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THE EFFECT OF THE MEDIUM ON THE DISSOCIATION OF THE *para*-CARBOXY ANILINE ION

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ABSTRACT

A calorimetric study of the dissociation of the *p*-carboxy aniline ion in water–DMSO mixtures, ranging from pure water up to 0.8 DMSO mole fraction, is presented. This compound is found to be a weaker base than the *m*-carboxy aniline in all solutions containing DMSO. Different behaviour has been observed in pure water, where the unstable zwitterion form greatly influences the aniline strength.

INTRODUCTION

A thermodynamic study of the dissociation of *meta*-carboxy aniline ion has been done [1] in water–dimethylsulfoxide (DMSO) mixtures. In water-rich solutions this compound displays a tautomeric zwitterion equilibrium $COOHPhNH_2 \rightleftarrows COO^-PhNH_3^+$ while in DMSO-rich solutions only the $COOHPhNH_2$ form is present. This suggests that the tautomeric effect influences the basicity of the compound only in water-rich solutions. In the other solutions the behaviour of the aniline is dominated by the σ-electron withdrawing effect of the carboxyl group which, in the *meta* position, stabilizes the benzene ring. The dissociation of the *para-*, *ortho-* and *meta*-hydroxy aniline ions have also been studied [2–4] in the same solutions and a sequence of basicity has been found. It is also noteworthy that for *meta*-hydroxy aniline an electrophilic attack by the proton on the benzene ring is likely to occur in the DMSO-rich solutions. Then in these solutions the *meta*-hydroxy aniline could be ring-protonated as happens in the gaseous phase [5], while for the *ortho-* and *para*-hydroxy isomers this is not true.

However, it could be inferred that the hydroxy and, generally, the carboxy anilines display "anomalous" behaviour because of the competition between basic and acidic functional groups. It seemed interesting to study the *para*-carboxy aniline in order to see whether it too displays a tautomeric effect, and how the carboxy and amino groups interact.

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EXPERIMENTAL

The calorimetric apparatus has been previously [6,7] described. DMSO (Carlo Erba RP grade) was purified according to the procedure [8] of Synnot and Butler, DMSO–water mixtures were prepared by weight from purified DMSO and CO_2-free, twice-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.0 to 0.8. An aqueous solution of 0.99 M HCl was prepared from a standard solution; its concentration was checked by potentiometric titration. The *p*-carboxy aniline was recrystallized from water–alcohol mixtures; its m.p. was checked before use. The compound was handled in a dry-box filled with dry nitrogen. The compound was also weighed in the dry-box.

The ionization process of the *p*-carboxy aniline ion ($COOHPhNH_3^+$) in the various water–DMSO mixtures at X mole fraction can be represented as

$$(COOHPhNH_3^+)_X \rightarrow (H^+)_X + (COOHPhNH_2)_X \qquad (1)$$

The molar enthalpy of ionization, $\Delta \overline{H}_1$, of $COOHPhNH_3^+$ was obtained [6,7] by measuring the molar enthalpy of solution, $\Delta \overline{H}_2$, of crystalline *p*-carboxy aniline in the mixed solvent of X mole fraction

$$COOHPhNH_{2(cry)} \rightarrow (COOHPhNH_2)_X \qquad (2)$$

and the molar enthalpy of neutralization, $\Delta \overline{H}_3$, of the same compound in the same mixture containing an excess of HCl

$$COOHPhNH_{2(cry)} + (H^+)_X \rightarrow (COOHPhNH_3^+)_X \qquad (3)$$

The molar enthalpy, $\Delta \overline{H}_1$, of process (1) can be obtained [6,7] by subtracting the two values $\Delta \overline{H}_2$ and $\Delta \overline{H}_3$.

In processes (2) and (3), concentrations ranging from 2×10^{-3} m to 4×10^{-3} m were used. Therefore, the $\Delta \overline{H}_1$ values can be considered at infinite dilution [6,7].

For each water–DMSO mixture at X mole fraction, these values refer to the ionization process of one mole of $COOHPhNH_3^+$, dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of $COOHPhNH_2$ molecules and one mole of protons solvated in the same amount of solvent.

RESULTS

Table 1 shows the ΔH_1^0, ΔH_2^0 and ΔH_3^0 values of processes (1), (2) and (3) obtained for the *p*-carboxy aniline ion.

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

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

TABLE 1

Enthalpy values of processes (1), (2) and (3) for the *para*-carboxy aniline ion and *para*-carboxy aniline, in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO} (kcal mol^{-1})	ΔH_1^0	ΔH_2^0	ΔH_3^0
0.0	1.68	6.49	4.81
0.1	0.75	6.76	6.01
0.2	0.19	5.48	5.29
0.3	0.04	3.33	3.29
0.4	0.06	1.49	1.43
0.5	0.08	0.10	0.02
0.6	0.1	−0.87	−0.97
0.7	0.12	−1.48	−1.60
0.8	0.15	−2.00	−2.15

These values are relative to the transfer of the ionization process, while the $\delta\Delta H_2^0$ and $\delta\Delta H_3^0$ values represent the transfer enthalpy of the substituted aniline and the substituted aniline ion, respectively, from pure water to mixed solvent. All these data are plotted against X_{DMSO} in Fig. 1.

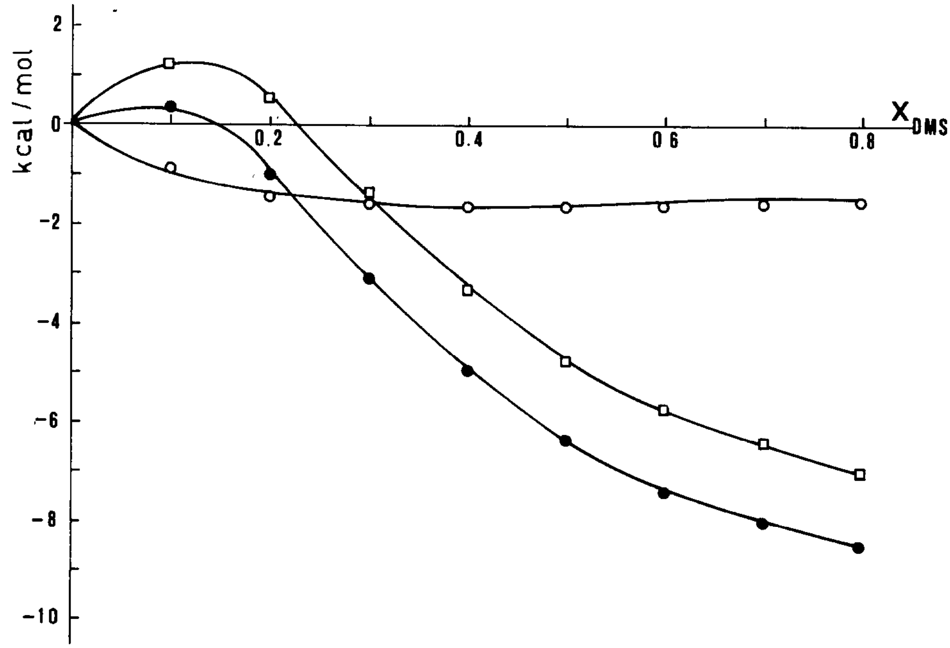
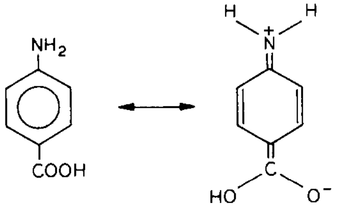


Fig. 1. (○), Enthalpy for the transfer of ionization of the *para*-carboxy aniline ion, $\delta\Delta H_1$; (●), transfer enthalpy of the *para*-carboxy aniline ion, $\delta\Delta H_2$; and (□), transfer enthalpy of *para*-carboxy aniline, $\delta\Delta H_3$, from pure water to DMSO–water solutions, shown as a function of mole fraction.

DISCUSSION

The $\delta\Delta H_1$ term, as shown in Fig. 1, is favourable to process (1) in the whole mole fraction range. This can be related to the desolvation of the aniline ion with respect to the undissociated aniline molecule. Thus, the dissociation process (1) is influenced more by the unfavourable interaction between the NH_3^+ group and the COOH substituent than by the stabilization represented by the resonance structure (I)



(I)

By comparing the *para-* and *meta-*carboxy anilines by means of the difference in the enthalpy of deprotonation $(\Delta H_1^0)_{p\text{-COOHPhNH}_3^+} - (\Delta H_1^0)_{m\text{-COOHPhNH}_3^+}$ (Fig. 2) it can be inferred that the *para* derivative is a weaker effective base in the whole mole fraction range, with the exception of 100% water, where the two bases differ by 0.08 kcal only. This can be explained by taking into account the difference in solvation enthalpy between the ions $\Delta H^0_{(p\text{-COOHPhNH}_3^+)-(m\text{-COOHPhNH}_3^+)}$ and the undissociated molecules $\Delta H^0_{(p\text{-COOHPhNH}_2)-(m\text{-COOHPhNH}_2)}$ (Fig. 2).

The greater solvation of the *p*-carboxy aniline is clearly the key effect for the relative weakness of the *para* aniline. However, in pure water there could be a very unstable zwitterion form tending to level the strength of the

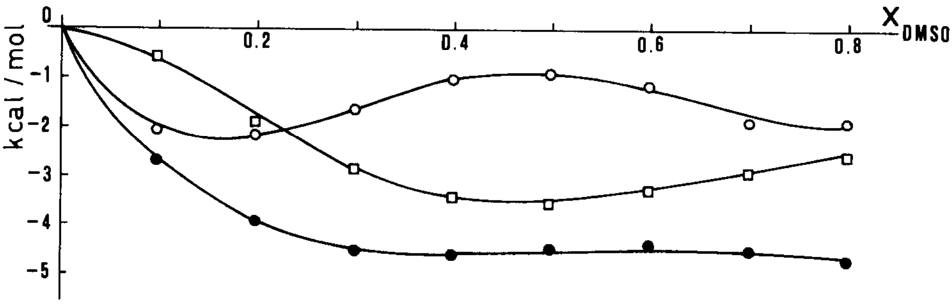


Fig. 2. (○), Difference in the enthalpy of deprotonation of *para-* and *meta-*carboxy aniline ions, $\Delta H_{1(p\text{-COOHPhNH}_3^+)} - \Delta H_{1(m\text{-COOHPhNH}_3^+)}$; (●), difference in the solvation enthalpy between the carboxy aniline couples, $\Delta H_{(p\text{-COOHPhNH}_2)-(m\text{-COOHPhNH}_2)}$; and (□), difference in the solvation enthalpy between the carboxy aniline ion couples, $\Delta H_{(p\text{-COOHPhNH}_3^+)-(m\text{-COOHPhNH}_3^+)}$, in various DMSO–water structures.

anilines. This difference sharply increases as far as $X_{\mathrm{DMSO}} = 0.1$. Beyond this mole fraction the difference becomes quite constant. It can be concluded that in DMSO–water solutions the zwitterion form of the *para* compound decreases more quickly than that of the *meta* form.

Finally, a comparison with the *para*-hydroxy·derivative was made by means of the difference in enthalpy of deprotonation $\Delta H_{1(\text{p-COOHPhNH}_3^+)} - \Delta H_{1(p\text{-OHPhNH}_3^+)}$ and in solvation enthalpy between the ions $\Delta H^0_{(p\text{-COOHPhNH}_3^+)-(p\text{-OHPhNH}_3^+)}$ and the undissociated molecules $\Delta H^0_{(p\text{-COOHPhNH}_2)-(p\text{-OHPhNH}_2)}$ (Fig. 3). The carboxy compound is a very weak aniline with respect to the hydroxy compound.

As previously shown [4] the undissociated molecule of *para*-hydroxy aniline is destabilized by the two π donor groups in the *para* position while for the *para*-carboxy aniline the contrary is true.

So the order of transfer, in the whole mole fraction, is COOH $\mathrm{PhNH_2}$ > $\mathrm{OHPhNH_2}$. Except in the case of water-rich solutions, the p-$\mathrm{COOHNH_3^+}$ anion too is more solvated than the p-$\mathrm{OHPhNH_3^+}$ one.

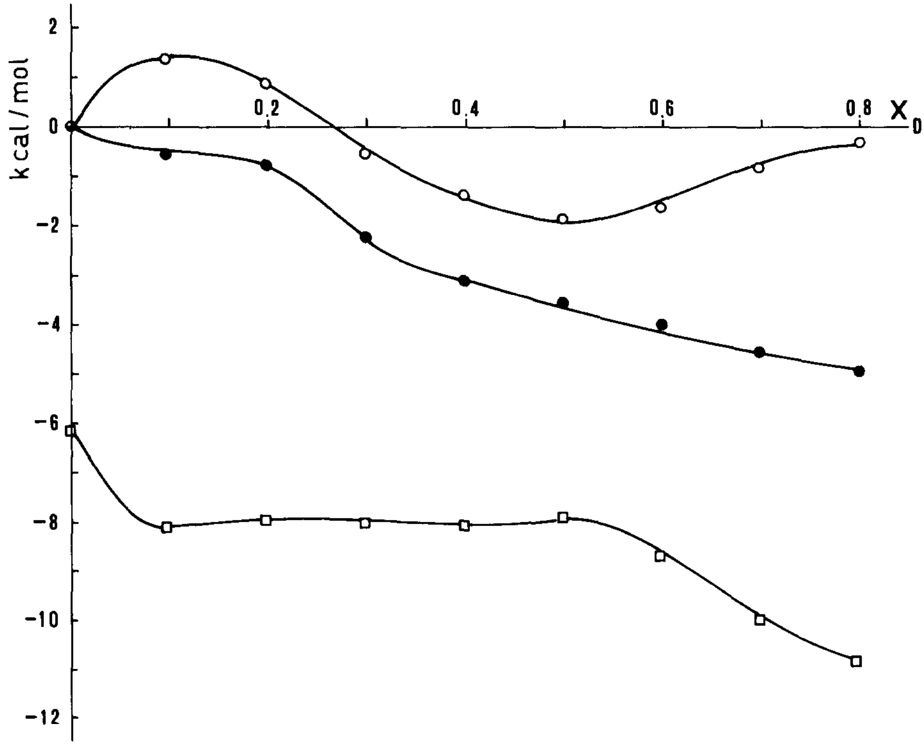


Fig. 3. (□), Difference in the enthalpy of deprotonation of *para*-hydroxy and carboxy aniline ions, $\Delta H_{1(p\text{-COOHPhNH}_3^+)} - \Delta H_{1(p\text{-OHPhNH}_3^+)}$; (○), difference in the solvation enthalpy between the hydroxy/carboxy aniline ion couples, $\Delta H_{(p\text{-COOHPhNH}_3^+)-(p\text{-OHPhNH}_3^+)}$; and (●), difference in the solvation enthalpy between the aniline couples, $\Delta H_{(p\text{-COOHPhNH}_2)-(p\text{-OHPhNH}_2)}$, in various DMSO–water mixtures.

Thus, the solvation of the *para*- and *meta*-carboxy/hydroxy anions and undissociated molecule couples is in opposite directions [1].

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