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THE EFFECT OF THE MEDIUM ON THE DISSOCIATION OF THE *ortho*-CARBOXY ANILINE ION. PRIMARY STERIC EFFECT AS A FACTOR IN THE IONIZATION PROCESS

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ABSTRACT

A calorimetric study of the dissociation of the *ortho*-carboxy aniline ion in water–DMSO mixtures, ranging from pure water up to 0.8 DMSO mole fraction is presented.

The primary steric effect is the key factor in the ionization process of the anilinium ion and seems to oppose the formation of the zwitterion in pure water.

INTRODUCTION

A thermodynamic study of the dissociation of *meta-*, *para-* and *ortho*-hydroxy and of *meta-* and *para*-carboxy aniline ions in water–dimethylsulfoxide (DMSO) solutions as a function of the mole fraction, has been performed in our laboratory [1–5]. This study has given further insight into the solvent effect on the acids and the conjugated bases.

The carboxy anilines [4,5] display an "anomalous" behavior because of the competition between basic and acid functional groups. Indeed a tautomeric effect, mostly in water-rich solutions, greatly influences the anilines strength and in pure water tends to equalize it. Furthermore, the carboxy compounds are very weak anilines with respect to the hydroxy compounds in the whole mole fraction range. This can be related to both the effects displayed by OH (σ acceptor and π donor) and COOH (σ and π acceptor) groups on $-NH_2$ in the *meta-* and *para*-derivatives.

As previously shown [3], the undissociated molecule of *para*-hydroxy aniline is destabilized by the two π donor groups in *para* position, while for the *para*-carboxy aniline the contrary is true. Thus the order of solvation, in the whole mole fraction, is $COOHPhNH_2 > OHPhNH_2$, with the exception of the water-rich solutions, the *p*-$COOHPhNH_3^+$ anion is also more solvated than the *p*-$OHPhNH_3^+$ anion. For the *meta* derivatives the order of solvation is $OHPhNH_2 > COOHPhNH_2$, because the interaction between the first group NH_2 and the second group COOH is dominated by the σ electron-withdrawing effect of the latter, which destabilizes the benzene ring. The contrary is true for the *meta*-hydroxy aniline; the π donor effect of the OH group stabilizes the benzene ring. Thus the greater solvation of the *para*-carboxy aniline ion and of the *meta*-hydroxy aniline are clearly the key effects for the relative weakness of the carboxy anilines.

It is also noteworthy that all these anilines are *N*-protonated with the exception of the *meta*-hydroxy derivative for which it may be supposed that an electrophilic attack of the proton occurs on the benzene ring.

Finally, for the *ortho*-hydroxy compound the hydroxyl group in the *ortho* position would conflict with the steric requirements of the NH_3^+ group and the resulting steric effect would partially oppose the formation of the anilinium ion and decrease the strength of the base.

In order to give a more complete picture of this class of anilines, the dissociation of the *ortho*-carboxy aniline ion has been examined. It seemed interesting to ascertain if this compound also displays a tautomeric effect and a primary steric effect as a factor in the ionization process.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been previously [1–5] described. DMSO (Carlo Erba RP grade) was purified according to the procedure [6] of Synnot and Butler and DMSO–water solutions 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 *ortho*-carboxy aniline was recrystallized from water–alcohol mixtures; its m.p. was checked before use. The compound was handled in a dry-box containing dry nitrogen. The weighing of the compound was also performed in the dry-box.

The ionization process of *ortho*-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 [1–5] by measuring the molar enthalpy of solution, $\Delta\overline{H}_2$, of crystalline carboxy aniline in the mixed solvent of *X* mole fraction

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

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

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

The molar enthalpy, $\Delta\overline{H}_1$, of process (1) can be obtained [1–5] 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} to 4×10^{-3} m were used. Therefore, the $\Delta\overline{H}_1$ values can be considered to be at infinite dilution [1–5].

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 *ortho*-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

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

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.

TABLE 1

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

X_{DMSO}	ΔH_1^0	ΔH_2^0	ΔH_3^0
0.0	0.49	5.40	4.91
0.1	0.58	7.00	6.42
0.2	0.40	6.72	6.32
0.3	0.11	4.89	4.78
0.4	0.02	3.08	3.06
0.5	0.09	1.89	1.80
0.6	0.11	1.02	0.91
0.7	0.04	0.36	0.32
0.8	0.01	0.03	0.02

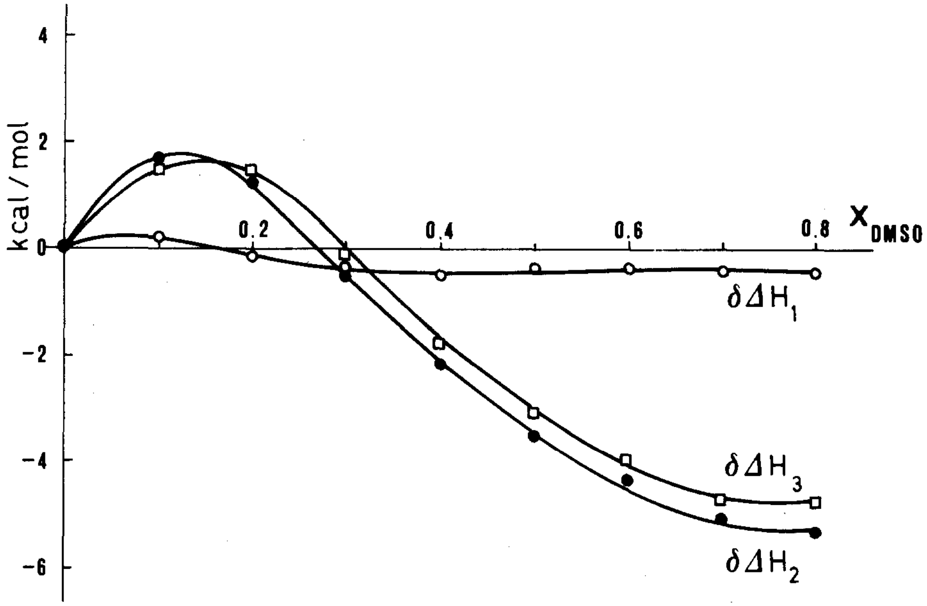


Fig. 1. Enthalpy for the transfer of the ionization of the *ortho*-carboxy aniline ion, $\delta\Delta H_1$ (○——○). Transfer enthalpies of the *ortho*-carboxy aniline ion, $\delta\Delta H_3$ (□——□), and *ortho*-carboxy aniline, $\delta\Delta H_2$ (●——●), from pure water to DMSO–water solutions as a function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

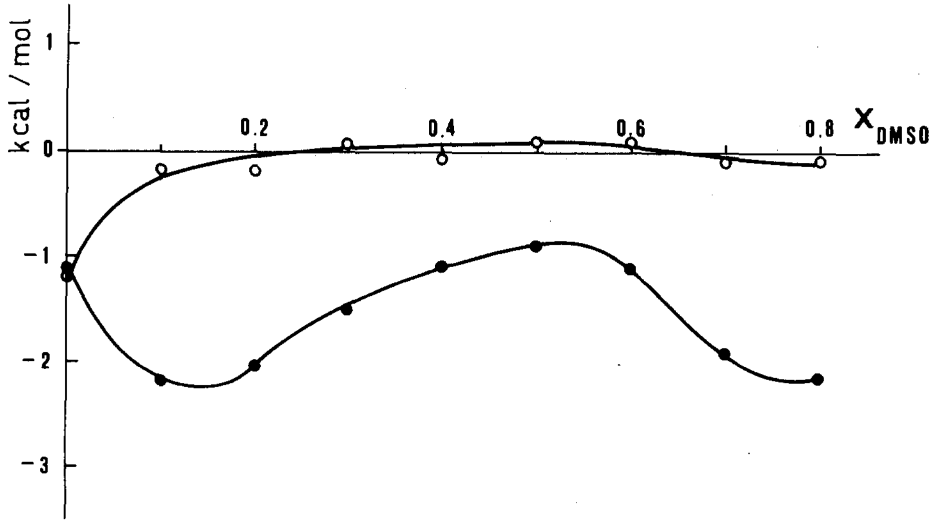
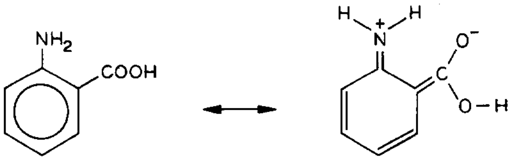


Fig. 2. Differences in the enthalpy of deprotonation of *ortho*-, *meta*- and *para*-carboxy aniline ions in various DMSO–water solutions, ○, $\Delta H_{1(o\text{-COOHPhNH}_3^+)} - \Delta H_{1(p\text{-COOHPhNH}_3^+)}$; ●, $\Delta H_{1(o\text{-COOHPhNH}_3^+)} - \Delta H_{1(m\text{-COOHPhNH}_3^+)}$.

DISCUSSION

The ΔH_1^0 term, as shown in Fig. 1, is favourable to process (1) apart from the range $0 \leqslant X_{\mathrm{DMSO}} \leqslant 0.1$.

These values are very small because both the aniline ion and the undissociated molecule display almost the same solvation. The reason for this could be found in the prevalence of the primary steric effect, both on the unfavorable interaction between the NH_3^+ group and the COOH substituent and on the stabilization represented by the resonance structure (I)



(I)

By comparing the *ortho* with the *para* and *meta* derivatives by means of the differences in the enthalpy of deprotonation $\Delta H^0_{1(o\text{-COOHPhNH}_3^+)} - \Delta H^0_{1(p\text{-COOHPhNH}_3^+)}$ and $\Delta H^0_{1(o\text{-COOHPhNH}_3^+)} - \Delta H^0_{1(m\text{-COOHPhNH}_3^+)}$ (Fig. 1), it can be inferred that the relative base effectiveness is in the sequence $m > o \equiv p$, with the exception of pure water where the sequence is $p \equiv m > o$.

This can be explained by taking into account the difference in solvation enthalpy between the ions $\Delta H^0_{(o\text{-COOHPhNH}_3^+)-(p\text{-COOHPhNH}_3^+)}$ and undissociated molecules $\Delta H^0_{(o\text{-COOHPhNH}_2)-(p\text{-COOHPhNH}_2)}$ (Fig. 3). It is clear that the greater solvation of ion and undissociated molecule of the *para* derivative are the key effects for the relative closeness of the *ortho* and *para* deprotonation enthalpies. However, in pure water one may gather that the hydration of the carboxyl group appears to enhance the primary steric effect accompanying the addition of the proton to the nitrogen atom. As a consequence, a transformation of the atom from its trivalent configuration in the free base to the bulkier tetrahedral configuration in the anilinium ion occurs. Therefore the carboxyl group in the *ortho* position decreases the strength of the

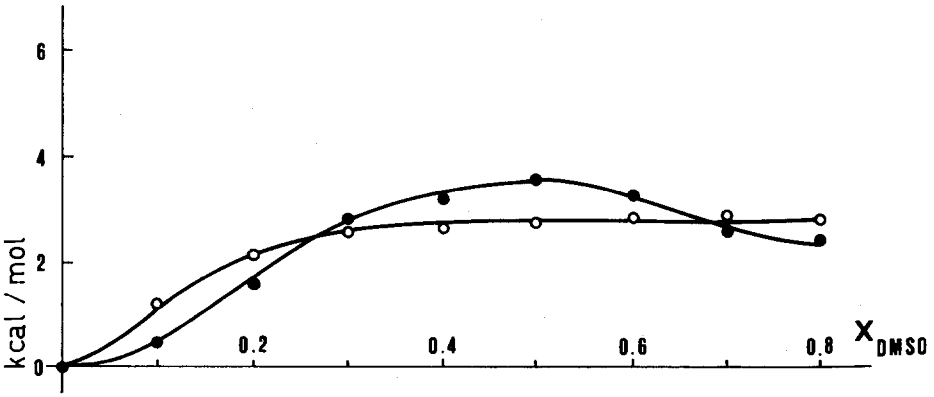


Fig. 3. Differences in the solvation enthalpies between the carboxy aniline ion couple and the carboxy aniline couple in various DMSO–water mixtures. ○, $\Delta H_{(o\text{-COOHPhNH}_2)-(p\text{-COOHPhNH}_2)}$; ●, $\Delta H_{(o\text{-COOHPhNH}_3^+)-(p\text{-COOHPhNH}_3^+)}$.

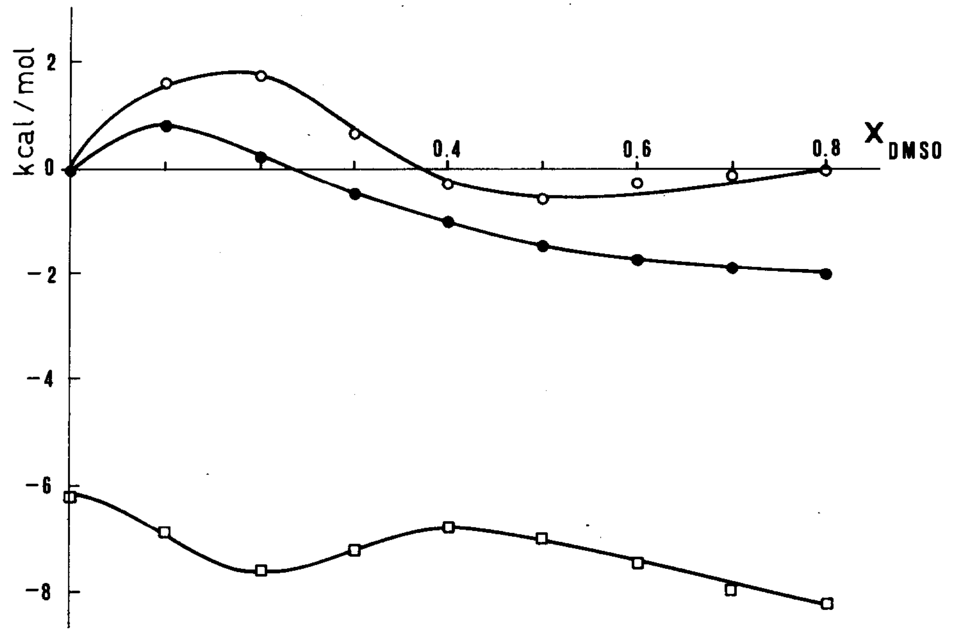


Fig. 4. Difference in the enthalpy of deprotonation of *ortho*-carboxy and -hydroxy aniline ion. Differences in the solvation enthalpies between the carboxy/hydroxy aniline ion couples and the carboxy/hydroxy aniline couples in various DMSO–water solutions. ○, $\Delta H_{(o\text{-COOHPhNH}_3^+)-(o\text{-OHPhNH}_3^+)}$; ●, $\Delta H_{(o\text{-COOHPhNH}_2)-(o\text{-OHPhNH}_2)}$; □, $\Delta H_{1(o\text{-COOHPhNH}_3^+)} - \Delta H_{1(o\text{-OHPhNH}_3^+)}$.

ortho with respect to the *meta* and *para* compounds. This effect, which also opposes the formation of the zwitterion in pure water, seems to be reduced in DMSO-rich solutions because of the diminished solvation of the carboxyl group.

Finally a comparison with the *ortho*-hydroxy derivative was made by means of the differences in enthalpy of deprotonation $\Delta H^0_{1(o\text{-COOHPhNH}_3^+)} - \Delta H^0_{1(o\text{-OHPhNH}_3^+)}$ and in solvation enthalpy between the ions $\Delta H^0_{(o\text{-COOHPhNH}_3^+)-(o\text{-OHPhNH}_3^+)}$ and the undissociated molecules $\Delta H^0_{(o\text{-COOHPhNH}_2)-(o\text{-OHPhNH}_2)}$ (Fig. 4). The carboxy compound is a very weak aniline with respect to the hydroxy compound. This means that the primary steric effect clearly prevails in the carboxy derivative. This is confirmed by the weaker solvation of the carboxy aniline and mostly of the carboxy aniline ion in the water-rich solutions.

In DMSO-rich solutions, where the primary steric effect is attenuated, the undissociated molecule of the *ortho*-carboxy aniline is stabilized by the π-acceptor and donor groups in the *ortho* position, while for the hydroxy derivative (two π-donors) the contrary is true.

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