Thermochimica Acta, 75 (1984) 341–346
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC STUDY OF THE DISSOCIATION OF THE 3-CARBOXY PYRIDINIUM ION. THE EFFECT OF THE HYDROGEN BOND ON THE BASE STRENGTH

F. RODANTE and M.G. BONICELLI

Dipartimento di Ingegneria Chimica, dei Materiali delle Materie Prime e Metallurgia, Università di Roma, Via del Castro Laurenziano 7, Roma (Italy)

(Received 22 November 1983)

ABSTRACT

A calorimetric study of the protonation of 3-carboxy pyridine is presented.

The solute–solvent interactions (hydrogen bonds and dipoles), more so than the effects intrinsic to the molecule (the greater degree of *s* character in the hybrid molecular orbital containing the lone pair), seems to have the main influence on the protonation of pyridine in the liquid phase.

INTRODUCTION

Substituted anilines are a large and important class of Brönsted bases, whose protonation has been studied [1–6] in aqueous solutions, in other solvents and in the gas phase.

As shown in an extended research performed in our laboratory [7–12] the isomers of the hydroxy and carboxy anilines display an "anomalous" behaviour because of the competition between the basic and acid functional groups.

This is true mostly for the carboxy derivatives which are weaker bases than the hydroxy ones in various water–dimethylsulfoxide (DMSO) solutions. Both solvents are excellent hydrogen bond acceptors, but only the water is a good hydrogen bond donor. Therefore, in these mixtures, the solvation of the ions (due to the hydrogen bond between the anilinium ion and the water and DMSO molecules) can be distinguished from that of the undissociated molecule (due to the hydrogen bond between the water and the neutral aniline).

Following this research, the behaviour of the substituted pyridines in the same solutions was studied.

Aromatic heterocycles differ considerably from aromatic hydrocarbons in that they contain at least one polar atom within the framework of the aromatic system. Large variations in σ and π electronic density may be expected in this class of compounds.

The lone-pair of pyridine, due to the N-double bond, is lodged in a hybrid molecular orbital which displays mostly *s* character, so that it becomes less favourable for bonding to the proton.

The $\sigma\pi$ orbitals of the pyridine are deformed by means of the attractive effect of the N-atom, thus, the ring is deactivated; this deactivation is enhanced by the electrophilic attack of the proton on the N-atom.

The aim of this work is to study the behaviour of 3-carboxy pyridine and compare it with that of *meta*-carboxy aniline.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus has been described previously [7–12]. DMSO (Carlo Erba, RP grade) was purified according to the procedure of Synnot and Butler [13]. 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 a standard solution; its concentration was checked by potentiometric titration. The 3-carboxy pyridine was recrystallized by water–alcohol mixtures; its m.p. was checked before use. 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 3-carboxy pyridine ion (m-COOHpyH$^+$) in the various water–DMSO mixtures at X mole fraction can be represented as

$$(\mathrm{COOHpyH^+})_X \rightarrow (\mathrm{H^+})_X + (\mathrm{COOHpy})_X \qquad (1)$$

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 3-carboxy pyridine in the mixed solvent of X mole fraction

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

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

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

The molar enthalpy, $\Delta\overline{H}_1$, of process (1) can be obtained [7–12] 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 ΔH_1 values can be considered at infinite dilution [7–12].

For each water–DMSO mixtures at X mole fraction, these values refer to the ionization process of one mole of COOHpyH$^+$, dissolved at infinite dilution in 1000 g of the mixed solvent yielding one mole of COOHpy molecules and one mole of protons solvated in the same amount of solvent.

TABLE 1

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

X_{DMSO}	ΔH_1^0	ΔH_2^0	ΔH_3^0
0.0	0.50	3.83	3.33
0.1	1.4	5.59	4.19
0.2	0.81	6.93	6.12
0.3	0.58	7.62	7.04
0.4	0.20	7.01	6.81
0.5	0.27	6.48	6.21
0.6	0.20	5.99	5.79
0.7	0.20	5.66	5.46
0.8	0.38	5.40	5.02

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 3-carboxy pyridine ion.

For the sake of comparison, it is convenient to express the ionization enthalpy values, ΔH_1^0, of the 3-carboxy pyridine ion as the difference between the values obtained in the mixed solvent at X mole fraction and in pure water, so that $\delta\Delta H_1^0 = (\Delta H_1^0)_X - (\Delta H_1^0)_{X=0}$.

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

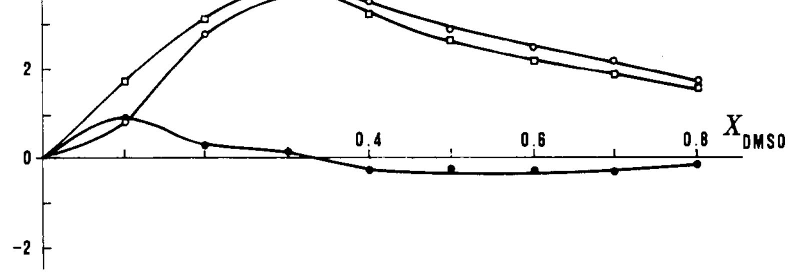

Fig. 1. Enthalpy for the transfer of the ionization of the 3-carboxy pyridine ion. Transfer enthalpies of the 3-carboxy pyridine ion and 3-carboxy pyridine from pure water to DMSO–water solutions as a function of the mole fraction.

pyridine and the substituted pyridinium ion, respectively, from pure water to mixed solvent.

All these data are plotted against X_{DMSO} in Fig. 1.

DISCUSSION

Both the undissociated molecule and ion, as shown in Fig. 1, are (always) desolvated in the whole mole fraction range.

The sequence of desolvation shows that the undissociated molecule is more desolvated than the ion up to 0.3 mole fraction. Beyond this mole fraction the reverse is true. This can be explained by means of the electronic effect of the substituent on the solute–solvent interactions at the N-atom and at the NH^+- group in the neutral pyridine and pyridinium ion, respectively. For an electron-withdrawing substituent such as a carboxyl group, the lone pair electron density at the N-atom is reduced and the interactions between the water molecules and the N-atom is weakened. The positive charge density at the NH^+-group of the pyridinium ion will be enhanced and solute–solvent interactions should be strengthened.

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 it is clear that the dipole–dipole interactions (due to the large dipoles of the carboxy pyridine and DMSO) are prevailing on the hydrogen bonding of pyridinium ion to the DMSO molecule.

Thus, the DMSO molecule seems to be a weaker hydrogen bond acceptor (by the pyridinium ion) than the water molecule.

On comparing 3-carboxy pyridine and *meta*-carboxy aniline by means of the difference in the enthalpy deprotonation $\Delta H^0_{1(3\text{-COOHpyH})^+} - \Delta H^0_{1(3\text{-COOHPhNH}_3^+)}$ (Fig. 2) it is inferred that the pyridine derivative is a weaker effective base than the *meta*-aniline derivative.

It is also well-known [14–16] that in the gas-phase the substituted pyridines are stronger bases than the substituted anilines. This clearly shows that the lower base strength, towards the solvated proton, of the pyridine with respect to the aniline cannot be ascribed to a greater degree of *s* character of the hybrid molecular orbital containing the lone pair.

So it can be concluded that the solute–solvent interactions are highly substantial effects in the protonation of the pyridine in the liquid phase. These effects overcome those intrinsically related to the molecule and the anion. The differences in solvation enthalpy between the ions, $\Delta H^0_{(\text{COOHpyH}^+)-(\text{COOHPhNH}_3^+)}$, and the undissociated molecules, $\Delta H^0_{(\text{COOHpyH})-(\text{COOHPhNH}_2)}$, were calculated as previously shown [7–12] and plotted in Fig. 2.

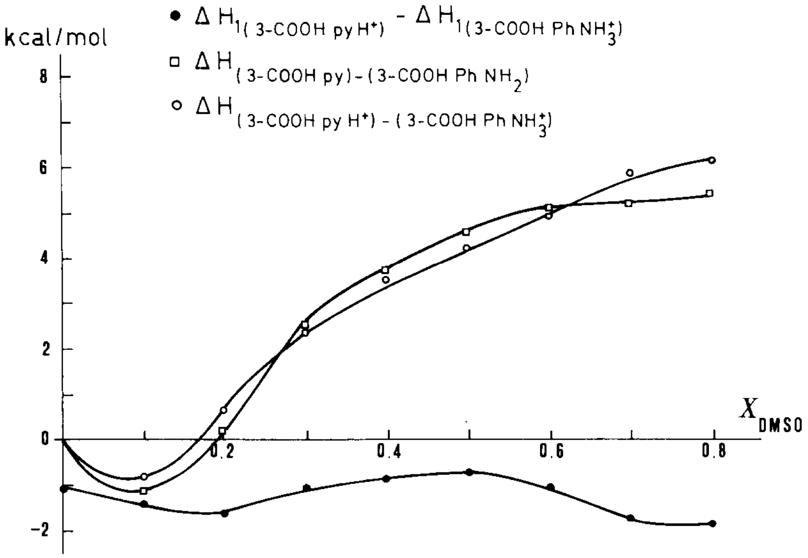

Fig. 2. Difference in the enthalpy of deprotonation of 3-carboxy pyridine and 3-carboxy aniline ions. Differences in the solvation enthalpies between the carboxy pyridine/aniline ions and undissociated molecules couples.

Figure 2 shows that the undissociated molecule and the anion of the pyridine are more desolvated than those of the substituted aniline with the exception of $0.0 \leqslant X_{\mathrm{DMSO}} \leqslant 0.2$, where the reverse is true.

Since the carboxyl group in the *meta* position [10] at the NH_2 group destabilizes the benzene ring, it can be concluded that the carboxyl group in the 3-substituted pyridine greatly inactivates and thus destabilizes the aromatic system. This is also true for the pyridinium ion.

Finally, the greater solvation of the pyridinium ion in water-rich solutions can be ascribed to the enhanced positive charge density at the NH^+ group, with a strengthened hydrogen bond.

The undissociated pyridine displays a tautomeric zwitterion equilibrium $COOHpy \rightleftarrows COO^-py$. It can be hypothesized that this zwitterion interacts with the water molecules to a greater extent than the zwitterion of the carboxy aniline.

ACKNOWLEDGEMENT

This work was carried out with the financial support of the Consiglio Nazionale delle Ricerche (C.N.R.) of Italy.

REFERENCES

1 J.-C. Halle, R. Shaal and A. Di Nallo, Anal. Chim. Acta, 60 (1972) 197.
2 T.W. Zawdzki, H.M. Papè, W.J. Canady and K.J. Leinler, Trans. Faraday Soc., 55 (1959) 1739.
3 S. Mékhopadhy and B. Nayak, Electrochim. Acta, 25 (1980) 807.
4 Y.K. Pollack, J.L. Deélin III, K.D. Summerhays, R.W. Taft and W.J. Here, J. Am. Chem. Soc., 99 (1977) 4583.
5 K.D. Summerhays, S.K. Pollack 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 F. Rodante and M.G. Bonicelli, Thermochim. Acta, 66 (1983) 225.
8 F. Rodante and M.G. Bonicelli, Thermochim. Acta, 67 (1983) 257.
9 F. Rodante and M.G. Bonicelli, Thermochim. Acta, 70 (1983) 339.
10 F. Rodante and M.G. Bonicelli, Thermochim. Acta, 71 (1983) 187.
11 F. Rodante and M.G. Bonicelli, Thermochim. Acta, 73 (1984) 193.
12 F. Rodante and M.G. Bonicelli, Thermochim. Acta, 74 (1984) 207.
13 J.C. Synnot and J.N. Butler, J. Phys. Chem., 73 (1969) 1470.
14 E.M. Arnett, B. Chawla, L. Bell, M. Toagepera, W.J. Here and R.W. Taft, J. Am. Chem. Soc., 99 (1977) 5729.
15 W.R. Davidson, J. Sunner and P. Kebarle, J. Am. Chem. Soc., 101 (1979) 1675.
16 E.M. Arnett and B. Chawla, J. Am. Chem. Soc., 101 (1979) 7140.