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Photochemical Reduction of Nitrobenzene and Its Reduction Intermediates. IX. The Photochemical Reduction of 4-Nitropyridine in a Hydrochloric Acid-Isopropyl Alcohol Solution[1]

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The photochemical reduction of 4-nitropyridine has been investigated in hydrochloric acid-isopropyl alcohol solutions. 4-Nitropyridine was not photoreduced in isopropyl alcohol, whereas when the photolysis was carried out in hydrochloric acid-isopropyl alcohol solutions, the photoreduction of 4-nitropyridine proceeded from its n,π^* triplet state to give 4-hydroxylaminopyridine in a quantitative yield. The quantum yields for the disappearance of 4-nitropyridine in hydrochloric acid-isopropyl alcohol solutions increased with the concentration of hydrochloric acid up to 3.6×10^{-2} mol l^{-1} ($\Phi=0.27$—0.94). These results suggest that the hydrogen abstraction of photoexcited 4-nitropyridine proceeds electrophilically because of the decrease in the electron density of the nitro group, in decrease resulting from the protonation of heterocyclic nitrogen and the n,π^* excitation of the nitro group.

It is well-known that aromatic nitro compounds are photoreduced in hydrogen-donative solvents to give the corresponding amino or hydroxylamino compounds.[2] Few investigation of the relationships between the electronic structures of photoexcited nitro compounds and their reactivities of hydrogen abstraction have, however, been done to date. Hurley and Testa[3] have reported that the reactivity of the hydrogen abstraction of the protonated nitrobenzene triplet is greater than that of the unprotonated nitrobenzene triplet. Janzen and Gerlock[4] reported the substituent effects on the photochemistry and nitroxide-radical formation of nitro aromatic compounds, as studied by electron-spin-resonance spin-trapping techniques. Meanwhile, we ourselves have reported that, when the photoreduction of *para*-substituted nitrobenzenes is done in isopropyl alcohol (IPA), there is a linear correlation between the log-values of the relative quantum yields of nitrobenzenes and the nitrobenzene and the Hammett constants (ρ: $+$); therefore, the hydrogen abstraction of photoexcited nitrobenzenes may proceed electrophilically.[1] On the other hand, 4-nitropyridine is not reduced photochemically in IPA, and it is photoreduced in hydrochloric acid (HCl) - IPA solutions to give 4-hydroxylaminopyridine in a quantitative yield.[5] These facts are very interesting and may prove useful in investigating the correlation between the reactivity of the photochemical reduction and the electronic structure of nitro aromatic compounds in the photoexcited states.

In this paper, we wish to report in detail our findings on the photoreduction of 4-nitropyridine and to discuss the photoreduction mechanism. Both the reporting and discussing were begun in a communication (Ref. 5).

Results

Photochemical Reduction of 4-Nitropyridine. Identification of the Reduction Products. Figure 1 shows the progressive spectral change during the course of the photolysis of a 2×10^{-3} mol l^{-1} solution of 4-nitropyridine in IPA on irradiation with an immersion-type 130-W high-pressure mercury lamp under a nitrogen atmosphere at room temperature. As Fig. 1 shows, no isosbestic points were observed on the spectra, and the reaction product (Product A) had an absorption at 250 mμ. "Product A" (mp>300°C, brown plate from ethanol) has not yet been identified; however, it is clearly not a reduction product of 4-nitropyridine, such as 4-hydroxylamino-, 4,4′-azoxy-, 4,4′-azo-, and/or 4-aminopyridine, as has been shown by a comparison of the UV spectra with those of authentic samples.

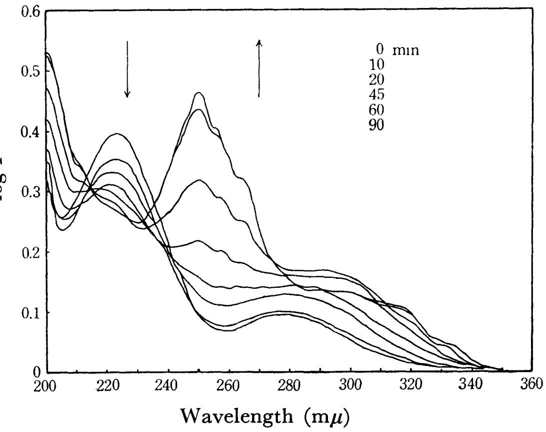

Fig. 1. The progressive spectral change of the photoreaction of 4-nitropyridine in IPA.

Meanwhile, the progressive spectral change during the reaction of a 2×10^{-3} mol l^{-1} solution of 4-nitropyridine in a 4 vol% concentrated HCl - IPA solution on irradiation with an immersion-type 130-W high pressure mercury lamp under a nitrogen atmosphere at room temperature is shown in Fig. 2. Two isosbestic points were observed at 214 and 244 mμ respectively. The absorption at 273 mμ (Product B) gradually in-

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1) Part VIII: S. Hashimoto and K. Kano, *Tetrahedron Lett.* **1970**, 3509.

2) Y. Ogata, *Kogyo Kagaku Zasshi*, **72**, 23 (1969); "The Chemistry of the Nitro and Nitroso Groups," ed. by H. Feuer, Interscience, New York (1969), p. 181.

3) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **89**, 6917 (1967).

4) E. G. Janzen and J. L. Gerlock, *ibid.*, **91**, 3108 (1969).

5) S. Hashimoto, K. Kano, and K. Ueda, *Tetrahedron Lett.*, **1969**, 2733.

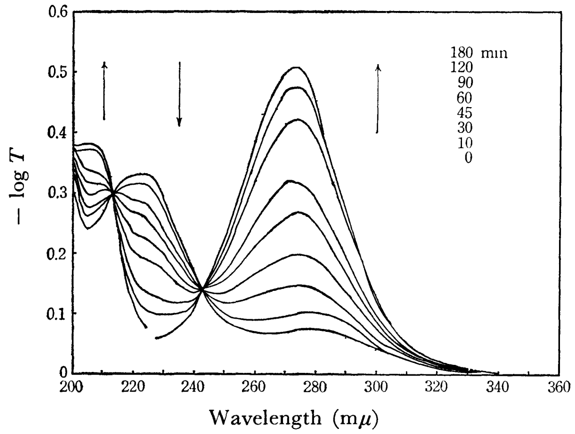

Fig. 2. The progressive spectral change of the photoreduction of 4-nitropyridine in HCl-IPA solution.

creased in intensity with the progress of the photolysis. "Product B" was converted by alkali to afford 4,4′-azopyridine (yield 32%), and then converted to 4,4′-azoxypyridine (yield 24%) on treatment in a neutral solution. It has been established that 4-hydroxylaminopyridine 1-oxide converts to 4,4′-azopyridine 1,1′-dioxide on treatment in an alkaline solution, and converts to 4,4′-azoxypyridine 1,1′-dioxide on treatment in a neutral solution,[6] while phenylhydroxylamine converts to azoxybenzene.[7] These facts suggest that "Product B", which is a precursor of 4,4′-azopyridine and 4,4′-azoxypyridine, is 4-hydroxylaminopyridine.

Effect of Triplet Quenchers. The quenching effects for the photoreduction of 4-nitropyridine in HCl-IPA solutions were investigated by using 1,3-pentadiene and/or oxygen as triplet quenchers.

A 2×10^{-3} mol l^{-1} solution of 4-nitropyridine in a 4 vol% concentrated HCl-IPA solution containing 1,3-pentadiene (2.5×10^{-2} mol l^{-1}) was irradiated with an immersion-type 130-W high-pressure mercury lamp under a nitrogen atmosphere at room temperature. In the photoreduction of 4-nitropyridine in the absence of 1,3-pentadiene, about 3.0 hr is required to complete the photolysis, but in the presence of 1,3-pentadiene, which is 1.5 times as large in quantity as 4-nitropyridine, about 4.5 hr is required. The photoreduction of 4-nitropyridine proceeded under irradiation by a near 316 mμ light, and we do not need consider the inner-filter effect by 1,3-pentadiene ($\lambda_{\max}^{\mathrm{IPA}}=223$ mμ) in this reaction. These facts suggest that the photoreduction of 4-nitropyridine is quenched by 1,3-pentadiene.

The quenching effect by oxygen was also studied. A 2×10^{-3} mol l^{-1} solution of 4-nitropyridine in a 4 vol% concentrated HCl - IPA solution was irradiated with an immersion-type 130-W high-pressure mercury lamp under an oxygen atmosphere at room temperature. The progressive spectral change during the photolysis is shown in Fig. 3. As Fig. 3 shows, the photochemical reaction of 4-nitropyridine under an oxygen atmosphere proceeded in a complicated way; finally, a product which had an absorption at 235 mμ was generated. The generation of 4-hydroxylaminopyridine was not observed on the UV spectrum. A reaction other than photoreduction might occur, and so it could not clarified whether or not the photoreduction of 4-nitropyridine was quenched by oxygen. Kaneko *et al.*[8] have reported that 4-nitropyridine 1-oxide is not reduced photochemically in ethanol under an oxygen atmosphere, and that 4-hydroxypyridine 1-oxide is thus prepared. The photolysis of 4-nitropyridine in oxygen-saturated solutions is now under investigation.

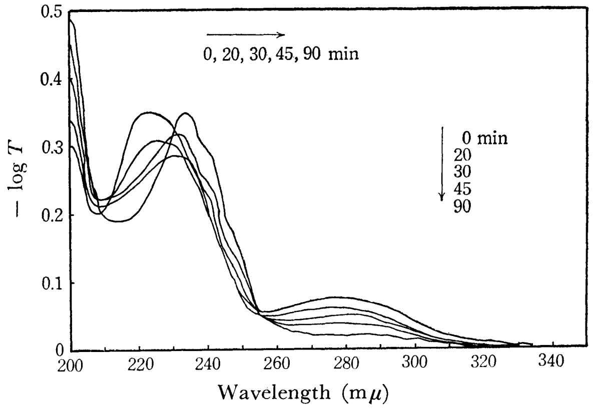

Fig. 3. The progressive spectral change of the photoreaction of 4-nitropyridine in HCl-IPA solution under an oxygen atmosphere.

The Role of HCl. The Quantum Yield for the Disappearance of 4-Nitropyridine. HCl plays an important role in the photochemical reduction of 4-nitropyridine. The quantum yields for the disappearance of 4-nitropyridine (Φ) were measured in order to clarify the role of HCl.

Several 1×10^{-3} mol l^{-1} solutions of 4-nitropyridine in 80% IPA-water solutions containing varying amounts of HCl were irradiated by a 316-mμ light under a nitrogen atmosphere at room temperature. Here, 4-hydroxylaminopyridine was the only product. The correlation between the quantum yields and the concentration of HCl is shown in Fig. 4. The quantum yields of the 4-nitropyridine disappearance increased

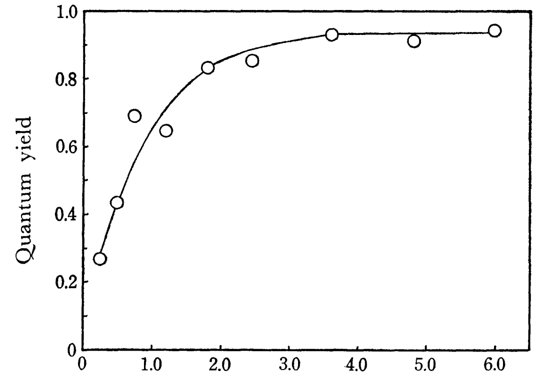

Fig. 4. The correlation of the quantum yields for the disappearance of 4-nitropyridine and the concentration of HCl.

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[6] F. Parisi, P. Bovina, and A. Quilico, *Gazz. Chim. Ital.*, **90**, 903 (1960).

[7] Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Amer. Chem. Soc.*, **79**, 3397 (1957); Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, *ibid.*, **86**, 3854 (1964).

[8] C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron Lett.*, **1967**, 775.

with the concentration of HCl up to 3.6×10^{-2} mol l^{-1}, and while they were constant above this concentration ($\Phi_{\text{av.}}=0.93$). The quantum yields of the 4-nitropyridine disappearance ($\Phi=0.27-0.94$) were greater than that of nitrobenzene in IPA ($\Phi=0.0114$)[9] and/or IPA - HCl solutions ($\Phi=0.04-0.14$).[3]

Discussion

It has been studied by several workers how aromatic nitro compounds, such as nitrobenzene,[9–11] *para*-substituted nitrobenzenes,[1,12] 1-nitronaphthalene,[13,14] and 4-nitropyridine 1-oxide,[15,16] are photoreduced in hydrogen-donative solvents to give the corresponding amino or hydroxylamino compounds. On the other hand, 4-nitropyridine was not photoreduced in IPA, but was reduced photochemically in HCl-IPA solutions under a nitrogen atmosphere to afford 4-hydroxylaminopyridine in a quantitative yield.

The photoreduction of 4-nitropyridine was quenched by 1,3-pentadiene; this suggested that the hydrogen abstraction proceeded from the excited triplet state of 4-nitropyridine. However, it seems that the quenching effect by 1,3-pentadiene is not significant in the photoreduction of 4-nitropyridine. This finding is similar to the oxygen quenching of the nitrobenzene triplet.[9] The photochemical behavior of nitro compounds in hydrogen-donative solvents may be written as in the following sequence:

$$\mathrm{N} + h\nu \xrightarrow{k_1} \mathrm{N}^{*(1)} \tag{1}$$

$$\mathrm{N}^{*(1)} \xrightarrow{k_2} \mathrm{N} \tag{2}$$

$$\mathrm{N}^{*(1)} \xrightarrow{k_3} \mathrm{N}^{*(3)} \tag{3}$$

$$\mathrm{N}^{*(3)} \xrightarrow{k_4} \mathrm{N} \tag{4}$$

$$\mathrm{N}^{*(3)} + \mathrm{Q} \xrightarrow{k_5} \mathrm{N} + \mathrm{Q} \tag{5}$$

$$\mathrm{N}^{*(3)} + \mathrm{AH} \xrightarrow{k_6} \mathrm{NH} + \mathrm{A} \tag{6}$$

A steady-state approximation for solutions containing quenchers such as 1,3-pentadiene and/or oxygen leads to this expression for the disappearance of nitro compounds:

$$\Phi = \frac{\Phi_T}{\left[1+\dfrac{k_4+k_5(\mathrm{Q})}{k_6(\mathrm{AH})}\right]}$$

where Φ is the quantum yield for the disappearance of nitro compounds, Φ_T is the yield of the triplet, (AH) is the concentration of the hydrogen-donative solvents, and (Q) is the concentration of the quenchers. It can be explained, in accounting for the ineffective oxygen quenching of the nitrobenzene triplet, that k_4 is greater than $k_5(\mathrm{Q})$.[9] In the photoreduction of 4-nitropyridine, however, k_4 may be small, since the quantum yield for the disappearance of 4-nitropyridine was about 0.9 in the absence of 1,3-pentadiene when an IPA solution of 4-nitropyridine containing 4 vol% concentrated HCl was irradiated with the 316 mμ light.[17] Therefore, it is reasonable to expect that $k_6(\mathrm{AH})$ will be greater than $k_5(\mathrm{Q})$.

Meanwhile, 4-nitropyridine in IPA absorbed broadly near the 340—420 mμ light. Since this weak band overlapped with the intense π,π^* band, it was impossible to distinguish the n,π^* band. It has been established that the hydrogen abstraction of photoexcited benzophenones proceeds from their n,π^* triplet states and that the reactivity of hydrogen abstraction falls off in their π,π^* triplet states.[18] By the way, the quantum yields for the diappearance of 4-nitropyridine in HCl-IPA solutions were strikingly large ($\Phi=0.27$—0.94). These facts suggest that the photoreduction of 4-nitropyridine proceeds from its n,π^* triplet state.

In the photoreduction of 4-nitropyridine to 4-hydroxylaminopyridine, HCl had to exist in the reaction system. The UV spectra of 4-nitropyridine in acidic IPA solutions, suggest that the protonation of heterocyclic nitrogen proceeded, while the protonation of the nitro group in the ground state does not occur, in the range of the HCl concentration used in our experiments, since the absorption of the conjugated acid of 4-nitropyridine at 280 mμ in IPA increased in its intensity with an increase in the acidity and the isosbestic point was observed at 248 mμ. These results suggest that 4-nitropyridine hydrochloride is reduced photochemically. It seemed that, since 4-nitropyridine partly forms its hydrochloride in the range of the HCl concentration from 0.24×10^{-2} to 3.6×10^{-2} mol l^{-1}, the quantum yield for the disappearance of 4-nitropyridine increased with the concentration of HCl; above this concentration, the formation of hydrochloride was perfect, and so the quantum yields became constant.

The electron density on the nitro group of 4-nitropyridine may be lower than that of nitrobenzene because of the electron-withdrawing effect of heterocyclic nitrogen. When the lone pair of heterocyclic nitrogen is protonated, the electron-withdrawing effect will be enhanced; therefore, the electron density on the nitro group of protonated 4-nitropyridine may be lower than that of unprotonated 4-nitropyridine.

Meanwhile, the n-π^* transition of the nitro group may be pictured as follows:[19]

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9) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966).

10) S. Hashimoto, J. Sunamoto, H. Fujii, and K. Kano, This Bulletin, **41**, 1249 (1968).

11) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc.*, **1968**, 1467.

12) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **90**, 1670 (1968).

13) S. Hashimoto and K. Kano, *Kogyo Kagaku Zasshi*, **72**, 188 (1969).

14) W. Trotter and A. C. Testa, *J. Phys. Chem.*, **74**, 845 (1970).

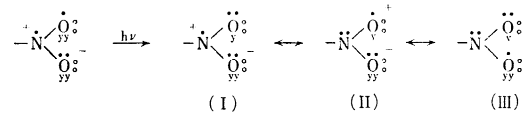
15) C. Kaneko, S. Yamada, I. Yokoe, N. Hata, and Y. Ubukata, *Tetrahedron Lett.*, **1966**, 4729.

16) N. Hata, E. Okutsu, and I. Tanaka, This Bulletin, **41**, 1769 (1968).

17) Although the quantum yield in the presence of 1,3-pentadiene could not determine exactly because of the difficulty of the determination of 4-nitropyridine, it was estimated to be about 0.6 when a solution of 4-nitropyridine (1×10^{-3} mol l^{-1}) in 4 vol% concentrated HCl-IPA solution containing 1,3-pentadiene (2.5×10^{-2} mol l^{-1}) was irradiated with the 316 mμ light.

18) T. Tezuka, *Yuki Gosei Kagaku Kyokai Shi*, **27**, 309 (1969).

19) "The Chemistry of the Nitro and Nitroso Groups," ed. by H. Feuer, Interscience, New York (1969), p. 169.



Ground state n,π^* Excited state

•: π electron; ∘: sp electron; y: p_y electron

The structure (I) and (III) imply that a nitro n,π^* excited state exhibits biradical properties. On the other hand, as is shown in the structure (II), n,π^* excitation removes an electron from the oxygen atom and promotes it to same π^* orbital, which is then shared by both atoms, formally leaving a 1/2 positive charge on oxygen. For these reasons, the n,π^* excited states of nitro compounds are similar to those of carbonyl compounds; therefore, it is reasonable to assume that the reactivity of the hydrogen abstraction of the n,π^* photoexcited nitro compounds is also similar to that of carbonyl compounds. Porter and Suppan[20)] have reported that the reactivity of the hydrogen abstraction of benzophenones may be classified, in decreasing order, as n,π^*, π,π^*, and charge-transfer (CT) states; these properties can be interpreted in term of the electron distribution in the lowest triplet level.

As has been mentioned above, the formal positive charge at oxygen atoms on the nitro group of 4-nitropyridine, may increase in this order: the unprotonated 4-nitropyridine, protonated 4-nitropyridine, and the n,π^* excited state of protonated 4-nitropyridine. In view of the above facts, it seems reasonable to assume that the hydrogen abstraction of photoexcited 4-nitropyridine may be dominated by the electron density on the oxygen of the nitro group, and that it proceeds electrophilically similarly to that of photoexcited benzophenones. This deduction may be supported by the fact that there is a linear correlation between the log-values of the quantum yields for the disappearence of *para*-substituted nitrobenzenes and the Hammett constants (ρ: +) when the photoreduction of *para*-substituted nitrobenzenes is done in IPA.[1)]

Experimental

Materials. The 4-nitropyridine was prepared according to the procedures described in the literature.[21)] Reagent-grade IPA was distilled prior to use. 1,3-Pentadiene commercially obtained was further purified by distillation (bp 42—45°C).

Determination of Quantum Yields. The 316-mμ light was isolated from a high-pressure 130-W mercury lamp with a combination filter of Toshiba UV-D25, an aqueous nickel sulfate solution, and carbon tetrachloride. The light intensities were determined with a potassium ferrioxalate actinometer described by Hatchard and Parker.[22)]

Analytical Procedures. The disappearance of 4-nitropyridine was determined by measuring the optical densities of photolyzed solutions. Polarographic analysis for following the 4-nitropyridine disappearance was also undertaken (pH=6.0, $E_{1/2}=-0.3$ V), but satisfying data could not obtained by this method. A Hitachi 124 spectrophotometer was used for the quantitative absorbance measurements and for following the progressive spectral change in the 4-nitropyridine photochemistry.

Preparation of 4,4′-Azoxypyridine and 4,4′-Azopyridine by the Photolysis of 4-Nitropyridine. A mixture of 0.62 g (5×10^{-3} mol) of 4-nitropyridine and 2.5 m*l* of concentrated HCl was exactly diluted to 1 *l* with IPA, and then irradiated with an immersion-type 130-W high-pressure mercury lamp for 10 hr under a nitrogen atmosphere at room temperature. After the irradiation, the photolyzed solution was evaporated to half of its volume *in vacuo*; the "reaction mixture" was thus obtained. The "reaction mixture" was neutralized with an aqueous sodium carbonate solution, and then evaporated to 100 m*l* of its volume. The brown residue thus obtained was heated to *ca.* 95°C for 2.5 hr and then extracted with chloroform. After the evaporation of the chloroform, the residue was recrystallized from water. The plate crystal thus obtained was identified as 4,4′-azoxypyridine; yield, 0.12 g (24%); mp 125—126.5°C. In mass spectroscopy, a molecular radical ion M$^+$ (*m/e* 200), was found corresponding to the molecular formula of $C_{10}H_8N_4O$.

Found: C, 60.10; H, 4.05; N, 28.12; O, 7.73%. Calcd for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99; O, 7.99%.

The UV and IR spectra of 4,4′-azoxypyridine are shown in Figs. 5 and 6.

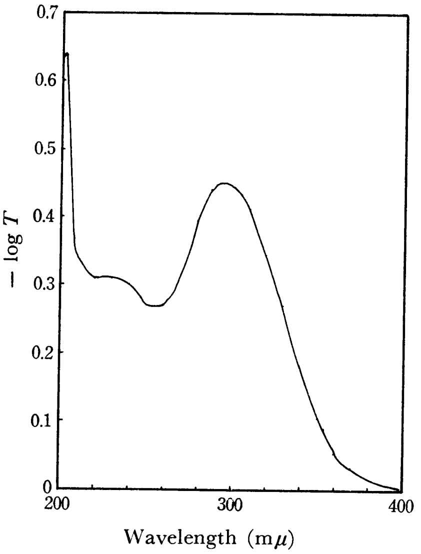


Fig. 5. UV-spectrum of 4,4′-azoxypyridine (4×10^{-5} mol l^{-1}).

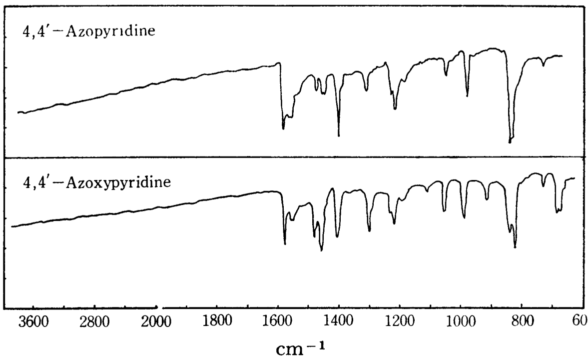


Fig. 6. IR-spectra of 4,4′-azoxypyridine and 4,4′-azopyridine (KBr).

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20) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

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

22) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

The "reaction mixture" was basified with 300 m*l* of a 33% aqueous sodium hydroxide solution, and then evaporated as far as possible. The redish-orange residue was dissolved in water and extracted with chloroform. After the evaporation of the chloroform, the residue was recrystallized from water. The redish-orange needles thus obtained were identified as 4,4′-azopyridine; yield, 0.15 g (32%); mp 109—110.5°C (lit,[6] mp 108—109°C). In mass spectroscopy, a molecular radical ion, M^+ (m/e 184), was found corresponding to the molecular formula of $C_{10}H_8N_4$.

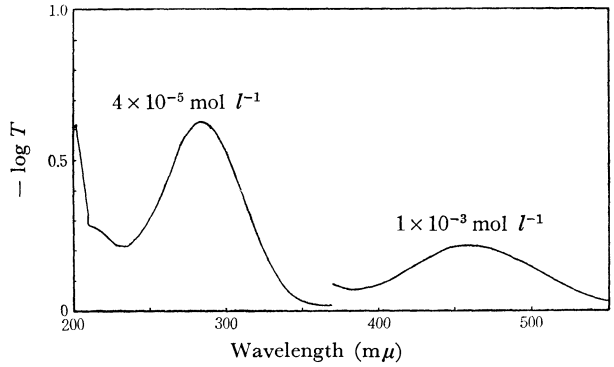

Fig. 7. UV-spectrum of 4,4′-azopyridine in IPA.

Found: C, 65.39; H, 4.22; N, 30.16%. Calcd for $C_{10}H_8N_4$: C, 65.20; H, 4.38; N, 30.42%.

The UV and IR spectra of 4,4′-azopyridine are shown in Figs. 7 and 6.

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