The Ultra-violet Absorption Spectrum of Pyridine N-oxide

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Introduction

Organo-chemical properties of pyridine N-oxide have been investigated by Ochiai and his coworkers(1). Recently, the ultra-violet absorption spectra of these compounds in solutions have been measured by Hirayama and Kubota(2,3). Generally, in the absorption spectra of π-conjugated compounds containing the heteroatoms, e.g., pyridine and diazines etc., there occur n-π^* electronic transitions as well as π-π^* transitions(4,5). In the present investigation, the absorption bands due to these two electronic transitions are observed with pyridine N-oxide both in solution of non-polar solvent and in vapor, and the effects of proton donors on these absorption bands are discussed.

Experimental

Solution Spectrum.—The spectrum of pyridine N-oxide in various solutions was measured with a Beckman quartz spectrophotometer model DU, using a fused quartz cell of 1 cm. path. N-hexane, ethyl alcohol and water were used as solvents. Measurements were limited to the region of wavelength shorter than 350 mμ.

Vapor Spectrum.—Ultra-violet absorption spectra of pure pyridine N-oxide vapor and of a mixture with ethyl alcohol in the vapor phase were photographed with a medium quartz spectrograph having a linear dispersion of about 16 Å per mm. at 3,100 Å. The absorption cell was a quartz tube 40 cm. in length, and 3 cm. in diameter, to which a side recess was attached at the middle part. The sample sealed in a thin-walled glass ampoule was inserted in the side recess, and then the cell was evacuated to the pressure of about 10^{-3} mm Hg. After sealing off the cell, the ampoule was broken, the vapor filling the cell at pressures corresponding to the temperatures of the sample.

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1) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

2) H. Hirayama and T. Kubota, *Annual Reports of* Shionogi *Research Laboratory*, **2**, 47 (1952).

3) T. Kubota, *J. Pharm. Soc. Japan*, **74**, 831 (1954).

4) M. Kasha, *Discus. Farad. Soc.*, **9**, 14 (1951).

5) F. Halverson and R.C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

In the case of mixed vapor, conc. alcohol solution of pyridine N-oxide (mole fraction, about 0.25) was used as the sample. Exposures were made against the hydrogen continium, varying the temperature of the sample from 0° to 110°C for the pure vapor, and from 10° to 120°C for the vapor mixture.

Results and Discussion

Solution Spectrum.—The absorption curves for various solutions are shown in Fig. 1.

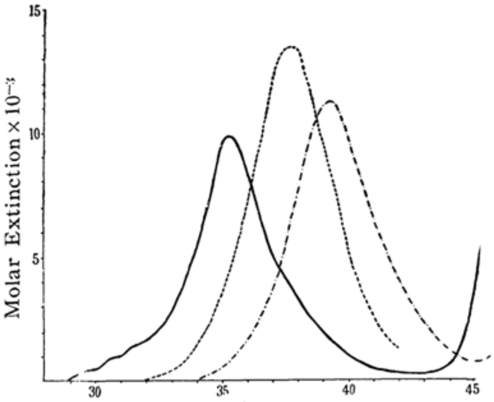

Fig. 1. Absorption spectrum of pyridine N-oxide.

——— *n*-hexane solution
------ ethyl alcohol solution
—·—·— water solution

As to the absorption of *n*-hexane solution, it appears that there are two absorption regions between 28,000 and 44,000 cm^{-1}; one of which is weak, accompanying a fine structure on longer wave-length end, and the other stronger having the maximum at 35,200 cm^{-1} (280 $m\mu$).

When either alcohol or water is used as the solvent, the absorption in the long wave-length region is not observed and the maximum shifts toward shorter wave-length side. Such a spectral behavior in pyridine N-oxide, supporting the assignment that weak long wave-length absorption is an n-π^* transition and the strong shorter wave-length absorption a π-π^* transition, may be explained as follows.

Pyridine N-oxide molecule has two pairs of 2p non-bonding electrons on the oxygen atom, one of which is considered to be in conjugation with the π-electron system of pyridine ring and the other to remain as a non-bonding pair. Generally, since the energy level of the non-bonding orbital lies above the highest π-level in the ground state, the n-π^* transition appears weakly in a longer wave-length region than the π-π^* transition. When proton donor such as alcohol or water is used as the solvent, the oxygen non-bonding orbital is largely stabilized in energy as a result of the formation of hydrogen bond[3]. Consequently, the n-π^* absorption disappears completely. At the same time, since the π-electron configuration will be perturbed by the formation of such a hydrogen bond, the π-π^* absorption shifts considerably to shorter wave-length, which is in agreement with our observation.

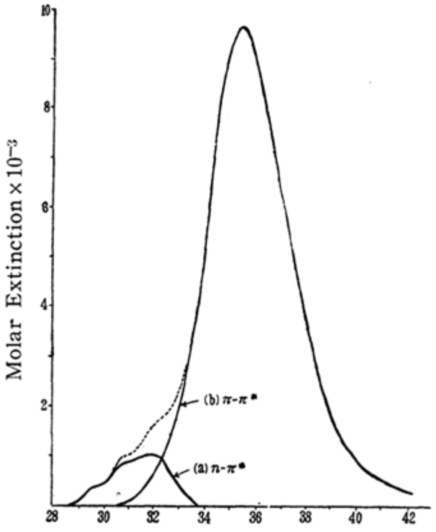

Fig. 2. Peak analysis of the absorption of *n*-hexane solution.

TABLE I

OSCILLATOR STRENGTH OF n-π^* AND π-π^* TRANSITIONS

Compound	$f(n\text{-}\pi^*)$	$f(\pi\text{-}\pi^*)$	$f(n\text{-}\pi^*)/f(\pi\text{-}\pi^*)$
Pyridine N-oxide	0.012	0.173	0.079
Pyridine[6]	0.003	0.041	0.073
Benzaldehyde[7]	0.0006	0.02	0.030
Acetophenone[7]	0.0006	0.014	0.043
P-benzoquinone[7]	0.0003	0.008	0.038

In order to estimate each absorption contribution from the n-π^* or π-π^* transition the peak analysis was made for the absorption of *n*-hexane solution according to the procedure given by Stephenson[6]. According to the well known equation,

$$f=4.32\times10^9\int\epsilon d\nu,$$

the oscillator strengths of the n-π^* and π-π^* transitions are calculated from the areas under the curves (a) and (b) in Fig. 2 respectively, their values being shown in Table I together with those for the other compounds[6,7]. As found from the table, while the f values for the n-π^* and π-π^* transitions are of considerably different orders for the

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6) H.P. Stephenson, *J. Chem. Phys.*, 22, 1077 (1954).
7) H.L. McMurry, *J. Chem. Phys.*, 9, 241 (1941).

different compounds, their ratio is in the same order of 10^{-2} for pyridine N-oxide as for the other compounds. This also gives supporting evidence for the assignment with respect to the n-π^* and π-π^* transitions mentioned above.

Vapor Spectrum.—The absorption spectra at different temperatures for pure and mixed vapors are sketched in Fig. 3 and Fig. 4, respectively. In the figures the lines show the main absorption bands and their heights the relative intensities, the shaded portions indicating regions of continuous absorption. The calculated vapor pressure values of pyridine N-oxide are given for the various temperatures in the last columns of Fig. 3 and Fig. 4.

In the region 29,000 cm^{-1}~48,000 cm^{-1} there are four absorption regions (I, II, III and IV regions in Fig. 3 or Fig. 4). The longest

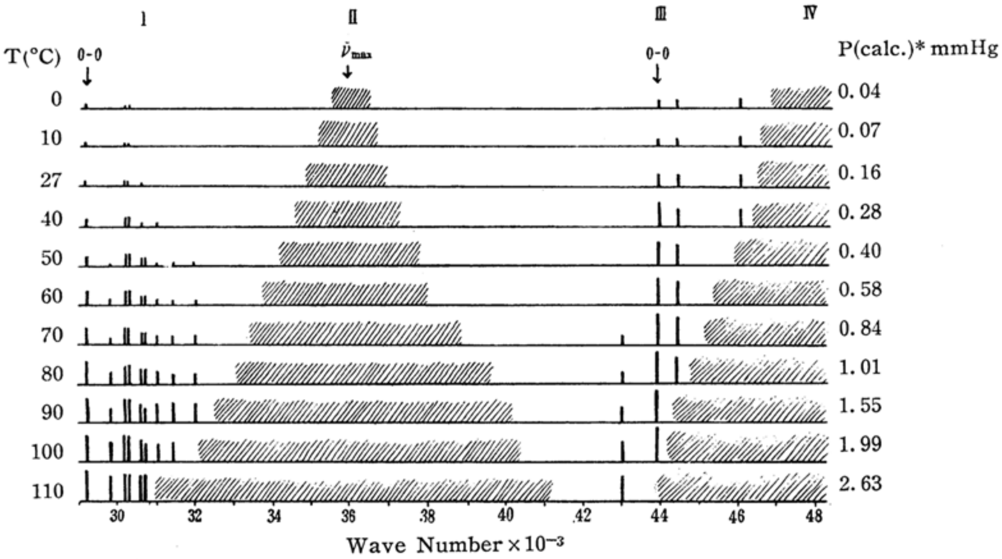

Fig. 3. Schematic absorption spectrum of pyridine N-oxide in pure vapor.

* Calculated by using the relation log P∝1/T and the boiling points of pyridine N-oxide (135° at 5 mm Hg, 113°C at 3mm Hg).

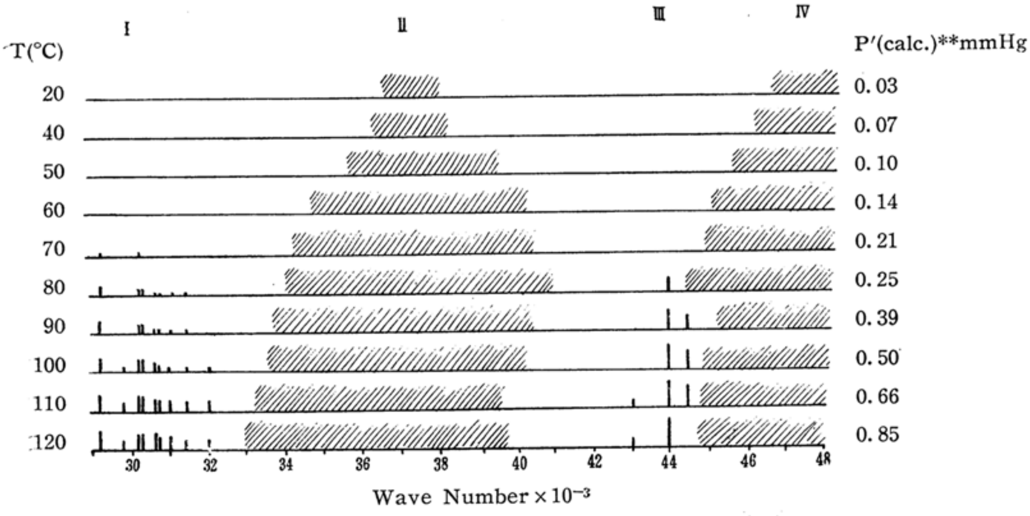

Fig. 4. Schematic absorption spectrum of pyridine N-oxide in vapor mixture with alcohol.

** The partial vapor pressure of pyridine N-oxide P′ is approximately given by P′=G×P, where G is the mol fraction of pyridine N-oxide in alcohol solution and P the vapor pressure of pyridine N-oxide.

wave-length region I is of a very sharp vibrational structure having the O-O band at 29,291 cm^{-1} [8], corresponding to the n-π^* absorption of n-hexane solution. The next, region II is continuous having its absorption maximum at about 35,960 cm^{-1}, corresponding to the π-π^* absorption of n-hexane solution. These spectral features fit in with Kasha's distinguishing criteria[4] that in vapor spectrum n-π^* absorption generally consists of very sharp bands and π-π^* absorption moderately broad or continuous bands. Thus, in accordance with the assignment for the solution spectrum, we confirm that the region I is an n-π^* transition and the region II a π-π^* transition.

Similarly, the region III is accompained by an extremely sharp vibrational structure having the O-O band at 43,884 cm^{-1} [8] and the region IV is continuous. These spectral appearances suggest that the former is an n-π^{**} transition and the latter is a π-π^{**} transition, where π^{**} is a π-level lying above the π^*-level related to the regions I and II.

Comparing the spectra of the pure vapor and the vapor mixture, we may notice that: (1) at low temperatures the n-π^* and n-π^{**} absorptions appear evidently in the former, but they are not observed in the latter, and (2) the π-π^* absorption in vapor mixture, lying at a little shorter wave-length than that for pure vapor at low temperatures, approaches to the position for pure vapor with increasing temperature. This spectral behavior is almost the same as in the case of solution spectrum and shows that, even in the state of vapor, pyridine N-oxide molecule forms hydrogen bond with alcohol molecule at low temperatures[3]. With increasing temperature, the hydrogen bond is broken due to thermal motion, and then the spectral feature of vapor mixture becomes identical with that of pure vapor.

Summary

The near ultra-violet absorption spectrum of pyridine N-oxide was measured in solution and vapor, and we concluded from the considerations of solvent effect, oscillator strength and the feature of vapor spectrum that the two of the four absorption regions are due to the excitation of the non-bonding electron, the others due to the excitation of π-electron. From the spectral behavior of pyridine N-oxide, it is also concluded that the pyridine N-oxide molecule forms hydrogen bond with alcohol or water molecule in vapor and solution state.

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[8] The detailed virbrational analysis is to be reported shortly.