

THERMODYNAMICS OF IONIZATION PROCESSES FOR HYDROXY-SUBSTITUTED BENZOIC ACIDS IN WATER–DIMETHYLSULFOXIDE MIXTURES AT 25°C

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(Received 21 May 1980)

ABSTRACT

The ionization and solution enthalpies of the hydroxybenzoic acids were measured calorimetrically at 25°C in water–dimethylsulfoxide mixtures ranging from pure water to 0.8 DMSO mole fraction.

In the same solutions, the ΔG° values for the ionization processes have been determined by potentiometric measurements.

The different enthalpy solvation values for the three hydroxy isomers were explained taking into account the prevalence of the resonance or the inductive effect as a function of the solvent composition.

The intramolecular hydrogen bond of the undissociated molecule seems to be responsible for the greater degree of ionization of *o*-hydroxybenzoic acid with respect to the *m* and *p*-hydroxy isomers.

INTRODUCTION

The ionization of chlorobenzoic and nitrobenzoic acids in water–dimethylsulfoxide mixtures has been the subject of extended research in our laboratory [1,2]. In the present work, the behaviour of the hydroxybenzoic acids in the same mixtures has been examined.

The difference in behaviour between the $\text{Cl}(\text{R}^+\text{I}^-)$ and the $\text{OH}(\text{R}^+\text{I}^-)$ can be related to the resonance effect and to the intramolecular and intermolecular hydrogen bonds displayed by the hydroxyl group.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [1,3]. DMSO (Carlo Erba RP grade) was purified according to the procedure of Synnot and Butler [4]. DMSO–water mixtures were prepared by weight from purified DMSO and CO_2 -free, twice-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.1 to 0.8. Aqueous solutions of 0.98 M HCl and 0.098 M NaOH were prepared from standard solutions and their concentrations were checked by potentiometric titrations. The *o*-, *m*- and *p*-hydroxy-

benzoic acids (all K and K products) were purified by crystallization from water—ether mixtures and their melting points checked before use.

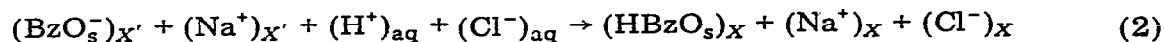
The NaBzO_s solutions (where the subscript indicates the substituted acids) were prepared by adding a NaOH solution of known molarity to the *o*-, *m*- and *p*-hydroxybenzoic acids dissolved in the mixed solvent. As a result of this addition, 100 g of the DMSO—water solution at X' mole fraction were obtained. The concentrations of the sodium salts were always in the range from 2×10^{-3} to 4×10^{-3} m. An amount of acid, about 4 or 5% of the original content, was not converted to salt and remained as free acid to avoid the presence of the free alkali.

The ionization process of HBzO_s in the various water—DMSO mixtures of X mole fraction can be represented as



The molar enthalpy of ionization $\Delta\bar{H}_1$, of HBzO_s was obtained by experimental measurement of

(a) the molar enthalpy of reaction, $\Delta\bar{H}_2$, of NaBzO_s dissolved in the mixed solvent of X' mole fraction, with 0.98 M HCl

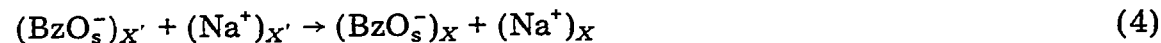


(b) the molar enthalpy of solution, $\Delta\bar{H}_3$, of the same amount of 0.98 M HCl in the same solvent mixture at X' mole fraction



From the dissociation constants of water (5) and the substituted hydroxybenzoic acids [6], it can also be inferred that the salts undergo very little hydrolysis ($\beta < 0.02\%$). Therefore, it is not necessary to correct the $\Delta\bar{H}_2$ values measured experimentally in process (2) for hydrolysis.

The molar enthalpy of process (1) can be obtained [1,2] by subtracting the two values $\Delta\bar{H}_3$ and $\Delta\bar{H}_2$ and by adding to this difference the $\Delta\bar{H}_4$ values related to the molar transfer enthalpy of NaBzO_s (at infinite dilution) from solvent X' to solvent X , viz.



It should be noted that the difference ($X' - X$) turns out to be very small for each couple: in the most unfavourable case, it was 2×10^{-4} when the DMSO final mole fraction was 0.8. The thermal effect of process (4) was calculated by using the experimental measurements published in this work.

For every one of the water—DMSO mixtures at X_{DMSO} mole fraction, the $\Delta\bar{H}_1$ values refer to the ionization of one mole of HBzO_s dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of protons and one mole of BzO_s^- ions solvated in the same amount of the solvent. In order to refer process (1) to one initial thermodynamic state only, we measured the solution enthalpies of the crystalline hydroxybenzoic acids, $\Delta\bar{H}_5$, in the

various solvent mixtures



so that the $\Delta\bar{H}_6 = \Delta\bar{H}_5 + \Delta\bar{H}_1$) values obtained for the process



refer to an identical initial thermodynamic state.

In processes (1) and (5), concentrations ranging from 2×10^{-3} to 4×10^{-3} m were used. Therefore the $\Delta\bar{H}$ values related to these processes were assumed to be equal to the ΔH° values [7].

All the measurements were carried out at 25°C , the average thermal jump in the cell during the experiments being about 0.1°C .

The ionization constants of the hydroxybenzoic acids at 25°C have been obtained from e.m.f. measurements of the cell



Potential measurements were made with an Orion 801 digital pH meter; the glass electrode was an Orion 91-01-00. The details of potentiometric measurements and the technique for obtaining the $\text{p}K_a$ values have been described previously [8,9]. The $\text{p}K_a$ values obtained from potentiometric measurements, were used to calculate ΔG° .

The initial standard state to which ΔG° values of ionization refer is defined to be an ideal 1 m solution of HBzO_s behaving as an infinitely dilute solution.

$T\Delta S^\circ$ values were calculated by using the Gibbs–Helmholtz equation.

RESULTS

Table 1 shows the ΔG° , ΔH° and $T\Delta S^\circ$ values of process (1) obtained for the three hydroxybenzoic acids.

For the ΔH° values, each number reported for process (1) is the difference between an average of at least six values relative to process (2) and a similar average for process (3); the standard deviations are indicated next to the tabulated values. The average standard deviation of the $\text{p}K_a$ values is 0.02 pK unit; the corresponding accuracy on the ΔG° values is ± 28 cal.

Tables 2 and 3 show the enthalpy values of processes (5) and (6).

For comparison, it is convenient to express the ionization enthalpy as the difference between the values obtained in the mixed solvent of X mole fraction and in pure water so that

$$\delta\Delta H_1^\circ = (\Delta H_1^\circ)_X - (\Delta H_1^\circ)_{X=0}$$

In a similar way, the values of $\delta\Delta G_1^\circ$ and $T\delta\Delta S_1^\circ$ can be defined and calculated.

These three values are relative to the transfer of the ionization process, while the $\delta\Delta H_5^\circ$ and $\delta\Delta H_6^\circ$ values represent the transfer enthalpy of the undissociated molecules and of the two ions H^+ and BzO_s^- , respectively, from

TABLE I

Enthalpy, entropy and free energy values of the ionization for *o*-, *m*- and *p*-hydroxybenzoic acids in DMSO—water solutions of various mole fractions at 25°C

All thermodynamic quantities are given in kcal mole⁻¹.

X_{DMSO}	<i>o</i> -Hydroxybenzoic acid			<i>m</i> -Hydroxybenzoic acid			<i>p</i> -Hydroxybenzoic acid		
	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$
0.0	4.10 ± 0.03	0.73 ± 0.01	-3.37 ± 0.03	5.56 ± 0.03	0.16 ± 0.01	-5.40 ± 0.03	6.25 ± 0.03	0.37 ± 0.02	-5.88 ± 0.04
0.1	4.44	0.79 ± 0.02	-3.65 ± 0.04	6.35	1.46 ± 0.01	-4.89 ± 0.03	0.03	1.16 ± 0.01	-5.79 ± 0.03
0.2	4.70	1.94 ± 0.02	-2.76 ± 0.04	7.11	4.36 ± 0.02	-2.75 ± 0.04	6.95	4.64 ± 0.02	-3.14 ± 0.04
0.3	5.17	3.36 ± 0.03	-1.81 ± 0.04	7.97	3.74 ± 0.03	-4.23 ± 0.04	7.78	6.14 ± 0.03	-2.78 ± 0.04
0.4	5.62	8.15 ± 0.02	2.53 ± 0.04	8.91	7.12 ± 0.01	-1.79 ± 0.03	8.92	8.58 ± 0.04	-1.09 ± 0.05
0.5	6.19	8.27 ± 0.04	2.08 ± 0.05	9.78	9.97 ± 0.02	0.19 ± 0.04	11.52	9.57 ± 0.03	-1.95 ± 0.04
0.6	6.72	8.46 ± 0.03	1.74 ± 0.04	10.86	12.34 ± 0.01	1.48 ± 0.03	11.77	10.04 ± 0.01	-1.77 ± 0.03
0.7	7.35	11.59 ± 0.05	4.22 ± 0.06	11.90	15.63 ± 0.04	3.73 ± 0.05	12.79	8.56 ± 0.02	-4.23 ± 0.04
0.8	7.90	9.96 ± 0.04	2.06 ± 0.05	12.70	13.80 ± 0.05	1.10 ± 0.06	13.67	11.89 ± 0.03	-1.78 ± 0.03

TABLE 2

Enthalpy values of the solution (ΔH_5^0) for *o*-, *m*- and *p*-hydroxybenzoic acids in DMSO—water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_5^0 (kcal mole ⁻¹)		
	<i>o</i> -Hydroxybenzoic acid	<i>m</i> -Hydroxybenzoic acid	<i>p</i> -Hydroxybenzoic acid
0.0	6.35 ± 0.01	6.18 ± 0.03	5.78 ± 0.02
0.1	7.30 ± 0.02	5.70 ± 0.02	5.60 ± 0.02
0.2	7.18 ± 0.01	4.97 ± 0.02	4.89 ± 0.01
0.3	6.30 ± 0.03	3.70 ± 0.02	3.70 ± 0.01
0.4	4.80 ± 0.01	2.00 ± 0.01	2.00 ± 0.02
0.5	3.01 ± 0.02	0.32 ± 0.01	-0.33 ± 0.01
0.6	1.90 ± 0.01	-0.80 ± 0.01	-1.30 ± 0.009
0.7	1.60 ± 0.01	-1.30 ± 0.01	-1.80 ± 0.01
0.8	1.46 ± 0.01	-1.46 ± 0.02	-2.08 ± 0.005

pure water to the mixed solvent. All these data are plotted against X_{DMSO} in Figs. 1–3.

DISCUSSION

A comparison of Figs. 1–3 suggests that the *o*-hydroxybenzoic acid, from the enthalpic point of view, undergoes ionization more easily than the *m*- and *p*-hydroxybenzoic acids. With respect to this point, *o*-hydroxybenzoic acid and *o*-chlorobenzoic acid behave in opposite ways.

TABLE 3

Enthalpy values of process (6) for *o*-, *m*- and *p*-hydroxybenzoic acids in DMSO—water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_6^0 (kcal mole ⁻¹)		
	<i>o</i> -Hydroxybenzoic acid	<i>m</i> -Hydroxybenzoic acid	<i>p</i> -Hydroxybenzoic acid
0.0	7.08 ± 0.01	6.34 ± 0.03	6.15 ± 0.03
0.1	8.09 ± 0.03	7.16 ± 0.04	6.76 ± 0.02
0.2	9.12 ± 0.02	9.33 ± 0.03	9.52 ± 0.02
0.3	9.66 ± 0.04	7.44 ± 0.04	9.84 ± 0.03
0.4	12.95 ± 0.02	9.12 ± 0.01	10.58 ± 0.04
0.5	11.28 ± 0.04	10.29 ± 0.02	9.24 ± 0.03
0.6	10.36 ± 0.03	11.54 ± 0.01	8.74 ± 0.01
0.7	13.19 ± 0.05	14.33 ± 0.04	6.76 ± 0.02
0.8	11.42 ± 0.04	12.34 ± 0.05	9.81 ± 0.03

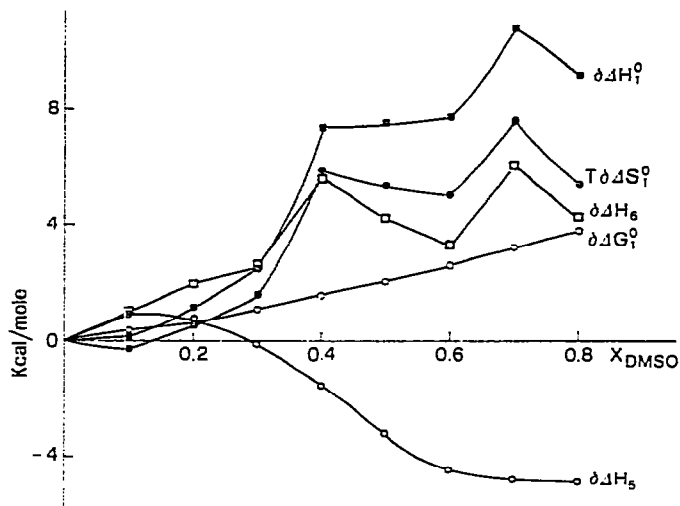


Fig. 1. Thermodynamic quantities for the transfer of *o*-hydroxybenzoic acid from pure water to DMSO—water mixtures as functions of the mole fraction at 25°C.

The different ionization of the three hydroxybenzoic acids can be ascribed to the different solvation which the molecules and the ions undergo in the mixtures.

The difference in solvation enthalpy between the *ortho*- and *meta*-solvated

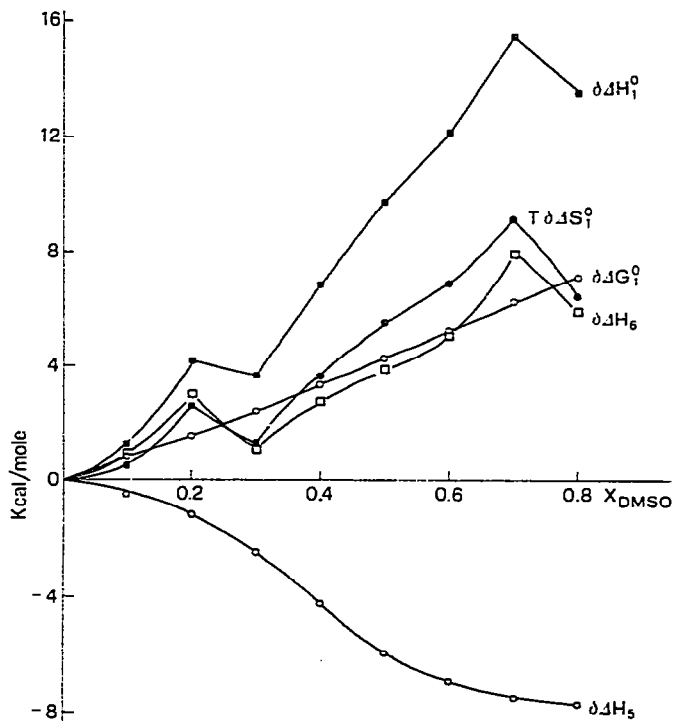


Fig. 2. Thermodynamic quantities for the transfer of *m*-hydroxybenzoic acid from pure water to DMSO—water mixtures as functions of the mole fraction at 25°C.

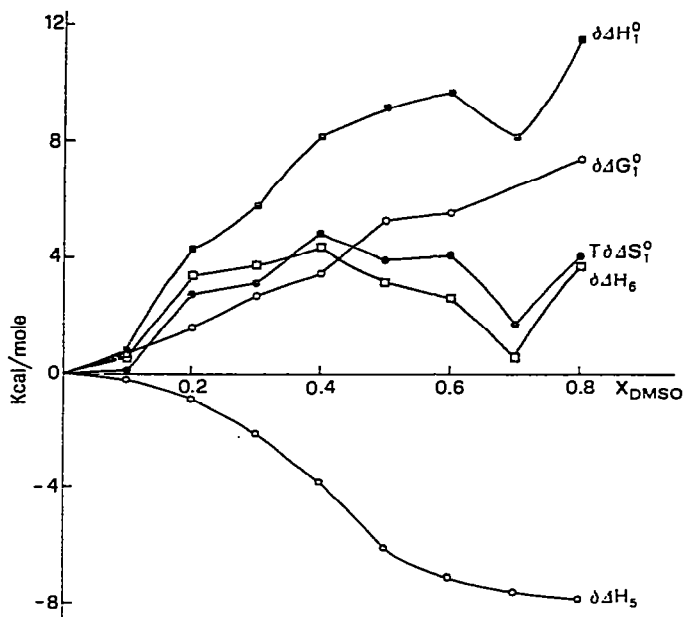


Fig. 3. Thermodynamic quantities for the transfer of *p*-hydroxybenzoic acid from pure water to DMSO—water mixtures as functions of the mole fraction at 25°C.

hydroxy anions, was calculated as

$$\Delta\bar{H}_{(oBzO^-)_X-(mBzO^-)_X} = \delta\Delta H_{6(oHBzO)}^0 - \delta\Delta H_{6(mHBzO)}^0 + \Delta\bar{H}_{(oBzO^-)_{aq.}-(mBzO^-)_{aq.}} \quad (7)$$

while the difference in the solvation enthalpy between the undissociated molecules is

$$\Delta\bar{H}_{(oHBzO)_X-(mHBzO)_X} = \delta\Delta H_{5(oHBzO)}^0 - \delta\Delta H_{5(mHBzO)}^0 + \Delta\bar{H}_{(oHBzO)_{aq.}-(mHBzO)_{aq.}} \quad (8)$$

The differences in solvation of the other couples were calculated in the same way. The last term on the right-hand sides of eqns. (7) and (8) was arbitrarily assumed to be equal to zero and the resulting $\Delta\bar{H}_{(oBzO^-)_X-(mBzO^-)_X}$ and $\Delta\bar{H}_{(oHBzO)_X-(mHBzO)_X}$ values are plotted in Fig. 4(a) and (b) as functions of the solvent composition. These values are supposed to approach very closely the true values [3].

The $\delta\Delta H_1^0$ values are much larger than the corresponding $\delta\Delta G_1^0$ and $T\delta\Delta S_1^0$ values. Thus the enthalpic term can be reasonably identified with the driving force of the ionization transfer process.

It is also possible that the heats of solution of undissociated organic acids have an endothermic maximum in water—alcohol mixtures. This fact could be due to a condition of maximum structure of the solvent [10]. According to Arnett et al. [11], the size of the maximum is roughly a function of the "volume" of the solute molecules. If this is true, the higher heat of solu-

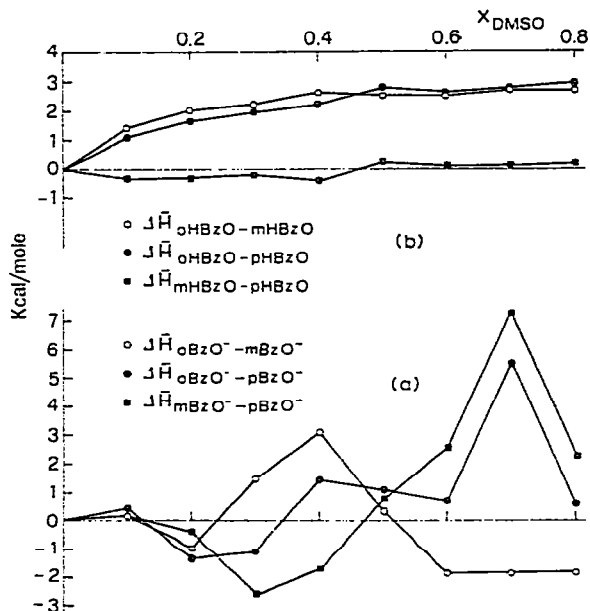
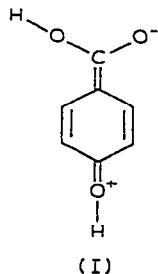


Fig. 4. Differences in the solvation enthalpy between (a) the hydroxy anion couples and (b) the undissociated hydroxy molecule couples in various DMSO–water mixtures. The differences in the hydration enthalpy both between the anion couples and the undissociated molecule couples are arbitrarily set equal to zero.

tion of *o*-hydroxybenzoic acid at 0.1 DMSO mole fraction, could be due to the larger “volume” of the *o*-hydroxybenzoic acid molecule with respect to the *meta* and *para* derivatives. Indeed, in the *o*-hydroxy isomer, both the COOH and OH groups have been shown to take part in a strong internal hydrogen bond. This fact, in turn, could be related to the better solvation, over the whole concentration range, of the *para* and *meta* undissociated molecules with respect to *ortho* compound.

For the *meta* and *para* undissociated molecules, the order of the transfer is $m\text{HBzO} > p\text{HBzO}$ in the range $0.0 < X_{\text{DMSO}} < 0.5$. In the range $0.5 < X_{\text{DMSO}} < 0.8$, the *meta* and *para* molecules display an inversion of solvation enthalpy so that the transfer sequence becomes $p\text{HBzO} > m\text{HBzO}$. Indeed, beyond $X_{\text{DMSO}} = 0.5$, the dipolar structure (I), which can be thought to be in resonance with the uncharged structure, interacts effectively with the



dipole of the DMSO molecules. From 0.0 to 0.5 mole fraction, the inductive effect (I^-) prevails in the *meta* position and so strengthens the intermolecular hydrogen bonds.

A comparison of the curves in Fig. 4(a) indicates, for the hydroxy anions, a continuous inversion of solvation enthalpy. In the mole fraction range from 0.0 to 0.12, the transfer of the anions decreases according to sequence $p\text{BzO}^- > m\text{BzO}^- > o\text{BzO}^-$, while from 0.12 to 0.34 the sequence becomes $m\text{BzO}^- > o\text{BzO}^- > p\text{BzO}^-$. Again, from 0.34 to 0.48 the order is $m\text{BzO}^- > p\text{BzO}^- > o\text{BzO}^-$. Above 0.48 mole fraction, the sequence observed is $p\text{BzO}^- > o\text{BzO}^- > m\text{BzO}^-$.

The hydroxyl group in the *para* position attracts the negative charge of the carboxylate group more weakly than in the *meta* position. Moreover, the resonance effect (R^+) in the *para* position decreases the inductive effect (I^-). For these reasons, in the water-rich mixtures, the *para* hydroxy anion interacts with the water molecules (hydrogen bond) to a greater extent than the *meta* anion.

In the *ortho* anion, the strong intramolecular hydrogen bond lowers the negative charge of the carboxylate group.

In the DMSO-rich solutions ($X_{\text{DMSO}} > 0.48$), the resonance effect prevails over the inductive effect thus allowing strong dipole-dipole interactions.

In the range from 0.12 to 0.34 X_{DMSO} , the drastic decrease in $\text{H}_2\text{O}/\text{DMSO}$ molar ratio from 9 : 1 to 2 : 1 affects to a greater extent the *p*-hydroxybenzoic anion. Finally, in the mole fraction range from 0.34 to 0.48 (molar ratio $\text{H}_2\text{O}/\text{DMSO}$ 1 : 1), the solution displays the maximum structure breaking and the maximum solvating power [1]; neither resonance nor inductive effect prevails.

Thus in the hydroxybenzoic anions and the corresponding undissociated molecules (except for the *o*-hydroxybenzoic acid) the prevalence of the inductive or resonance effect is a function of the solvent composition.

In the chlorobenzoic anions, the inductive effect always prevails, while in the undissociated chlorobenzoic molecules, the resonance prevails at all mole fractions [1].

It is clear that the greater ionization of the *o*-hydroxy compound with respect to the *meta* and *para* derivatives derives chiefly from the greater desolvation of the undissociated molecules.

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