this last mole fraction. The σ_p values (always negative) show a maximum at $X_\mathrm{DMSO} = 0.5$. These trends can be related to the fact [14] that only if the field effects are much larger than those of resonance can σ values be expected to be independent of or slightly affected by the solvent.

TABLE 1

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

x_{DMSO}	*m*-OH			*p*-OH		
	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$	$\rho\sigma$	$\rho_H\sigma_H$	$\rho_S\sigma_S$
0.0	0.125	−0.044	0.168	−0.381	−0.198	−0.183
0.1	0.015	−0.716	0.731	−0.425	−0.497	0.718
0.2	0.000	−2.315	2.314	−0.491	−2.515	2.024
0.3	0.015	−1.365	1.379	−0.682	−3.119	2.438
0.4	0.015	−4.695	3.456	−0.542	−4.508	3.966
0.5	0.066	−4.828	4.893	−1.209	−5.539	3.330
0.6	−0.044	−6.631	6.585	−0.711	−4.941	4.230
0.7	−0.117	−8.313	8.194	−0.770	−3.125	2.356
0.8	−0.154	−5.666	5.510	−0.865	−4.265	3.400

If it is assumed that the inductive and field effects are the same in both the *para* and *meta* positions, $\sigma_m - \sigma_p$ should then be a measure of the resonance effect (see Table 3). The $\sigma_m - \sigma_p$ values display a decreasing electron-releasing resonance effect as the DMSO content increases, except at $x_{DMSO} = 0.5$ where the resonance shows a maximum. This behaviour can be related to a typical feature of DMSO—water solutions [5—7]. Indeed, at $x_{DMSO} = 0.5$, the maximum structure-breaking displayed by the solution increases the solvation power of the mixture towards the anions so that the maximum solute—solvent interaction is found at the indicated mole fraction.

The σ values of the *meta* derivative display a limited dependence on the medium effect and have positive values up to 0.57 DMSO mole fraction. Thus, for this isomer it seems reasonable to assume that both eqns. (1) and (2) are valid, from 0.1 to 0.57 mole fraction. σ_H and σ_s values have been calculated in this range. Using the values from Table 1 it is also possible

TABLE 2

σ Values calculated by using the Hammett equation for *m*- and *p*-hydroxybenzoic acids in water—DMSO mixtures at 25°C

x_{DMSO}	*m*-OH σ_m	*p*-OH σ_p
0.0	0.125	−0.381
0.1	0.012	−0.350
0.2	0.000	−0.363
0.3	0.010	−0.438
0.4	0.009	−0.331
0.5	0.038	−0.691
0.6	−0.023	−0.376
0.7	−0.057	−0.373
0.8	−0.067	−0.299

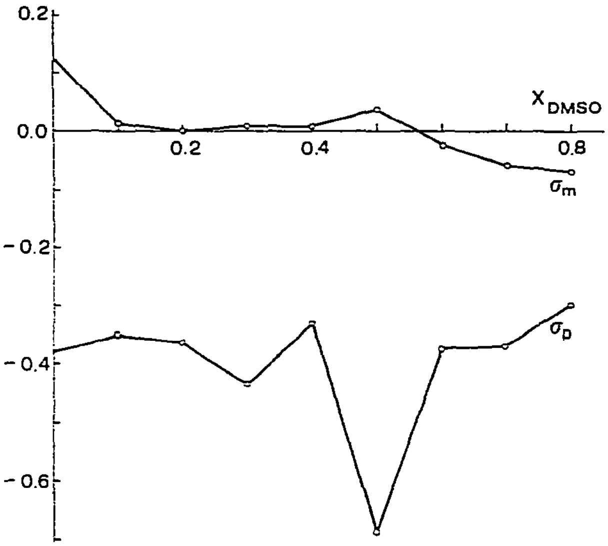

Fig. 1. Variation of the σ values for *m*- and *p*-hydroxybenzoic acids as a function of the mole fraction at 25°C.

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	0.506
0.1	0.363
0.2	0.363
0.3	0.448
0.4	0.340
0.5	0.729
0.6	0.353
0.7	0.316
0.8	0.235

TABLE 4

σ and ρ values calculated by using enthalpic and entropic equations for *m*-hydroxybenzoic acid in water—dimethylsulfoxide mixtures at 25°C

X_{DMSO}	σ_s	σ_H	ρ_s
0.0	0.168	−0.044	1
0.1	0.090	0.017	8.120
0.2	0.077	0.020	30.050
0.3	0.088	0.017	15.670
0.4	0.087	0.017	29.720
0.5	0.119	0.009	41.11

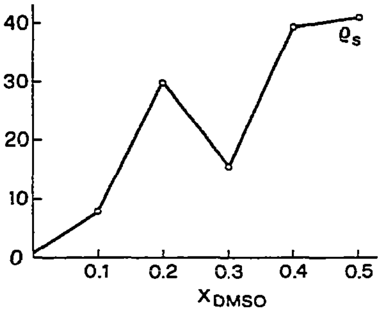

Fig. 2. Variation of the ρ_s values for *m*-hydroxybenzoic acid as a function of the mole fraction at 25°C.

to calculate the ρ_s values. σ_H, σ_s and ρ_s values are given in Table 4 and ρ_s values are plotted against X_{DMSO} in Fig. 2.

The greater extent of the effect of the σ_s with respect to the σ_H values indicates that the external contributions are entropy controlled and therefore chiefly inductive in character [12], so that the solute—solvent interactions are exclusively discussed in terms of ρ_s change.

The entropy reaction constant values of the *meta*-hydroxybenzoic acid are much greater than those of the *meta*-chloro and nitrobenzoic acids throughout the mole fraction range.

For the σ_s values of the three *meta* derivatives the following order is observed [1,2] for all mole fractions: $\sigma_{NO_2} > \sigma_{Cl} > \sigma_{OH}$. On the basis of the inductive effect values the following order of entropy reaction constants can be expected: $\rho_{NO_2} > \rho_{Cl} > \rho_{OH}$ while the observed order is: $\rho_{OH} > \rho_{Cl} > \rho_{NO_2}$. This behaviour can be ascribed to the drastic solvation of the *m*-hydroxy anion with respect to the unsubstituted anion. This fact, in turn, is in agreement with the hypothesis that, for the hydroxy derivatives, the hydrogen bonding of the hydroxyl group to solvent molecules is more important than the interactions of the nitro and chloro groups with the same molecules.

The *para*-hydroxy derivatives display negative values throughout the mole fraction range. This fact was related to the electron-releasing resonance effect which overlaps and prevails over the inductive effect.

The substituents with negative values exhibit an "abnormal" enthalpy—entropy relationship [11] and so eqn. (2) was not used. It has also been shown how compensation [15] of $\delta\Delta H^0$ and $\delta\Delta S^0$ may lead to an approximate linear free energy relationship such as $-\delta\Delta G^0 = 2.303RT\rho\sigma$.

In order to assess the relative contributions of enthalpy and entropy to the substituent effect the following equations are used [12]

$$f_H = \frac{|\sigma_H|}{|\sigma_H| + |\sigma_S|} \qquad (7a)$$

$$f_s = \frac{|\sigma_S|}{|\sigma_S| + |\sigma_H|} \qquad (7b)$$

TABLE 5

σ and ρ values calcualted by using entropic equations for *p*-hydroxybenzoic acid in water—dimethylsulfoxide mixtures at 25°C

X_{DMSO}	σ_s	ρ_s
0.0	−0.183	1
0.1	−0.309	−2.324
0.2	−0.322	−6.286
0.3	−0.404	−6.035
0.4	−0.287	−13.819
0.5	−0.682	−4.882
0.6	−0.336	−12.589
0.7	−0.333	−7.075
0.8	−0.252	−13.492

We also observe that, in water and at 25° C, for the *meta*-hydroxy compound the entropic contribution f_s is equal to 80% of the total substituent effect, while for the *para*-hydroxy isomer the enthalpic contribution $f_H = 0.52$ prevails. This clearly shows that the resonance contribution to the substituent effect for the *p*-OH isomer is larger than that of the *m*-OH isomer. Indeed the resonance is mainly related to the enthalpic term. The σ and σ_s values for the *para*-hydroxy acid show [12] rather good correlation in the water solvent if eqn. (1) is used.

We observe that the σ_p values are greatly affected by the solvent composition only in the 0.43—0.58 mole fraction range. Thus we believe that eqns. (1) and (6b) give an approximate trend for the σ_s and ρ_s values only in the above-mentioned mole fraction range (see Table 5).

A plot of ρ_s vs. X_{DMSO} is shown in Fig. 3. The dotted line represents those values of ρ_s which are most uncertain because of the greater influence of the solvent.

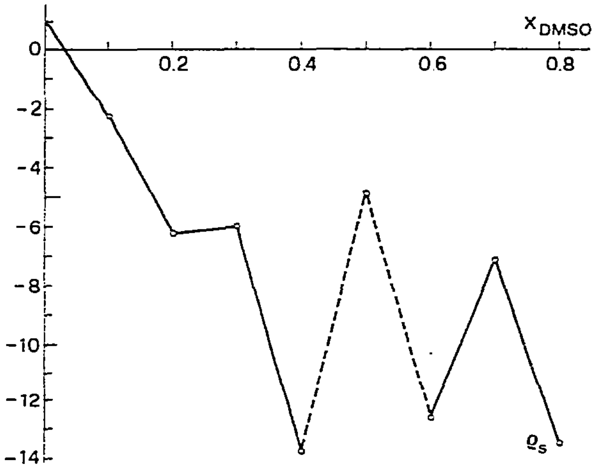

Fig. 3. Variation of the ρ_s values for *p*-hydroxybenzoic acid as a function of the mole fraction at 25°C.

The electron-releasing resonance effect decreases the equilibrium constant by increasing and thus localizing the negative charge of the carboxylate group. Indeed the OH—PhCOO$^-$ anion acts as a stronger base then the unsubstituted anion.

The ρ_s negative values increase as the H_2O content decreases. This can be related to enhanced anion desolvation which, in turn, yields an increasing differentiation in the acidity of hydroxy substituted and benzoic acid. At $X_{DMSO} = 0.5$ a drastic increase in the electron-releasing resonance effect produces a sharp decrease for the ρ_s values due to enhanced solute—solvent interactions.

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