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MEDIUM EFFECT ON THE DISSOCIATION OF THE *meta*-HYDROXYANILINE ION

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ABSTRACT

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

The solution and neutralization heats of *m*-hydroxyaniline have also been obtained.

On the basis of these measurements, an electrophilic attack of the proton on the benzene ring could be hypothesized.

INTRODUCTION

A thermodynamic study of the dissociation of both the *para*- and *ortho*-hydroxyaniline ions in water–dimethylsulfoxide (DMSO) mixtures was recently performed in our laboratory [1,2]. *Para*-hydroxyaniline is a more effective base in the whole mole fraction range. This was mostly ascribed to an increasing primary steric effect accompanying the addition of the proton to the nitrogen atom of the *ortho* compound. Therefore, the hydroxyl group in the *ortho* position would partially hinder the formation of the aniline ion and decrease the strength of the base. This effect, together with the σ-electron-withdrawing inductive effect and the steric inhibition of resonance, can be responsible for the reduced basicity of the *ortho* compound.

As shown previously [3], in the gaseous phase, *para*- and *ortho*-hydroxyanilines are *N*-protonated while *meta*-hydroxyaniline is ring protonated.

In aqueous solutions, all three anilines [3] are *N*-protonated since strong hydrogen bonds are formed between the water molecules and the substituted aniline ion. The interaction of water with the delocalized charge of the ring protonated ion should be very weak [1].

The dissociation study of the *meta*-hydroxyaniline ion in various DMSO–water mixtures, should determine whether or not the *N*-protonation remains in the DMSO-rich solutions. Indeed, DMSO is an excellent hydrogen bond acceptor but a very weak hydrogen bond donor. It also shows a greater dipole ($D = 3.96$) than that of water ($D = 1.95$).

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EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [4,5]. DMSO (Carlo Erba, RP grade) was purified according to the procedure [6] 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 0.1 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 *m*-hydroxyaniline was recrystallized from water–alcohol mixtures and purified by sublimation; its m.p. was checked before use. After distillation the compound was handled in a dry-box filled with dry nitrogen. The weighing of the compound was also performed in the dry-box.

The ionization process of the *m*-hydroxyaniline ion ($OHPhNH_3^+$) in the various water–DMSO mixtures of X mole fraction can be represented by

$$(OHPhNH_3^+)_X \rightarrow (H^+)_X + (OHPhNH_2)_X \qquad (1)$$

The molar enthalpy of ionization, $\Delta \overline{H}_1$, of $OHPhNH_3^+$ was obtained [4,5] by experimental measurement of the molar enthalpy of solution, $\Delta \overline{H}_2$, of crystalline *m*-hydroxyaniline in the mixed solvent of X mole fraction, represented by

$$OHPhNH_{2(cr.)} \rightarrow (OHPhNH_2)_X \qquad (2)$$

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

$$OHPhNH_{2(cr.)} + (H^+)_X \rightarrow (OHPhNH_3^+)_X \qquad (3)$$

The molar enthalpy, $\Delta \overline{H}_1$, of process (1) can be obtained [4,5] 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 at infinite dilution [4,5]. For every one of the water–DMSO mixtures at X mole fraction, these values refer to the ionization process of one mole of $OHPhNH_3^+$, dissolved at infinite dilution in 1000 g of the mixed solvent, yielding one mole of $OHPhNH_2$ molecules and one mole of protons solvated in the same amount of the solvent.

RESULTS

Table 1 shows the ΔH_1^0, ΔH_2^0 and ΔH_3^0 values of processes (1)–(3) obtained for the *m*-hydroxyaniline ion.

For comparison, it is convenient to express the ionization enthalpy values, ΔH_1^0 of the *m*-substituted aniline ion as the difference between the values

TABLE 1

Enthalpy values of processes (1)–(3) for the *m*-hydroxyaniline ion and *m*-hydroxyaniline in DMSO–water solutions of various mole fractions at 25°C

X_{DMSO}	ΔH_1^0 (kcal mole^{-1})	ΔH_2^0 (kcal mole^{-1})	ΔH_3^0 (kcal mole^{-1})
0.0	6.69	6.38	−0.31
0.1	6.51	6.18	−0.33
0.2	5.52	5.06	−0.46
0.3	4.58	3.74	−0.84
0.4	4.08	2.51	−1.58
0.5	4.12	1.49	−2.63
0.6	4.48	0.71	−3.77
0.7	4.82	0.16	−4.66
0.8	4.80	−0.19	−4.99

obtained in the mixed solvent at X mole fraction and in pure water, so that

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

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 of the substituted aniline ion, respectively, from pure water to mixed solvent. All these data are plotted against X_{DMSO} in Fig. 1.

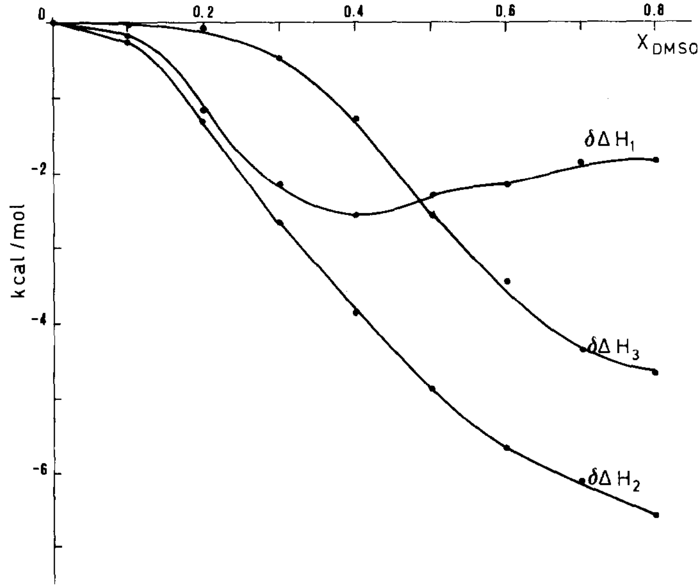


Fig. 1. Enthalpy for the transfer of the ionization of the *m*-hydroxyaniline ion. Transfer enthalpies of the *m*-hydroxyaniline ion and of *m*-hydroxyaniline from pure water to DMSO–water solutions as a function of the mole fraction.

DISCUSSION

In contrast to the *p*- and *o*-hydroxyaniline ions, the *m*-hydroxyaniline ion dissociation is always favoured by an increase in the DMSO content in the solvent mixtures (Fig. 1). This can be ascribed to the fact that the aniline molecule is much more solvated than the aniline cation in the whole mole fraction range. Therefore, one may gather that the solvation of the undissociated molecule is the key factor in the *m*-hydroxyaniline dissociation.

By comparing *para*- and *ortho*-hydroxyanilines with *meta*-hydroxyaniline by means of the differences in the enthalpy of deprotonation, $(\Delta H_1^0)_p - (\Delta H_1^0)_m$, $(\Delta H_1^0)_o - (\Delta H_1^0)_m$ (Fig. 2), it can be inferred that the *meta* derivative is the weakest effective base in the whole mole fraction range.

The differences in solvation enthalpy between the *meta / para*, $\Delta H^0_{(m\text{-OHPhNH}_3^+)-(p\text{-OHPhNH}_3^+)}$, and *meta / ortho*, $\Delta H^0_{(m\text{-OHPhNH}_3^+)-(o\text{-OHPhNH}_3^+)}$, couples for the aniline ions were calculated as shown previously [1,2] and plotted in Figs. 3 and 4. In the same way, the differences in solvation enthalpy between the *meta/para*, $\Delta H^0_{(m\text{-OHPhNH}_2)-(p\text{-OHPhNH}_2)}$, and *meta/ ortho*, $\Delta H^0_{(m\text{-OHPhNH}_2)-(o\text{-OHPhNH}_2)}$, couples for the undissociated molecules were calculated and plotted in Figs. 3 and 4.

Figures 3 and 4 show that in the whole mole fraction range the transfer of the aniline ions decrease according to the sequence $p\text{-NH}_3^+ > o\text{-NH}_3^+ > m\text{-NH}_3^+$, while for the undissociated molecule the order of transfer is $m\text{-NH}_2 >$

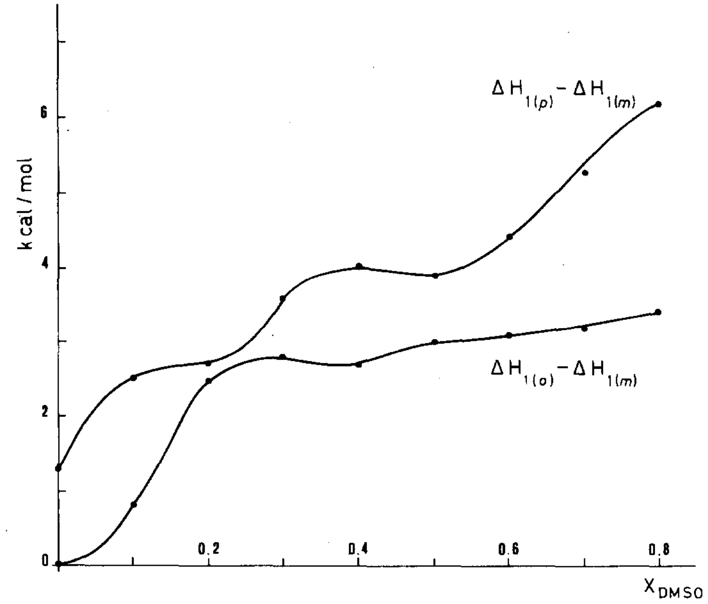


Fig. 2. Differences in the enthalpy of deprotonation of *meta*-, *para*- and *ortho*-hydroxyaniline ions as a function of the mole fraction.

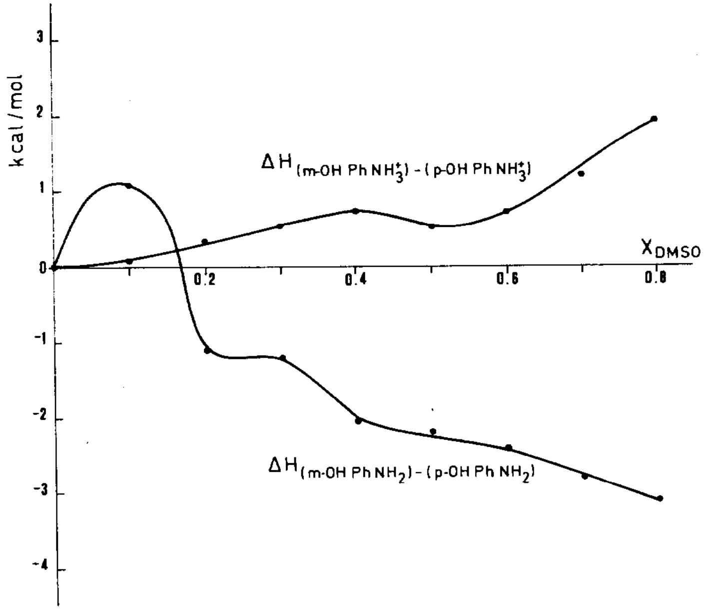


Fig. 3. Differences in the solvation enthalpies between the hydroxyaniline ion couples and the hydroxyaniline couples in various DMSO–water mixtures. The differences in the hydration enthalpy both between the aniline ion couples and the aniline couples are arbitrarily set equal to zero.

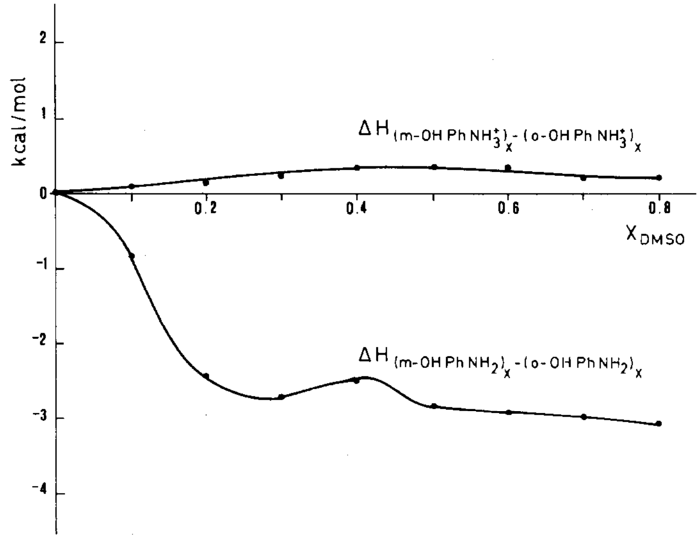
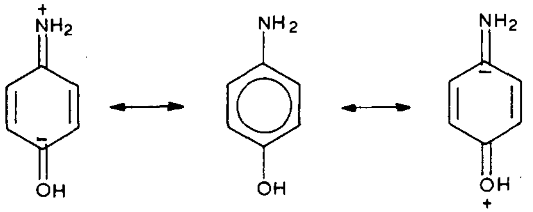


Fig. 4. Differences in the solvation enthalpies between the hydroxyaniline ion couples and the hydroxyaniline couples in various DMSO–water solutions. The differences in the hydration enthalpy both between the aniline ion couples and the aniline couples are arbitrarily set equal to zero.

p-$NH_2 > o$-NH_2. Furthermore, it is noteworthy that the molecule solvation clearly prevails on the anion solvation.

It is also known [7] that, in the gaseous phase, the enhanced stabilization of the undissociated molecule of *meta*-hydroxyaniline with respect to *para*-hydroxyaniline is connected to the more favourable interaction between the NH_2 and OH groups (both σ-acceptor and π-donor).

The destabilizing interaction of two π-donors in *para* disubstituted benzene may be represented by



whereby the substituents compete with each other for conjugation with the ring.

The favourable interaction at the *meta* position is not readily rationalized in terms of resonance.

Indeed, this interaction should occur, according to the Perturbation Molecular Orbital Theory, between the lone pair of the hydroxyl group and the important orbitals in mono-amino substituted benzene, viz. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

For the *ortho* compound, the destabilizing interaction of the two π-donors may be partially reduced by the steric inhibition of resonance.

As shown, the *meta*-hydroxyaniline ion displays the weakest solvation while for *meta*-hydroxyaniline the contrary is true, particularly in DMSO-rich solutions. This could mean that the large dipole of the DMSO stabilizes the benzene charge of the *m*-hydroxyaniline. It may be supposed that an electrophilic attack of the proton occurs on the benzene ring.

It is also known [8] that hydrogen bonding solvents promote substituent protonation because of the strong hydrogen bonds that can be formed with the hydrogen atoms of the amino group. So, *m*-hydroxyaniline is *N*-protonated in water, but this is not true in solutions rich in DMSO to which a superior ability in accepting hydrogen bonds should be ascribed.

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