

CALORIMETRIC BASICITY SCALE FOR SOME ANILINE AND PYRIDINE ISOMERS IN LIQUID PHASE. SUBSTITUENT, TAUTOMERIC, STERIC AND HYDROGEN BOND EFFECTS

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 10 February 1984)

ABSTRACT

A calorimetric basicity scale for six anilines and two pyridines in liquid phase is presented.

The substantial effects influencing the basicity order were found to be: (1) substituent effect; (2) steric effect; (3) tautomeric effect; (4) hydrogen bond effect.

This scale emphasizes the prevalence of each of the four effects considered at different solvent compositions.

INTRODUCTION

The chemical properties of compounds belonging to related series have been found to exhibit large differences in the gas phase compared to the corresponding properties in liquid phase. In the latter, the trends in acid–base reactivity usually differ widely from the more regular trends observed in the gas phase.

Some authors have carried out comprehensive reviews related to this subject [1–3]. A large number of effects are responsible for this difference. A substantial effect is represented by the features of the solvent in which the reactions take place.

Recently in our laboratory an extensive research on the basicity of some anilines and pyridines has been carried out [4–11].

The protonation of six anilines and two pyridines was studied mostly from the calorimetric point of view in water–dimethylsulfoxide (DMSO) mixtures ranging from pure water up to 0.8 mole fraction DMSO.

The choice of this medium was suggested by the very different behaviour of the two liquids towards the anions and the undissociated molecules.

The substantial effects influencing the aniline and pyridine isomers in this system were found to be: (1) substituent effect; (2) steric effect; (3) tautomeric effect; (4) hydrogen bond effect.

It is the aim of this paper to summarize the information on the mechanisms leading to the observed sequence of basicity for these compounds in this particular liquid phase.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO–water solutions, and the technique for obtaining the thermodynamic values for aniline and pyridine isomers have been described previously [4–11].

DISCUSSION

The compounds examined were: *meta*-, *para*-, *ortho*-hydroxy and -carboxy anilines and 2- and 3-carboxy pyridines.

An analysis follows of each effect on all the compounds studied.

Substituent effect

For the hydroxy substituted anilines there is a destabilizing interaction of two π -donor for the *para* derivative [4] because the substituents, (both π -donor) compete with each other for conjugation with the ring. For the *ortho* compound [5], the destabilizing interaction of the two π -donors may be partially reduced by the steric inhibition of resonance. For the *meta* derivative [6] a favourable interaction occurs, 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 *meta*-carboxy derivative [7], according to the Perturbation Molecular Theory, the interaction between the first group, NH_2 , and the second group, COOH , is dominated by the σ -electron-withdrawing effect of the latter, which destabilizes the benzene ring while for the *para*-carboxy aniline [8] (π -donor and -acceptor) the contrary is true.

In DMSO-rich solutions, where the primary steric effect is attenuated, the undissociated molecule of *ortho*-carboxy aniline [9] is stabilized by π -acceptor and -donor groups.

Finally, the carboxy group in the 3- [10] and 2-pyridine [11] greatly unactivates and thus destabilizes the aromatic system.

Steric effect

The hydroxy [5] and, particularly, the carboxy [9] groups in the *ortho* position decrease the strength of the basicity by virtue of the transformation of the nitrogen atom from its trivalent configuration in the free base to the bulkier tetrahedral configuration in the anilinium ion.

No steric effect was found for the 2-carboxy pyridine [11].

Tautomeric effect

A predominant zwitterion form in pure water, greatly solvated by water molecules, weakens the basicity strength of the *meta*-carboxy aniline [7]. In pure water there is a very unstable zwitterion form, for the *para*-aniline [8], tending to level the strength of *para* and *meta* derivatives.

By the difference in enthalpy of deprotonation it can be concluded that in DMSO–water solutions the zwitterion form of the *para* compound decreases more quickly than that of the *meta* form.

The primary steric effect which opposes the formation of the zwitterion of the *ortho* compound [9] in pure water, seems to be reduced in DMSO-rich solutions because of the diminished solvation of the carboxyl group.

It was also shown that the zwitterion of the 2-carboxy pyridine [11] interacts with the water molecules to a greater extent than the zwitterion of the 3-carboxy pyridine.

Hydrogen bond effect

Both solvents, H₂O and DMSO, are excellent hydrogen bond acceptors but only H₂O is also a good hydrogen bond donor. Therefore, in these mixtures one can distinguish the solvation of the ions (due to the hydrogen bond formed between the anilinium and pyridinium ions and the water and DMSO molecules) from that of the undissociated molecules (due to the hydrogen bond formed between the water and the neutral anilines and pyridines).

The hydrogen bond appears to be the key-factor in the solvation effect.

Therefore, with the exception of the *m*-hydroxyaniline (which was found to be ring protonated), the *m*-carboxy aniline and the *o*-carboxy aniline [9] (where the primary steric effect is the prevailing factor), all the compounds display a greater solvation for the ions mostly in the water-rich solutions. In these solutions the 2- [11] and 3-carboxy pyridines [10] display a stronger hydrogen bond than the anilines, this being ascribed to the enhanced positive charge density at the NH⁺ group.

On the basis of these effects, it is possible to give a satisfactory explanation of the calorimetric basicity scale found.

It is well-known that in the gas phase the substituted pyridines [9–10] are stronger bases than the substituted anilines.

In the DMSO–water solutions the order based on the protonation enthalpy is: *p*-OHphNH₂ > *o*-OHphNH₂ > *m*-OHphNH₂ > *m*-COOHphNH₂ > 3-COOHpy > *p*-COOHphNH₂ = *o*-COOHphNH₂ = 2-COOHpy.

By comparing *para*- [4] and *ortho*-hydroxy [5] anilines with *meta*-hydroxy aniline [6], it can be inferred that the *meta* derivative is the weakest base in the whole mole fraction range.

The solvation of the ions decreases according to the sequence *p*-NH₃⁺ > *o*-

$\text{NH}_3^+ > m\text{-NH}_3^+$, while for the undissociated molecule the order of transfer is $m\text{-NH}_2 > p\text{-NH}_2 > o\text{-NH}_2$. Thus, it is clear that the molecule solvation effect clearly prevails on the other effects for the *meta* derivative. For this derivative, it may be assumed that, particularly in DMSO-rich solutions, the benzene charge is so stabilized that an electrophilic attack of the proton on the ring, instead of on the nitrogen atom, occurs.

The primary steric effect is mostly responsible for the reduced basicity of the *ortho* compound with respect to the *para*. For the latter, the stronger basicity strength can clearly be related to the absence of a substantial effect.

The greater solvation of the *p*-carboxy aniline [8] (due to the π -resonance stabilization) is clearly the key-factor causing its relative weakness with respect to the *meta* carboxy and hydroxy anilines [7]. Therefore, the substituent effect prevails in this compound.

However, in pure water the tautomeric effect, due to a very unstable zwitterion form, tends to level the strength of the two carboxy anilines. The greater solvation of the ion and the undissociated molecule of the *para* derivative with respect to the *ortho* derivative (which displays a large primary steric effect) is the key-factor making the basicity strength of the *ortho* and *para* derivatives comparable.

In pure water the hydration of the carboxyl group enhances the primary steric effect and decreases the strength of the *ortho* [9] with respect to the *meta* compound [7].

It should also be noted that in the liquid phase the 3-carboxy pyridine is a weaker base than the *meta*-carboxy aniline but a stronger base than the *para*- and *ortho*-carboxy anilines [9].

In water-rich solutions the principal effect on the pyridine protonation is the substituent effect through hydrogen bonding of the pyridinium ion to water. It can be concluded, therefore, that the solute-solvent interactions are stronger effects than the σ -electron-withdrawing effect of the *meta*-carboxy aniline [7] but a weaker effect than the π -resonance substituent and primary steric effects of the *para* [8] and *ortho* [9] anilines, respectively.

The equivalent basicity strength of the *ortho*-carboxy aniline [9] and 2-carboxy pyridine [11] can be ascribed to the fact that the large primary steric effect of the *ortho*-carboxy aniline is balanced by the strong solute-solvent interactions of the 2-pyridine.

Finally, it must be stressed that the DMSO-water system is useful in supplying a calorimetric basicity scale which emphasizes the prevalence of one of the four effects considered at different mole fractions.

REFERENCES

- 1 A. Mucci, R. Domain and R.L. Benoit, *Can. J. Chem.*, 58 (1980) 953.
- 2 R.L. Benoit, M.J. Mackinnon and L. Bergeron, *Can. J. Chem.*, 58 (1981) 1501.

- 3 E.M. Arnett, R. Quirk and J. Burke, *J. Am. Chem. Soc.*, 92 (1970) 1260.
- 4 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 66 (1983) 225.
- 5 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 67 (1983) 257.
- 6 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 70 (1983) 339.
- 7 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 71 (1983) 187.
- 8 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 73 (1984) 193.
- 9 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 74 (1984) 207.
- 10 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 75 (1984) 341.
- 11 F. Rodante and M.G. Bonicelli, *Thermochim. Acta*, 77 (1984) 327.