The Primary Photochemical Process of 4-Nitropyridine *N*-Oxide II. Decay Kinetics of the Photochemical Intermediates[1]

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In order to clarify the primary photochemical process of 4-nitropyridine *N*-oxide in solution, kinetic flash spectrophotometric studies were carried out under various conditions. The flash excitation of 4-nitropyridine *N*-oxide in alcoholic solution resulted in three transient species in the spectral region between 360 nm and 580 nm; one of them was a weak absorption at about 530 nm (transient species A and A′), and the other, a stronger one around 380 nm (transient species B). The experiments on the decay kinetics of these transients revealed that the photochemical reaction of 4-nitropyridine *N*-oxide in an alcoholic solution proceeded through these intermediate species originating from the excited singlet state; Process I (the photochemical formation of 4-hydroxypyridine *N*-oxide nitrate) involved the bimolecular interaction between an intermediate A′ and unexcited molecule, while Process II (the photochemical formation of 4-hydroxylaminopyridine *N*-oxide) was initiated by a hydrogen-atom abstraction from a solvent molecule by an intermediate B which was produced from another intermediate A. The two intermediates A and A′ were reasonably assumed to be formed concurrently from the excited singlet state of 4-nitropyridine *N*-oxide.

4-Nitropyridine *N*-oxide changes upon irradiation of 313 nm light in ethanol to give 4-hydroxypyridine *N*-oxide nitrate (Process I) or 4-hydroxylaminopyridine *N*-oxide (Process II), depending on the reaction conditions.[2-5] As has been described in a previous paper,[5] the observation of the transient absorption in the region between 360 nm and 580 nm and the measurements of the quantum yields under various conditions led to the conclusions that Processes I and II both proceed *via* some intermediate species originating from the excited singlet state of 4-nitropyridine *N*-oxide; Process I being due to a bimolecular interaction between an intermediate and an unexcited molecule, and Process II involving a hydrogen abstraction of an intermediate from an alcoholic solvent.

The purpose of the present investigation is to clarify whether or not the transient species observed in a flash photolysis of 4-nitropyridine *N*-oxide are actually responsible for Processes I and II, and then to obtain some information on the primary process.

Experimental

Materials. The 4-nitropyridine *N*-oxide used in this experiment was synthesized by nitrating the pyridine *N*-oxide according to the method given in the literature,[6] and the product was purified by recrystallization from acetone several times. The solvents used for the flash experiments were reagent-grade methanol, ethanol, isopropanol, and glycerol, all of which were used without further purification.

Flash Spectrophotometric Experiment. A sample solution contained in a quartz reaction cell (8 cm in length and 2 cm in diameter) was deaerated by flushing the cell with nitrogen. A quartz flash photolysis lamp (10 cm in length and 2 cm in diameter) filled with xenon gas was operated at 11 kV and 2 μF, dissipating an energy of 120 J; the duration of the flash was 10 μsec. The absorption spectra of transient species and their decays were determined with a xenon lamp (Toshiba 500 W) or a tungsten lamp (60 W), a plane grating spectrograph (Shimadzu GE-100), a photomultiplier tube (RCA 1P28), and a synchroscope (Toshiba 3054).

Results and Discussion

Figures 1 and 2 show the absorption spectra of the transient species produced by a flash excitation of 4-nitropyridine *N*-oxide in deaerated ethanol or glycerol at room temperature; the spectrum was plotted immediately after the flash and also at some specified time interval following the flash. As can be seen from the figures, two absorption systems were observed in the region between 360 nm and 580 nm; one of them was a weak absorption at about 530 nm, and the other, stronger one around 380 nm. Both absorptions were reduced to some extent in their intensity

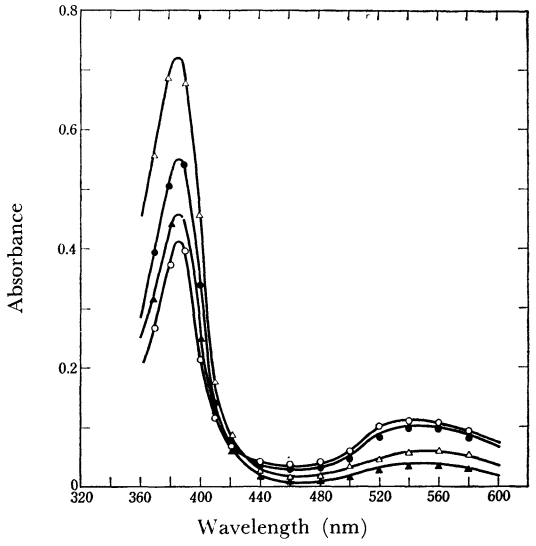


Fig. 1. Absorption spectrum of the transient species in 3.0×10^{-5}M 4-nitropyridine *N*-oxide in ethanol at room temperature.
(1) -○-, (2) -●-, (3) -△-, and (4) -▲- indicate the spectrum taken at 40 μsec, 60 μsec, 200 μsec, and 1 msec, respectively, after the flash.

1) Part I: N. Hata, E. Okutsu, and I. Tanaka, This Bulletin, **41**, 1769 (1968).
2) C. Kaneko, S. Yamada, I. Yokoe, N. Hata, and Y. Ubukata, *Tetrahedron Lett.*, **1966**, 4729.
3) C. Kaneko, S. Yamada, and I. Yokoe, *Chem. Pharm. Bull.* (Tokyo), **15**, 356 (1767).
4) C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron Lett.*, **1967**, 775.
5) N. Hata, E. Okutsu, and I. Tanaka, This Bulletin, **41**, 1769 (1968).
6) E. Ochiai, *J. Org. Chem.*, **18**, 535 (1953).

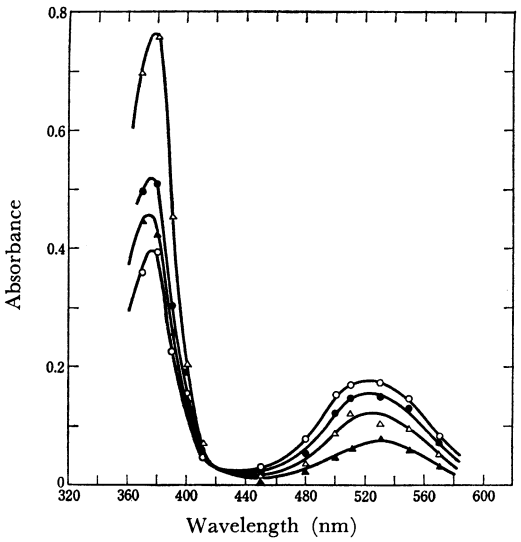


Fig. 2. Absorption spectrum of the transient species in 3.0×10^{-5}M 4-nitropyridine *N*-oxide in glycerol at room temperature.
(1) -○-, (2) -●-, (3) -△-, and (4) -▲- indicate the spectrum taken at 40 μsec, 60 μsec, 200 μsec, and 1 msec, after the flash.

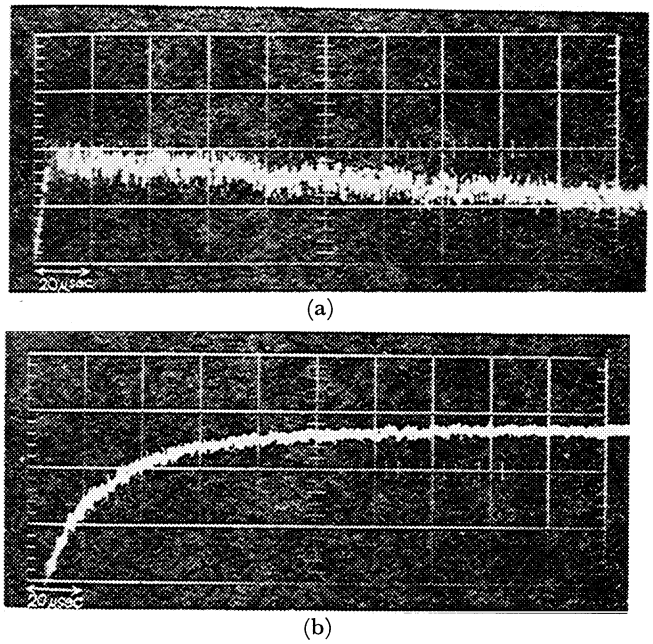


Fig. 3. Oscilloscope traces of transient absorption at 530 nm and 380 nm in ethanol (3.0×10^{-5}M) at room temperature. Horizontal scale, 20 μsec/division; Vertical scale, transmitted light intensity (downward).
(a): at 530 nm, (b) at 380 nm

in an oxygen-saturated solution, but they were not quenched completely. In addition, it may be inferred from these figures that the decay of the 530-nm species was followed by the formation of the 380-nm species. Figure 3 presents some typical pictures of oscilloscope traces taken at 530 nm and 380 nm after flash illumination of a 3.0×10^{-5} M solution of 4-nitropyridine *N*-oxide in deaerated ethanol. It is clear that an appreciable time was required for the appearance of the 380-nm species, while the formation of the 530-nm species was instantaneous-within the time of the flash. Quite similar results were also obtained in a methanol or an isopropanol solution. These observations indicate that the transient absorption which appeared around 530 nm was due to species different from those of the 380 nm absorption.

Next, kinetic examinations of the transients produced by flash illumination in deaerated solutions such as methanol, ethanol, isopropanol, and glycerol were carried out by measuring photoelectrically the time dependence of the absorption intensity (D) at 530 nm and 380 nm under various conditions.

Figure 4(a) shows the results when the first-order rate law was applied for the decay of the transients at 530 nm, while the second-order rate plots are shown

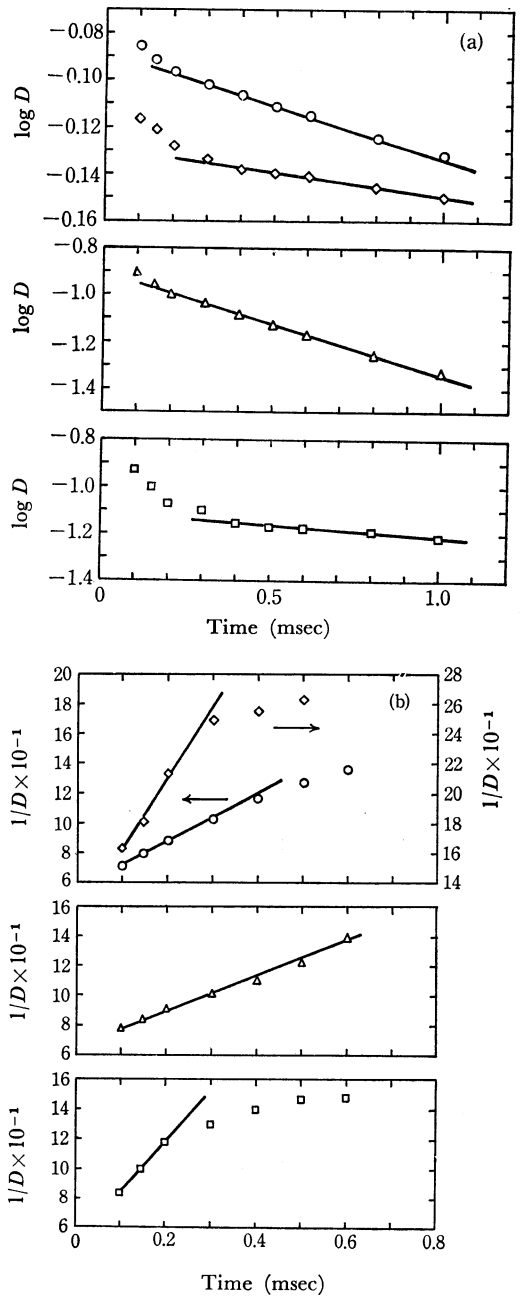


Fig. 4. First- and second-order rate plots for the decay of the transient absorption at 530 nm in various solvents at room temperature.
-◇-: in methanol, -○-: in ethanol, -△-: in isopropanol, -□-: in glycerol.
(a) first-order rate plots, (b) second-order rate plots.

in Fig.4(b). There, the second-order rate plot in Fig. 4(b) seems to require some considerations, because the slope at the first (initial) stage of decay is greater than that at the second stage in the cases of methanol, ethanol, and glycerol solution.

Generally, when any transient species, say X, is able to decay according to both the first- and second-order processes, the decay rate is expressed as follows:

$$-\mathrm{d[X]}/\mathrm{d}t = k_1[\mathrm{X}] + k_2[\mathrm{X}]^2 \quad (1)$$

where k_1 and k_2 represent, respectively, the first- and second-order rate constants. The slope of the first-order rate plot is given by Eq. (2). Thus, the slope at the first stage of decay must be greater than that at the second stage.

$$-\mathrm{d}(\ln[\mathrm{X}])/\mathrm{d}t = k_1 + k_2[\mathrm{X}] \quad (2)$$

Equation (3) gives a slope of the second-order rate plot, indicating that the slope at the second stage of decay can be expected to be greater than that of the first stage.

$$\mathrm{d}(1/[\mathrm{X}])/\mathrm{d}t = k_1/[\mathrm{X}] + k_2 \quad (3)$$

These general relations were applied to the present experimental results. Tentatively, let us suppose that the transient absorption around 530 nm is due to a single species which decays according to both the first- and second-order rate laws. On this assumption, the first-order rate plot in Fig.4(a) is consistent with Eq.(2), whereas the second-order rate plot in Fig.4(b) is in conflict with Eq.(3). For this reason, it seems most reasonable to conclude that the 530 nm absorption should be ascribed to two transient species which decay with different first-order rate constants. Therefore, the faster species is referred to as the intermediate A (rate constant, k_A) and the slower one as the intermediate A′ (rate constant, $k_{A'}$). The values of these rate constants, as evaluated from the decay curve in Fig. 4(a), are given in Table 1.

TABLE 1. RATE CONSTANTS OF THE INTERMEDIATE SPECIES A, A′, AND B IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

Solvent	$k_A(\mathrm{sec}^{-1})$ $\times 10^{-4}$	$k_{A'}(\mathrm{sec}^{-1})$ $\times 10^{-2}$	$k_B(\mathrm{sec}^{-1})$ $\times 10^{-1}$	$k_B^f(\mathrm{sec}^{-1})$ $\times 10^{-4}$
Methanol	2.4	2.3	0.17	5.0
Ethanol	0.90	9.2	1.2	1.5
Isopropanol	0.48	9.2	3.1	0.82
Glycerol	1.0	2.0	0.25	1.1

Figures 5 and 6 show the first- and second-order rate plots for the transient absorption around 380 nm. There, a single straight-line relation was obtained by plotting log D against the time in an isopropanol or glycerol solution, while in a methanol or ethanol solution the decay curve followed, at the first stage of decay, the second-order rate law and, at the second stage, the first-order kinetics. Moreover, in the case of a methanol or ethanol solution, the first- and second-order rate plots were fairly consistent with Eqs.(2) and (3). From these results, it may be concluded that the transient absorption around 380 nm is due to a single species which decays according to the first-order kinetics, but that there is a small contribution from the second-order process in the case of a methanol

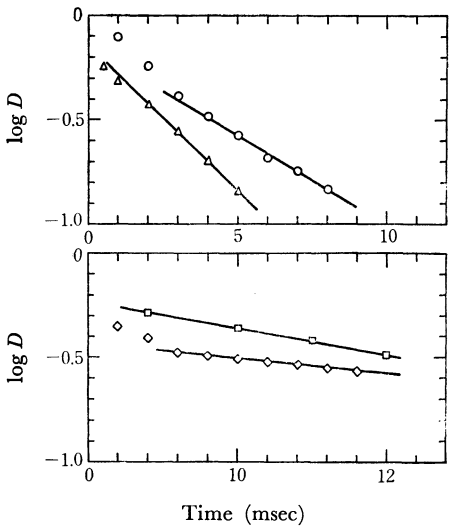


Fig. 5. First-order rate plots for the decay of the transient absorption at 380 nm in various solvents at room temperature.
-◇-: in methanol, -○-: in ethanol, -△-: in isopropanol, -□-: in glycerol.

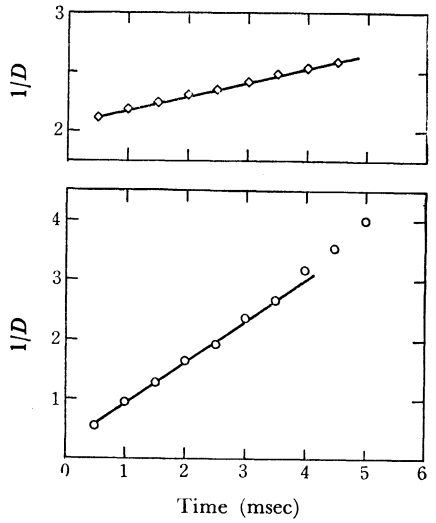


Fig. 6. Second-order rate plots for the decay of the transient absorption at 380 nm in methanol (-◇-) and in ethanol (-○-).

or ethanol solution. Therefore, the transient species is referred to as the intermediate B, and the first-order rate constants, k_B, estimated from the straight-line portion of the curve in Fig. 5 are given in Table 1.

The rate constant of the formation of the intermediate B, k_B^f, was evaluated from the rise in the transient absorption at 380 nm (Fig.3). The values thus obtained of k_B^f in various solutions are listed in Table 1. In Table 1 the decay rate of the intermediate A may be found to agree closely with that of the formation of the intermediate B. This suggests that the species B is produced directly from the intermediate A.

Although the decay rate of the intermediate B increased when the solvent was changed from methanol to ethanol and then to isopropanol, such a solvent dependency of the decay rate was not found in the case of the intermediate A or A′ (Table 1). The data imply that the intermediate B is probably responsible

for Process II, which involves a hydrogen-atom abstraction from the solvent alcohol, as has been reported previously.[5] Generally, when any transient species can abstract a hydrogen atom from a hydrogen donor, its decay rate may be expected to increase in proportion to the concentration of the hydrogen donor. In order to confirm which intermediate, A, A′, or B, is involved in the hydrogen-atom abstraction from the solvent alcohol, therefore, the decay rates of these species were determined as a function of the concentration of isopropanol added as a hydrogen donor in a methanol solution; the results are shown in Fig.7. The decay

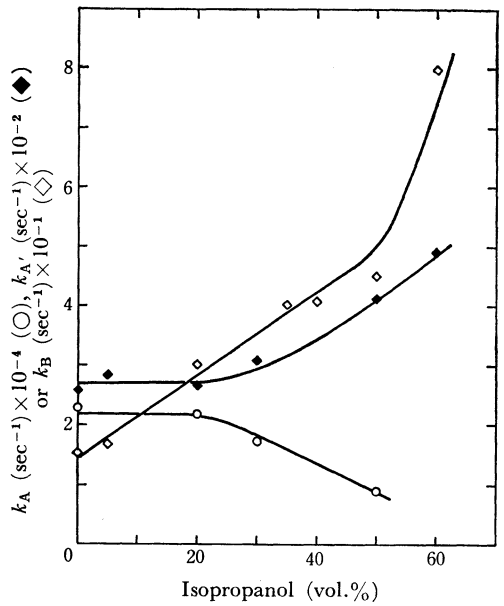


Fig. 7. Effect of an addition of isopropanol on the first-order decay rates of the intermediate species A, A′, and B in methanol.
-○-: intermediate species A, -◆-: intermediate species A′, -◇-: intermediate species B.

rate of the intermediate B increased proportionately with the amounts of isopropanol added, while the decay of the intermediate A or A′ was independent of the addition of isopropanol up to about 20 vol.%. Consequently, it appears plausible that the intermediate B is responsible for Process II. When the amounts of isopropanol added exceeded *ca* 40% in volume, however, the decay rates of these species showed a great change and approached the value in the case of the isopropanol solution.

In a previous paper,[5] on the basis of the concentration and temperature dependences of the quantum yield of the 4-nitropyridine *N*-oxide disappearance, Process I has been inferred to proceed *via* a transient complex formed from the interaction of an intermediate, say Y, originating from the excited singlet state (S_1) with an unexcited molecule (S_0), as described in the following sequence:

	Rate
$Y \rightarrow S_0$ (or chemical change)	$k_Y^a[Y]$
$S_0 + Y \rightarrow (S_0Y)$	$k_Y^b[S_0][Y]$
$(S_0Y) + S_0 \rightarrow Y + S_0 + S_0$	$k_Y^c[(S_0Y)][S_0]$
$(S_0Y) \rightarrow$ Process I	

If these steps are actually involved in Process I, and if one of the three transients, A, A′, and B, observed here corresponds to the intermediate Y described above, then its decay rate (k_Y) may be expected to vary with an increased concentration of 4-nitropyridine *N*-oxide following Eq.(4).

$$k_Y = k_Y^a + k_Y^b[S_0] - k_Y^c[(S_0Y)][S_0]/[Y] \quad (4)$$

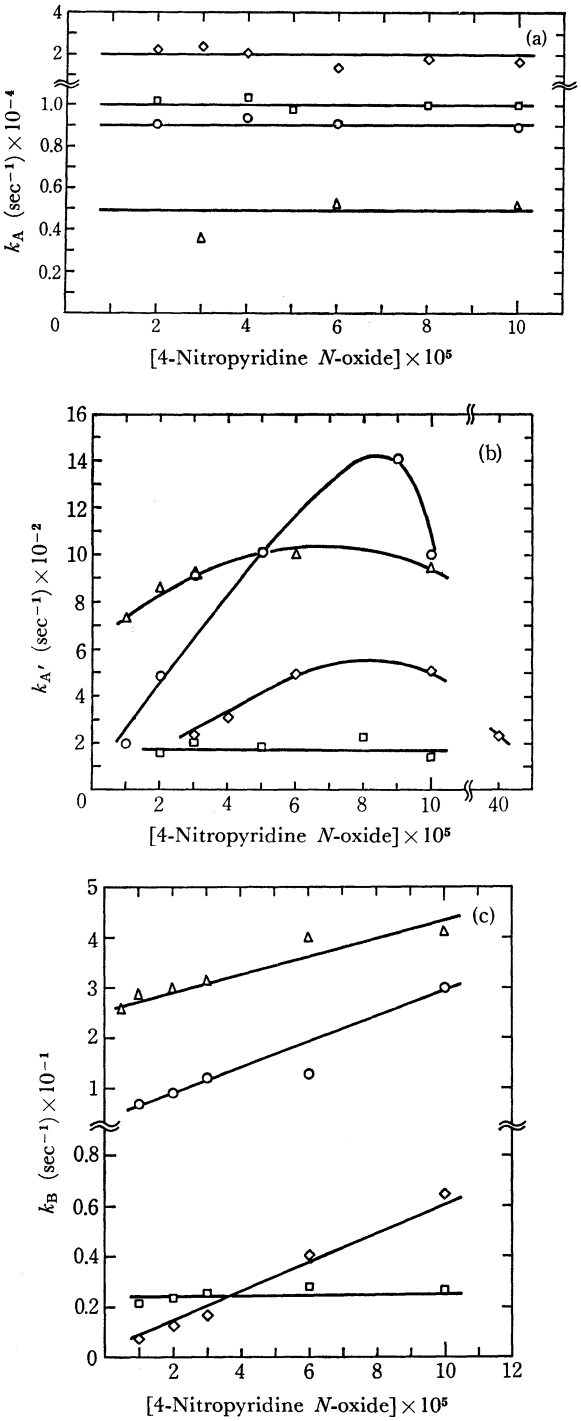
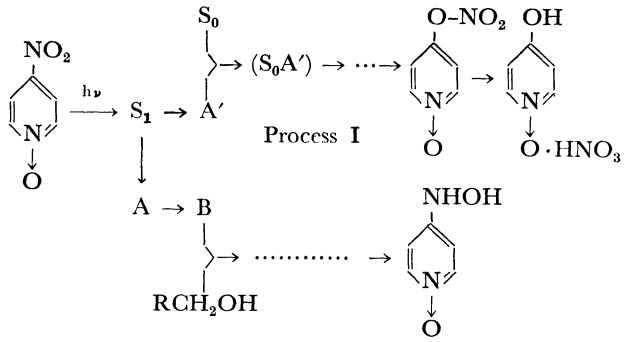


Fig. 8. First-order decay rates of the intermediate species A, A′, and B *versus* initial concentration of 4-nitropyridine *N*-oxide.
-◇-: in methanol, -○-: in ethanol, -△-: in isopropanol, -□-: in glycerol.
(a) intermediate species A, (b) intermediate species A′, (c) intermediate species B.

For this reason, the effect of the initial concentration of 4-nitropyridine *N*-oxide on the decay rates of the intermediates, A, A′, and B, was examined in deaerated ethanol. With an increase in the concentration of 4-nitropyridine *N*-oxide, as Fig. 8 shows, the decay rate of the intermediate A′ increased until it approached a steady value, and then decreased; such a concentration-dependence of the decay rate is consistent with Eq.(4). On the other hand, the decay rate of the intermediate B increased linearly with an increase in the concentration of 4-nitropyridine *N*-oxide, while that of the intermediate A remained unchanged, in the range of concentrations used in this experiment. These resluts support the idea that the intermediate A′ is responsible for Process I, and that this process proceeds through the formation of a transient complex (S_0A').

From the experimental results presented above, the following scheme seems to be reasonable for the primary photochemical process of 4-nitropyridine *N*-oxide in an alcoholic solution;[7] a partial modification is made of a scheme proposed in a previous paper.[5] The 4-nitropyridine *N*-oxide excited into the S_1 state by absorbing the ultraviolet light (>300 nm) is converted into the intermediate A (530nm), followed by transformation to the intermediate B (380 nm),



which then abstracts a hydrogen atom from an alcoholic solvent to lead to Process II. Here, it seems to be of particular interest that 4-nitropyridine *N*-oxide is photochemically reduced *via* some intermediates originating from the excited singlet state, since the photochemical reduction of aromatic nitro compound generally proceeds through the lowest triplet state.[8] As will be reported in a later paper,[9] however, it has become apparent from the studies of the biacetyl sensitization that the photoreduction of 4-nitropyridine *N*-oxide is also capable of proceeding *via* the lowest triplet state. The intermediate A′ (530 nm), which is also considered to result from the S_1 state, would interact with the ground state molecule, S_0, to give a transient complex (S_0A'), through which Process I proceeds. The end product of Process I, the 4-hydroxypyridine *N*-oxide nitrate, has been demonstrated to result from a hydrolysis of the nitric acid ester of 4-hydroxypyridine *N*-oxide generated during the photoreactions.[3] Accordingly, certain reactions taking place within the transient complex (S_0A') appear to lead to the formation of this nitric acid ester, although the mechanism is entirely ambiguous at present. The 4-hydroxylaminopyridine *N*-oxide formed by Process II may be converted photochemically to 4-nitropyridine *N*-oxide under an oxygen atmosphere.[10] Hence, the ultraviolet irradiation of the 4-nitropyridine *N*-oxide in an atmosphere of oxygen is expected to give 4-hydroxypyridine *N*-oxide nitrate as the major product; in fact, its yield has been reported to be 60–65% in an ethanol solution.[3] On the contrary, the 4-hydroxylaminopyridine *N*-oxide is expected to be the main product under a nitrogen atmosphere, particularly in the case of a concentrated solution of 4-nitropyridine *N*-oxide, because most of the transient complex (S_0A') is quenched by collision with an unexcited *N*-oxide molecule; Process II thus becomes more likely. The experiments performed under such conditions support this idea.[2,5]

Meanwhile, as has been suggested by Kaneko *et al.*[3,4] the Nef-type mechanism is also anticipated to be responsible to some extent for the formation of 4-hydroxypyridine *N*-oxide nitrate; especially, the photoreaction of 3,5-dimethyl 4-nitropyridine *N*-oxide has been considered to be due to this mechanism.[4] It seems, therefore, that further studies are necessary in order to elucidate the mechanism of Process I.

As to the structure of the intermediates, A, A′, and B, involved in Process I or II, we could not draw any conclusions from only the present experimental results. As judged from the facts that 4-nitropyridine *N*-oxide undergoes a photochemical change in a moiety of the nitro group, but not of the N→O group, however, it may be assumed that the nitro group in each of these intermediates is considerably different from a normal one in structure. In addition, the fact that the absorption spectrum of the intermediate A (530 nm) exists in the same region as that of the intermediate A′ suggests that their electronic structures are quite similar to each other. On the other hand, the absorption band of the intermediate B (380 nm) is located rather close to that of 4-nitropyridine *N*-oxide (330 nm), which probably means

7) Considered from the fact that the transient absorptions are always observed regardless of the presence or absence of oxygen in solution, the intermediate species A, A′, and B are assumed to originate from the excited singlet state (S_1) but not the lowest triplet state.

8) a) Nitrobenzene and 1-nitronaphthalene : R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966), *ibid.*, **89**, 6917 (1967), S. Hashimoto, J. Sunamoto, H. Fujii, and K. Kano, This Bulletin, **41**, 1249 (1968), J. A. Barltrop, and N. J. Bunce, *J. Chem. Soc., C*, **1968** 1467, W. Trotter and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 7044 (1968), R. Hurley and A. C. Testa, *ibid.*, **90**, 1949 (1968), S. Hashimoto and K. Kano, *Kogyo Kagaku Zasshi*, **72**, 188 (1969), W. Trotter and A. C. Testa, *J. Phys. Chem.*, **74**, 845 (1970); b) 4-Nitropyridine : S. Hashimoto, K. Kano, and K. Ueda, *Tetrahedron Lett.*, **1969**, 2733. This Bulletin, **44**, 1102 (1971). c) About the photochemistry of aromatic nitro compounds see, for example, H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups," Part 1, ed. by H. Feuer, Interscience Publishers, New York, (1969), Chapter 4.

9) I. Ono and N. Hata, This Bulletin, in press.

10) The photochemical conversion of 4-hydroxylaminopyridine *N*-oxide to 4-nitropyridine *N*-oxide in ethanol under an oxygen atmosphere has been reported by Kaneko *et al.*[3]

that the nitro group of the intermediate B structurally a little resembles that of unexcited 4-nitropyridine *N*-oxide. In order to clarify the structure of the intermediates, A, A′, and B, it seems to be important to elucidate in detail the reaction mechanism for both Processes I and II; along this line further studies are now in progress.

In conclusion, the authors wish to express their hearty thanks to Professor Ikuzo Tanaka of Tokyo Institute of Technology for his encouragement and Professor Shiro Matsumoto of this university for his permission to use a flash-photolysis apparatus.