CALORIMETRIC STUDY OF THE IONIZATION PROCESS FOR 2,4-DIHYDROXY BENZOIC ACID

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ABSTRACT

A calorimetric study of the ionization process of 2,4-dihydroxy benzoic acid, in water–DMSO mixtures, ranging from pure water up to 0.8 mole fraction, is presented.

This compound is a less effective acid than 2,3-dihydroxy benzoic acid up to 0.6 mole fraction. Beyond this mole fraction a reversal of acid strength occurs. The solvation of the undissociated molecule seems to be the key factor of the difference in acid strength of the two dihydroxy derivatives, while between the corresponding monosubstituted compounds the anion solvation plays a prevailing role.

INTRODUCTION

A systematic study of the ionization processes of disubstituted benzoic derivatives [1–3] and (disubstituted) phenol derivatives [4,5] in water–dimethylsulfoxide (DMSO) mixtures have recently been started in our laboratory. The aim of this research is to compare the disubstituted derivatives with the corresponding monosubstituted derivatives in order to give a more complete understanding of the effect of an additional substituent group on interactions between the first substituent and the functional group.

As shown [1], the additivity principle is partially valid for the 3,5-dinitrobenzoic acid, while for the 2,6-dihydroxy benzoic acid it is not true [2]. This can be ascribed to the fact that for compounds containing two groups in the *ortho* position with respect to the carboxyl group often the additivity principle is seriously violated.

The calorimetric study of the 2,4- and 2,5-dinitro phenols shows that the second group in the *para* and *meta* positions, respectively, represents the key factor in the ionization process of the two compounds.

Finally, the introduction of the second hydroxyl group in the *meta* position destabilizes the benzene ring [3] to a lesser degree than the (second) hydroxyl in the *ortho* position.

This work is aimed at comparing the effect of the second hydroxyl group in the *para* position with that in the *meta* position.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been previously described [1,2]. DMSO (Carlo Erba RP grade) was purified according to the procedure of Synnot and Butler [6]. DMSO–water mixtures were prepared by weighing purified DMSO and CO_2-free twice-distilled water. The mole fraction of DMSO in these mixtures ranges from 0.0 to 0.8. Aqueous solutions of 1 M HCl and 0.1 M NaOH were prepared from standard solutions; their concentrations were checked by potentiometric titrations. The 2,4-dihydroxy benzoic acid (Fluka) was purified by crystallization from water–ether mixtures; its m.p. was checked before use. The 2,4-$(OH)_2PhCOONa$ solutions were prepared by adding an NaOH solution of known molarity to 2,4-dihydroxy benzoic acid dissolved in the mixed solvent. As a result of this addition 100 g of DMSO–water solution at X mole fraction was obtained.

The ionization process of the 2,4-dihydroxy benzoic acid, in the various water–DMSO mixtures of X mole fraction can be represented by
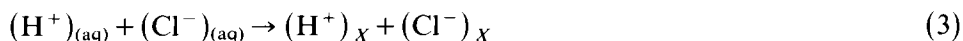
$$[2,4\text{-}(OH)_2PhCOOH]_X \rightarrow [2,4\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \tag{1}$$
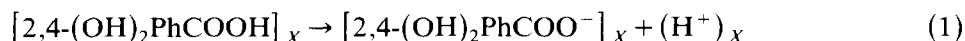
The molar enthalpy, $\Delta\overline{H}_1$, of the ionization of 2,4-$(OH)_2PhCOOH$ was obtained [1,2] by the experimental procedure described.

(a) The molar enthalpy of reaction, $\Delta\overline{H}_2$, of 2,4-$(OH)_2PhCOONa$, dissolved in the mixed solvent of X' mole fraction, with 1 M HCl was measured

$$[2,4\text{-}(OH)_2PhCOO^-]_{X'} + (Na^+)_{X'} + (H^+)_{(aq)} + (Cl^-)_{aq}$$

$$\rightarrow [2,4\text{-}(OH)_2PhCOOH]_X + (Na^+)_X + (Cl^-)_X \tag{2}$$
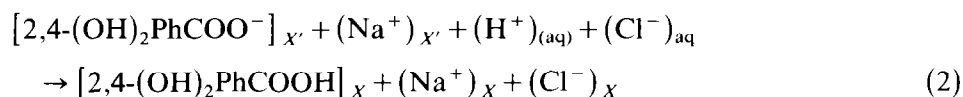
(b) The molar enthalpy of solution, $\Delta\overline{H}_3$, of the same amount of 1 M HCl, in the same solvent mixture at X mole fraction, was measured

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

(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 $[2,4\text{-}(OH)_2PhCOONa]_X$ (at infinite dilution) from the solvent of X' to the solvent of X mole fraction

$$[2,4\text{-}(OH)_2PhCOO^-]_{X'} + (Na^+)_{X'} \rightarrow [2,4\text{-}(OH)_2PhCOO^-]_X + (Na^+)_X \tag{4}$$
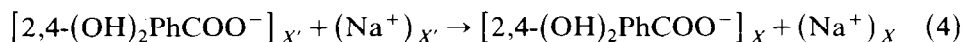
For every one of the water–DMSO mixtures at X_{DMSO} mole fraction, the $\Delta\overline{H}_1$ values refer to the ionization of 1 mol of 2,4-$(OH)_2PhCOOH$ dissolved

at infinite dilution in 1000 g of mixed solvent, yielding 1 mol of [2,4-$(OH)_2PhCOO^-]_X$ ions and 1 mol 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 2,4-$(OH)_2PhCOOH$ in the various solvent mixtures were measured

$$2,4\text{-}(OH)_2PhCOOH_{(cry)} \rightarrow [2,4\text{-}(OH)_2PhCOOH]_X \tag{5}$$
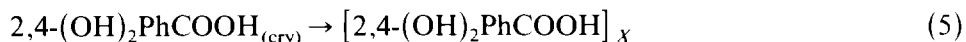
so that the $\Delta \text{-} \overline{H}_6 = \Delta \overline{H}_5 + \Delta \overline{H}_1$ values obtained for the process

$$2,4\text{-}(OH)_2PhCOOH_{(cry)} \rightarrow [2,4\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \tag{6}$$
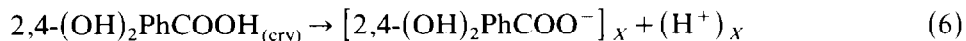
refer to an identical initial thermodynamic state.

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

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 2,4-dihydroxy benzoic 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 $\delta \Delta H_1^0 = (\Delta H_1^0)_X - (\Delta H_1^0)_{X=0}$.

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

All these data are plotted in Fig. 1.

TABLE 1

Enthalpy values of processes (1), (5) and (6) for the 2,4-dihydroxy benzoic acid in DMSO–water solutions of various mole fraction

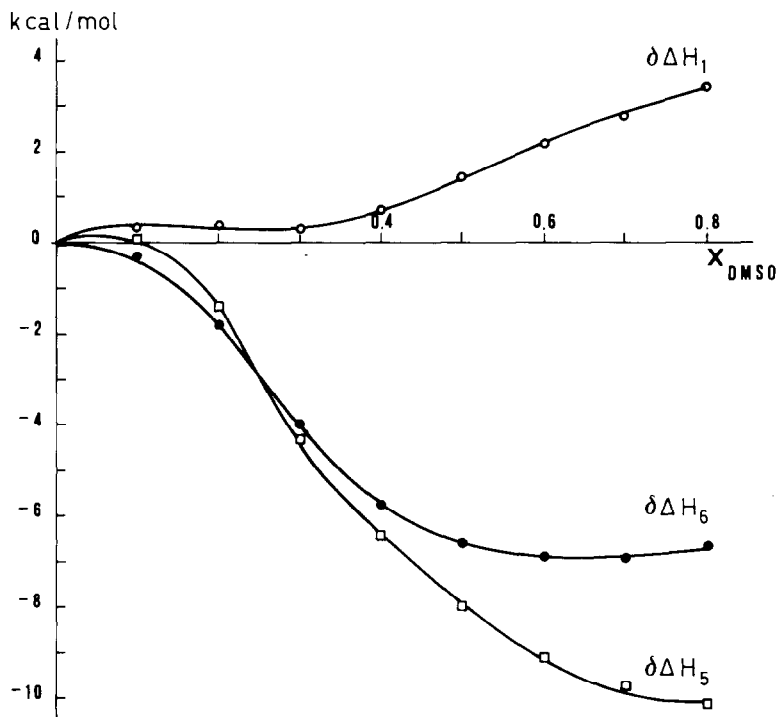| X_{DMSO}	ΔH_1^0	ΔH_5^0	ΔH_6^0
0.0	0.45	7.15	7.60
0.1	0.74	7.03	7.77
0.2	0.87	5.35	6.22
0.3	0.71	2.81	3.52
0.4	1.19	0.67	1.86
0.5	1.87	−0.89	0.98
0.6	2.77	−1.94	0.83
0.7	3.20	−2.53	0.67
0.8	3.95	−2.93	1.02

Fig. 1. Enthalpy for the transfer of the ionization and transfer enthalpies of the undissociated molecule and the ion of the 2,4-dihydroxy benzoic acid.

DISCUSSION

The $\delta\Delta H_1^0$ term (Fig. 1) is unfavourable to process (1), this being due to the greater solvation of the undissociated molecule with respect to that of the anion. Therefore, the second hydroxyl group in the *para* position stabilizes the benzene ring. For the same reason the 2,4-dihydroxy derivative is a less effective acid up to 0.6 mole fraction, than the 2,3-dihydroxy benzoic acid. This can be demonstrated by comparing 2,4-dihydroxy and 2,3-dihydroxy benzoic acid, by means of the difference in the enthalpy ionization $\Delta H_{1(2,4-(OH)_2PhCOOH)_x}^0 - \Delta H_{1(2,3-(OH)_2PhCOOH)_x}^0$ (Fig. 2). Therefore, the difference in solvation enthalpy between the ions $\Delta H_{(2,4-(OH)_2PhCOO^-)_x-(2,3-(OH)_2PhCOO^-)_x}^0$ and the undissociated molecules $\Delta H_{(2,4-(OH)_2PhCOOH)_x-(2,3-(OH)_2PhCOOH)_x}^0$ shows that (Fig. 2) the undissociated molecule of the 2,4-dihydroxy derivative is always more solvated than that of the 2,3-dihydroxy benzoic acid, thus, confirming the stabilization effect of the second hydroxyl group in the *para* position. The relative solvation of the undissociated molecules is also greater than that of the anions with an exception at $X_{DMSO} = 0.6-0.8$ where a reversal of the solvation trend occurs, so that the acidity strength of the two dihydroxy derivatives is also reversed.

kcal / mol

$\square$ $\Delta H_{1[2,4(OH)_2PhCOOH]}$ $- \Delta H_{1[2,3(OH)_2PhCOOH]}$

$\bullet$ $\Delta H_{[2,4(OH)_2PhCOO^-]-[2,3(OH)_2PhCOO^-]}$

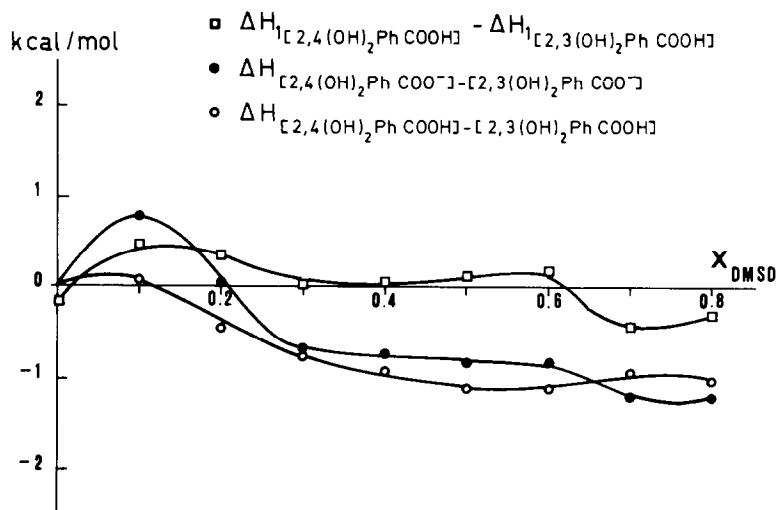$\circ$ $\Delta H_{[2,4(OH)_2PhCOOH]-[2,3(OH)_2PhCOOH]}$

Fig. 2. Differences in the enthalpy of ionization and in solvation enthalpies between the undissociated molecule couples and the anion couples of the 2,4-dihydroxy and 2,3-dihydroxy benzoic acids in various DMSO–water mixtures.

By comparing the 3- and 4-monosubstituted compounds by means of the difference in the enthalpy of ionization $\Delta H^0_{1(3\text{-OHPhCOOH})} - \Delta H^0_{1(4\text{-OHPhCOOH})}$ (Fig. 3) it can be shown that the *meta* derivative is a more effective acid than the *para* derivative up to 0.5 mole fraction. Beyond this mole fraction the

kcal / mol

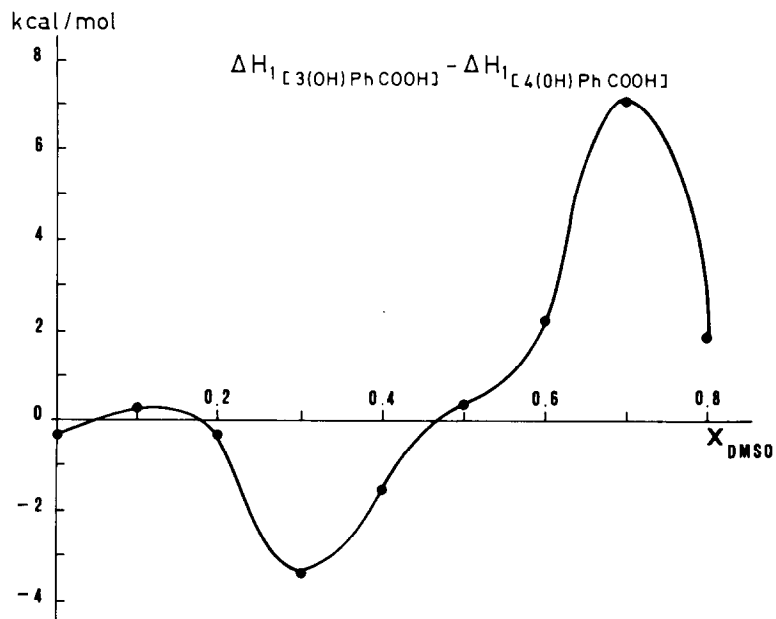$\Delta H_{1[3(OH)PhCOOH]} - \Delta H_{1[4(OH)PhCOOH]}$

Fig. 3. Difference in the enthalpy of ionization of the 3-hydroxy and 4-hydroxy benzoic acids in various DMSO–water mixtures.

contrary is true. As shown previously [3] the anions solvation is the factor prevailing in the comparison of the acidity strength between the 2,6- and the 2,3-dihydroxy derivative, while for the corresponding monosubstituted derivatives (2 and 3) the greater ionization of the *ortho*-hydroxy derivative with respect to the *meta* compound derives chiefly from the greater desolvation of the undissociated molecule [7].

A comparison was made of the differences in the enthalpy of ionization and in the relative solation of the anions and the undissociated molecules of the mono- [7] and dihydroxy derivatives for the couples 2,4/2,3 dihydroxy, and 4/3 monohydroxy.

It is noted that in this case the solvation of the undissociated molecule is the key factor for the disubstituted compound while for the monosubstituted compound the anions play a major role. It seems reasonable to assume that the latter is the more likely behaviour for the dihydroxy derivative. This is due to the interaction between the two substituted groups in the undissociated molecule driving the ionization processes, an exception being the 2,6-dihydroxy benzoic acid. Indeed, for the latter the strong internal hydrogen bonds greatly stabilize the anion. This hypothesis justifies more detailed consideration.

ACKNOWLEDGEMENT

REFERENCES

1 F. Rodante, G. Ceccaroni and F. Fantauzzi, Thermochim. Acta, 65 (1983) 295.
2 F. Rodante and G. Ceccaroni, Thermochim. Acta, 72 (1984) 335.
3 F. Rodante and G. Ceccaroni, Thermochim. Acta, 75 (1984) 115.
4 F. Rodante, G. Ceccaroni and F. Fantauzzi, Thermochim. Acta, 70 (1983) 83.
5 F. Rodante, G. Ceccaroni and F. Fantauzzi, Thermochim. Acta, 70 (1983) 91.
6 J.C. Synnot and J.N. Butler, J. Phys. Chem., 73 (1979) 1470.
7 F. Rodante, G. Ceccaroni and M.G. Bonicelli, Thermochim. Acta, 42 (1980) 223.