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THERMODYNAMICS OF THE IONIZATION PROCESS FOR 3,5-DINITROBENZOIC ACID. THE ADDITIVE EFFECT OF A *META* SUBSTITUENT ON THE ACID STRENGTH

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ABSTRACT

The ionization and solution enthalpies of 3,5-dinitrobenzoic acid were measured calorimetrically at 25°C in water–DMSO mixtures ranging from 0.1 up to 0.8 mole fraction of DMSO.

The ΔG^0 values for the ionization process have been determined for these solutions by potentiometric measurements.

An attempt has also been made to compare the observed substituent constants to those predicted on the assumption of the additivity principle.

INTRODUCTION

The ionization processes of some monosubstituted phenols and benzoic acids in water–dimethylsulfoxide (DMSO) mixtures [1–5] and some linear free-energy relationships [6–10] for the same compounds have been the subject of an extended research in this laboratory.

In the present work the behaviour of 3,5-dinitrobenzoic acid has been examined in the same mixtures. An attempt has also been made to compare the observed substituent constants, $\Sigma\sigma$, to those predicted on the assumption of a strictly additive effect.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [1–5]. DMSO (Carlo Erba, RP grade) was purified according to the procedure of Synnot and Batler [11]. 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 0.1 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 3,5-dinitrobenzoic acid (K and K product) was purified by crystallization from water–alcohol mixtures; its melting point was checked before use. The $(NO_2)_2PhCOONa$ solutions were prepared by adding a NaOH solution of known molarity to 3,5-dinitrobenzoic 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 3,5-dinitrobenzoic acid, in the various water–DMSO mixtures of X mole fraction can be represented by

$$[3{,}5\text{-}(NO_2)_2PhCOOH]_X \rightarrow [3{,}5\text{-}(NO_2)_2PhCOO^-]_X + (H^+)_X \tag{1}$$

The molar enthalpy, $\Delta \overline{H}_1$, of ionization of 3,5-$(NO_2)_2PhCOOH$ was obtained [1–5] by the experimental procedure described.

(a) The molar enthalpy of reaction, $\Delta \overline{H}_2$, of 3,5-$(NO_2)_2PhCOONa$, dissolved in the mixed solvent of X' mole fraction, with 0.99 M HCl was measured.

$$\begin{aligned}&[3{,}5\text{-}(NO_2)_2PhCOO^-]_{X'} + (Na^+)_{X'} + (H^+)_{aq} + (Cl^-)_{aq} \rightarrow \\ &\quad [3{,}5\text{-}(NO_2)_2PhCOOH]_X + (Na^+)_X + (Cl^-)_X\end{aligned} \tag{2}$$

(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 enthapy of 3,5-$(NO_2)_2PhCOONa$ (at infinite dilution) from solvent X' to solvent X.

$$[3{,}5\text{-}(NO_2)_2PhCOO^-]_{X'} + (Na^+)_{X'} \rightarrow [3{,}5\text{-}(NO_2)_2PhCOO^-]_X + (Na^+)_X \tag{4}$$

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 3,5-$(NO_2)_2PhCOOH$ dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of protons and one mole of 3,5-$(NO_2)_2PhCOO^-$ ions solvated in the same amount of the solvent.

For a better understanding of the $\Delta \overline{H}_1$ values obtained in the different solvent mixtures, the solution enthalpies of crystalline 3,5-$(NO_2)_2PhCOOH$ in the various solvent mixtures were measured.

$$3{,}5\text{-}(NO_2)_2PhCOOH_{cr.} \rightarrow [3{,}5\text{-}(NO_2)_2PhCOOH]_X \tag{5}$$

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

$$3{,}5\text{-}(NO_2)_2PhCOOH_{cr.} \rightarrow [3{,}5\text{-}(NO_2)_2PhCOO^-]_X + (H^+)_X \qquad (6)$$

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 $\Delta \bar{H}_1$ values related to these processes were assumed to be equal to the ΔH^0 values [1–5].

The ionization constants of the 3,5-dinitrobenzoic acid at 25°C have been obtained from e.m.f. measurements of the cell

$$\text{Ag, AgCl} \mid 3{,}5\text{-}(NO_2)_2PhCOOH_{(m_1)} \,\vdots\, 3{,}5\text{-}(NO_2)_2PhCOONa_{(m_2)}$$

$$\vdots\, NaCl_{(m_3)} \mid \begin{smallmatrix}\text{Glass}\\ \text{electrode}\end{smallmatrix}$$

Potential measurements were made with an Orion 801 digital pH meter; the glass electrode was an Orion 91-01-00. Details of the potentiometric measurements have been described previously [12,13]. The pK_a values obtained from potentiometric measurements were used to calculate the ΔG^0 values at different temperatures. These values may be related to T according to Ives and Pryor [14], by the equation

$$\Delta G^0 = a + bT + cT^2$$

where the coefficients a, b and c were obtained by the least-squares method. $T\Delta S^0$ values were calculated using the ΔG^0 and ΔH^0 values. The initial standard state to which ΔG^0 values of ionization refer is defined to be an ideal 1 m solution of $3{,}5\text{-}(NO_2)_2PhCOOH$ behaving as an infinitely dilute solution.

RESULTS

Table 1 shows the ΔG^0, ΔH^0 and $T\Delta S^0$ values of process (1) obtained for the dinitro-substituted benzoic acid. Table 2 shows the enthalpy values of processes (5) and (6).

Due to the very limited solubility in water of the dinitrobenzoic acid, it is impossible to obtain, in aqueous solutions, reliable results for the enthalpic effects. So, it is convenient to express, for comparison purposes, the ionization enthalpy as the difference between the values obtained in the mixed solvent at X mole fraction and in the solution at $X_{DMSO} = 0.1$.

$$\delta \Delta H_1 = (\Delta H_1^0)_X - (\Delta H_1^0)_{X=0.1}$$

In a similar way, the values of $\delta \Delta G_1^0$ and $T\delta \Delta S_1^0$ can be defined and calculated. These three 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 $3{,}5\text{-}(NO_2)_2PhCOO^-$,

TABLE 1

Free energy, enthalpy and entropy values of the ionization for 3,5-dinitrobenzoic acid in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔG^0 (kcal mole^{-1})	ΔH^0 (kcal mole^{-1})	$T\Delta S^0$ (kcal mole^{-1})
0.1	4.13	0.90	−3.23
0.2	4.60	1.99	−2.61
0.3	5.35	3.63	−1.72
0.4	6.04	5.51	−0.53
0.5	6.37	7.33	0.96
0.6	7.27	8.77	1.50
0.7	7.67	9.53	1.86
0.8	8.27	9.30	1.03

TABLE 2

Enthalpy values of processes (5) and (6) for 3,5-dinitrobenzoic acid, in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_5^0 (kcal mole^{-1})	ΔH_6^0 (kcal mole^{-1})
0.1	6.46	7.36
0.2	6.85	8.84
0.3	6.39	10.02
0.4	5.38	10.89
0.5	4.12	11.45
0.6	2.93	11.70
0.7	2.11	11.64
0.8	1.96	12.26

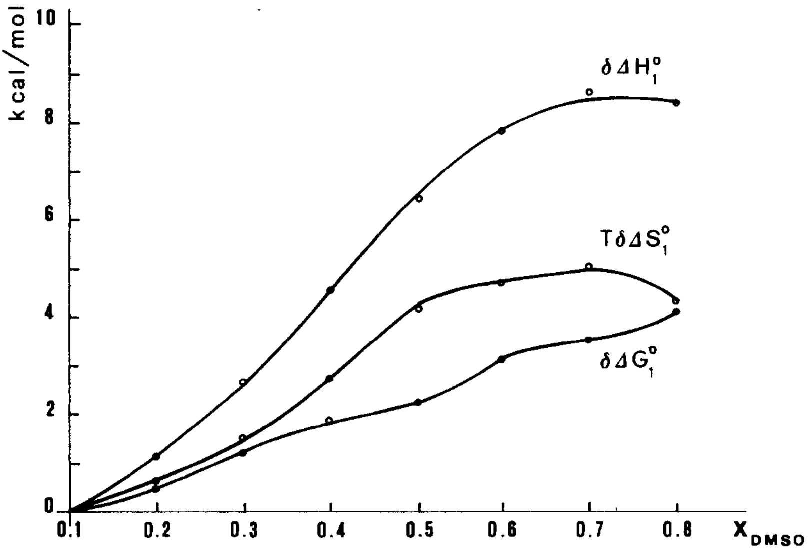

Fig. 1. Thermodynamic quantities for the transfer of the ionization of 3,5-dinitrobenzoic acid from $X_{\mathrm{DMSO}} = 0.1$ to DMSO–water mixtures as a function of the mole fraction at 25°C.

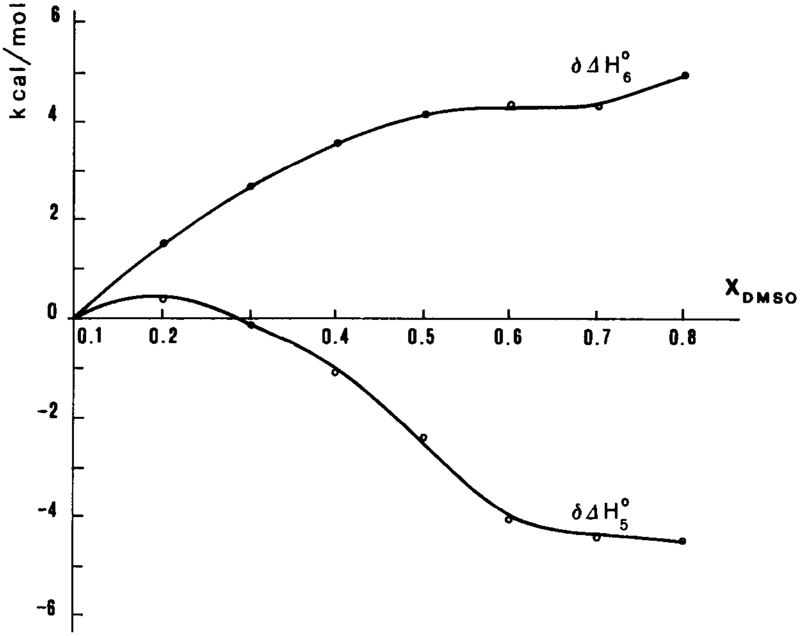

Fig. 2. Transfer enthalpies of the undissociated molecule and of the two ions H^+ and 3,5-NO_2PhCOO^- from $X_{DMSO} = 0.1$ to DMSO–water mixtures as a function of the mole fractions at 25°C.

respectively, from solution at $X_{DMSO} = 0.1$ to the mixed solvent.

All these data are plotted vs. X_{DMSO} in Figs. 1 and 2.

DISCUSSION

Figure 1 shows that the enthalpic term is the driving force of the ionization process.

It can also be inferred (Fig. 2) that from the enthalpic point of view, the desolvation of the 3,5-dinitrobenzoic anion plays a more important role than the solvation of the undissociated molecule for $X_{DMSO} \leqslant 0.5$. Beyond this mole fraction the values of the solvation and desolvation become quite similar.

It is also clear that the different transfer solvation enthalpies of the anions play a major role in the differentiation of the acidity between the 3,5-dinitro and 3-nitrobenzoic acids. This difference, $\Delta H^0_{(3,5\text{-}(NO_2)_2PhCOO^-)_x-(3\text{-}NO_2PhCOO^-)_x}$, was calculated as shown previously [1–5]. In this case, however, the reference state is the DMSO–water solution with $X_{DMSO} = 0.1$. In the same way the difference in solvation enthalpy between the undissociated molecules, $\Delta H^0_{(3,5\text{-}(NO_2)_2PhCOOH)_x-(3\text{-}NO_2PhCOOH)_x}$, was calculated. Figure 3 shows how the dinitrobenzoic anion is solvated to a larger extent than the nitrobenzoic anion, with a sharp maximum at $\Delta X_{\mathrm{DMSO}} = 0.4$–$0.6$. This fact can be almost exclusively ascribed to the inductive effect (I^-) of the nitro group. Indeed, this attracts the negative charge of the monosubstituted anion more weakly than the disubstituted anion, thus allowing stronger anion–water interactions. For this reason, as the H_2O content ($X_{\mathrm{DMSO}} > 0.1$) decreases, the 3-nitrobenzoic anion becomes more desolvated than the 3,5-dinitrobenzoic anion. This trend goes on up to $\Delta X_{\mathrm{DMSO}} = 0.4$–$0.5$, where the desolvation of the 3-nitrobenzoic anion relative to the 3,5-dinitrobenzoic anion shows a sharp maximum. With a further increase in the DMSO content, the solvation of the two ions becomes similar.

The principle of the additivity has been examined for the free energy of ionization of disubstituted benzoic acids in aqueous solutions and in other solvent systems [15–17]. In the present work the equation $-\delta\Delta G^0 = \rho\Sigma\sigma$ [18] has been used to calculate the substituent constants, $\Sigma\sigma$, for the 3,5-$(NO_2)_2PhCOOH$ in the whole mole fraction range. Values of $\delta\Delta G^0 = \Delta G^0_{3,5\text{-}(NO_2)_2PhCOOH} - \Delta G^0_{PhCOOH}$ were calculated by using the free energy values of this work as well as those calculated previously [4].

The values of the reaction constants, ρ, for the monobenzoic derivatives have been reported in previous works [6,7,10]. If the additivity principle is assumed, the $\Sigma\sigma$ values will be equal to $2\sigma_m$ values at the various mole

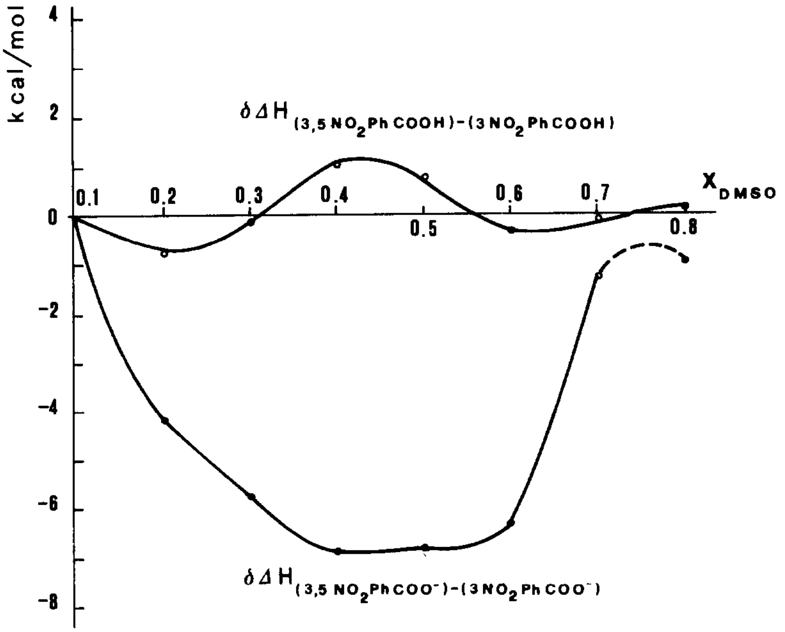

Fig. 3. Differences in the solvation enthalpy between the anions and between the undissociated molecules of 3,5-dinitrobenzoic acid and 3-nitrobenzoic acid, in various DMSO–water mixtures.

TABLE 3

$\Sigma\sigma$ values observed and predicted on the assumption of the additivity principle

X_{DMSO}	$\Sigma\sigma_{\text{observed}}$	$\Sigma\sigma_{\text{predicted}}$
0.1	1.35	1.47
0.2	1.36	1.55
0.3	1.25	1.51
0.4	1.29	1.61
0.5	1.47	1.64
0.6	1.37	1.63
0.7	1.45	1.60
0.8	1.35	1.49

fractions [7]. The observed and predicted $2\sigma_m$ values are reported in Table 3. It can be observed that for $X_{\text{DMSO}} < 0.2$ and $X_{\text{DMSO}} > 0.6$ there is agreement within 10%. In the range of mole fraction $\Delta X_{\text{DMSO}} = 0.2$–$0.6$, the additivity principle is seriously violated. This is worth a more detailed consideration.

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