UV-Spectroscopic Study of the Influence of Traces of Water on the Protolytic Equilibria of Substituted Pyridine N-Oxides in Aprotic Solvents

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Using a UV-spectrophotometric method, an attempt has been made to estimate quantitatively the influence of traces of water in aprotic solvents on the acidic-basic equilibria involving heterocyclic N-oxides. The N-oxides under study were pyridine N-oxide (PyO), 4-methoxy-pyridine N-oxide (4-MeOPyO), and 2-, 3-, and 4-picoline N-oxide (2-, 3-, and 4-PicO). For particular N-oxide the UV-spectra of acetonitrile solutions containing the free base and/or its simple or semiperchlorate have been recorded. To carry out the calculations various equilibrium models which include the protolytic equilibrium with water and basic species present in the solvent have been tested using the program STOICHIO which is based on nonlinear regression analysis. It turned out that apart from the acidic-basic dissociation of a protonated N-oxide and cationic homoconjugation (the equilibria which are usually considered in such systems) it is absolutely necessary to take into account the protolytic equilibrium between the cationic acid and water present as impurity. Implications concerning investigations of other equilibrium systems in aprotic solvents and, in particular, the quality of the acidity constants for the calibration agents used in potentiometry are discussed.

KEY WORDS: Protolytic equilibria; aprotic solvents; traces of water; equilibrium constants; heterocyclic N-oxides.

1. Introduction

Studies of the protolytic equilibria of organic compounds give such important physicochemical parameters as pK_a values or the association constants of hydrogen bonded complexes.⁽¹⁻³⁾ They are carried out mainly in aqueous solutions.⁽⁴⁻⁶⁾ However, the equilibria

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range for protons in water is much smaller than in nonaqueous solutions, due to the high polarity and the considerable ability for proton exchange of this solvent. The first feature makes the dissociation of ionic pairs favorable, while the second one implies that the homo- and heteroconjugated species are not likely to be formed. Therefore, the only equilibrium which can be considered in aqueous solutions is in fact the proton exchange between water and the species studied.

To obtain more information concerning any given equilibria, aprotic solvents must be used. It must be kept in mind, however, that if a solvent of a very low polarity is chosen, the possible equilibria are complex due to the formation of associates of varying degrees of complexity. Polar aprotic solvent, such as acetonitrile, propylene carbonate, *etc.*, are the most suitable for this work. In particular, a great part of our studies of the proton - N-oxide equilibria was performed in acetonitrile, as this aprotic solvent has moderate polarity.

Apart from the equilibria of interest, one must not forget that species present as impurities can also take part in the acidic-basic equilibrium system. In the case of acetonitrile it would seem that N-bases like ammonia which is present owing to hydrolysis should first be considered.⁽⁷⁻⁸⁾ However, while samples of commercial acetonitrile contain 5×10^{-6} to $5\times10^{-5}M$ of basic impurities (*i.e.*, ammonia and alkylamines),⁽⁹⁾ the special purification procedures developed by Coetzee⁽⁷⁻¹⁰⁾ and others,⁽¹¹⁻¹³⁾ reduce the content of ammonia below $10^{-6}M$, *i.e.*, usually well below the range of the concentrations of the species under study. On the other hand, water which is always present even in the most rigorously dried solvent, also can take part in the equilibria. In the case of acetonitrile even the application of the purification procedures mentioned above reduces the concentration of water not lower than 16 ppm ($10^{-3}M$).⁽¹¹⁻¹³⁾

This small amount of water can be neglected when amphiprotic solvents are considered which are able to exchange the proton themselves. In contrast, water as an additional acidic-basic agent can change qualitatively the equilibrium scheme in an aprotic solvent. Using techniques such as potentiometry usually requires comparatively high concentrations of the species of interest (*i.e.*, 5×10^{-4} to $10^{-2}M$) as compared to other instrumental techniques such as spectrophotometry. Consequently, the presence of water does not significantly influence the results owing to the difference between the basicity of water and the compounds investigated. On the other hand, UV-spectrophotometry is also frequently used to study the acidic-basic equilibria in aprotic solvents and is a technique which gives the most visual and direct picture

of the species present in a system. Due to high molar absorption coefficients of the species derived from the organic acids and bases, the range of concentrations is several orders of magnitude smaller than that applied in potentiometry. Spectrophotometry is, moreover, very frequently used to determine the acidity constants of the agents applied to calibrate electrodes for potentiometric measurements. In this case, it is important to note that water is a base whose strength is comparable with the basicity of the species of interest (for example the picrate anion). Omitting the equilibria which involve water must thus lead to incorrect values of other equilibrium constants and even to a false model of other equilibria. A good illustration of this observation is the "time evolution" of the pK_a value of picric acid in acetonitrile: 4.0,⁽¹⁴⁾ 5.6,⁽¹⁵⁾ 6.6,⁽¹⁶⁾ 8.9⁽⁸⁾ and $11.0^{(17)}$ Such "increase" in pK_a can be explained by the fact that gradually improved methods of purification of acetonitrile were applied in the studies mentioned above which made possible the more and more accurately purified solvent to be obtained.

Although there is a great number of papers which deal with the protolytic equilibria in aprotic solvents, few papers published till now take into account the possible presence of water in a quantitative way.⁽¹⁸⁻²⁰⁾ For the reasons given above, we thought it worthwhile to make an attempt to estimate quantitatively the influence of traces of water on the protolytic equilibria in the aprotic solvent acetonitrile.

As model compounds we have chosen pyridine N-oxide and its 4methoxy-, 2-, 3-, and 4-methyl substituted derivatives. These compounds differ sufficiently in their acidic-basic properties and, moreover, the equilibrium scheme is complex enough, owing to the formation of homocomplexed cations [see the equilibria in Eqs. (1-4)].

It is well-known⁽²¹⁻²⁴⁾ that heterocyclic amine N-oxides form two types of solid salts with perchloric acid: simple perchlorates which contain simple cations of protonated N-oxides, BH⁺, and semiperchlorates (the basic salts) which contain homoconjuated cations, BHB⁺ (B stands for N-oxide molecule). Therefore, for the sources of protonated forms of N-oxides we used both types of perchlorates. The perchlorate anion is particularly recommended owing to its low ability to affect cationanion association as well as anionic homoconjugation. In acetonitrile solutions containing both protonated and nonprotonated forms of Noxides the following equilibria are usually considered

$$BH^+ + ClO_4^- = BH^+ClO_4^-$$
(1)

$$BHB^{+} + ClO_{4}^{-} = BHB^{+}ClO_{4}^{-}$$
(2)

$$BH^+ = B + H^+ \tag{3}$$

$$BH^+ + B = BHB^+ \tag{4}$$

In this scheme the first two equilibria are ionic association leading to simple (1) and semiperchlorate (2), respectively. Taking into account the published data for amines,^(7,25) it can be assumed that these equilibria are almost completely shifted to the left in the concentrations range used. Conductometric studies⁽²⁶⁻²⁸⁾ confirm this assumption. Equilibrium (3) is simply a dissociation of acid conjugated to Noxide, while equilibrium (4) is homoconjugation between free base and its protonated form.

2. Experimental

Pyridine N-oxide was synthesized and purified by the method of Ochiai.⁽²⁹⁾ 2-, 3-, and 4-picoline N-oxides (Fluka AG) were purified as described previously.⁽³⁰⁾ 4-Methoxy pyridine N-oxide (Aldrich C.O.) has been crystallized twice from acetone. Simple perchlorates of pyridine N-oxide, 2-, 3-, and 4-picoline N-oxide, and 4-methoxy-pyridine N-oxide were synthesized as described previously.^(30,31)

Semiperchlorates^(30,31) of pyridine N-oxide, 2-, 3-, and 4-picoline and 4-methoxypyridine N-oxide were obtained as described previously. Elementary analysis has been carried out for all the compounds studied. The results are in good agreement with the calculated compositions (*i.e.*, the errors were less than 0.05%).

Spectrophotometric grade acetonitrile (Fluka AG) was kept over 4Å molecular sieves and subsequently purified using the modified Coetzee procedure.⁽¹⁰⁾ The solvent was dried with CaH₂ (10 g-dm⁻³) for 48 h, decanted, fractionally distilled from P_2O_5 (3 g-dm⁻³), refluxed over calcium hydride (5 g-dm⁻³) for several hours and fractionally distilled (very slowly). The purified solvent has a specific conductivity of 4×10⁻⁸ S-cm⁻¹ and its UV-spectrum shows no significant absorption in the visible region.

The UV-spectrum of acetonitrile showed no significant absorption in the region under study. Absorption spectra were recorded on a SPECORD M 40 spectrophotometer equipped with a thermostated cell compartment at 25°C using cells of 0.5 and 1.0 cm length.

3. Results and Discussion

In our previous papers⁽³⁰⁻³²⁾ we described the spectral characteristics of substituted pyridine N-oxides, as well as their simple and



Fig. 1. The UV-spectra of solutions of 4-picoline N-oxide perchlorate in acetonitrile. The concentrations of the subsequent solutions are: 1, 9.7×10^{-6} ; 2, 2.02×10^{-5} ; 3, 4.05×10^{-5} ; 4, 6.07×10^{-5} ; 5, 7.86×10^{-5} ; 6, 1.01×10^{-4} ; and 7, $2.04 \times 10^{-4}M$.



Fig. 2. The UV-spectra of solutions of 4-picoline N-oxide semiperchlorate in acetonitrile. The concentrations are: 1, 8.72×10^{-5} ; 2, 1.0×10^{-4} ; 3, 1.41×10^{-4} ; 4, 2.0×10^{-4} ; 5, 2.67×10^{-4} ; and 6, $3.21 \times 10^{-4}M$.

homoconjugated proton complexes and compared them with the results of theoretical calculations. As has already been mentioned, the main aim of our present study was to determine the influence of water on the equilibrium scheme of the solutions of substituted pyridine N-oxides and their proton complexes in acetonitrile. Moreover, taking into account that it is not only one external base present in acetonitrile, we have also tried to evaluate the role of basic impurities.

We recorded the absorption spectra of three series of solutions. The first and the second consisted of solutions of variable concentration



Fig. 3. The UV-spectra of solutions of 4-picoline N-oxide perchlorate ($C = 4.09 \times 10^{-4}M$) in the presence of 4-picoline N-oxide in acetonitrile. The concentrations of 4-picoline N-oxide are: 1, 1.55×10^{-4} ; 2, 2.24×10^{-4} ; 3, 2.88×10^{-4} ; 4, 3.48×10^{-4} ; and 5, $4.09 \times 10^{-4}M$.

of simple and semiperchlorate, respectively. Solutions of the third series contained simple perchlorate in constant concentration and a gradually increasing amount of free base. For each system under study we took absorbances measured at five or six different wavelengths chosen to cover the regions of absorption of all the possible individuals present in the system.

Typical series of absorption spectra, for the 4-PicO system as an example, are in Figs. 1-3. Calculations were carried out using the program STOICHIO,⁽³³⁾ which is based on nonlinear confluence analysis. This means that not only absorbances, but also the characteristics of the composition of the solutions can be treated as quantities contributing to error.

In the case of spectrophotometry the program determines the parameters by minimizing the sum of squares given by (5).

$$\phi = \sum_{i} \left[\sum_{j} W_{j}^{A} (\hat{A}_{ij} - A(\overline{P}, \overline{K} \,\overline{\varepsilon}_{j}, \overline{\omega}_{i})^{2} + \sum_{k} W_{k}^{\omega} (\hat{\omega}_{ik} - \omega_{ik})^{2} \right]$$
(5)

where A_{ij} is the value of absorbance measured for i^{th} solution at j^{th} wavelength, ω_{ij} is j^{th} composition of the i^{th} solution (for example the mass of the reagent, *etc.*), $\overline{\omega}_i = (\omega_{i1}, \omega_{i2}, \ldots, \omega_{i,n(i)})$ is the vector of the characteristics of the composition of i^{th} solution (*i.e.*, the mass of a solid reagent, concentration, *etc.*). ^ denotes the corresponding experimental value, \overline{P} is the vector of the stoichiometric coefficients to be determined (if any), \overline{K} is the vector of the equilibrium constants to be determined, ε_{ij}



Fig. 4. comparison of theoretical (×) and experiental (•) values of absorbances for proton, 4-PicO system for $\lambda = 248$ nm: a) absorbance vs. the concentration of BH⁺ for the first series of solutions in the case of the simplest model; b) absorbance vs. the concentration of BH⁺ for the first series of solutions containing only perchlorate in the case of the model containing the proton exchange with water; c) absorbance vs. the concentration of BHB⁺ for the series of solutions containing BHB⁺ only and vs. the concentrations of B for the solutions containing BH⁺ and B, respectively. The model containing the proton exchange with water has been used in the calculations.

is the molar absorption coefficient of j^{th} species at the i^{th} wavelength, $\overline{\varepsilon}_i = \varepsilon_{i1}, \varepsilon_{i2}, \ldots, \varepsilon_{in}$) is the vector of the absorption coefficients of the species for i^{th} wavelength, *n* being the number of species, W_j^{A} is the statistical weight of absorbances of j^{th} wavelength, W_j^{∞} is the statistical weight of the composition characteristics of the j^{th} group.

In all the cases considered in this paper the stoichiometric coefficients were not determined directly due to the fact that we had few acceptable equilibrium models to choose from. The second reason was the great number of parameters to be determined (*i.e.*, the molar absorption coefficients and the equilibrium constants).

When carrying out the regression analysis, it is essential to estimate correctly the ratio of the standard deviations of the quantities considered. In our calculations we estimated the standard deviation in absorbance to be 0.02, taking into account the precision of measurements. The total concentrations of species other than impurities were considered as error free.

As the protonated forms of all the N-oxides are weak acids, their acidity constants have no influence on the results of the absorption measurements, provided that simple acid-base dissociation is considered. Therefore we have taken the respective values from potentiometric measurements.⁽²⁶⁻²⁸⁾



Fig. 5. The UV-spectra of solutions of 4-picoline N-oxide perchlorate ($C = 5.35 \times 10^{-5} M$) in acetonitrile in the presence of added water. The concentrations of water are: 1, 2.78×10^{-3} ; 2, 5.55×10^{-3} ; 3, 8.33×10^{-3} ; and 4, $1.11 \times 10^{-2} M$.

The simplest equilibrium model tested consisted of acidic-basic dissociation of a protonated N-oxide and cationic homoconjugation (equilibrium 3 and 4, respectively). It can be observed, however, that such a model cannot explain the concentration dependence of the spectra of 1:1 perchlorates. Consider the case of 4-PicO (Fig. 1), for which we performed detailed sample calculations. In the case of the least concentrations the spectrum resembles that of 4-PicO, while by increasing the concentration its characteristic redox band at 276 nm becomes hidden under the increased band of the cation (see Ref. 32 for detailed spectral characteristics of substituted pyridine N-oxides and their proton complexes). It is improbable that the free N-oxide appears as a result of the acid-base dissociation of the cationic acid in acetonitrile, as the acidity constant is too low (of order $10^{-11(26-28)}$) to provide sufficient free base even for the lowest concentrations considered. The results of STOICHIO calculations fully confirm this observation. The agreement between theory and experiment is poor, especially in the case of dilute solutions of 1:1 perchlorate (see Fig. 4a). This is consistent with the comments in the Introduction, as water can be expected to act as a proton acceptor here. Thus, to improve our model we first added the equilibrium between water and protonated Noxide which was in fact including in the equilibrium scheme the dissociation of hydronic cation

$$H_3O_{(s)}^{\dagger} = H_2O_{(s)} + H_{(s)}^{\dagger}$$
 (6)

To get a quantitative confirmation, we have recorded the spectra of 4-picoline N-oxide perchlorate solutions with gradually increased amounts of water (Fig. 5). As shown, the band for the free base is en-

N-Oxide	Results of Calog K_{HOMO}	lculations pK _{H3O} +	Potentiometr log <i>K</i> _{HOMO}	ric Data pK _a	σ _A
4-MeOPyO	3.74(0.15)	8.34(0.92)	4.02(0.01)	12.21(0.01)	0.07
4-PicO	3.93(0.14)	7.98(0.71)	3.57(0.01)	11.00(0.01)	0.04
3-PicO	4.27(0.66)	7.8(1.0)	3.35(0.01)	10.31(0.01)	0.07
2-PicO	4.15(0.72)	7.81(0.34)	3.25(0.01)	10.23(0.01)	0.04
PyO	4.06(0.65)	7.78(0.43)	3.22(0.01)	10.04(0.01)	0.02

Table I. Results of Calculations for Proton - N-Oxide Systems

 by Including the Protolytic Equilibrium with Water

 ${}^{a}\sigma_{A}$ is the standard deviation in absorbance averaged over all the wavelengths.

hanced as the concentration of water increases. This indicates that, under the conditions applied, water is a strong enough base to extract a proton from the acid conjugated to N-oxide. Because the exact concentration of water was unknown, we assumed an average concentration of $0.001M^{(11-13)}$ with a standard deviation of 0.0008M and treated the total concentration of water in each solution as a quantity subject to error. As shown in Fig. 4b for 4-PicO as an example, the agreement between theoretical and experimental values of absorbance is improved with respect to the first model, especially for the lowest concentrations of BH⁺. This can serve as a confirmation of our extended model. In Fig. 4c we can see the agreement between theory and experiment for the B and BHB⁺ containing series of solutions. The results of calculations for all the compounds studied are in Table I.

The next step was to evaluate the role of ammonia and other basic species present in acetonitrile. The assumption that the effect of impurities is entirely due to the presence of ammonia has proved to be false. First, Fig. 5 gives a direct evidence that adding water in concentrations of order of $10^{-3}M$ apparently increases the ratio [B]/[BH⁺]. Second, replacing equilibrium (6) with the acid dissociation of the NH[±] cation and assuming the analytical concentration of ammonia even as high as $10^{-5}M$ (the upper limit of its amount in purified acetonitrile) gave a pK_a for the ammonium ion of 13.4, *i.e.* far from the value of 16.5 reported by Coetzee.^(7,34) Our next attempt was thus including both water and ammonia species in the equilibrium model. However, this did not substantially improve the fit to the experimental data and, moreover, the least-squares did not converge when both acidity constants were determined simultaneously. This means that it is excessive to include more than one additional base in the system, though the presence of ammonia cannot be unambiguously rejected. If this species is present in our system, the pK_a value of H_3O^+ determined should rather be regarded as an "overall constant" referring to all the potential bases present in acetonitrile as impurities. On the other hand, as water definitely prevails at significant concentration, this constant is most probably close to that for H_3O^+ .

The pK_a value of H_3O^+ in acetonitrile has been determined previously by Kolthoff et al.^(18,19) by combined spectrophotometric and potentiometric methods and found to be of about 2.0. However, in processing their results of the potentiometric measurements the authors used the pK_a of indicators fixed on an underestimated value of the picric acid pK_a of 8.9,⁽⁸⁾ while the correct value is 11.0.⁽¹⁷⁾ We can conclude that their value should in fact be about 4.0. In view of this, our value of about 8 seems too high, but can clearly be overestimated due to the influence of ammonia. On the other hand, from the comparison of the water pK_a for H_3O^+ (about -1.7) and those of acids conjugated to the least basic N-oxides: 4-NO₂PyO (-1.7)⁽³⁵⁾ and 4-CNPyO (-1.1)⁽³⁶⁾ and from the assumption that the relations between the pK_a values in various solvents are conserved to some extent, it can be inferred that the acetonitrile pK_a value of H₃O⁺ should also be comparable to that of the cationic acids of the N-oxides mentioned which are 5.7 and 6.3, respectively.⁽²⁶⁾ These members are closer to our value.

Looking for the next equilibria which would have some influence on the results, we considered the possibility of hydration of N-oxides or their conjugated acids given by

$$B + H_2 O = B H_2 O \tag{7}$$

$$BH^+ + H_2O = BH_3O^+ \tag{8}$$

To get some preliminary information on the hydration of free bases we have recorded the spectra of acetonitrile solutions of 4-picoline N-oxide with various amounts of water. The spectra are shown in Fig. 6. As can be seen they depend on the concentration of water. From these data we calculated the equilibrium constant of equilibrium (7) of 0.96 with standard deviation of 0.24. This indicates that the hydration of the free base is negligible for the concentration of water and free base of about 0.001*M*, concentrations of which can be found in our main series of solutions. Nevertheless, we have tested such a model for picoline N-oxides. However, the agreement between theory and experiment has not improved, and the parameters have become indeterminable. Including equilibrium (8) gives a similar result.



Fig. 6. The UV-spectra of solutions of 4-picoline N-oxide ($C = 7.04 \times 10^{-5} M$) in acetonitrile in the presence of added water. The concentrations of water are: 1, 2.78×10^{-3} ; 2, 5.55×10^{-3} ; 3, 8.33×10^{-3} ; 4, 1.11×10^{-2} ; and 5, $1.67 \times 10^{-2} M$.

From our considerations it can be concluded that the most probable model of equilibria of dilute solutions containing N-oxide and its conjugated acid is the one composed of equilibrium (3), (4), and (6). For enough basic N-oxides, however, dissociation of BH⁺ is not much advanced and therefore we should take into account the proton exchange between BH⁺ and H₂O, which is a combination of (3) and (6) instead of those two equilibria separately

$$BH^{+} + H_{2}O = B + H_{3}O^{+}$$
(9)

The results of our investigation enable one to conclude that it is absolutely necessary to consider the protolytic equilibria with water present as impurity as far as dilute solutions of weak acidic-basic systems in aprotic solvents are concerned, if one wants to get a correct picture of the equilibria of interest. Obviously, the necessary extension of the equilibrium model must involve diminishing the accuracy of the equilibrium parameters determined.

Another important point is that omitting the influence of water on the equilibria leads to false values of acidity constants of reagents used in potentiometry and, consequently, to false values of equilibrium constants obtained with the use of this method.

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