

Experimental Studies on the UV-Spectra of Several Substituted Pyridine N-Oxides and Conjugated Cationic Acids in Acetonitrile

Lech Chmurzynski

Department of Chemistry, University of Gdansk, Sobieskiego 18, 80-952 Gdansk, Poland
Tel.: +48-58-415271; Fax: +48-58-410357 (lesiu@sun1.chem.univ.gda.pl)

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Abstract: The ultraviolet spectra of heterocyclic N-oxides of pyridine N-oxide series and the conjugated cationic acids (simple cations of protonated N-oxides) in acetonitrile as the representative of polar aprotic solvents, were determined. The obtained spectra of N-oxides studied (mainly tri-substituted pyridine N-oxides) and their cations obtained by the protonation of free N-oxides by the excess of perchloric acid, have been collected and discussed. Taking into account the spectroscopic results, a scheme of acid-base equilibria in polar aprotic solvents has been discussed. The influence of the traces of water on acid-base equilibria in non-aqueous media has been stressed.

Keywords: UV spectra, pyridine N-oxides, cationic acids, perchloric acid, acetonitrile.

Introduction

It is well known [1-5] that the derivatives of pyridine N-oxide in polar aprotic solvents such as acetonitrile, in addition to proton-exchange equilibria with the solvent leading to the formation of simple BH^+ cations, Eq. (1), also form hydrogen-bonded complexes containing two molecules of base and one proton; the so-called cationic homocomplexes BHB^+ , Eq. (2), and heterocomplexes BHB_1^+ , where B and B_1 stand for N-oxide molecules. Moreover, hetero-cyclic N-oxides form two types of salts with strong inorganic acids (e.g. perchloric acid) in the solid state *i.e.* simple salts (perchlorates) containing cations of protonated N-oxides, BH^+ , and basic salts (semiperchlorates) which contain homocomplex cations,

BHB^+ [6,7]. The hydrogen bond in homocomplex cation is exceptionally short, as revealed by X-ray crystallography [8], which results in its exceptionally high strength, leading to the presence of a considerable amount of homoconjugated cations even in solvents with relatively high dielectric constants [1]. For this reason, simple and complex perchlorates seem to be good sources of simple and homocomplex cations formed by substituted pyridine N-oxides in solutions. However, due to the presence of acid-base equilibria (acid dissociation and, especially, cationic homoconjugation) in non-aqueous media (e.g. acetonitrile), among simple BH^+ and complex cations, the molecules of free N-oxide are present at equilibrium [1,9]. Consequently, the recorded spectra of the solutions of salts studied do not represent the spectra of species considered,

i.e. the simple and complex cations of heterocyclic N-oxides. To shift the equilibria of the acid dissociation of protonated N-oxides (B denotes N-oxide, BH⁺ simple cation, BHB⁺ homoconjugated cation and SH solvent):



towards cationic acids and the equilibria of cationic homoconjugation:



towards homoconjugated cations, concentrations of respective salts as high as possible have to be used.

However, due to the high values of absorption coefficients, the concentrations of solution used are limited. Furthermore, the spectra of homoconjugated cations can be observed spectrophotometrically for the most basic N-oxides only. Moreover, some substituted (especially di- and tri-substituted) pyridine N-oxides do not form complex salts in solid state due to steric hindrances (which was the case for N-oxides studied).

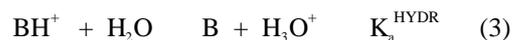
Less complicated is the situation in the case of simple salts. For respectively basic N-oxides the equilibrium of the acidic dissociation of protonated N-oxides, Eq. (1), is almost completely shifted towards cationic acids. However, for the N-oxides of medium and low basicity whose protonated forms are relatively strong acids in non-aqueous solutions, the concentrations of free bases are respectively high at the salt concentration range used in spectrophotometrical measurements. Therefore, to avoid such situation and obtain the spectra of the protonated N-oxides of medium and low basicity, the 0.1 M solution of perchloric acid in acetonitrile has to be used as the protonating agent. To obtain comparable results, the solutions containing N-oxides studied and the excess of perchloric acid instead of simple salts were also applied in the case N-oxides of sufficient basicity. The use of perchloric acid is particularly recommended since it is virtually completely dissociated [9] in acetonitrile solutions and the perchlorate anion has low ability to affect cation-anion association. Moreover, the perchlorate anion shows no tendency towards anionic homoconjugation [10].

The main aim of this study was to determine the UV-spectral characteristic of heterocyclic N-oxides of pyridine N-oxide series and their conjugated cations (simple cations obtained by protonation of N-oxides studied) in acetonitrile as the representative of polar aprotic solvents [11-12]. The main series of N-oxides studied were tri-substituted pyridine N-oxide derivatives: 2,6-dimethyl-4-nitropyridine N-oxide (2,6Me₂4NO₂PyO), **1**, 2,6-dimethyl-4-chloropyridine N-oxide (2,6Me₂4ClPyO), **2**, 2,4,6-trimethylpyridine N-oxide (2,4,6Me₃PyO), **3**, and 2,6-dimethyl-4-methoxypyridine N-oxide (2,6Me₂4MeOPyO), **4**, as well as mono-substituted pyridine N-oxide with respectively

long chain-substituent in position 4, namely 4-undecylpyridine N-oxide (4C₁₁H₂₃PyO), **5**.

Results and Discussion

In the first step of this study the acetonitrile spectra for the simple perchlorates of N-oxides studied were recorded and compared with those obtained in acetonitrile solutions containing respective N-oxide and the excess of perchloric acid. It turned out that the spectral characteristics obtained for the acetonitrile solutions of simple cations in two various ways were different. Even in the cases of most basic N-oxides studied, the bands which are characteristic for free N-oxides were observed in the spectra of simple perchlorates. Since it is not possible that the free N-oxides appear in solutions studied in the case of alkyl-substituted pyridine N-oxides such as 2,6Me₂4MeOPyO, 2,4,6Me₃PyO and 4C₁₁H₂₃PyO (for which the acidity constant in acetonitrile is expected to be of the order of that characteristic for pyridine N-oxide *i.e.* 10⁻¹¹ and even lower, being too low to provide sufficient amounts of N-oxide even for the lowest concentrations studied) the presence of the N-oxide bands can be explained in terms of the equilibrium between protonated N-oxides and water present in the non-aqueous solvent:



in which water acts as a proton acceptor. This observation confirms our earlier finding regarding the role of the equilibrium of the dissociation of the hydronic cation in non-aqueous solutions [13]. Moreover, it affords another reason for recording the spectra of simple cations BH⁺ in the solutions containing free N-oxides studied and the large excess of perchloric acid to obtain the best approximation of the spectra of protonated N-oxides.

The spectral data for substituted pyridine N-oxides studied are shown in Table 2. In general, the spectra of tri-substituted pyridine N-oxides have the same spectral structure as those of pyridine N-oxide and mono-substituted derivatives which depends on the type of substituent [9,14]. In the case of pyridine N-oxide it has been found [15] that UV spectrum of the free base consists of two intensive bands of which the long-wave band is of the ^{-*} type [16] (charge transfer from the oxygen atom of N-oxide to the ring) and short-wave band is the same type as ¹L_b pyridine band. It is well-known that passing from vacuum to the solvents of increasing polarity results in the blue-shifting of the long-wave CT bands of pyridine N-oxide [17] and its mono-substituted derivatives [18]. This rule is performed for many aprotic solvents. For example, the maximum absorption position of the long-wave band of pyridine N-oxide being 289 nm in the vacuum [15], 282 nm in non-polar aprotic solvents as n-hexane [17] and n-heptane [19] shifts to 275 nm in the

polar aprotic solvents as acetonitrile [15]. Moreover, in the case of polar amphiprotic solvents such as methanol [20], ethanol [21] and water [22], the band considered shifts further towards shorter waves up to 264.5, 263 and 254 nm, respectively. However, the causes of both above-mentioned short-wave shifts are different. In the case of aprotic solvents, the basic factors causing the short-wave

shifts are electrostatic interactions of dipole-dipole type and dispersion forces [17,23]. As far as the amphiprotic solvents are concerned the blue shift is caused by the phenomenon of forming the hydrogen bond between N-oxide and solvent molecules [17,24]. The value of the blue shift depends on "hydrogen bonding power" (which is proportional to the solvent and hydrogen bond polarity).

Table 1. Structures, full names, abbreviations and numbers used in text for N-oxides studied.

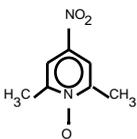
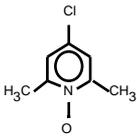
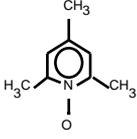
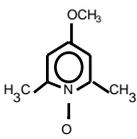
	2,6-dimethyl-4-nitropyridine N-oxide	2,6Me ₂ 4NO ₂ PyO	1
	2,6-dimethyl-4-chloropyridine N-oxide	2,6Me ₂ 4ClPyO	2
	2,4,6-trimethylpyridine N-oxide	2,4,6Me ₃ PyO	3
	2,6-dimethyl-4-methoxypyridine N-oxide	2,6Me ₂ 4MeOPyO	4
	4-undecylpyridine N-oxide	4C ₁₁ H ₂₃ PyO	5

Table 2. UV spectral characteristics of free and protonated substituted pyridine N-oxides.

N-oxide	Concentration [M]	λ_{max} [nm]	$\epsilon_{10^{-4}}$ [mol ⁻¹ cm ⁻¹ dm ³]
2,6Me ₂ 4NO ₂ PyO	2.531 10 ⁻⁵	245.0 349.5	7.11 14.23
2,6Me ₂ 4NO ₂ PyO 1 M HClO ₄	7.125 10 ⁻⁵	236.0 299.5	8.42 4.70
4C ₁₁ H ₂₃ PyO	1.770 10 ⁻⁵	214.0 218.0 278.5	14.69 13.56 16.38
4C ₁₁ H ₂₃ PyO 1 M HClO ₄	5.228 10 ⁻⁵	230.4 255.0	12.60 3.06
2,6Me ₂ 4ClPyO	2.753 10 ⁻⁵	214.8 224.0 276.0	21.09 21.82 16.00
2,6Me ₂ 4ClPyO 1M HClO ₄	7.981 10 ⁻⁵	232.5 269.5 276.0	10.60 6.51 6.29
2,4,6Me ₃ PyO	2.970 10 ⁻⁵	221.0 270.0	19.87 10.77
2,4,6Me ₃ PyO 1 M HClO ₄	9.610 10 ⁻⁵	217.0 270.6	5.20 6.25
2,6Me ₂ 4MeOPyO	2.831 10 ⁻⁵	213.5 272.0	23.67 14.13
2,6Me ₂ 4MeOPyO 1 M HClO ₄	2.874 10 ⁻⁵	233.5 315.5	41.75 4.17

In the case of the protonated forms of pyridine N-oxide the inversion of bands due to protonation takes place [15]. The long-wave band shifts towards the shorter waves, while the 1L_b band towards the longer ones. Moreover, a significant decrease in the intensity of bands caused by protonation is observed [15]. The phenomena found experimentally have been confirmed by the results of CNDO/S-CI semi-empirical calculations [15]. Moreover, such inversion of bands was observed in an other aprotic solvent, sulfolane [25]. However, in non-aqueous solvents this can only be caused by such very strong acids as perchloric [15], methansulfonic [25] and trimethansulfonic [25]. On the contrary, acetic acid and its halogene-substituted derivatives are not sufficiently strong proton-donor agents to cause inversion the bands of pyridine N-oxide [24].

The above described observations concerning the influence of solvation on the spectra of pyridine N-oxide and its conjugated cations have been confirmed [26] by the results of the CNDO/S-CI-nPDQ [27] semi-empirical studies on the solvation effect by acetonitrile molecules on the UV-spectra of species studied. It has been found [26] that all the bands of all the above-mentioned species considered are blue shifted on solvation. The most significant, however, is the shift of the long-wave - * band of pyridine N-oxide.

In the case of N-oxides which contain conjugated substituents (e.g. methoxy-, N,N'-dimethylamine- and nitro- groups) the situation is much more complex and depends on the substituent. Generally, in the spectra of free N-oxides the intense long-wave band has a redox character (it is worth noting that the substituent also contributes to this charge transfer [14]) and is strongly red-shifted, owing to conjugation. The next intense band, the short-wave one, mainly has the character of the 1L_b pyridine band, being blue-shifted with respect to pyridine. However, due to conjugation it is not as strongly blue-shifted as for non-conjugated N-oxides. For protonated conjugated N-oxides the same intense bands are observed as for protonated non-conjugated N-oxides. However, the redox band is not so largely blue-shifted and the 1L_b band remains on shorter wavelengths. Consequently, in the case of a strong conjugation effect an inverse of band due to protonation is not observed [14]. Moreover, for protonated N-oxides which contain chromophore groups the bands characteristic of these chromophores can be distinguished [9].

In the case of the tri-substituted N-oxides studied which cannot exert the mesomeric effect, i.e. $4C_{11}H_{23}PyO$ and $2,4,6Me_3PyO$, the longest intensive band is (as in the case of pyridine N-oxide) of the * type and has a redox character (mainly charge-transfer from oxygen to the ring). The second one, the short-wave band, is the same as the 1L_b transition band of pyridine. Consequently, the inversion of bands and a significant decrease in the intensity of all

bands considered is observed. Summing up, the N-oxides considered and their protonated forms have the same spectral characteristic as pyridine N-oxide (as well as its mono-substituted non-conjugated derivatives) and conjugated cationic acids.

For free $2,6Me_24ClPyO$ and $2,6Me_24MeOPyO$ the conjugation effect is not evident even for long-wave bands, their positions (276 and 272 nm, respectively) being almost the same as for pyridine N-oxide (275 nm). However, for protonated $2,6Me_24ClPyO$ the conjugation effect can be observed for the 1L_b (long-wave) band which is not as strongly blue-shifted (with respect to pyridine) as in the case of non-conjugated N-oxides. A stronger conjugation effect can be observed in the case of protonated $2,6Me_24MeOPyO$ for which the 1L_b band is strongly red-shifted as compared with non-conjugated N-oxides, its position being at 315.5 nm.

In the case of $2,6Me_24NO_2PyO$ the conjugation effect is very strong and therefore the redox band is shifted as far as 349.5 nm. From the positions of the band for protonated N-oxide it can be concluded that, as in the case of 4-nitropyridine N-oxide [9], the protonation is not able, due to strong conjugation effect, to reverse the sequence of the bands of N-oxide considered.

Summing up, it has been found that the following tri-substituted N-oxides: 4-undecylpyridine N-oxide and 2,4,6-trimethylpyridine N-oxide, as well as their protonated forms have the same UV-spectral structure as pyridine N-oxide and conjugated cationic acid. In the case of the three remaining N-oxides, i.e. 2,6-dimethyl-4-chloropyridine N-oxide, 2,6-dimethyl-4-methoxypyridine N-oxide and 2,6-dimethyl-4-nitropyridine N-oxide, as well as the cationic acids conjugated with them, the influence of the conjugation on their UV-spectral characteristics has been observed, the strongest one being in the case of $2,6Me_24NO_2PyO$.

Moreover, it turned out that basing on the UV-spectral data in acetonitrile the scheme of the fundamental acidic-basic equilibria of substituted pyridine N-oxides in polar aprotic solvents has been extended. To explain the experimentally observed sequence of the bands of the species studied, apart from the acidic dissociation of protonated N-oxide (1) and cationic homoconjugation (2) (the equilibria which are usually considered in such systems) it is necessary to accept the protolytic equilibrium (3) between the cationic acid and traces of water present in the non-aqueous solvent as impurity. On the basis of pKa and protolytic reaction constants determined it was found that the protolytic equilibria with traces of water have to be considered, as far as dilute solutions of weak acid-base systems in aprotic solvents are concerned [13]. Omitting the influence of water on the fundamental equilibria leads to false values of equilibrium constants.

It is worth mentioning that on the other hand, the influence of the reactions of the hydration of free (4) and protonated N-oxides (5):



on acidic-basic equilibria considered was found to be negligible [13].

Experimental Section

Chemicals

Compounds

The majority of the tri-substituted pyridine N-oxides studied, namely 2,6Me₂4NO₂PyO [29], 2,6Me₂4ClPyO [30], 2,4,6Me₃PyO [31] and 4C₁₁H₂₃PyO [32] were synthesized according to standard Ochiai method [33] or its modifications [29-32]. Melting points for the 2,6Me₂4NO₂PyO and 2,6Me₂4ClPyO crystallized from acetone were 437 K (lit. 436-437 [33]) and 370 K (lit. 374 K [30]), respectively, whereas boiling points for the 2,4,6Me₃PyO and 4C₁₁H₂₃PyO were 418-420 K at 15 mm Hg (lit. 419 K at 15 mm Hg [31] and 449 K at 0.2 mm Hg (lit. melting point N-oxide chloride is 399 K [34]).

The monohydrate of 4-methoxy-2,6-dimethylpyridine N-oxide (Me₂MeOPyO) was prepared from 2,6-dimethylpyridine *via* 4-nitro,2,6-dimethylpyridine N-oxide by standard methods, *i.e.* 2,6-dimethylpyridine was oxidated using glacial acetic acid and 30% H₂O₂ as oxidizing agents, the obtained 2,6-dimethylpyridine N-oxide was nitrated using the mixture of nitric and sulfuric acids, and finally the nitro- group in 4-nitro,2,6-dimethylpyridine N-oxide was substituted by methoxy-group [33]. The anhydrous N-oxide Me₂MeOPyO was obtained by sublimation (at 348-353 K, 0.1 mm Hg), mp 373.5-374 K.

Simple perchlorates of the N-oxides studied were synthesized as were those of PyO and its methyl-substituted derivatives [18].

Solvent

Spectrophotometric grade acetonitrile (Fluka AG) was kept over 3Å molecular sieves. The UV spectrum of the solvent showed no significant absorption in the region studied.

Experimental procedures

The UV spectra were recorded on a SPECORD M-40 spectrophotometer equipped with a thermostated cell

compartment at 298 K with the use of the quartz cells of a 1 cm light path.

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Sample Availability: Available from the authors.