Thermochimica Acta, 88 (1985) 347–353
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC STUDY OF THE IONIZATION PROCESS FOR 2,5-DIHYDROXYBENZOIC ACID. RESONANCE EFFECT. A CALORIMETRIC ACIDITY SCALE FOR DIHYDROXY-SUBSTITUTED BENZOIC DERIVATIVES

F. RODANTE, M. TOCCI and A. ONOFRI

Dipartimento di Ingegneria Chimica dei Materiali, delle Materie Prime e Metallurgia, Università di Roma, Via del Castro Laurenziano 7, Roma (Italy)

(Received 10 December 1984)

ABSTRACT

A calorimetric study of the ionization process of 2,5-dihydroxybenzoic acid, in water–DMSO mixtures, ranging from pure water up to 0.8 mole fraction is presented.

This compound shows a very different behaviour with respect to the 2,3-dihydroxy derivative because of the two hydroxyl groups which, in the relative *para* position, stabilize and delocalize the charge on the anion. For this reason, 2,5-$(OH)_2PhCOOH$ is, with the exception of 2,6-$(OH)_2PhCOOH$, the strongest acid in an acidity scale of dihydroxy derivatives.

INTRODUCTION

The group of mono- and disubstituted hydroxyl compounds has been systematically studied in our laboratory [1–5]. The dissociation processes, in water–dimethylsulfoxide (DMSO) mixtures of the *ortho-*, *meta-* and *para*-monohydroxy derivatives have been compared with those of the corresponding disubstituted 2,6-, 2,4- and 2,3-dihydroxybenzoic derivatives. In this way it is possible to obtain a more complete understanding of the effect of an additional substituent group on the interactions between the first and the functional groups.

The trend in ionization of the 2,6-dihydroxy derivative [3] is very different from that typical of all other mono- and disubstituted benzoic derivatives previously studied. This is due to two internal hydrogen bonds formed between the carboxyl and the hydroxyl groups. It was also noted that the solvation of the undissociated molecules is the key-factor in disubstituted benzoic dissociation. This is linked to the interaction between the two disubstituted groups which, in the undissociated molecules, drive the ionization processes, an exception being the 2,6-dihydroxybenzoic acid.

The 2,5-dihydroxy derivative seems to be a very interesting compound. The two hydroxyl groups, in the relative *para* position, stabilize the benzene ring by means of a resonance effect both in the anion and in the undissociated molecule.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been previously described [1–5]. 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 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 where checked by potentiometric titrations. The 2,5-dihydroxybenzoic acid (Fluka) was purified by crystallization from water–ether mixtures and its m.p. checked before use.

The 2,5-$(OH)_2PhCOONa$ solutions were prepared by adding an NaOH solution of known molarity to 2,5-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 2,5-dihydroxybenzoic acid in the various water–DMSO mixtures of X mole fraction can be represented by

$$[2,5\text{-}(HO)_2PhCOOH]_X \rightarrow [2,5\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \qquad (1)$$

The molar enthalpy, $\Delta \bar{H}_1$, of the ionization of 2,5-$(OH)_2PhCOOH$ was obtained by the experimental procedure described below.

(a) The molar enthalpy of reaction, $\Delta \bar{H}_2$, of 2,5-$(OH)_2COONa$, dissolved in the mixed solvent of X' mole fraction, with 0.99 M HCl was measured

$$[2,5\text{-}(OH)_2PhCOO^-]_{X'} + (Na^+)_{X'} + (H^+)_{aq} + (Cl^-)_{aq}$$
$$\rightarrow [2,5\text{-}(OH)_2PhCOOH]_X + (Na^+)_X + (Cl^-)_X \qquad (2)$$

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

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

(c) The molar enthalpy of process (1) can be obtained 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 relating to the molar transfer enthalpy of 2,5-$(OH)_2PhCOONa$ (at infinite dilution) from a solvent with mole fraction X' to a solvent with mole fraction X

$$[2,5\text{-}(OH)_2PhCOO^-]_{X'} + (Na^+)_{X'} \rightarrow [2,5\text{-}(OH)_2PhCOO^-]_X + (Na^+)_X \qquad (4)$$

For each water–DMSO mixture at X_{DMSO} mole fraction, the $\Delta \bar{H}_1$ values refer to the ionization of one mole of $[2,5\text{-}(OH)_2PhCOOH]_X$ dissolved at infinite dilution in 1000 g of mixed solvent, yielding one mole of $[2,5\text{-}(OH)_2PhCOO^-]_X$ ions and one mole of protons solvated in the same amount of solvent.

For a better understanding of the $\Delta\bar{H}_1$ values obtained in the different solvent mixtures, the solution enthalpies of crystalline $2,5\text{-}(OH)_2PhCOOH$ in the various solvent mixtures were measured

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

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

$$2,5\text{-}(OH)_2PhCOOH_{cry} \rightarrow [2,5\text{-}(OH)_2PhCOO^-]_X + (H^+)_X \qquad (6)$$

refer to an identical thermodynamic state.

In processes (2) and (5) concentrations ranging from 2×10^{-3} to 4×10^{-3} M were used. Therefore, the $\Delta\bar{H}$ values relating 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), respectively, obtained for $2,5\text{-}(OH)_2PhCOOH$.

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 those 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 the two ions H^+ and $[2,5\text{-}(OH)_2PhCOO^-]_X$, 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 $2,5\text{-}(OH)_2PhCOOH$ in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_1^0	ΔH_2^0	ΔH_3^0
0.0	0.39	7.01	7.40
0.1	0.59	6.98	7.57
0.2	0.67	5.53	6.20
0.3	0.71	3.06	3.77
0.4	0.75	0.98	1.73
0.5	0.97	−0.47	0.50
0.6	1.56	−1.35	0.21
0.7	2.27	−1.90	0.37
0.8	2.94	−2.40	0.54

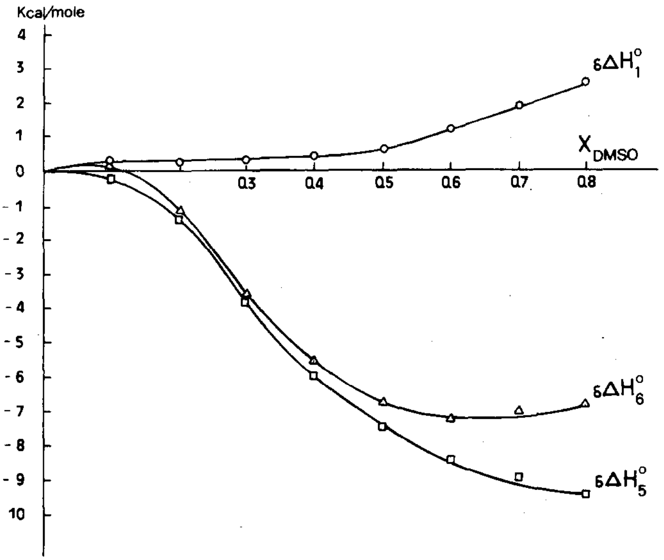

Fig. 1. Enthalpy for the transfer of the ionization and transfer enthalpies of the undissociated molecule and the ion of 2,5-dihydroxybenzoic acid.

DISCUSSION

The $\delta\Delta H_1^0$ term (Fig. 1) is not favourable for process (1), this being due to the greater solvation of the undissociated molecule with respect to the anion. Therefore, the second hydroxyl group in position 5 stabilizes the undissociated molecule to a greater degree than the anion, this being so in DMSO-rich solutions.

A calorimetric acidity scale could be useful for understanding the different effects of the hydroxyl groups at the different positions in the benzene ring. In this way a more complete explanation of the effect of the hydroxyl group at position 5 can also be obtained. For this purpose, the ionization

TABLE 2

Differences in the solvation enthalpies between the anion couples of 2,6-, 2,5-, 2,4- and 2,3-dihydroxybenzoic acids

X_{DMSO}	$\Delta H_{6(2,6)-(2,5)}$	$\Delta H_{6(2,5)-(2,4)}$	$\Delta H_{6(2,5)-(2,3)}$
0.1	−0.02	0	0.76
0.2	0.06	−0.18	0.33
0.3	−0.29	−0.45	−0.15
0.4	−0.17	−0.07	−0.65
0.5	−0.13	−0.28	−1.11
0.6	−0.40	−0.42	−1.18
0.7	−0.55	−0.1	−1.30
0.8	−0.69	−0.27	−1.51

TABLE 3

Differences in the solvation enthalpies between the undissociated molecules couples of 2,6-, 2,5-, 2,4- and 2,3-dihydroxybenzoic acids

X_{DMSO}	$\Delta H_{5(2,6)-(2,5)}$	$\Delta H_{5(2,5)-(2,4)}$	$\Delta H_{5(2,5)-(2,3)}$
0.1	0.28	−0.15	−0.22
0.2	0.51	0.32	−0.04
0.3	0.23	0.39	−0.35
0.4	0.36	0.45	−0.41
0.5	0.62	0.56	−0.52
0.6	0.88	0.73	−0.37
0.7	1.35	0.77	−0.14
0.8	1.78	0.68	−0.35

values of 2,6-$(OH)_2PhCOOH$, 2,4-$(OH)_2PhCOOH$ and 2,5-$(OH)_2PhCOOH$ are given in Table 2. The order based on the ionization enthalpy is 2,6-$(OH)_2PhCOOH$ > 2,5-$(OH)_2PhCOOH$ > 2,3-$(OH)_2PhCOOH$ > 2,4-$(OH)_2$-PhCOOH.

The 2,5-dihydroxy derivative is, as it can be shown, with the exception of 2,6-$(OH)_2PhCOOH$, the strongest acid. This can be explained taking into account the differences in solvation between the ions and the undissociated molecules of all the hydroxyl derivatives (Tables 2 and 3, Figs. 2–4).

A comparison of 2,5-$(OH)_2PhCOOH$ with 2,6-$(OH)_2PhCOOH$ (Fig. 2) shows that the solvations of the ions and undissociated molecules favour the greater ionization of 2,6-$(OH)_2PhCOOH$. It is also clear that the undissociated molecule solvations play an important role. The same behaviour is displayed by the 2,5- and 2,4-dihydroxy derivatives (Fig. 3). The 2,4-undissociated molecule is solvated to a greater degree by virtue of the second hydroxyl group in the *para* position [5], so these derivatives behave like many of the dihydroxy derivatives.

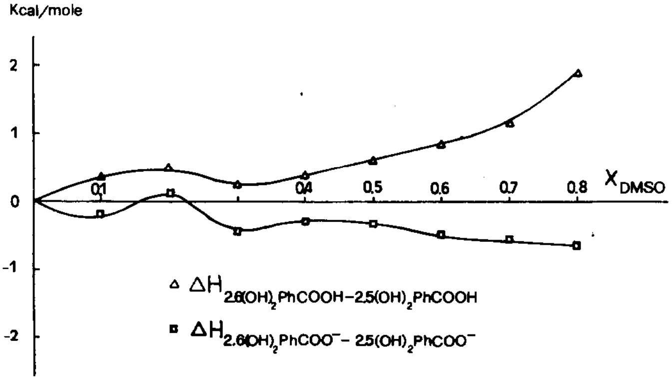

Fig. 2. Differences in solvation enthalpies between the undissociated molecule couples and the anion couples of 2,6- and 2,5-dihydroxybenzoic acids in various DMSO–water solutions.

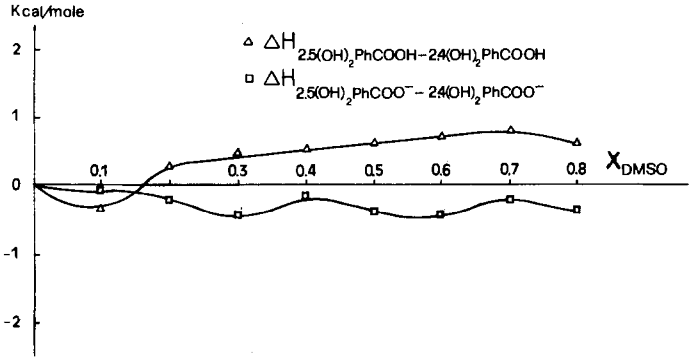

Fig. 3. Differences in solvation enthalpies between the undissociated molecule couple and the anion couples of 2,5- and 2,4-dihydroxybenzoic acids in various DMSO–water solutions.

This is not true when comparing the 2,5-$(OH)_2PhCOOH$ and 2,3-$(OH)_2PhCOOH$ compounds [Fig. 4]. The effect of the second hydroxyl group in position 5 is very different from that in position 3. Beyond $X = 0.3$ both the anion and the undissociated molecule of 2,5-$(OH)_2PhCOOH$ are more solvated than those of 2,3-$(OH)_2PhCOOH$, the major role being played, in this case, by the anions' relative solvation.

This fact can be ascribed to the stabilization and delocalization of the charge of the 2,3-anion caused by the hydroxyl groups in the relative *para* position. For this reason the 2,5-dihydroxy anion displays a greater solvation in DMSO-rich solutions where dipole–dipole interactions are prevalent.

It can therefore be concluded that the 2,6- (always) and 2,5- (sometimes) derivatives differ from the likely behaviour of the dihydroxy derivatives, because of the stabilization and delocalization of the charge on the anions. The reason for this is provided, for the former, by the hydrogen bonds in the *ortho* position [3] and for the latter by the two hydroxyl groups in the relative *para* position.

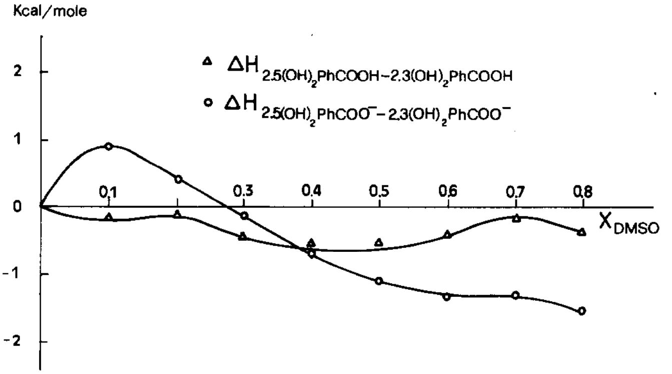

Fig. 4. Differences in solvation enthalpies between the undissociated molecule couples and the anion couples of 2,5- and 2,3-dihydroxybenzoic acids in various DMSO–water solutions.

REFERENCES

1 F. Rodante, G. Ceccaroni and M.G. Bonicelli, Thermochim. Acta, 42 (1980) 223.
2 F. Rodante, M.G. Bonicelli and G. Ceccaroni, Thermochim. Acta, 43 (1981) 199.
3 F. Rodante and G. Ceccaroni, Thermochim. Acta, 72 (1984) 335.
4 F. Rodante and G. Ceccaroni, Thermochim. Acta, 75 (1984) 115.
5 F. Rodante and G. Ceccaroni, Thermochim. Acta, 76 (1984) 139.
6 J.C. Synnot and J.N. Butler, J. Phys. Chem., 73 (1969) 1470.