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THE EFFECT OF MEDIUM ON THE DISSOCIATION OF THE *ORTHO*-HYDROXYANILINIUM 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*-hydroxyanilinium ion in water–DMSO mixtures is presented.

The heats of neutralization of *ortho*-hydroxyaniline and its heats of solution have been obtained.

The primary steric effect seems to be an important factor in the ionization process of the anilinium ion.

INTRODUCTION

Substituted anilines have formed a subject of extended research. Their protonation has been studied in aqueous solutions and in other solvents [1–3].

Recent advances in the gas phase have shown that some substituted anilines are *N*-protonated, while others are ring-protonated [4]. Mono-hydration equilibria in the gas phase have also been measured for several protonated anilines, $BH^+ + OH_2 \rightarrow (BHOH_2^+)$, and the hydration energies have been obtained [4]. The latter, together with the gas-phase basicities of anilines, allow us to determine whether a change of the protonation site from ring to nitrogen atom has occurred or not.

π-Electron-donating substituents, such as the hydroxyl group in the *para* position, stabilize the nitrogen-protonated base while in the *meta* position, the ring protonated base is favored.

In aqueous solutions all these anilines are *N*-protonated since strong hydrogen bonds are formed between the water molecules and the substituted anilinium ion. The interaction of water with the delocalized charge of the ring-protonated ions should be very weak.

A thermodynamic study of the dissociation of the *para*-hydroxyanilinium ion in water–DMSO (dimethylsulfoxide) solutions was performed in our laboratory [5].

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A nitrogen-protonation of the *para* compound was also found in the DMSO-rich solutions. This means that the dipole displayed by the anilinium cation allows a large interaction of the cation with the DMSO molecules.

The dissociation study of the *ortho*-hydroxyanilinium ion in the same solution should give some information about the primary steric effect displayed by the *ortho* group, which is an important factor in the basic strength of the *ortho* substituted anilines.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [6,7]. 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 0.1 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 *ortho*-hydroxyaniline was recrystallized from water–alcohol mixtures; its melting point was checked before use. The compound was handled in a dry-box filled with dry nitrogen. Weighing of the compound was also performed in the dry-box.

The ionization process of the *ortho*-hydroxyanilinium cation ($OHPhNH_3^+$) in the various water–DMSO mixtures of X mole fraction can be represented as

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

The molar enthalpy, $\Delta\overline{H}_1$, for the ionization of $OHPhNH_3^+$ was obtained [6,7] by experimental measurement of:

(a) the molar enthalpy of solution, $\Delta\overline{H}_2$, of crystalline *ortho*-hydroxy aniline in the mixed solvent of X mole fraction

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

(b) the molar enthalpy of neutralization, $\Delta\overline{H}_3$, of the *para* compound in the same mixture containing an excess of HCl

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

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 every one of the water–DMSO mixtures at X_{DMSO} mole fraction, the 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 solvent.

TABLE 1

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

x_{DMSO}	ΔH_1^0	ΔH_2^0	ΔH_3^0
0.0	6.65	5.91	−0.74
0.1	7.34	6.55	−0.79
0.2	7.98	6.99	−0.99
0.3	7.39	5.93	−1.46
0.4	6.83	4.57	−2.26
0.5	7.11	3.87	−3.33
0.6	7.61	3.15	−4.46
0.7	7.99	2.67	−5.32
0.8	8.17	2.52	−5.65

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 *ortho*-hydroxyanilinium ion.

For comparison, it is convenient to express the ionization enthalpy values,

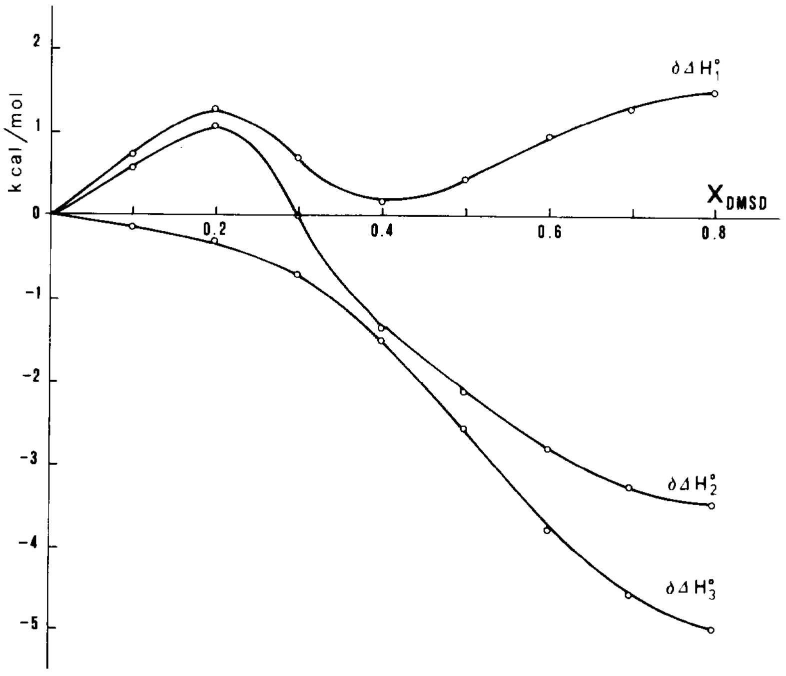

Fig. 1. Enthalpy for the transfer of the ionization of the *ortho*-hydroxyanilinium ion. Transfer enthalpies of the *ortho*-hydroxyanilinium ion and *ortho*-hydroxyaniline from pure water to DMSO–water solutions as a function of the mole fraction.

ΔH_1^0, of the hydroxy substituted anilinium ion as the difference between the values obtained in the mixed solvent at X mole fraction and in pure water so that

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

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

DISCUSSION

From an enthalpic point of view, the substituted anilinium ion dissociation is always hindered by increasing the DMSO content in the solvent mixtures (Fig. 1).

Figure 1 also shows that the anilinium cation is more solvated than the aniline molecule in the whole mole-fraction range, with the exception of $0.4 \leqslant X_{\text{DMSO}} \leqslant 0.5$. This could be ascribed, in the DMSO-rich solutions, to the dipole displayed by the anilinium cation and to the consequent interaction between the latter and the dipoles of the DMSO molecules.

In the water-rich solutions, the maximum of desolvation of the substituted aniline is related to its maximum endothermic heat of solution, due, in turn, to a condition of maximum structure of the solvent and to the "volume" of the *ortho*-substituted compound [9].

By comparing the *para* and *ortho*-hydroxyanilines, by means of the difference in the enthalpy of deprotonation $(\Delta H_1^0)_{\text{p}} - (\Delta H_1^0)_{\text{o}}$ (Fig. 2), it can be inferred that the former is a more effective base in the whole mole-fraction range.

The difference in solvation enthalpy between the *para*-hydroxy and *ortho*-

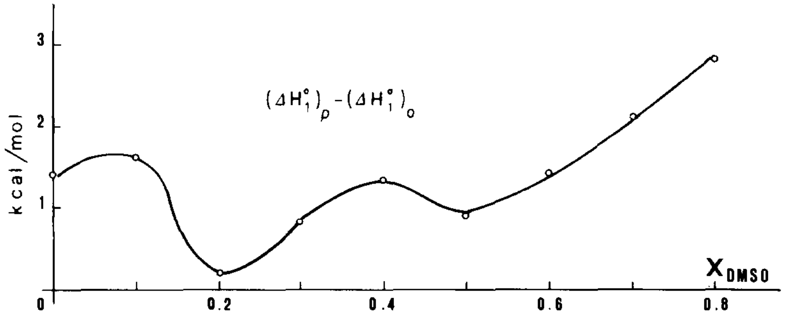

Fig. 2. Difference in the enthalpy of deprotonation of *para* and *ortho*-hydroxyanilinium ions as a function of the mole fraction.

hydroxyanilinium ions was calculated as [9]

$$\Delta H^0_{(p\text{-OHPhNH}_3^+)_X-(o\text{-OHPhNH}_3^+)_X} = \delta\Delta H^0_{3(p\text{-OHPhNH}_3^+)} - \delta\Delta H^0_{3(o\text{-OHPhNH}_3^+)} + \Delta H^0_{(p\text{-OHPhNH}_3^+)_{\text{aq.}}-(o\text{-OHPhNH}_3^+)_{\text{aq.}}} \qquad (4)$$

while the difference in solvation enthalpy between the undissociated molecules is

$$\Delta H^0_{(p\text{-OHPhNH}_2)_X-(o\text{-OHPhNH}_2)_X} = \delta\Delta H^0_{2(p\text{-OHPhNH}_2)} - \delta\Delta H^0_{2(o\text{-OHPhNH}_2)} + \Delta H^0_{(p\text{-OHPhNH}_2)_{\text{aq.}}-(o\text{-OHPhNH}_2)_{\text{aq.}}} \qquad (5)$$

The last term on the right-hand sides of eqns. (4) and (5) was arbitrarily assumed to be equal to zero and the resulting $\Delta H^0_{(p\text{-OHPhNH}_3^+)_X-(o\text{-OHPhNH}_3^+)_X}$ and $\Delta H^0_{(p\text{-OHPhNH}_2)_X-(o\text{-OHPhNH}_2)_X}$ are plotted in Fig. 3 as a function of the solvent composition.

Figure 3 shows how the *para*-anilinium ion and *para*-aniline are always solvated to a greater extent than the *ortho*-anilinium ion and *ortho*-aniline.

In the DMSO-rich solutions there is a maximum in the difference of

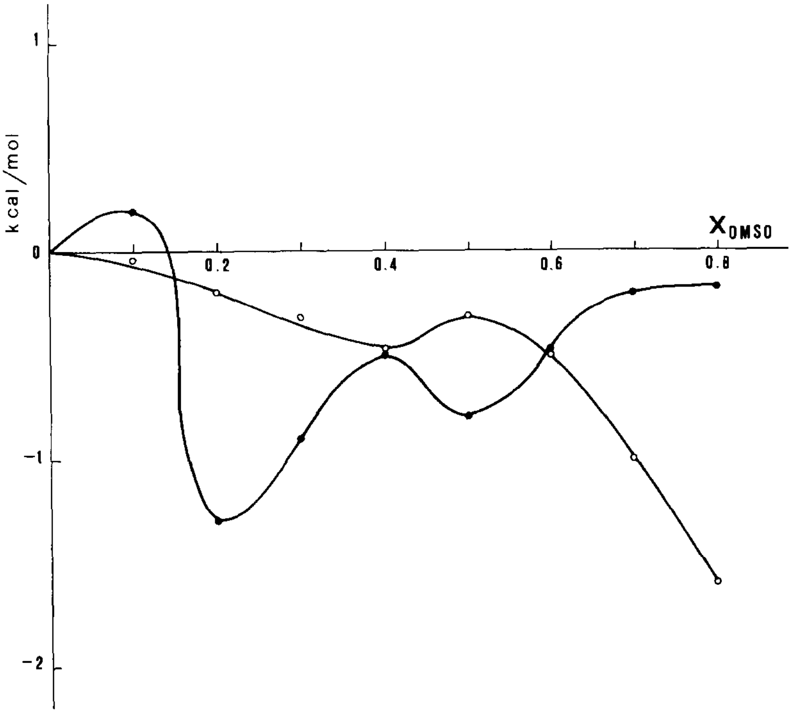

Fig. 3. Differences in the solvation enthalpies between the hydroxyanilinium couples and the hydroxyaniline couples in various DMSO–water mixtures. The differences in the hydration enthalpy both between the anilinium couples and the aniline couples are arbitrarily set equal to zero. ○, $\Delta H_{(p\text{-OHPhNH}_3^+)_X-(o\text{-OHPhNH}_3^+)_X}$; ●, $\Delta H_{(p\text{-OHPhNH}_2^+)_X-(o\text{-OHPhNH}_2^+)_X}$.

solvation enthalpies between the *para* and *ortho*-anilinium ions due to the greater interaction of the former with the dipoles of DMSO.

At $X_{\mathrm{DMSO}} = 0.2$ there is a maximum in the difference of the solvation enthalpies between *para* and *ortho*-aniline molecules, due to the foregoing maximum heat of solution.

It is noteworthy that at this mole fraction the basicities of *ortho* and *para*-anilines are quite similar.

On the basis of these observations, one may gather that for the *ortho* compound there is an increase in the primary steric effect [10–12] 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 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. 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.

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