# THE EFFECT OF MEDIUM ON THE DISSOCIATION OF THE p-HYDROXYANILINE ION

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(Received 20 January 1983)

ABSTRACT

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

The heats of neutralization of p-hydroxyaniline and its heats of solution have been obtained by calorimetric measurements.

The entropy term can be identified as the driving force of the dissociation process.

INTRODUCTION

Substituted anilines are a large and important class of Bronsted bases, whose protonation has been studied in aqueous solutions and in other solvents [1–3].

Recent advances in gas-phase chemistry provide a large fund of information about the intrinsic basicities of some substituted anilines [4–6].

In the gas phase, some of the substituted anilines are N-protonated, while others are ring protonated. In aqueous solutions, all these anilines are N-protonated.

In the comparison of substituted amines and anilines, protonation in water, non-aqueous solvents (DMSO, PC) and gas phase was used [7,8] for understanding the solvent effect both on the bases, B, and on the conjugated acids, $BH^+$.

A thermodynamic study of the dissociation variation of the p-hydroxy-aniline ion in water–DMSO(dimethylsulfoxide) solutions, as a function of the mole fraction should give further insight into the solvent effect on the acid and the conjugated base.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [9,10]. DMSO (Carlo Erba, RP grade) was purified according to the procedure [11] 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 $p$-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 $p$-hydroxyaniline ion ($OHPhNH_3^+$) in the various water–DMSO mixtures of $X$ mole fraction can be represented as

$$(OHPhNH_3^+)_X \rightarrow (H^+)_X + (OHPhNH_2)_X \tag{1}$$

The molar enthalpy of ionization, $\Delta \overline{H}_1$, of $OHPhH_3^+$ was obtained [9,10] by experimental measurement of the molar enthalpy of solution, $\Delta \overline{H}_2$, of crystalline $p$-hydroxyaniline in the mixed solvent of $X$ mole fraction

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

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

$$OHPhNH_{2(cr.)} \rightarrow OHPhNH_3^+ \tag{3}$$

The molar enthalpy, $\Delta \overline{H}_1$, of process (1) can be obtained [9,10] by subtracting the two values $\Delta \overline{H}_2$ and $\Delta \overline{H}_3$.

In processes (2) and (3), concentrations ranging from $2 \times 10^{-3}$ m to $4 \times 10^{-3}$ m were used. Therefore, the $\Delta \overline{H}_1$ values can be considered at infinite dilution [9,10]. For every one of the water–DMSO mixtures at $X_{DMSO}$ 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.

In the literature [1] the $pK_a/1$ values of process(1) at 20°C are reported for $p$-hydroxyaniline. From these data and from the $\Delta H_1^0$ values reported in Table 1, the $pK_a/1$ values at 25°C were calculated, using the equation

$$pK_{25°C} = pK_{20°C} - \frac{\Delta H_1^0 \Delta T}{1.987 \cdot T_1 T_2 \times 2.303}$$

From the $pK_a/1$ value at 25°C, the free energy, $\Delta G_1^0$, relative to process(1) and the $T\Delta S_1^0$ values were calculated using the Gibbs–Helmholtz equation.

The initial standard state to which $\Delta G_1^0$ values of ionization refer is defined to be an ideal 1 m solution of $OHPhNH_3^+$ behaving as an infinitely dilute solution.

RESULTS

Table 1 gives the $\Delta G_1^0$, $\Delta H_1^0$ and $T\Delta S_1^0$ values of process (1) obtained for the $p$-hydroxyaniline ion. Table 2 shows the enthalpy values of processes (2) and (3).

For comparison it is convenient to express the ionization enthalpy values, $\Delta H_1^0$, of the hydroxy substituted aniline ion as a difference between the values obtained in the mixed solvent at $X$ mole fraction and in pure water so that

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

In a similar way, the values of $\delta\Delta G_1^0$ and $T\delta\Delta S_1^0$ can be defined and

TABLE 1

Free energy, enthalpy and entropy values for the ionization of the $p$-hydroxyaniline ion, in DMSO–water solutions of various mole fractions at 25°C All thermodynamic quantities are given in kcal mole$^{-1}$.

| $X_{DMSO}$ | $\Delta G_1^0$ | $\Delta H_1^0$ | $T\Delta S_1^0$ |
|---|---|---|---|
| 0.0 | 7.70 | 8.00 | 0.31 |
| 0.1 | 7.22 | 8.96 | 1.74 |
| 0.2 | 6.92 | 8.19 | 1.27 |
| 0.3 | 6.75 | 8.14 | 1.39 |
| 0.4 | 6.73 | 8.12 | 1.39 |
| 0.5 | 6.73 | 7.98 | 1.25 |
| 0.6 | 6.86 | 8.92 | 2.06 |
| 0.7 | 7.03 | 10.13 | 3.10 |
| 0.8 | 7.30 | 10.97 | 3.67 |

TABLE 2

Enthalpy values of processes (2) and (3) for the $p$-hydroxyaniline ion, in DMSO–water solutions of various mole fractions at 25°C

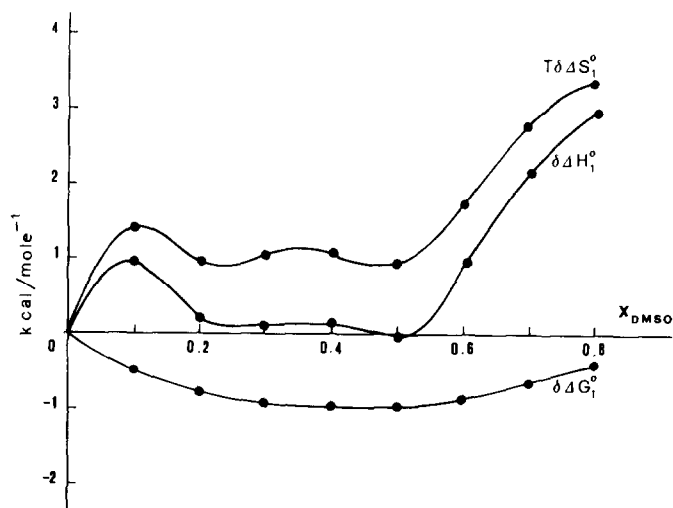| $X_{DMSO}$ | $\Delta H_2^0$ (kcal mole$^{-1}$) | $\Delta H_3^0$ (kcal mole$^{-1}$) |
|---|---|---|
| 0.0 | 6.06 | − 1.94 |
| 0.1 | 6.94 | − 2.02 |
| 0.2 | 5.83 | − 2.36 |
| 0.3 | 5.21 | − 2.93 |
| 0.4 | 4.21 | − 3.91 |
| 0.5 | 3.18 | − 4.80 |
| 0.6 | 2.78 | − 6.14 |
| 0.7 | 2.61 | − 7.52 |
| 0.8 | 2.50 | − 8.47 |

Fig. 1. Thermodynamic quantities for the transfer of the ionization of the *p*-hydroxyaniline ion from pure water to DMSO–water mixtures as a function of the mole fraction.

calculated. These three 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
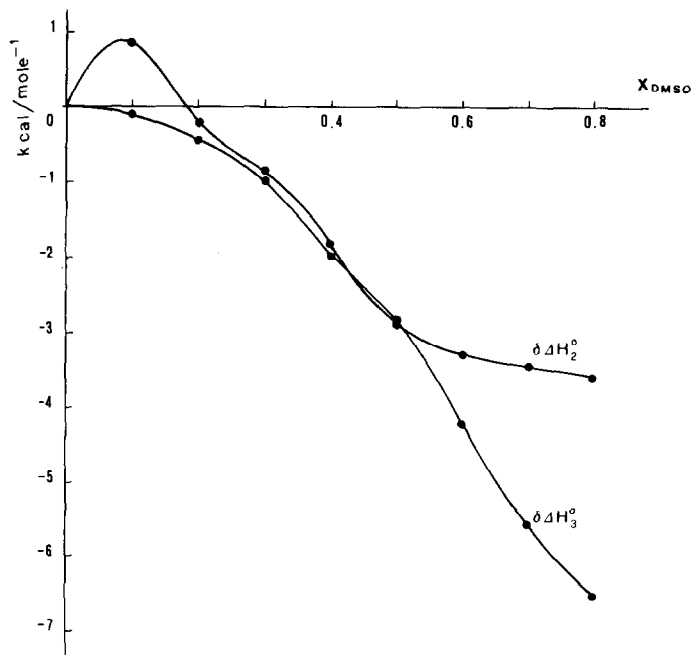


Fig. 2. Transfer enthalpies of *p*-hydroxyaniline and the *p*-hydroxyaniline ion from pure water to DMSO–water mixtures as a function of the mole fraction.

pure water to mixed solvent. All these data are plotted vs. $X_{DMSO}$ in Figs. 1 and 2.

DISCUSSION

From Fig. 1 it can be inferred that the $\delta\Delta H_1^0$ values are smaller than the corresponding $\delta\Delta G_1^0$ and $T\delta\Delta S_1^0$ for $0.15 \leqslant X_{DMSO} \leqslant 0.5$, while out of this range the values of the entropy and enthalpy terms become larger than those of the free energy term.

The $\delta\Delta H_1^0$ values show that dissociation of the substituted aniline is always hindered by an increase of DMSO in the solvent mixtures, while the terms $T\delta\Delta S_1^0$ and $\delta\Delta G_1^0$ are always favourable to process (1). It is also noteworthy that in this case the entropy term can be reasonably identified with the driving force of process (1).

The enthalpy trend can be explained taking into account the enthalpy of solvation undergone by the hydroxyaniline and the hydroxyaniline ion.

Figure 2 shows that the solvation enthalpies are quite similar for aniline and the aniline ion for $0.2 \leqslant X_{DMSO} \leqslant 0.5$, while, out of this range of mole fractions the aniline ion is more solvated than the aniline molecule. This can be ascribed to the greater dipole displayed by the aniline cation and the consequently greater interaction with the DMSO molecules.

In the water-rich solutions, the greater 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 [12].

As shown, the entropy term $T\delta\Delta S_1^0$ is always favourable to process (1) with a sharp increase in water-rich and DMSO-rich solutions. This fact agrees with the typical structural features of the DMSO–water mixtures [13–15] which show two zones (0–0.15 and 0.5–0.8) with an ordered structure and one (0.15–0.5) with a disordered structure.

ACKNOWLEDGEMENT

REFERENCES

1 J.C. Hallè, R. Shall and A. DiNallo, Anal. Chim. Acta, 60 (1972) 197.
2 T.W. Zawidzki, H.M. Papè, W.J. Canady and K.J. Laindler, Trans. Faraday Soc., 55 (1959) 1739.
3 S. Mukhopadhyay and B. Nayak, Electrochim. Acta, 25 (1980) 807.

4 Y.K. Pollak, J.L. Deulin III, K.D. Summerhays, R.W. Taft and W.J. Hehre, J. Am. Chem. Soc., 99 (1977) 4583.

5 K.D. Summerhays, S.K. Pollak and R.W. Taft, J. Am. Chem. Soc., 99 (1977) 4585.

6 Y.K. Lou, K. Nishizawa, T. Tse, R.S. Brown and P. Kebarle, J. Am. Chem. Soc., 103 (1981) 6291.

7 A. Mucci, R. Domain and R.L. Benoit, Can. J. Chem., 50 (1980) 953.

8 R.L. Benoit, M.J. Mackinnom and L. Bergeron, Can. J. Chem., 59 (1981) 1501.

9 F. Rodante, Thermochim. Acta, 23 (1978) 311.

10 F. Rodante, Thermochim. Acta, 32 (1979) 293.

11 J.C. Synnot and J.N. Butler, J. Phys. Chem., 73 (1979) 1470.

12 F. Rodante, G. Ceccaroni and M.G. Bonicelli, Thermochim. Acta, 42 (1980) 223.

13 F. Fiordiponti, F. Rallo and F. Rodante, Gazz. Chim. Ital., 104 (1974) 649.

14 F. Rodante, F. Rallo and P. Fiordiponti, Thermochim. Acta, 6 (1973) 369.

15 F. Rodante, and P. Fiordiponti, Thermochim. Acta, 19 (1977) 13.