CALORIMETRIC STUDY OF THE IONIZATION PROCESS FOR 2,6-DIHYDROXYBENZOIC ACID. THE EFFECT OF THE INTERNAL HYDROGEN BOND ON ACID STRENGTH

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ABSTRACT

The ionization and solution enthalpies of 2,6-dihydroxybenzoic acid were measured calorimetrically at 25°C in water–DMSO mixtures, ranging from pure water up to 0.8 mole fraction of DMSO.

The trend of the ionization as a function of the DMSO mole fraction is very different from those of all the monosubstituted-benzoic acids previously studied. This is due to the two internal hydrogen bonds formed between the carboxyl group and the hydroxyl groups.

INTRODUCTION

The ionization process of 3,5-dinitrobenzoic acid has been examined in dimethylsulphoxide (DMSO)–water solutions [1]. The two nitro groups, in *meta* positions, give rise to an additive (σ) inductive effect. More precisely, the additive principle was found to be effective (for the free energy values) in water-rich ($x_{DMSO} < 0.2$) and DMSO-rich ($x_{DMSO} > 0.6$) mixtures. On the other hand, in the range of mole fraction $\Delta x_{DMSO} = 0.2$–0.6 the additive principle is seriously violated.

In the present work the behaviour of 2,6-dihydroxybenzoic acid has been examined in the same mixtures.

The *ortho*-hydroxybenzoic acid shows strong intramolecular and intermolecular hydrogen bonding [2,3], which distinguishes the *ortho* from the *meta* and *para* compounds.

It seemed reasonable to expect the *ortho*-dihydroxy compound to display a very different behaviour with respect to other disubstituted compounds. Indeed, both hydroxyl groups should form a strong internal hydrogen bond with the carboxyl group.

EXPERIMENTAL PROCEDURE

The calorimetric apparatus has been previously described [1–3]. DMSO (Carlo Erba RP grade) was purified according to the procedure of Synnot and Butler [4]. DMSO–water mixtures were prepared by weighing purified DMSO and CO_2-free twice-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.0 to 0.8. Aqueous solutions of 0.99 M HCl and 0.098 M NaOH were prepared from standard solutions; their concentrations were checked by potentiometric titration. The 2,6-dihydroxybenzoic acid (Fluka) was purified by crystallization from water–ether mixtures, and its melting point checked before use. The 2,6-$(OH)_2$PhCOONa solutions were prepared by adding a NaOH solution of known molarity to 2,6-dihydroxy-benzoic acid dissolved in the mixed solvent. As a result of this addition, 100 g of a DMSO–water solution at x mole fraction was obtained.

The ionization process of 2,6-dihydroxybenzoic acid in the various water–DMSO mixtures of x mole fraction can be represented by

$$[2,6\text{-}(OH)_2PhCOOH]_x \rightarrow [2,6\text{-}(OH)_2PhCOO^-]_x + (H^+)_x \qquad (1)$$
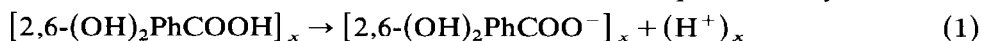
The molar enthalpy, $\Delta \overline{H}_1$, of ionization of 2,6-$(OH)_2$PhCOOH was obtained by the experimental procedure described [1–3].

(a) The molar enthalpy of reaction, $\Delta \overline{H}_2$, of 2,6-$(OH)_2$PhCOONa, dissolved in the mixed solvent of x' mole fraction, with 0.99 M HCl was measured

$$[2,6\text{-}(OH)_2PhCOO^-]_{x'} + (Na^+)_{x'} + (H^+)_{aq} + (Cl^-)_{aq}$$
$$\rightarrow [2,6\text{-}(OH)_2PhCOOH]_x + (Na^+)_x + (Cl^-)_x \qquad (2)$$
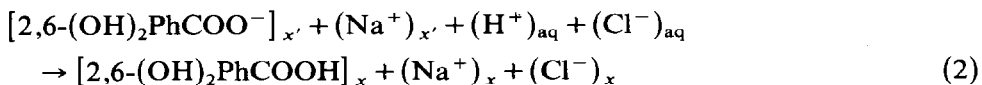
(b) The molar enthalpy of solution, ΔH_3, of the same amount of 0.99 M HCl, in the same solvent mixture at x' mole fraction, was measured

$$(H^+)_{aq} + (Cl^-)_{aq} \rightarrow (H^+)_x + (Cl^-)_x \qquad (3)$$

(c) The molar enthalpy of process (1) can be obtained by subtracting the two values $\Delta \overline{H}_3$ and $\Delta \overline{H}_2$, and by adding to their difference the $\Delta \overline{H}_4$ values related to the molar transfer enthalpy of [2,6-$(OH)_2$PhCOONa], at infinite dilution, from solvent x' to solvent x.

$$[2,6\text{-}(OH)_2PhCOO^-]_{x'} + (Na^+)_{x'} \rightarrow [2,6\text{-}(OH)_2PhCOO^-]_x + (Na^+)_x \qquad (4)$$
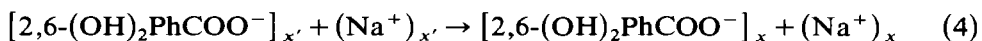
For each of the water–DMSO mixtures at x_{DMSO} mole fraction, the $\Delta \overline{H}_1$ values refer to the ionization of one mole of [2,6-$(OH)_2$PhCOOH] dissolved at infinite dilution in 1000 g of mixed solvent, yielding one mole of [2,6-$(OH)_2$PhCOO$^-$] ions and one mole of protons solvated in the same amount of solvent.

For a better understanding of the $\Delta \overline{H}_1$ values obtained in the different solvent mixtures, the solution enthalpies of crystalline 2,6-$(OH)_2$PhCOOH in the various solvent mixtures were measured.

$$2,6\text{-}(OH)_2PhCOOH_{(c)} \rightarrow [2,6\text{-}(OH)_2PhCOOH]_x \qquad (5)$$

Hence, $\Delta \overline{H}_6 = \Delta \overline{H}_5 + \Delta \overline{H}_1$ values obtained for the process

$$2,6\text{-(OH)}_2\text{PhCOOH}_{(c)} \rightarrow \left[2,6\text{-(OH)}_2\text{PhCOO}^-\right]_x + \left(\text{H}^+\right)_x \qquad (6)$$

refer to an identical initial thermodynamic state.

In processes (2) and (5) concentrations ranging from 2×10^{-3} to 4×10^{-3} m were used. Therefore, the $\Delta \overline{H}_1$ values related to these processes were assumed to be equal to the ΔH^0 values [1–3].

RESULTS

Table 1 shows the ΔH_1^0, ΔH_5^0 and ΔH_6^0 values of processes (1), (5) and (6) obtained for 2,6-dihydroxybenzoic acid.

For the sake of comparison, it is convenient to express the ionization enthalpy values, ΔH_1^0, as the difference between the values obtained in the mixed solvent at x mole fraction and in pure water so that

$$\delta \Delta H_1^0 = \left(\Delta H_1^0\right)_x - \left(\Delta H_1^0\right)_{x=0}$$

These values are relative to the transfer of the ionization process, while the $\delta \Delta H_5^0$ and $\delta \Delta H_6^0$ values represent the transfer enthalpy of the undissociated molecules and of the two ions H^+ and $2,6\text{-(OH)}_2\text{PhCOO}^-$, respectively, from pure water to mixed solvent. These data are plotted in Figs. 1 and 2.

DISCUSSION

The $\delta \Delta H_1^0$ term, as shown in Fig. 1, is favourable to process (1) in the complete mole fraction range with the exception of $0.7 < x_{\text{DMSO}} < 0.8$. This trend is very different from that of the *ortho*-hydroxybenzoic acid and from those of all the monosubstituted benzoic acid derivatives, which have been

TABLE 1

Enthalpy values of processes (1), (5) and (6) for 2,6-dihydroxybenzoic acid in DMSO–water solutions of various mole fractions at 25°C

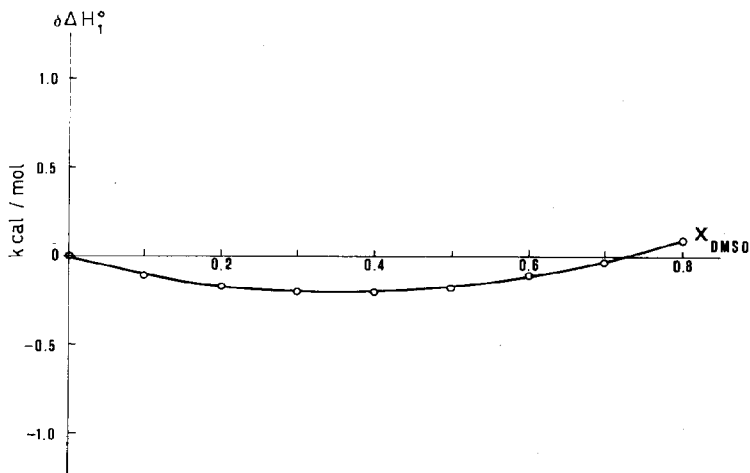| x_{DMSO}	ΔH_1^0	ΔH_5^0	ΔH_6^0
0.0	0.14	7.12	7.26
0.1	0.04	7.37	7.41
0.2	−0.03	6.15	6.12
0.3	−0.06	3.40	3.34
0.4	−0.06	1.48	1.42
0.5	−0.03	0.26	0.23
0.6	0.03	−0.36	−0.33
0.7	0.12	−0.44	−0.32
0.8	0.23	−0.51	−0.28

Fig. 1. Enthalpy for the transfer of the ionization of 2,6-dihydroxybenzoic acid as a function of mole fraction.

the subject of extensive research in our laboratory [5–9], and also differs from the disubstituted nitrobenzoic acid [1].

The enthalpy trend can be explained by taking into account the solvation enthalpies of the 2,6-dihydroxybenzoic acid and 2,6-dihydroxybenzoic anion.
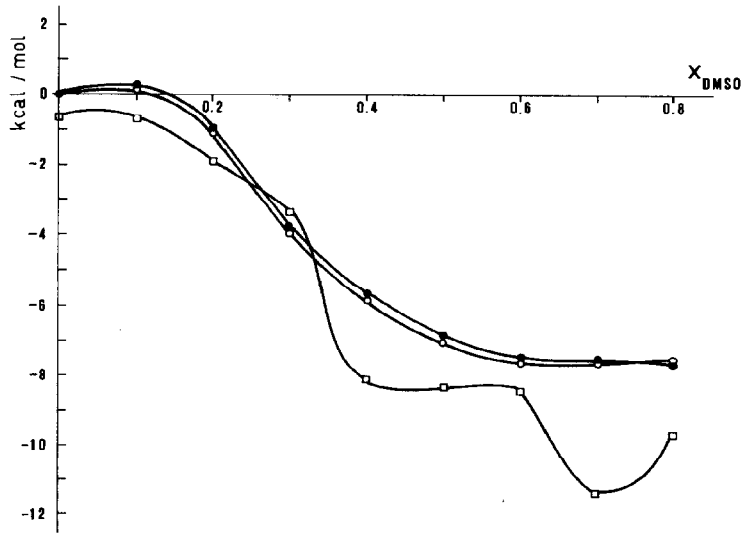

Fig. 2. Transfer enthalpies of the undissociated molecule and ions of 2,6-dihydroxybenzoic acid as a function of mole fraction. Difference in the enthalpy of ionization of 2,6-dihydroxy- and 2-hydroxybenzoic acid as a function of the mole fraction. ●, $\delta \Delta H_5^0$; ○, $\delta \Delta H_6^0$; □, $\Delta H_{2,6(OH)_2PhCOOH}^0 - \Delta H_{2(OH)PhCOOH}^0$.
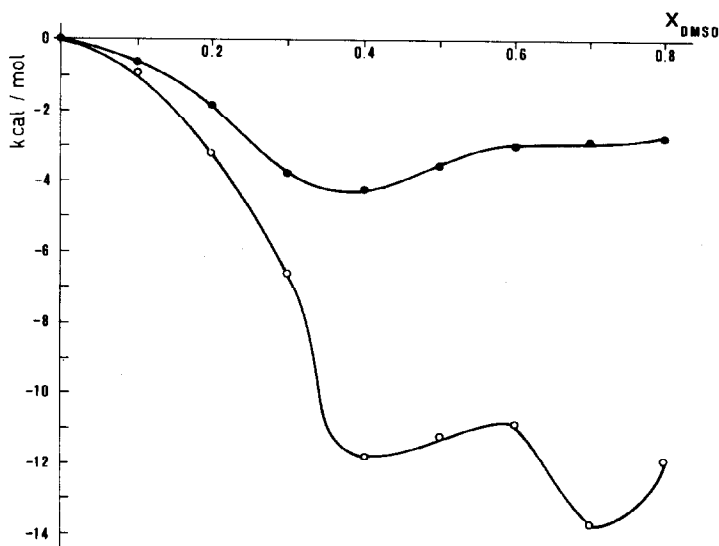
Fig. 3. Differences in the solvation enthalpies of the undissociated molecule couples and the anion couples of 2,6-dihydroxy- and 2-hydroxybenzoic acids in various DMSO–water mixtures. $\bigcirc$, $\Delta H^0_{(2,6(OH)_2PhCOO^-)-(2(OH)PhCOO^-)}$; $\bullet$, $\Delta H^0_{(2,6(OH)_2PhCOOH)-(2(OH)PhCOOH)}$.

Figure 2 shows that the 2,6-dihydroxybenzoic anion is more solvated than the 2,6-dihydroxybenzoic acid in the complete mole fraction range with the exception of $0.7 < x_{DMSO} < 0.8$.

It is also clear that the differentiation of the acidity between the 2,6-dihydroxy- and 2-hydroxybenzoic acid (Fig. 2) is mainly related to the transfer solvation enthalpy of the anions. This difference, $\Delta H^0_{[2,6(OH)_2PhCOO^-]_x-[2(OH)PhCOO^-]_x}$, together with the difference in the solvation enthalpy between the undissociated molecules, $\Delta H^0_{[2,6(OH)_2PhCOOH]_x-[2(OH)PhCOOH]_x}$, was calculated as previously shown [7–9] and plotted in Fig. 3.

Figure 3 shows that the dihydroxybenzoic anion is more solvated than the hydroxybenzoic anion with a sharp maximum at $\Delta x_{DMSO} = 0.4$–0.8. This fact can be ascribed to the stabilization and delocalization of the charge of the anion by means of the two internal hydrogen bonds. For these reasons the dihydroxy anion displays a greater solvation in DMSO-rich solutions, where the dipole–dipole interactions are prevalent. The equation

$$\delta\Delta G^0 = \rho_0\Sigma\sigma_0^2 + 2fF + \sigma_0^1 - \sigma_p + 2\delta E_s \tag{7}$$

was used to calculate the substituent constants, $\Sigma\sigma_0^2$, for the 2,6-(OH)$_2$PhCOOH in water. If the additive principle is assumed, the same value could be equal to $2\sigma_0^2$. The two values are found to be 0.842 and -0.868.

Thus the 2,6-dihydroxy compound shows a remarkable discrepancy between calculated and predicted values in water, while for the 3,5-dinitrobenzoic acid there is agreement to within 6%. This can be ascribed to the fact that for compounds containing two groups *ortho* to the carboxyl group the additive principle is frequently seriously violated. Furthermore, eqn. (7), obtained by modifying the equation used for mono *ortho*-hydroxybenzoic acid [3], is not likely to be effective.

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