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CALORIMETRIC STUDY OF THE IONIZATION PROCESS FOR 2,3-DIHYDROXYBENZOIC ACID

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ABSTRACT

A calorimetric study of the ionization process of 2,3-dihydroxybenzoic acid was performed in water–DMSO mixtures ranging from pure water up to a 0.8 mole fraction of DMSO.

A comparison of the ionization processes of the 2,6-dihydroxybenzoic acid with the 2- and 3-monohydroxy substituted benzoic acids was also presented.

INTRODUCTION

The thermodynamic study of the ionization processes of *ortho*-, *meta*- and *para*-hydroxybenzoic acids in water–dimethylsulfoxide (DMSO) mixtures has been the subject of a research recently carried out in our laboratory [1,2].

A calorimetric study of the ionization process of 2,6-dihydroxybenzoic acid was also performed [3]. The trend of the ionization as a function of the DMSO mole fraction of the disubstituted hydroxybenzoic acid is very different from that of the monohydroxy substituted benzoic acid [1] and from all the mono-benzoic acids previously studied [4–6]. This is due to the two internal hydrogen bonds formed between the carboxyl and the hydroxyl groups. It was interesting to study the behaviour of other dihydroxy substituted benzoic acids and compare them with the corresponding monohydroxy substituted benzoic acids in order to supply a more complete picture of this class of compounds.

In the present work, the behaviour of 2,3-dihydroxybenzoic acid has been examined.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been previously described [1]. DMSO (Carlo Erba RP grade) was purified according to the procedure of Synnot

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and Butler [7]. DMSO–water mixtures were prepared by weighing purified DMSO and CO_2-free doubly-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 titrations. The 2,3-dihydroxybenzoic acid (Fluka) was purified by crystallization from water–ether mixtures and its m.p. checked before use. The 2,3-$(OH)_2$PhCOONa solutions were prepared by adding an NaOH solution of known molarity to 2,3-dihydroxybenzoic acid dissolved in the DMSO–water mixture. As a result of this addition 100 g of DMSO–water solution at X mole fraction was obtained.

The ionization process of 2,3-dihydroxybenzoic acid, in the various water–DMSO mixtures of X mole fraction can be represented by

$$[2,3\text{-}(OH)_2PhCOOH]_X \rightarrow [2,3\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \tag{1}$$

The molar enthalpy, $\Delta \overline{H}_1$, of the ionization of 2,3-$(OH)_2$PhCOOH was obtained [1] by the experimental procedure described.

(a) The molar enthalpy of reaction, ΔH_2, of 2,3-$(OH)_2$PhCOONa, dissolved in the mixed solvent of X' mole fraction, with 0.99 M HCl was measured

$$\begin{aligned}&[2,3\text{-}(OH)_2PhCOO^-]_{X'} + (Na^+)_{X'} + (H^+)_{aq} + (Cl^-)_{aq}\\ &\quad \rightarrow [2,3\text{-}(OH)_2PhCOOH]_X + (Na^+)_X + (Cl^-)_X\end{aligned} \tag{2}$$

(b) The molar enthalpy of solution, $\Delta \overline{H}_3$, of the same amount of 0.99 M HCl, in the same solvent mixture at X' mole fraction, was measured

$$(H^+)_{aq} + (Cl^-)_{aq} \rightarrow (H^+)_X + (Cl^-)_X \tag{3}$$

(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 this difference the $\Delta \overline{H}_4$ values related to the molar transfer enthalpy of 2,3-$(OH)_2$PhCOONa (at infinite dilution) from a solvent with mole fraction X' to a solvent with mole fraction X

$$[2,3\text{-}(OH)_2PhCOO^-]_{X'} + (Na^+)_{X'} \rightarrow [2,3\text{-}(OH)_2PhCOO^-]_X + (Na^+)_X \tag{4}$$

For every one of the water–DMSO mixtures at X_{DMSO} mole fraction, the $\Delta \overline{H}_1$ values refer to the ionization of one mole of $[2,3\text{-}(OH)_2PhCOOH]_X$ dissolved at infinite dilution in 1000 g of mixed solvent, yielding one mole of $[2,3\text{-}(OH)_2PhCOO^-]_X$ 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 2,3-$(OH)_2$PhCOOH in the various solvent mixtures were measured

$$2,3\text{-}(OH)_2PhCOOH_{cry} \rightarrow [2,3\text{-}(OH)_2PhCOOH]_X \tag{5}$$

TABLE 1

Enthalpy values of processes (1), (5) and (6) for the 2,3-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	0.57	6.88	7.45
0.1	0.23	6.63	6.86
0.2	0.48	5.44	5.92
0.3	0.69	3.28	3.97
0.4	1.17	1.26	2.43
0.5	1.74	−0.08	1.66
0.6	2.55	−1.11	1.44
0.7	3.63	−1.89	1.74
0.8	4.29	−2.18	2.11

so that the $\Delta H_6 = \Delta H_5 + \Delta H_1$ values obtained for the process

$$2,3\text{-}(OH)_2PhCOOH_{cry} \rightarrow [2,3\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \qquad (6)$$

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.

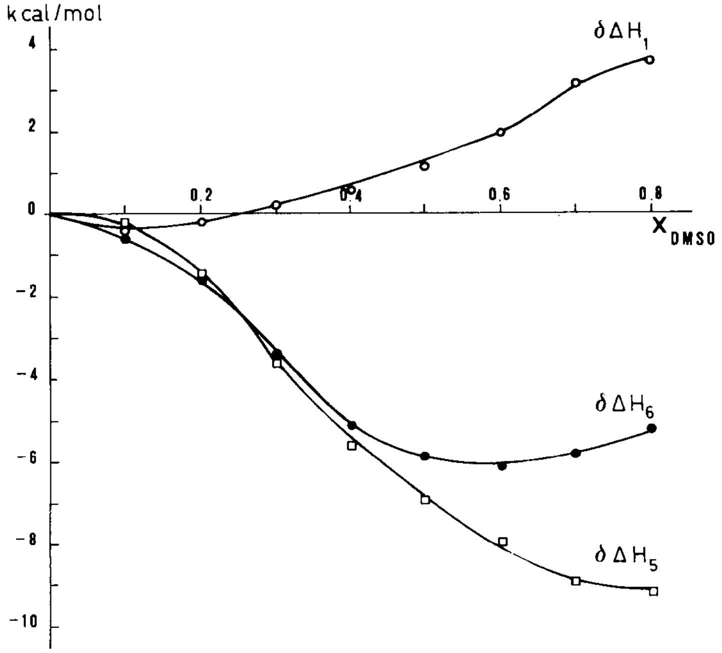

Fig. 1. Enthalpy for the transfer of the ionization and transfer enthalpies of the undissociated molecule and the ion of the 2,3-dihydroxybenzoic acid.

RESULTS

Table 1 shows the ΔH_1^0, ΔH_5^0 and ΔH_6^0 values of processes (1), (5) and (6) obtained for the 2,3-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 $\delta\Delta H_1^0 = (\Delta H_1^0)_X - (\Delta H_1^0)_{X=0}$.

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 $[2,3\text{-}(OH)_2PhCOO^-]_X$, respectively from pure water to mixed solvent.

All these data are plotted in Fig. 1.

DISCUSSION

The $\delta\Delta H_1^0$ term, as shown in Fig. 1, is favourable to process (1) only in the water-rich solutions ($0.0 < X_{DMSO} < 0.2$) while for the DMSO-rich solutions the contrary is true. This can be ascribed to the fact that in these two solution ranges the undissociated molecules and the ions invert the order of solvation.

By comparing the 2,3-dihydroxy- and the 2,6-dihydroxybenzoic acids, by means of the difference in the enthalpy of ionization $(\Delta H_1^0)_{2,3\text{-}(OH)_2PhCOOH} - (\Delta H_1^0)_{2,6\text{-}(OH)_2PhCOOH}$ (Fig. 2) it can be inferred that the latter is a more effective acid over the whole mole fraction range. The difference in solvation enthalpy between the ions

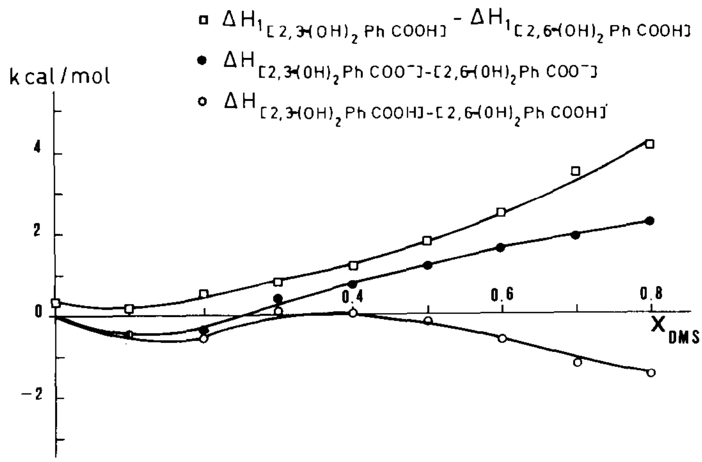

Fig. 2. Differences in the enthalpy of ionization and in solvation enthalpies between the undissociated molecule couples and the anion couples of the 2,3-dihydroxy- and 2,6-dihydroxybenzoic acids in various DMSO–water solutions.

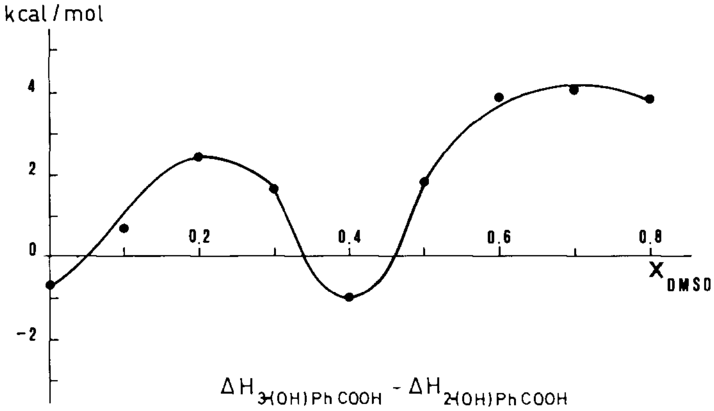

Fig. 3. Differences in the enthalpy of ionization of the 3-hydroxy- and 2-hydroxybenzoic acids in various DMSO–water mixtures.

$\Delta H^0_{(2,3\text{-}(OH)_2PhCOO^-)_x-(2,6\text{-}(OH)_2PhCOO^-)_x}$ and the undissociated molecules $\Delta H^0_{(2,3\text{-}(OH)_2PhCOOH)_x-(2,6\text{-}(OH)_2PhCOOH)_x}$ of the 2,3-dihydroxy- and 2,6-dihydroxybenzoic acids shows that the greater solvation of the 2,6-dihydroxy anion and of the 2,3-dihydroxy undissociated molecule explains the greater acidity observed for the 2,6-dihydroxy derivative.

It is noteworthy that the solvation of the 2,6-dihydroxy anion plays a major role mostly in DMSO-rich solutions, where the stabilization and delocalization of the charge of the anion, due to the two internal hydrogen bonds, are enhanced and the dipole–dipole interactions are prevalent.

Although the introduction of the second hydroxyl group in the *meta* position destabilizes the benzene ring, the steric effect of the two hydroxyl groups in the *ortho* position makes this molecule less solvated than that of the 2,3-hydroxy derivative.

A comparison between the differences in the enthalpy ionization of the $\Delta H^0_{1(3\text{-}(OH)PhCOOH)_x} - \Delta H^0_{1(2\text{-}(OH)PhCOOH)_x}$ (Fig. 3) and $\Delta H^0_{1(2,3\text{-}(OH)_2PhCOOH)_x} - \Delta H^0_{1(2,6\text{-}(OH)_2PhCOOH)_x}$ (Fig. 2) can be obtained by considering the relative solvation of the anions and undissociated molecule of the mono- [2] and dihydroxy- (this work) derivatives.

Therefore, for the mono derivatives the greater ionization of the *ortho*-hydroxy compound with respect the *meta*-derivative comes chiefly from the greater desolvation of the undissociated molecule. On the contrary the key-factor of the greater strength of the 2,6-dihydroxybenzoic acid is represented again by the internal hydrogen bond.

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