ABSORPTION SPECTRA OF SOME PYRIDINE AND PYRIDINE N-OXIDE DERIVATIVES IN OLEUM

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The absorption spectra of a number of pyridine and pyridine N-oxide derivatives in media of different acidity functions have been investigated. The bathochromic shift of the short-wave absorption band in oleum is interpreted as a consequence of the addition of a proton to the conjugate acid. The formation of a hydrogen bond between the 3-hydroxy derivative of the heterocyclic compounds investigated and the oleum, appearing as a hypsochromic shift of the long-wave absorption band, has been detected. This phenomenon is absent in the case of the 2-methoxy derivative.

Pyridine, pyridine N-oxide, and their derivatives possess basic properties. In the spectra of the conjugate acids of derivatives of these heterocycles the short-wave band is shifted bathochromically [1] in comparison with the spectra of the neutral molecules and there is no change in the position of the long-wave band. Calculation has confirmed that protonation has little effect on the position of the absorption bands, although they are due to different types of electronic transitions in the cation and in the neutral base [2]. The spectra of derivatives of pyridine and of its N-oxide in oleum have not been described previously. We have compared the absorption spectra of methyl and hydroxy derivatives of pyridine and of pyridine N-oxide in water and in media of different acidity functions: +1.09, −2.12, −4.78, −7.58, −9.06, and −11.98. The results obtained are given in Tables 1 and 2. Since the electronic structures of pyridine and benzene are similar, we applied to the spectra of the heterocycles under consideration the classification of the bands adopted for benzene, namely, the short-wave band was denoted by K and the long-wave band by B.

TABLE 1. Dependence of the Position of the K and B Absorption Bands of Pyridine, Pyridine N-Oxide, and Their 2-Methyl-Substituted Derivatives on the Acidity of the Solvent

Acidity function, H_0	λ_{max} (log ε)							
	pyridine		2-methylpyridine		pyridine N-oxide		2-methylpyridine N-oxide	
	K	B	K	B	K	B	K	B
*	199 (3,46)	256 (3,61)	202 (3,51)	262 (3,57)	207 (4,20)	255 (3,99)	208 (3,98)	252 (3,63)
+1,09	202 (3,40)	256 (3,69)	204 (3,41)	263 (3,75)	207 (4,06)	255 (3,95)	209 (4,04)	254 (3,69)
−2,12	202 (3,39)	256 (3,65)	204 (3,66)	262 (3,90)	219 (3,70)	259 (3,43)	219 (3,50)	265 (3,55)
−4,78	202 (3,38)	256 (3,69)	205 (3,53)	264 (3,80)	219 (3,70)	259 (3,48)	214 (3,50)	265 (3,55)
−7,58	202 (3,44)	256 (3,71)	205 (3,42)	264 (3,84)	216 (3,58)	257 (3,43)	211 (3,58)	264 (3,63)
−9,06	202 (3,42)	256 (3,74)	204 (3,42)	263 (3,80)	216 (3,42)	257 (3,27)	206 (3,83)	263 (3,62)
−11,98	205 (3,13)	256 (3,67)	208 (3,11)	263 (3,65)	217 (3,60)	257 (3,55)	213 (3,67)	265 (3,86)

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* Solvent: water.

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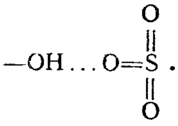
TABLE 2. Dependence of the Positions of the K and B Absorption Bands in Derivatives of 3-Hydroxypyridine and 3-Hydroxypyridine N-Oxide on the Acidity of the Solvent

Acidity function, H_0	Position of the methyl	λ_{max} (log ε) of the derivatives			
		3-hydroxypyridine		3-hydroxypyridine N-oxide	
		K	B	K	B
+1,09	—	202 (4,12)	284 (3,83)	206 (4,17)	254 (3,74)
	—2—	202 (4,13)	286 (3,87)	206 (4,33)	254 (3,65)
	—6—	202 (4,35)	291 (3,94)	205 (4,31)	251 (3,65)
	—2,6—	202 (4,25)	295 (4,06)	204 (4,31)	251 (3,05)
−2,12	—	198 (4,25)	282 (3,72)	203 (4,34)	285 (3,70)
	—2—	199 (4,32)	287 (3,94)	203 (4,48)	290 (3,91)
	—6—	200 (4,43)	290 (3,95)	203 (4,42)	292 (3,77)
	—2,6—	200 (4,51)	295 (4,14)	203 (4,41)	296 (3,95)
−4,78	—	198 (4,27)	282 (3,83)	202 (4,37)	285 (3,75)
	—2—	199 (4,36)	286 (3,98)	203 (4,45)	288 (4,95)
	—6—	200 (4,45)	289 (3,96)	202 (4,42)	289 (3,78)
	—2,6—	200 (4,44)	295 (4,18)	203 (4,63)	298 (3,90)
−7,58	—	198 (4,23)	280 (3,76)	201 (4,31)	283 (3,75)
	—2—	199 (4,26)	285 (3,74)	202 (4,42)	286 (3,76)
	—6—	200 (4,45)	288 (3,88)	201 (4,32)	288 (3,78)
	—2,6—	201 (3,34)	291 (4,28)	202 (4,63)	292 (4,10)
−9,06	—	198 (4,27)	280 (3,82)	201 (4,37)	282 (3,77)
	—2—	199 (4,47)	285 (4,02)	202 (4,40)	287 (3,91)
	—6—	200 (4,44)	286 (3,99)	203 (4,46)	290 (3,81)
	—2,6—	199 (3,91)	294 (3,65)	204 (2,23)	291 (4,02)
−11,98	—	210 (3,22)	261 (3,73)	218 (3,61)	263 (3,61)
	—2—	210 (4,53)	268 (4,83)	214 (3,91)	272 (4,12)
	—6—	211 (4,40)	269 (3,98)	213 (4,57)	271 (4,58)
	—2,6—	213 (4,33)	276 (4,66)	214 (4,49)	278 (4,74)

TABLE 3. Compositions of the Solvents and Their Acidity Functions

Solvent	Acidity function, H_0
0,1 *N* HCl	+1,09[8]
H_2SO_4 : H_2O = 1 4	−2,12
H_2SO_4 : H_2O = 2 . 3	−4,78
H_2SO_4 : H_2O = 4 . 1	−7,58
H_2SO_4 cp-grade	−9,06
7.3% oleum	−11,98

As can be seen from Table 1, the K band of pyridine and of its 2-methyl derivative is shifted bathochromically twice: the first time on comparing the absorption spectra in water and in hydrochloric acid, and the second time with an increase in the acidity function of the solvent from −9.06 to −11.98. In the spectrum of pyridine N-oxide and its 2-methyl derivative the pattern is somewhat more complicated. Since these are weaker bases than pyridine [3], after a first bathochromic shift which takes place at $H_0 = -2.12$, the K band undergoes a second hypsochromic shift, and in oleum shifts secondarily in the red direction. In the spectra of the 3-hydroxy derivatives of the compounds studied in oleum there is likewise a bathochromic shift of the K band (see Table 2). The bathochromic shift of the K band of the conjugate acids of the pyridine and pyridine N-oxide derivatives observed in a medium of high acidity is apparently a consequence of a change in the structure of the molecule through the addition of a second proton. In favor of this hypothesis is the synthesis of double salts of pyridine N-oxide [4]. Furthermore, according to Denis and Gilberg [5], in the pyridine cation about 80% of the charge on the proton is delocalized on the protonated pyridine molecule, with 60% retained by the nitrogen and 20% by the two neighboring carbon atoms. The latter makes the addition of a proton to the conjugate acids of pyridine and its derivatives in a medium of high acidity function probable.

Since in a neutral medium an equilibrium between neutral and bipolar structures is characteristic for derivatives of 3-hydroxypyridine [6] and of pyridine N-oxide [7], Table 2 does not give the absorption bands in water. In the absorption spectra of the hydroxy derivatives in oleum, the B band is shifted 10-20 nm in the short-wave direction. When the hydrogen of the hydroxy group is replaced by a methyl group, the blue shift of the long-wave band disappears (see Fig. 1). The hypsochromic shift of the B band is probably due to the interaction of the hydroxy group in position 3 with the solvent in the manner of  $-\mathrm{OH}\ldots\mathrm{O}{=}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}}$. Judging from the magnitude of the effect (see Table 1), no similar bond arises between the solvent and the hydroxy group formed as a result of the protonation of the N-oxide group. When an elec-

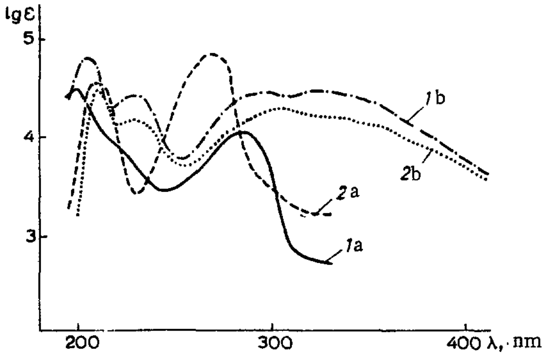


Fig. 1. Absorption spectrum in kh. ch. ["chemically pure"] sulfuric acid (1) and in oleum (2) of 3-hydroxy-2-methylpyridine N-oxide (a) and of 3-methoxy-2-methylpyridine N-oxide (b).

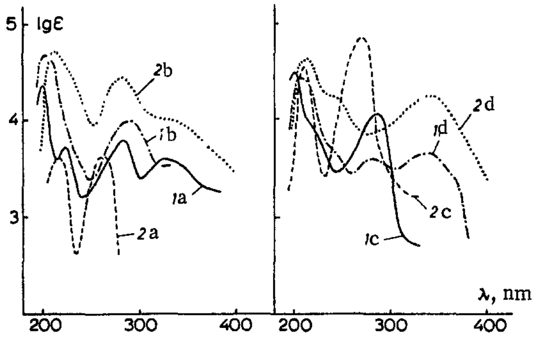


Fig. 2. Absorption spectra in cp-grade sulfuric acid (1) and in oleum (2) of 3-hydroxypyridine N-oxide (a), 3-hydroxy-2-nitropyridine N-oxide (b), 3-hydroxy-2-methylpyridine (c), and 3-hydroxy-2-methyl-4-nitropyridine (g).

tron-accepting nitro group is present in the molecule, the position of the B band is stabilized (Fig. 2), apparently as a consequence of the formation of an intramolecular hydrogen bond between the nitro and hydroxy groups in the ortho position to one another [7].

EXPERIMENTAL

The absorption spectra of the purified pyridine and pyridine N-oxide derivatives were taken on an SF-8 spectrophotometer in rectangular quartz cells with a layer thickness of 1 cm. The concentration of the solutions was 10^{-5} M. As standards were used solvents with definite values of the acidity function. The compositions of the solvents are given in Table 3.

The acidity functions of the solvents prepared from sulfuric acid were determined as described by Paul and Long [9].

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