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The Primary Photochemical Process of 4-Nitropyridine *N*-Oxide

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In order to clarify the primary photochemical process of 4-nitropyridine *N*-oxide in solution, investigations by means of a steady-light irradiation and a flash spectroscopic method were carried out. 4-Nitropyridine *N*-oxide changes photochemically to 4-hydroxypyridine *N*-oxide nitrate (Process I) or 4-hydroxylaminopyridine *N*-oxide (Process II), depending on the reaction conditions. In either case, Process I and Process II, the photochemical reaction was found to proceed through the common intermediate species A. We concluded from the experimental results that Process I involves a bimolecular interaction between the intermediate A and the unexcited 4-nitropyridine *N*-oxide molecule, while Process II involves a hydrogen-abstracting reaction from a solvent molecule.

Recently, pyridine and quinoline-*N*-oxides and their several derivatives have been reported by various workers to cause a photochemical change in the N-O group when they are irradiated with ultraviolet light in either a solution or vapor.[1-4] The introduction of nitro group into the 4-position of pyridine *N*-oxide, has been found to cause a photochemical change completely different from those of pyridine- and 2-picoline-*N*-oxides in solution.[5,6] That is, 4-nitropyridine *N*-oxide in ethanol changes photochemically in two

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1) N. Hata and I. Tanaka, *J. Chem. Phys.*, **36**, 2072 (1962); N. Hata, This Bulletin, **34**, 1440, 1444 (1961).

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5) C. Kaneko, S. Yamada and I. Yokoe, Symposium on Photochemistry, Osaka, October, 1966.

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ways, depending on the reaction conditions, to give 4-hydroxypyridine *N*-oxide nitrate or 4-hydroxylaminopyridine *N*-oxide, while the N-O group remains unchanged.[5,6] Therefore, in order to clarify the primary process of such an interesting photochemical reaction of 4-nitropyridine *N*-oxide, we carried out investigations by means of a steady-light irradiation and also a flash spectroscopic method in solution.

Experimental

Materials. The 4-nitropyridine *N*-oxide used in this experiment was synthesized by Ochiai's method,[7] and the product was purified by several recrystallizations from acetone. Ethanol and glycerol were reagent-grade products of Wako Pure Chemical Industries, the spectro-grade ethanol was also used.

Steady-light Experiment. The light source employed was a Toshiba high-pressure mercury lamp (H-400 P), while for the 3130 Å irradiation a filter combination of a nickel sulfate solution with a UV-31 Toshiba filter was used. Sample solutions in various concentrations were added to the quartz cylindrical reaction cell and then placed in a thermostated box with two quartz windows, through which collimated light passed to irradiate the sample solutions. In order to determine the quantum yield of the 4-nitropyridine *N*-oxide disappearance, the light intensity was measured with a potassium ferrioxalate actinometer. The absorption spectra were taken with a Hitachi recording spectro-photometer, EPS-2 U.

Flash Spectroscopic Experiment. The photolysis flash lamp consisted of a quartz tube 200 mm in length and about 20 mm in diameter, filled with xenon gas to about 150 mmHg. By discharging a bank of a condenser with a capacity of 25 μF charged to 4 kV, 200 joules of energy were dissipated; the half-width of the discharge time was about 50 microseconds. The reaction cell, consisting of a quartz tube 70 mm in length and 20 mm in diameter, was set parallel to the photolysis lamp. The reaction cell and the photolysis lamp were surrounded by a reflection plate. The flash lamp for the spectrograph was constructed much like to the photolysis lamp, but the capacity was 8 μF charged to 3.2 kV, the energy was about 40 joules, and the half-width of the discharge time was about 20 microseconds.

Experimental Results

Before describing the experimental results, it will be usefull for understanding the primary photochemical process of 4-nitropyridine *N*-oxide to mention briefly the photochemical reaction in an ethanol solution. The absorption spectrum of 4-nitropyridine *N*-oxide (*ca.* 10^{-4}—10^{-3} mol l^{-1} in ethanol) decreases progressively in intensity, and a new absorption band with its maximum at 269 mμ appears, as the irradiation time increases. Figure 1 shows the results for the 5×10^{-5} mol·l^{-1} ethanol solution. After concentrating the irradiated solution under reduced pressure, the oily residues (Prod. X) are gradually crystallized to afford 4-hydroxypyridine *N*-oxide nitrate.[7] This photochemical reaction is referred to as Process I. When the concentrated ethanol solution of 4-nitropyridne *N*-oxide (*ca.* 10^{-2} mol l^{-1}) is irradiated with a 3130 A light in a nitrogen atmosphere, however, the nitro group of the 4-position is photochemically reduced to yield 4-hydroxylaminopyridine *N*-oxide.[6] The progressive change in the absorption spectrum of 4-nitropyridine *N*-oxide at 3130 Å irradiation is shown in Fig. 2, where two isosbestic points are observed at 254 mμ and 308 mμ.[6] This photochemical reaction is referred to as Process II.

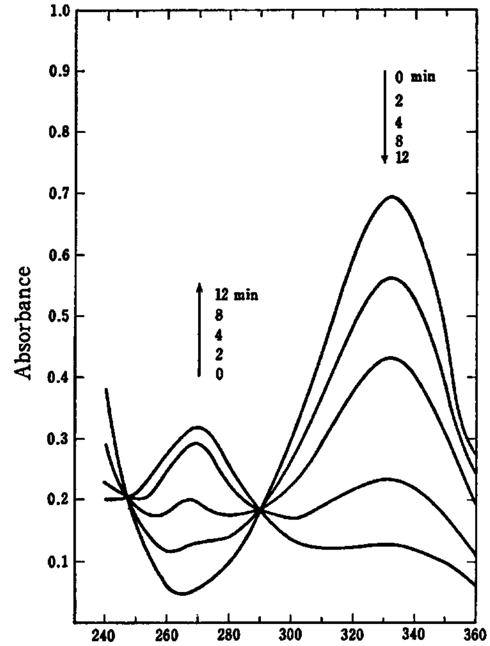
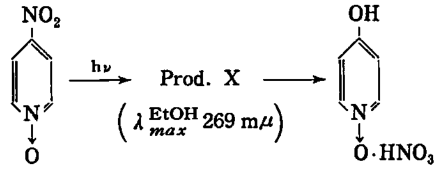


Fig. 1. The progressive spectral change of 4-nitropyridine *N*-oxide on 3130 Å irradiation in ethanol (5×10^{-5} mol l^{-1}).
Numbers refer to irradiation time.



Process I

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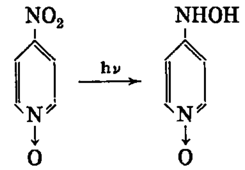
[7] E. Ochiai, *J. Org. Chem.*, **18**, 535 (1953).

Process II



In order to examine the concentration dependency of the photochemical reaction, the 3130 Å irradiation was carried out in ethanol solutions with various concentrations of 4-nitropyridine *N*-oxide. Whether Process I or Process II was determined from the ultraviolet absorption spectrum of the irradiated solution, the results thus obtained are shown schematically in Fig. 3. As can be seen from Fig. 3, Process II proceeds both in a solution with an extremely low concentration (less than *ca.* 2×10^{-5} mol l^{-1}) and in a solution with a high concentration (over *ca.* 10^{-4} mol l^{-1}), whereas Process I proceeds strikingly in a solution with a medium concentration (*ca.* 10^{-4}—10^{-5} mol l^{-1}). The results obtained for the deaerated solution indicate that Process II can be facilitated by excluding any oxygen dissolved in the solution, and that Process I can proceed even in a deaerated solution.

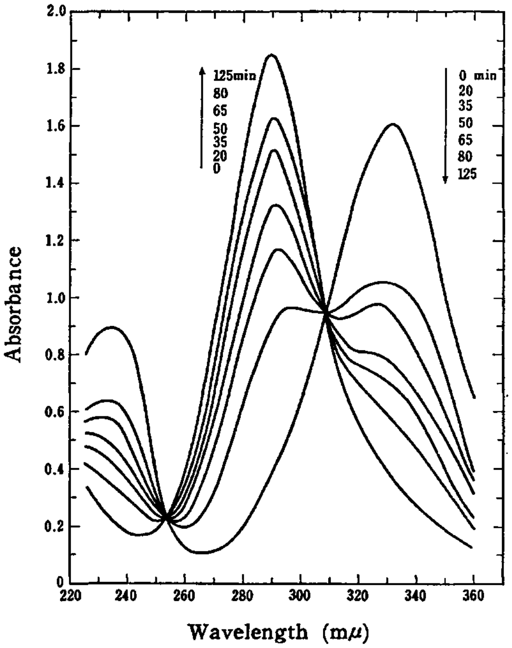


Fig. 2. The progressive spectral change of 4-nitropyridine *N*-oxide on 3130 A irradiation in ethanol (1.8×10^{-2} mol l^{-1}). Numbers refer to irradiation time.

Next, we examined the effect of the viscosity on the photochemical process and the effect of the concentration on the quantum yield of the 4-nitropyridine *N*-oxide disappearance. Figure 4 shows the progressive spectral change in 4-nitropyridine *N*-oxide when it is irradiated with 3130 Å light in glycerol and also in a glycerol solution mixed with various amounts of ethanol. Although Process II proceeded in a highly viscous solution, a lowering of the viscosity of the solution was observed to lead to a switch in the photochemical reaction from Process II to Process I. As is shown in Fig. 5, the quantum yield of 4-nitropyridine *N*-oxide disappearance in ethanol, where Process I takes place, increased markedly with an increase in the concentration, giving a maximum value (1.6—1.8) in the region of about 6×10^{-4} mol·l^{-1}. A further increase in the concentration caused a decrease in the quantum yield. On the other hand, the quantum yield in glycerol, where Process II takes place, was independent of the concentration and showed an average value of about 0.7. Figure 6 shows the temperature dependence of the quantum yield where the quantum yield of 4-nitropyridine *N*-oxide disappearance was observed to increase with a rise in the temperature. Although the quantum yield mentioned above was measured in a solution which had not

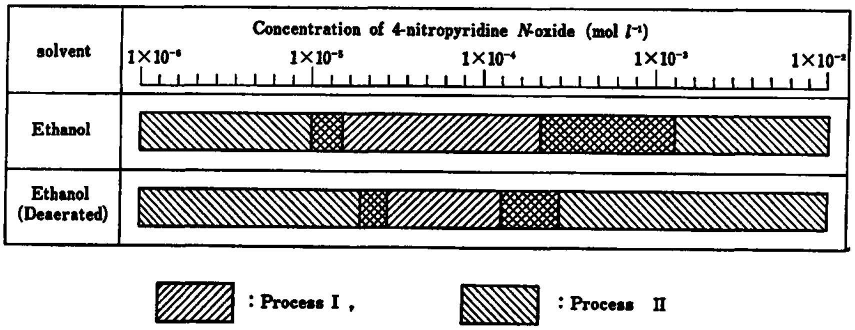
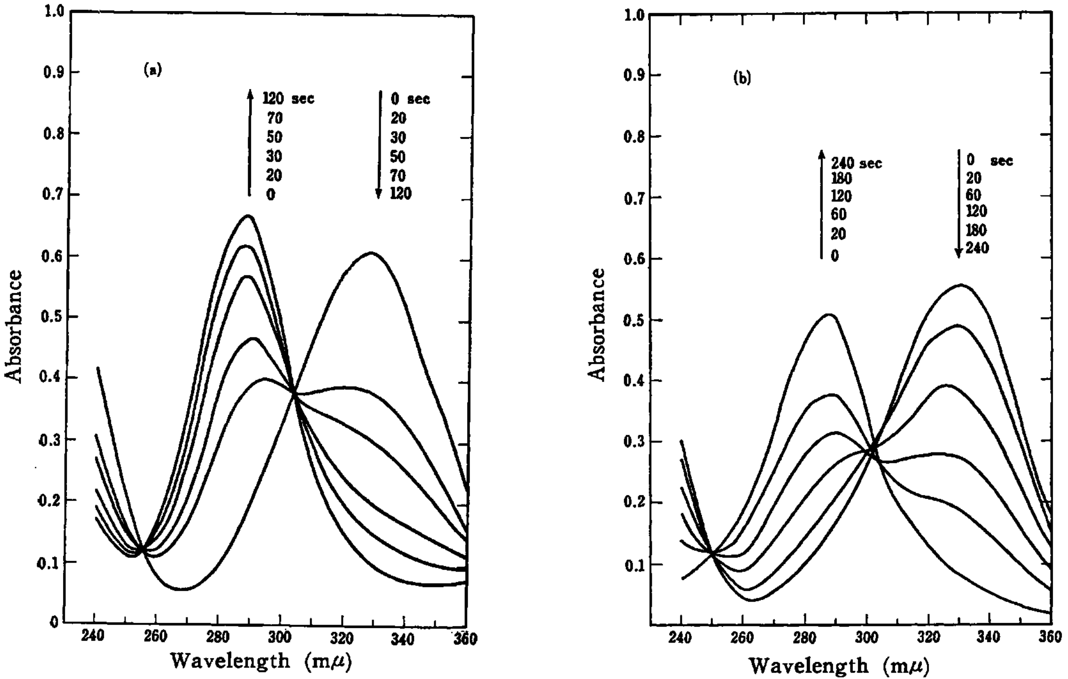
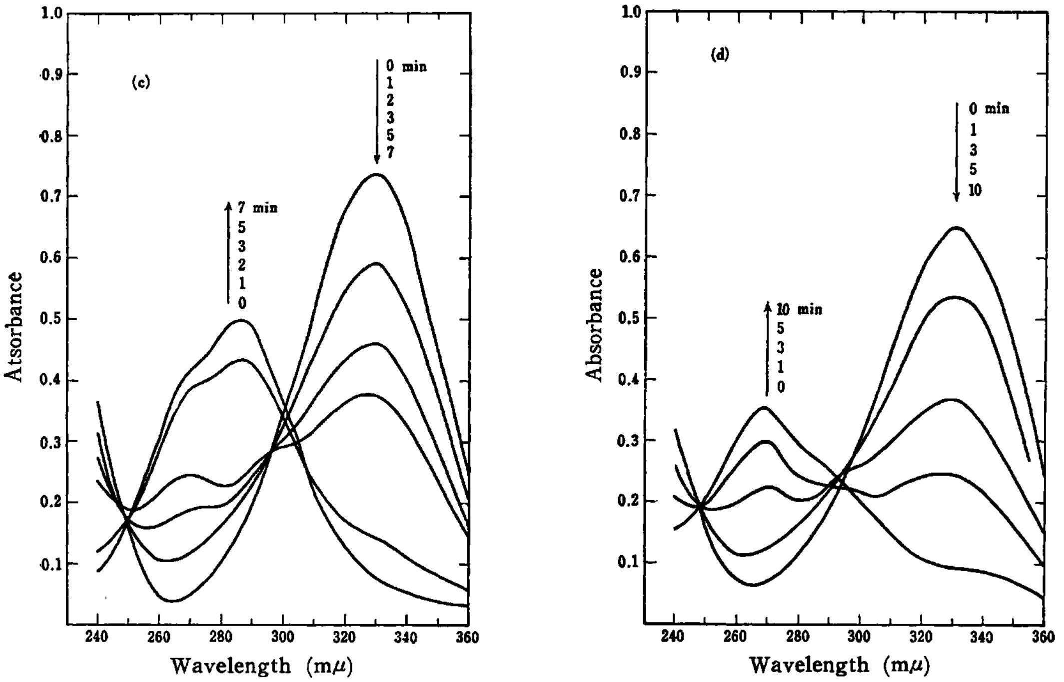


Fig. 3. Schematic representation of the photochemical processes of 4-nitropyridine *N*-oxide in ethanol.



(a) glycerol

(b) glycerol (1 vol) and ethanol (1 vol)



(c) glycerol (2 vol) and ethanol (3 vol)

(d) glycerol (1 vol) and ethanol (2 vol)

Fig. 4. The progressive spectral change of 4-nitropyridine *N*-oxide on 3130 Å irradiation in viscous solution (*ca.* 5×10^{-5} mol l^{-1}).
Numbers refer to irradiation time.

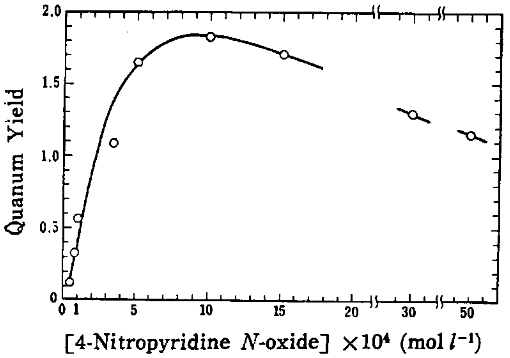


Fig. 5. Quantum yield (Φ) *versus* concentration of 4-nitropyridine *N*-oxide at 30°C in ethanol.

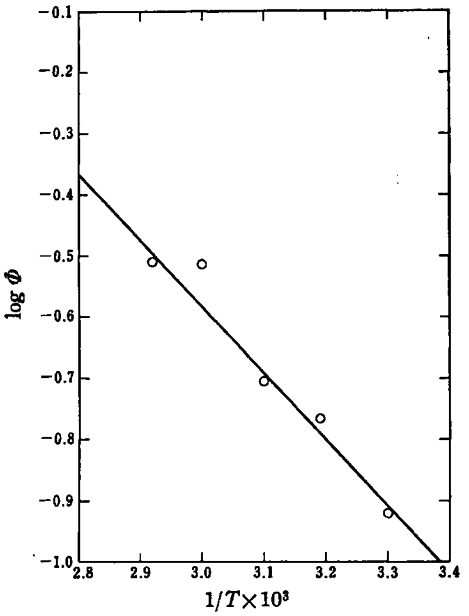


Fig. 6. Quantum yield (Φ) *versus* temperature in ethanol (5×10^{-5} mol l^{-1}).

been degassed, a comparison with the results for a solution degassed by flushing with nitrogen at 30°C indicated that there is possibly no effect of the oxygen dissolved in the solution on the quantum yield.

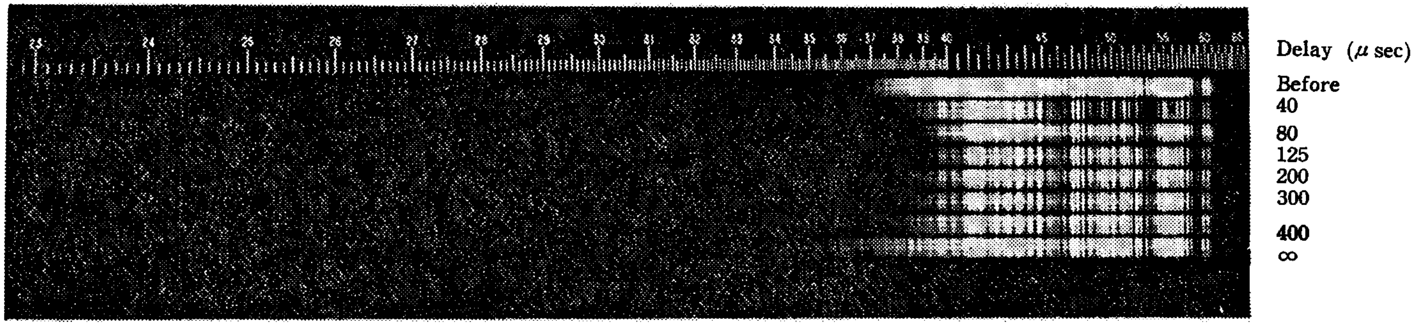
Finally, in order to get information on the photochemical intermediate which may be formed during the reaction, the flash spectroscopic examination was carried out in both ethanol and glycerol. In the case of a 5×10^{-5} mol l^{-1} ethanol solution (Fig. 7 (a)), transient absorptions were observed around 370 mμ and 570 mμ, but they disappeared within about 10^{-4} sec to give a shorter wavelength absorption (260 mμ—270 mμ) corresponding to the Prod. X being formed in Process I. In the case of a glycerol solution (4×10^{-5} mol l^{-1}), the same transient absorptions as in the case of an ethanol solution appeared around 370 mμ and 570 mμ, as is shown in Fig. 7 (b); these absorptions decayed within about 10^{-4} sec to give the absorption of 4-hydroxylaminopyridine *N*-oxide via Process II. Figure 7 (c) shows the results for the flash illumination in a very dilute ethanol solution (2×10^{-5} mol l^{-1}), which indicated the appearance of the same transient absorption, followed by Process I and Process II. In all these experiments, the transient absorption common to all three cases was independent of the presence or absence of oxygen in the solution.

Discussion

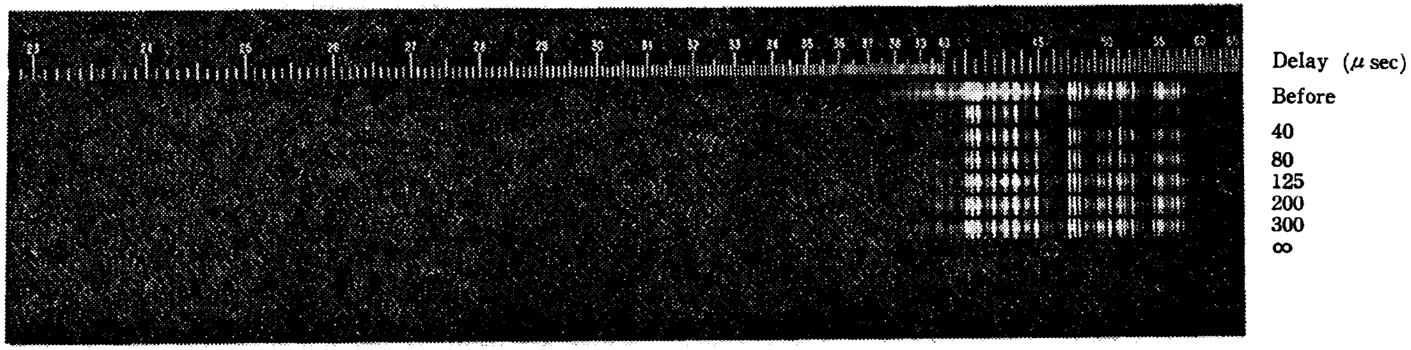
In the present paper, we propose the primary process shown schematically in Fig. 8 for the photochemical reaction of 4-nitropyridine *N*-oxide in solution, where S_0 and S_1 denote, respectively, the ground and the lowest excited singlet-state molecules, while both A and B represent intermediate species.

The following conclusions have been drawn from the flash spectroscopic experiments: 1) Both Process I and Process II proceed through the intermediate A. 2) The absorption spectrum of the intermediate A is always observed around 370 mμ and 570 mμ, regardless of the dissolved oxygen in solution, possibly meaning that the intermediate A is not a triplet state. 3) The intermediate A has a relatively long lifetime (*ca.* 10^{-4} sec), which suggests the possibility of a bimolecular interaction between the intermediate A and unexcited 4-nitropyridine *N*-oxide (S_0).

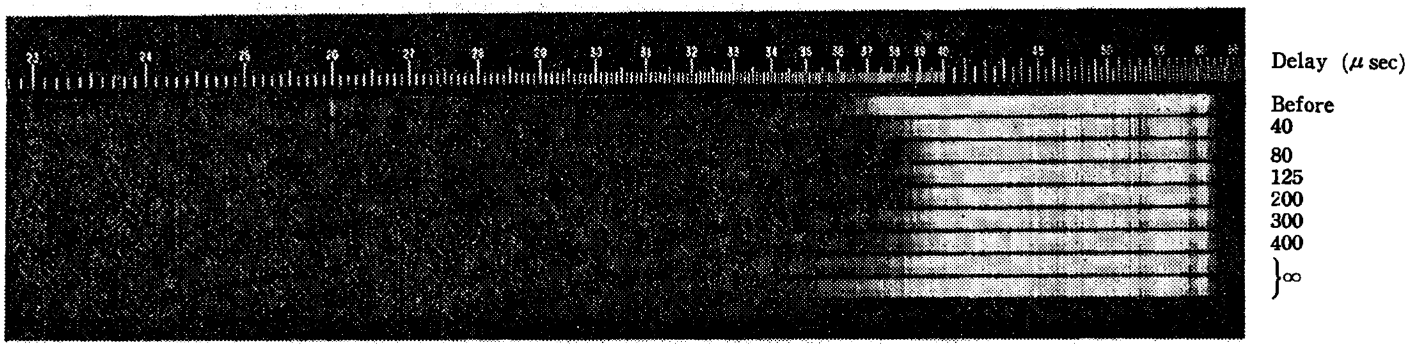
It is very difficult to bring the intermediate A together with an unexcited *N*-oxide molecule (S_0) in a glycerol solution because of the high viscosity of the solvent. As has been reported in a previous paper,[6] Process II involves a hydrogen atom-abstracting process from a solvent molecule, and thus an intermediate A probably abstracts a hydrogen atom from a glycerol molecule to form 4-hydroxylaminopyridine *N*-oxide finally. As to the hydrogen atom-abstracting species, however, it is not possible to say anything about whether it is an intermediate A or an intermediate B transformed further from an intermediate A. In any case, the intermediate A is responsible for Process II. Similarly, in a very dilute solution of 4-nitropyridine *N*-oxide the intermediate, either A or B, is considered to make an abstraction of a hydrogen atom from an ethanol molecule before colliding with an unexcited *N*-oxide molecule (S_0). In fact, the experimental results show that only Process II takes place in these solutions.



(a) 5×10^{-5} mol l^{-1} ethanol solution



(b) 4×10^{-5} mol l^{-1} glycerol solution



(c) 2×10^{-5}mol l^{-1} ethanol solution

Fig. 7. Flash photolysis of 4-nitropyridine *N*-oxide.

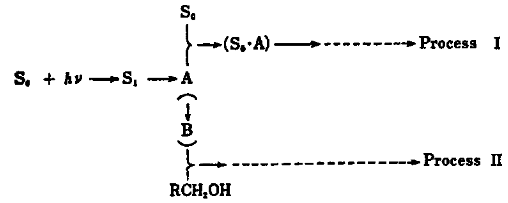


Fig. 8. The primary photochemical process of 4-nitropyridine *N*-oxide in solution.

On the other hand, as the concentration of 4-nitropyridine *N*-oxide in ethanol increases, the possibility of a collisional encounter of the intermediate A with an unexcited *N*-oxide molecule (S_0) becomes more likely; therefore, a bimolecular reaction between them can be expected to take place. This is confirmed by the experimental results on the concentration dependence of the photochemical reaction (Fig. 3) and on the quantum yield of 4-nitropyridine disappearance (Fig. 5). Moreover, further support for it is given by the following experimental results: 1) As the viscosity of the glycerol solution is lowered by adding various amounts of ethanol, the photochemical reaction is converted from Process II to Process I (Fig. 4). 2) The quantum yield of the 4-nitropyridine *N*-oxide disappearance in an ethanol solution increases gradually with a rise in the tempreature (Fig. 6), from which fact the activation energy is estimated to be about 5 kcal mol^{-1}, which is considered to correspond to the activation energy of diffusion.

However, the following experimental results are not clearly explained: 1) In a very concentrated ethanol solution Process I does not proceed; rather, Process II takes place. 2) In connection with 1), the quantum yield of the 4-nitropyridine *N*-oxide disappearance decreases with an increase in the concentration after reaching its maximum value. One possible explanation for these facts is to assume the formation of a transient weak complex between A and S_0. That is, with an increase in the concentration, most of the weak complex formed may be quenched by collision with an unexcited *N*-oxide molecule (S_0), thus reproducing S_0 and A, and the intermediate species, A, thus reproduced may be responsible for Process II. Further studies of these points, including the details of Process I and II and the nature of the intermediate A, are now in progress and will be reported on later.

In conclusion, the authors wish to express their hearty thanks to Professor S. Kato of Osaka University and Dr. Y. Mori of the Tokyo Institute of Technology for their valuable suggestions.