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DISSOCIATION OF 2-CARBOXY-PYRIDINE ION. PRIMARY STERIC EFFECT AND SOLUTE–SOLVENT INTERACTIONS AS IONIZATION FACTOR FOR *ortho* PYRIDINE AND ANILINE

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ABSTRACT

A calorimetric study of the protonation of 2-carboxy pyridine is presented. 2-Carboxy pyridine and the *ortho*-carboxy aniline are bases of equal strength. This is due to the fact that the primary steric effect of the *ortho*-carboxy aniline is offset by the strong solute–solvent interactions of the 2-carboxy pyridine.

INTRODUCTION

The protonation of some substituted anilines in various water–dimethylsulphoxide (DMSO) solutions has been the subject of a research carried out in this laboratory [1–6].

This study has supplied substantial information on the effects influencing the aniline strength. This latter depends on a wide range of effects: (a) the σ and π effects of the substituents on the functional groups; (b) the features of the two solvents (both excellent hydrogen bond acceptors but only one is a good hydrogen bond donor); (c) a tautomeric effect between the undissociated molecule and the zwitterion form. A very particular case, however, can be represented by the primary steric effect, which occurs in the *ortho*-substituted anilines.

The proton addition to the nitrogen atom leads to the transformation of the latter from the trivalent to the bulkier tetrahedral configuration. Therefore, the primary steric effect clearly prevails in the carboxy derivative with respect to the hydroxy derivative.

In the same solutions the behaviour of 3-carboxy pyridine was studied [7]. For this compound the solute–solvent interactions (hydrogen bonds and dipoles) more than the effects intrinsic to the molecule (the greater degree of *s* character in the hybrid molecular orbital containing the lone pair) seem to be the key effects of the protonation of the pyridine derivative in the liquid phase.

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This work investigates the behaviour of the 2-carboxy pyridine in confrontation with *ortho*-aniline derivatives. It was particularly interesting to study the primary steric effect between the carboxyl group and the NH_2 and N groups which display a very different bulk.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been previously described [1–7]. DMSO (Carlo Erba RP grade) was purified according to the procedure of Synnot and Butler [8]. 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 1 M HCl was prepared from standard solution; its concentration was checked by potentiometric titration. The 2-carboxy pyridine 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 2-carboxy pyridine ion ($COOHpyH^+$) in the various water–DMSO mixtures at X mole fraction can be represented as

$$(COOHpyH^+)_X \rightarrow (H^+)_X + (COOHPhy)_X \qquad (1)$$

The molar enthalpy of ionization, $\Delta\overline{H}_1$, of $COOHpyH^+$ was obtained by measuring the molar enthalpy of solution, $\Delta\overline{H}_2$, of the 2-carboxy pyridine in the mixed solvent of X mole fraction

$$COOHpy_{(cry)} \rightarrow (COOHpy)_X \qquad (2)$$

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

$$COOHpy_{(cry)} + (H^+) \rightarrow (COOHpyH^+)_X \qquad (3)$$

The molar enthalpy, $\Delta\overline{H}_1$, of process (1) can be obtained 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 [1–7].

For each water–DMSO mixture at X mole fraction, these values refer to the ionization process of 1 mol $COOHpyH^+$, dissolved at infinite dilution in 1000 g mixed solvent, yielding 1 mol COOHpy molecules and 1 mol 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 2-carboxy pyridine ion.

TABLE 1

Enthalpy values of processes (1)–(3) for 2-carboxy pyridine in DMSO–water mixtures of various mole fraction at 25°C

X_{DMSO}	ΔH_1^0	ΔH_2^0	ΔH_3^0
0.0	0.47	3.15	2.68
0.1	0.87	4.35	3.48
0.2	0.38	5.26	4.88
0.3	0.15	5.68	5.53
0.4	0.16	5.80	5.64
0.5	0.21	5.64	5.43
0.6	0.19	5.02	4.83
0.7	0.30	4.81	4.51
0.8	0.29	4.67	4.38

For the sake of comparison, it is covenient to express the ionization enthalpy values, ΔH_1^0, of the 2-carboxy pyridine ion as the difference between the values obtained in the mixed solvent at X mole fraction and in pure water, hence

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

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

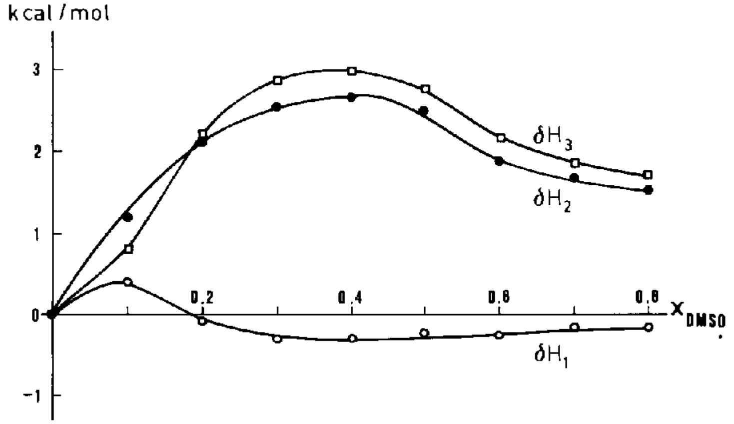

Fig. 1. Enthalpy for the transfer of the ionization of the 2-carboxy pyridine ion. Transfer enthalpies of the 2-carboxy pyridine ion and 2-carboxy pyridine from pure water to DMSO–water mixtures as a function of the mole fraction.

DISCUSSION

As previously shown for the 3-carboxy pyridine [7] both the undissociated molecule and the ion are desolvated over the whole mole fraction range (Fig. 1). In the water-rich solutions (up to 0.1 mole fraction) the undissociated molecule is more desolvated than the ion. The electron-withdrawing effect of the carboxyl group reduces the lone pair electron density and the interactions between the water molecules and the N atom are weakened. On the contrary, the positive charge density at the NH^+ group of the pyridinium ion will be enhanced and the solute–solvent interactions will be strengthened. Therefore, in the water-rich solutions the principal effect of substituent on the pyridine protonation is through hydrogen bonding of the pyridinium ion to water.

In the DMSO-rich solutions the dipole–dipole interactions (due to the large dipole of the carboxy pyridine and DMSO) prevail on the hydrogen bonding of the pyridinium ion to the DMSO molecule.

By comparing the 2-carboxy pyridine and 3-carboxy pyridine by means of the difference in the enthalpy of deprotonation $\Delta H^0_{(2\text{-COOHpyH}^+)} - \Delta H^0_{(3\text{-COOHpyH}^+)}$ (Fig. 2) it can be inferred that the 2-carboxy pyridine is a weaker effective base than the 3-carboxy pyridine in the water-rich solutions. This can be explained by taking into account the difference in solvation enthalpy between the ions $\Delta H^0_{(2\text{-COOHpyH}^+)-(3\text{-COOHpyH}^+)}$ and undissociated molecules $\Delta H^0_{(2\text{-COOHpy})-(3\text{-COOHpyH}^+)}$ (Fig. 2).

It is clear that the greater solvation of the 2-carboxy undissociated molecule is the key effect for the relative strength of the two bases. It can be hypothesized that the zwitterion of the 2-carboxy pyridine interacts with the water molecules to a greater extent than the 3-carboxy pyridine.

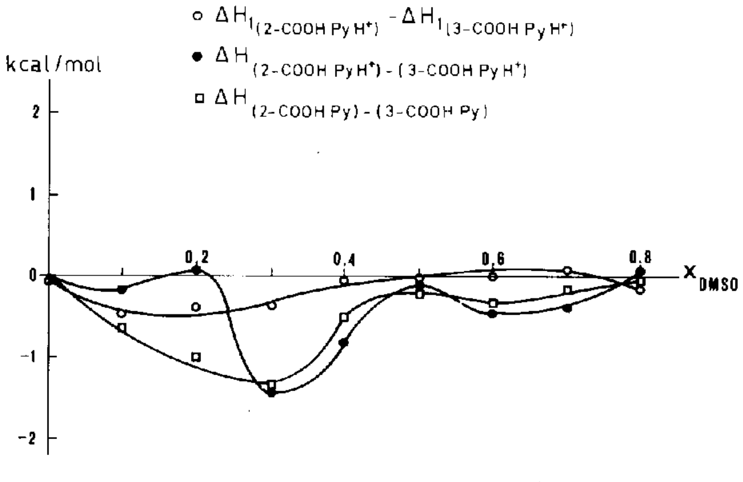

Fig. 2. Difference in the enthalpy of deprotonation of 2- and 3-carboxy pyridine ions. Differences in the solvation enthalpies between the 2- and 3-pyridine ions and the 2- and 3-pyridines.

It also seemed interesting to compare the 2-COOHpy with the *ortho*-carboxy aniline. It is known that in the gas phase the substituted pyridines are stronger bases than the substituted anilines, while in the liquid phase the opposite is true. The difference in the enthalpy of deprotonation, $\Delta H^0_{1(2\text{-COOHpyH}^+)} - \Delta H^0_{1(o\text{-COOHPhNH}_3^+)}$, however, displays that the 2-carboxy pyridine and the *ortho*-carboxy aniline are bases of equal strength (Fig. 3).

This can be explained by taking into account the relative solvation enthalpy between the ion $\Delta H^0_{(\text{COOHpyH}^+)-(\text{COOHPhNH}_3^+)}$ and the undissociated molecule $\Delta H^0_{(\text{COOHpy})-(\text{COOHPhNH}_2)}$. In water-rich solutions both pyridine and pyridinium ion are more solvated than the corresponding aniline and anilinium ion. The greater solvation of the pyridinium ion can be ascribed to the enhanced positive charge density at the NH^+ group leading to a strengthened hydrogen bond. For the pyridine it can be hypothesized that the zwitterion strongly interacts with water. Furthermore, in water-rich solutions the hydration of the carboxyl enhances the primary steric effect. This effect seems to be reduced in DMSO-rich solutions because of the diminished solvation of the carboxyl group. In the same solutions it could also be hypothesized that the carboxyl group in position 2 greatly deactivates and, thus, destabilizes the aromatic system for the pyridine and the pyridinium ion.

It can be concluded that the large primary steric effect of *ortho*-carboxy aniline is balanced by the strong solute–solvent interaction of 2-pyridine.

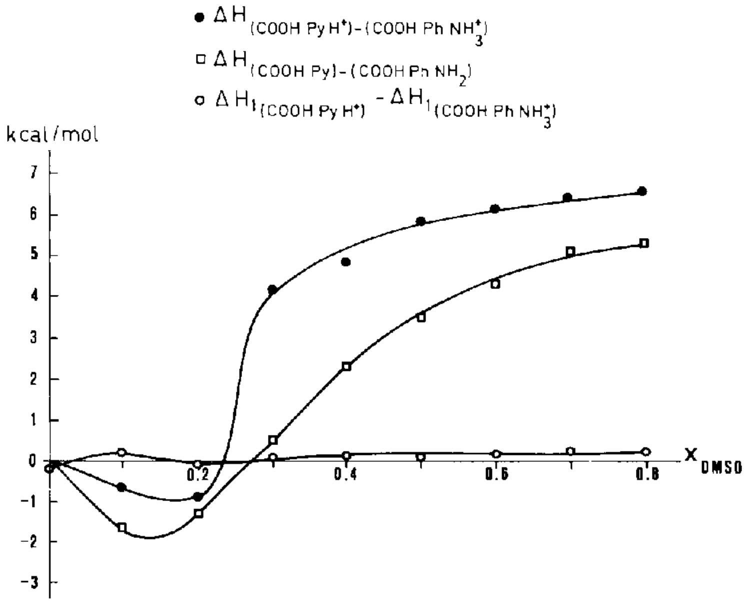

Fig. 3. Difference in the enthalpy of deprotonation of 2-carboxy pyridine and *ortho*-carboxy aniline ions. Differences in the solvation enthalpies between carboxy pyridine/aniline ions and undissociated molecule couples.

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