meric benzenoid compounds, permit an energetically, especially favorable distribution of charges.

Acknowledgments.—Several interesting discussions with Dr. G. E. Philbrook of the University of Georgia are gratefully acknowledged; they provided much of the stimulation needed to attack this problem.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra of Substituted Pyridine 1-Oxides and their Conjugate Acids

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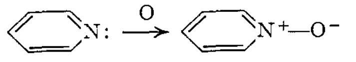
RECEIVED SEPTEMBER 27, 1954

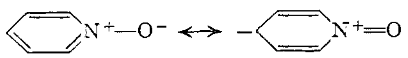
The ultraviolet absorption spectra of pyridine 1-oxide and of its conjugate acid, 1-hydroxypyridinium ion, have been determined in water and in 50% sulfuric acid, respectively, and are compared with the spectra of pyridine and pyridinium ion The effect of substituents in the 3- and 4-position on the spectra of pyridine 1-oxide and of its conjugate acid are determined. The spectra of isoquinoline 2-oxide and of its conjugate acid are also reported.

The ultraviolet absorption spectrum of pyridine is well known.[2] Its most outstanding feature is a band near 256 mμ with a molar extinction coefficient ϵ_{max} 2.66 × 10^3, both values in aqueous solution. This band shows a well defined vibrational structure. In acidic solution, where the species present is pyridinium ion, the wave length of this band is unaltered, but ϵ_{max} is increased twofold, to 5.32 × 10^3, and the vibrational structure is greatly decreased.[2a] The difference between the two spectra must be ascribed to the tying up of the unshared electron pair of the nitrogen atom, and to the introduction of the formal positive charge at this atom.

An alternate way of tying up the lone pair consists of oxidizing pyridine to its 1-oxide.



The spectrum of the latter compound is shown in Fig. 1 (*cf.* Table I). It shows a single very intense band, devoid of all vibrational structure, at almost the same wave length as the bands of pyridine and pyridinium ion, but of much higher ϵ_{max}. The intensity difference between pyridinium ion and pyridine 1-oxide can be understood since the latter compound has an appreciably larger conjugated system, due to the contributions of structures of the types I and II.[3] The spectrum also shows that a



I II

further band is present at the far ultraviolet end of the range accessible with the available equipment. The band maximum probably lies at 205 mμ, and has a molar extinction of about 1.7 × 10^4.

Introduction of various substituents in the 3-position does not greatly affect either the wave length or the intensity of the 254 mμ band of pyridine 1-oxide. Substituents in the 4-position have a somewhat larger effect in increasing the intensity of the absorption, up to almost twofold, and leading to a red-shift of up to 26 mμ (*cf.* Table I). The shorter wave length band appears to be somewhat more susceptible to effects of substituents, particularly those in the 3-position.

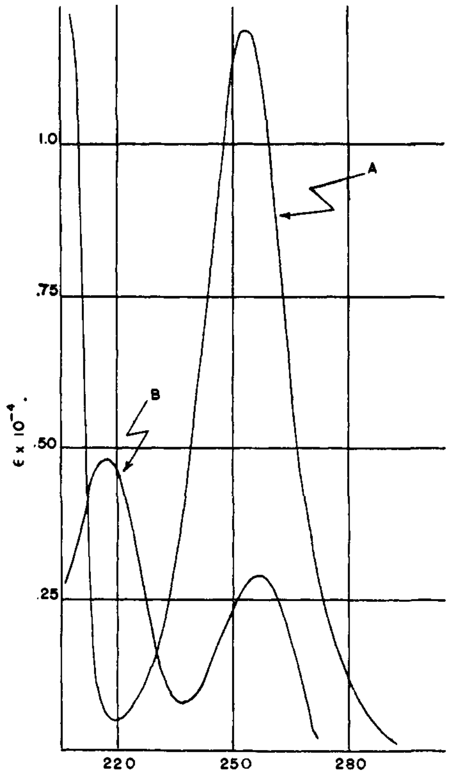


Fig. 1.—The spectra of pyridine 1-oxide in water (A), and of 1-hydroxypyridinium ion in 62% sulfuric acid (B).

As commonly found in spectroscopic investigations, the nitro group exerts a profound effect; the spectrum of 4-nitropyridine 1-oxide is shown in Fig. 2.

From the intensity, from the effect of substituents on the wave length (red-shift), and from the

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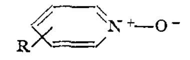
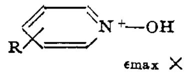
[2] (a) E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 410 (1949); (b) *cf.* also H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

[3] H. H. Jaffé, THIS JOURNAL, **76**, 3527 (1954).

TABLE I

THE ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED PYRIDINE 1-OXIDES AND THEIR CONJUGATE ACIDS





	λ, mμ	εmax × 10⁻⁴	λ, mμ	εmax × 10⁻⁴
H	254	1.19	217; 257	0.49; 0.29
3-CH_3	209; 254	1.98; 1.17	220; 263	0.42; 0.35
3-COOH	220; 260[a]	2.24; 1.02[a]	(218)[b]; 265	(0.69); 0.21
3-COO^-	216; 257	2.18; 1.09	.....	......
3-OH[c]	225; 263	1.45; 1.04		
3-$NHCOCH_3$	240; (254)[b]; 295	2.53; (1.50); 0.17		
3-NH_2	234; (252)[b]; 314	2.28; (1.15); 0.27		
3-NH_3^+			222; 261	0.51; 0.26
4-CH_3	206; 256	1.87; 1.43	226; 254	0.83; 0.27
4-COOH	216; 280[a]	1.12; 1.71[a]	232; 272	0.96; 0.35
4-COO^-	212; 273	1.51; 1.60	.....	......
4-OH	262[d]	1.35[d]	240	1.05
4-O^-	272	1.77	.....	......
4-NH_2	276[e]	1.90[e]	268[e]	1.61[e]
4-NO_2	226; 313	0.80; 1.25	244; (280)[b]	0.82; (0.38)
3,4-$(CH)_4$[f]	218; 250	2.33; 3.10	212; 234	2.05; 4.74
	294	0.86	280; 330	0.27; 0.36

[a] These data are corrected for the ionic species present at equilibrium. [b] Inflection points. [c] These data are taken from the graphs of E. Shaw, THIS JOURNAL, **71**, 67 (1949); the solvent was alcohol. Shaw states that in water, $\lambda_{max} = 255$ mμ. [d] In alcohol, Shaw finds $\lambda_{max} = 268$ mμ, $\epsilon_{max} = 1.4 \times 10^4$; *cf.* the reference in footnote *c*. [e] The wave lengths agree well with those reported by H. Hirayama and T. Kubota, *J. Pharm. Soc. Japan*, **73**, 140 (1953); our ϵ_{max}-values are about 5% lower than those reported by the Japanese authors. [f] Isoquinoline 2-oxide and its conjugate acid.

behavior on addition of a proton (*cf.* below), it appears likely that the electronic transition responsible for the 254 mμ band of pyridine 1-oxide is closely related to the bands at essentially the same wave length in pyridine and pyridinium ion. This transition has the nature of a π-π* transition in pyridine,[4] and the data presented here are consistent with this interpretation.

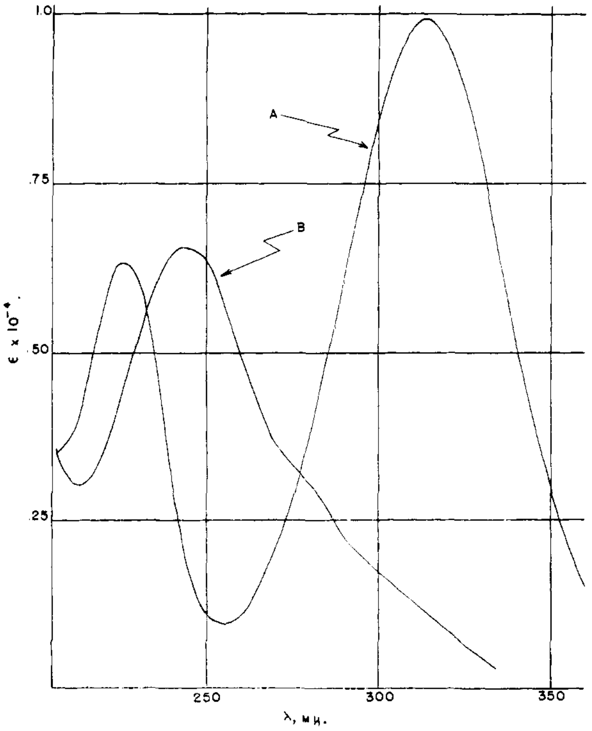
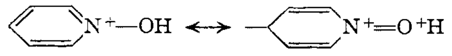


Fig. 2.—The spectra of 4-nitropyridine 1-oxide in water (A), and of its conjugate acid in 62% sulfuric acid (B).

Pyridine 1-oxide is a weak base,[5] and in moderately acidic solutions is present as the conjugate acid, 1-hydroxypyridinium ion, III. The longest wave length absorption band of III is found at



III IV

about the same wave length as the corresponding band of pyridine 1-oxide, but has a much lower molar extinction (*cf.* Fig. 1 and Table I). The latter fact is not surprising since the only resonance involving the hydroxy group analogous to structure II is the high energy structure IV. The intensity of the band in III is even lower than that of the corresponding band of pyridinium ion. A further band appears in the spectrum of III at 218 mμ with ϵ_{max} 0.49 × 10^4. This band probably corresponds to the same transition responsible for the 205 mμ band in pyridine 1-oxide, although the intensity is greatly decreased.

Introduction of substituents into the 3- or 4-position of 1-hydroxypyridinium ion does not greatly affect the 257 mμ band (*cf.* Table I), with the exception of those substituents (*e.g.*, 4-OH and 4-NH_2) which are able to donate electrons to the ring nitrogen atom by a resonance effect. Just as in the free bases, the short wave length band appears somewhat more sensitive to the effect of substituents. The spectra of the 4-hydroxy and 4-amino derivatives of III resemble those of the corresponding free bases, except for a blue-shift and slight reduction in intensity (*cf.* Fig. 3 and Table I). It can hardly be decided at this time whether we are actually dealing with a blue-shift of the band of the free base, or whether a transition of fundamentally different nature, say due to the resonance V → VI, is responsible for the band. The effect of the nitro group on the spectrum of III does not resem-

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(4) This assignment has recently been reviewed, *cf.* reference 1b.

(5) H. H. Jaffé and G. O. Doak, THIS JOURNAL, **77**, 4441 (1955).

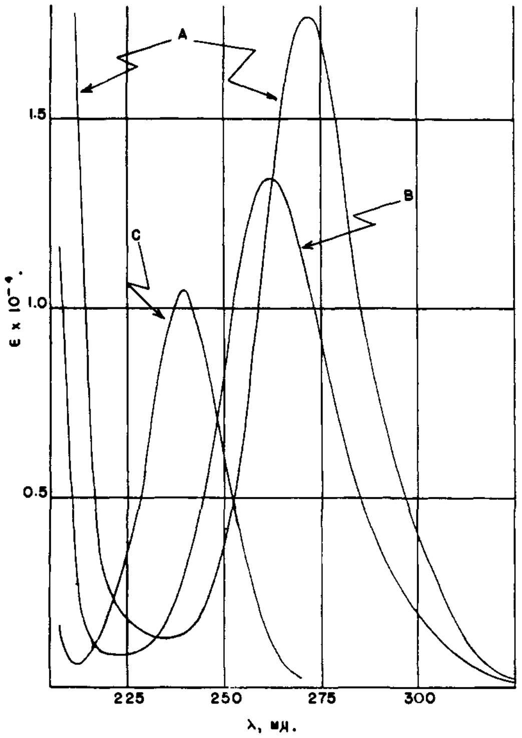

Fig. 3.—The spectra of 4-hydroxypyridine 1-oxide in water (B), its conjugate acid in 62% sulfuric acid (C), and its conjugate base in 0.1 *N* sodium hydroxide (A).

ble that of the other substituents; the spectrum of 4-nitro-1-hydroxypyridinium ion is shown in Fig. 2.

V VI

The spectra of isoquinoline 2-oxide and of its conjugate acid are shown in Fig. 4. The spectra are much more complex than those of the corresponding pyridine and quinoline[6] derivatives. Each compound has three bands, at least one of which has very high intensity. No analysis of these spectra will be attempted at this time.

Experimental

The preparations of the compounds used in this investigation were reported previously.[3,5] All spectra were determined at 25° with a Beckman D.U. spectrophotometer, using 1-cm. cells. Concentrations were adjusted so that the optical density at the various peaks was between 0.3 and 0.7. The spectra of the N-oxide free bases were determined in aqueous solution, although the solutions contained, in some cases, up to 2% alcohol used to dissolve the compounds. The spectra of the 1-hydroxypyridinium ions were determined in mixtures of equal volumes of water and sulfuric acid (about 62 wt. % H_2SO_4); this concentration of acid was sufficient to convert all of the free bases to their conjugate acids.[5] The N-oxides of nicotinic and isonicotinic acids in dilute aqueous solution (3.5×10^5 *M*) are completely ionized. The spectra of the free acids were obtained by correcting extinction values from solutions in dilute (0.1 *N*) sulfuric acid for both the 1-hydroxypyridinium and the nicotinate (isonicotinate) ions present at equilibrium. These concentrations were calculated from equilibrium constants reported elsewhere.[5]

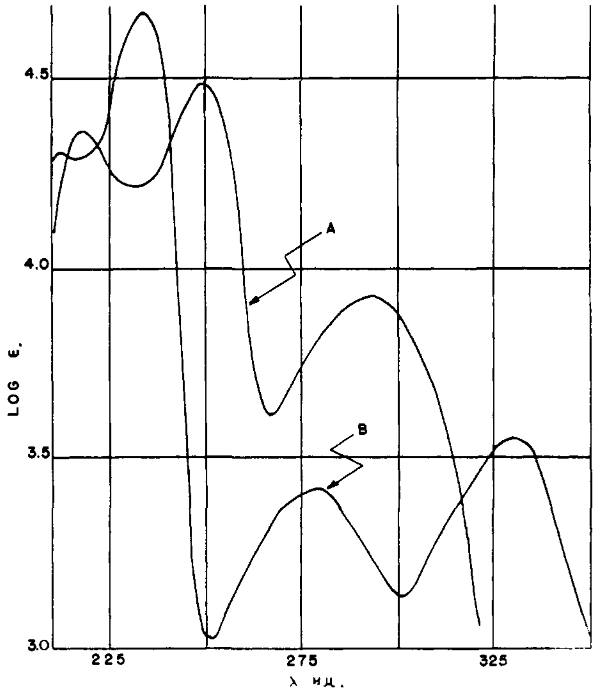

Fig. 4.—The spectra of isoquinoline 2-oxide in water (A), and its conjugate acid in 62% sulfuric acid (B).

Acknowledgments.—The author is indebted to Dr. Hertha Sponer and Dr. H. P. Stephenson for an interesting discussion of the spectra of pyridine bases and of the present results. The skilled technical assistance of Mrs. Caroline Sasser is gratefully acknowledged.

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[6] H. Hirayama and T. Kubota, *J. Pharm. Soc. Japan*, **72**, 1025 (1952).