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The Primary Photochemical Process of 4-Nitropyridine *N*-Oxide. III. Its Photochemical Behavior in an Aqueous Solution

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4-Nitropyridine *N*-oxide does not undergo photochemical changes in an aqueous solution. When small amounts of 2-propanol or tetrahydrofuran were added to a deaerated solution, however, the 4-nitropyridine *N*-oxide was found to be reduced photochemically to afford 4-hydroxylaminopyridine *N*-oxide. From the measurements of the quantum yields and from flash-spectroscopic experiments under various conditions, such a photoinduced reduction of 4-nitropyridine *N*-oxide in deaerated water was revealed to be initiated by a hydrogen-atom abstraction from a 2-propanol or tetrahydrofuran by the triplet species. The situation was quite different from the case of an alcoholic solution, in which some intermediate species originating from the excited singlet state was responsible for the photoreduction.

As has been described in a previous paper,[1] the photochemical reaction of 4-nitropyridine *N*-oxide in alcohol (methanol, ethanol, 2-propanol, or glycerol) involves some intermediate species, A, A′, or B, originating from the excited singlet state; Process I (the photochemical formation of 4-hydroxypyridine *N*-oxide nitrate) proceeds *via* a transient complex between the intermediate A′ and the unexcited molecule, while Process II (the photochemical formation of 4-hydroxylaminopyridine *N*-oxide) is initiated by a hydrogen-atom abstraction from a solvent molecule by the intermediate B, which is produced from another intermediate, A.

However, the 4-nitropyridine *N*-oxide in water is quite stable to light.[2] Considering the fact that even Process I does not proceed in an aqueous solution, the primary process may be inferred to be quite different from that in alcohol. In order to make this point

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[1] N. Hata, I. Ono, and T. Tsuchiya, This Bulletin, **45**, 2386 (1972).

[2] C. Kaneko, S. Yamada, I. Yokoe, N. Hata, and Y. Ubukata, *Tetrahedron Lett.*, **1966**, 4729.

clear, therefore, the present authors have carried out investigations by means of both steady-light irradiation and flash spectroscopy for the 4-nitropyridine *N*-oxide in deaerated water.

Experimental

The 4-nitropyridine *N*-oxide used in this experiment was synthesized and purified according to the method given in the literature.[3] Reagent-grade tetrahydrofuran and 2-propanol (Wako Pure Chemical Industries) were used without further purification.

The apparatus and procedures for both the steady-light and flash experiments were the same as those reported previously.[1,4]

Results and Discussion

Photochemical changes were not induced for the 4-nitropyridine *N*-oxide when it was irradiated with 313 nm light in deaerated water. The introduction of small amounts of 2-propanol or tetrahydrofuran (THF) into the solution, however, was found to result in the photochemical reduction of 4-nitropyridine *N*-oxide to the 4-hydroxylaminopyridine *N*-oxide, while no such production occurred when *tert*-butyl alcohol was added instead of 2-propanol or THF. Such a photoinduced reaction of 4-nitropyridine *N*-oxide in an aqueous solution was completely prevented by the dissolved oxygen. As an example, Fig. 1 shows the progressive spectral change of 4-nitropyridine *N*-oxide (7.0×10^{-5} M) in deaerated water containing 1.2×10^{-1} M THF on 313 nm irradiation. As can be seen from the figure, as the irradiation time increased the absorption spectrum of 4-nitropyridine *N*-oxide decreased progressively in intensity and a new absorption band with its maximum at 283 nm appeared, which coincided with that of 4-hydroxylaminopyridine *N*-oxide.

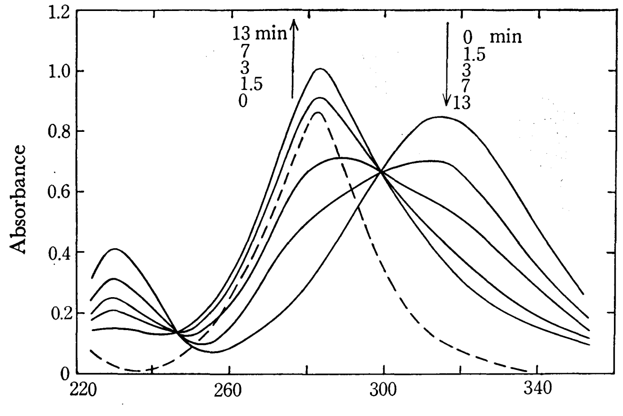

Fig. 1. The progressive spectral change of 4-nitropyridine *N*-oxide in deaerated water (7.0×10^{-5} M) containing a 1.2×10^{-1} M THF on 313 nm irradiation. Numbers refer to the irradiation time. The broken curve represents the absorption spectrum of 4-hydroxylaminopyridine *N*-oxide in water (4.7×10^{-5} M).

The quantum yields (Φ) of the disappearance of 4-nitropyridine *N*-oxide were determined as a function of the concentration of 2-propanol or THF added as the reducing agent, or of the concentration of the hydrogen-donor (RH) in an aqueous solution (7.0×10^{-5} M) at room temperature. Figure 2 shows the results thus obtained; a linear relationship may be seen to exist between the reciprocals of Φ and [RH].

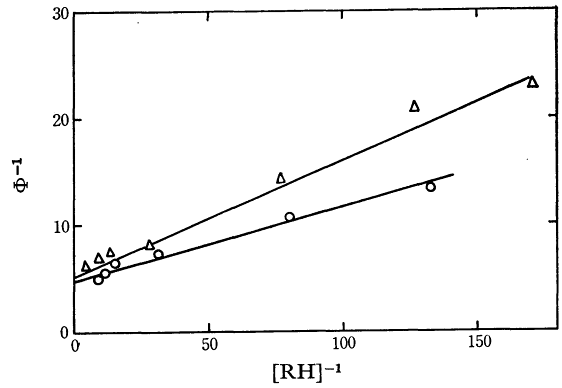

Fig. 2. Quantum yield (Φ) *vs.* concentration of hydrogen-donor (-○-: THF, -△-: 2-propanol) in deaerated aqueous solution (7.0×10^{-5} M) at room temperature, on 313 nm irradiation.

Next, in order to clarify whether or not the photochemical process of 4-nitropyridine *N*-oxide in water involves the same intermediates as in the case of an alcoholic solution, flash-spectroscopic examinations were undertaken in a deaerated aqueous solution at room temperature. Figure 3 shows the absorption spectra of the transient species produced by a flash illumination, where the spectrum was plotted after the flash and also at a specified time interval following the flash. Thus, the transient absorptions were observed around 380 and 550 nm, but they completely disappeared in the presence of oxygen. The decay analyses for these transient absorptions were carried out by applying the first-order rate law at various wavelengths; two examples, at 380 nm and at 540 nm, are presented in Fig. 4. It is clear from the figure that the decay curve for the 540 or 380 nm absorption can be resolved into

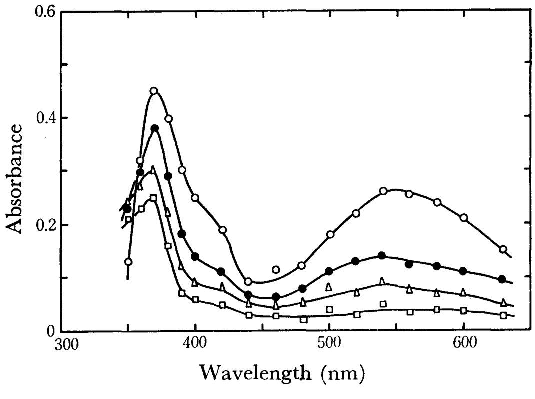

Fig. 3. Transient spectra of 4-nitropyridine *N*-oxide in deaerated water (7.0×10^{-5} M) at room temperature. (1) -○-, (2) -●-, (3) -△-, and (4) -□- indicate the spectrum taken at 20 μsec, 60 μsec, 100 μsec, and 200 μsec, respectively, after the flash.

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

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

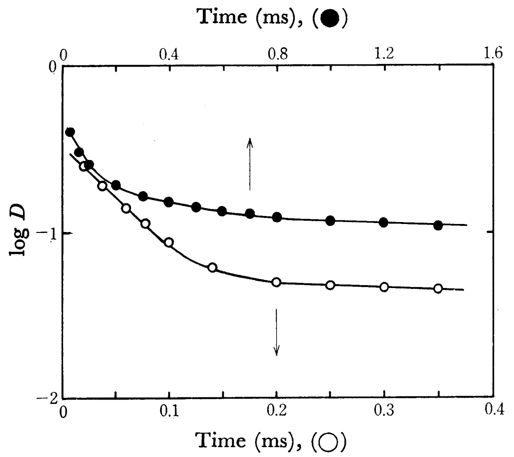

Fig. 4. Decay analysis for the transient absorption at 380 nm (●) and 540 nm (○).

a two- or three-component decay. Consequently, the transient absorptions were revealed to be due to three intermediate species, X, Y, and Z; their individual spectra are shown in Fig. 5. The intermediate X, with its absorptions around 380 and 550 nm, decayed with a rate constant (k_X) of $3.3\times10^4\,s^{-1}$, whereas the intermediates Y and Z (about 370 nm) decayed with rate constants (k_Y and k_Z) of $3.8\times10^3\,s^{-1}$ and $7.0\times10^2\,s^{-1}$ respectively.

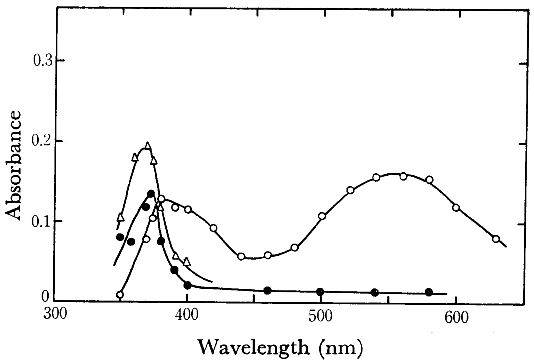

Fig. 5. Absorption spectra of the intermediate species X (-○-), Y (-●-) and Z (-△-) resolved by the decay analyses at different wavelengths.

Then, the effect of a hydrogen-donor on the decay rate was investigated in order to elucidate which intermediate is responsible for the photochemical reduction of 4-nitropyridine *N*-oxide. The decay rate (k_X) of the intermediate X, as is shown in Fig. 6, increased linearly with an increase in the concentration of THF, while that (k_Y or k_Z) of the intermediate Y or Z was independent of the concentration of THF. Quite similar results were also obtained when the 2-propanol was added as a hydrogen-donor instead of THF.[5] These results lead to the conclusion that the intermediate X is responsible for the hydrogen-atom abstraction from a THF or 2-propanol.

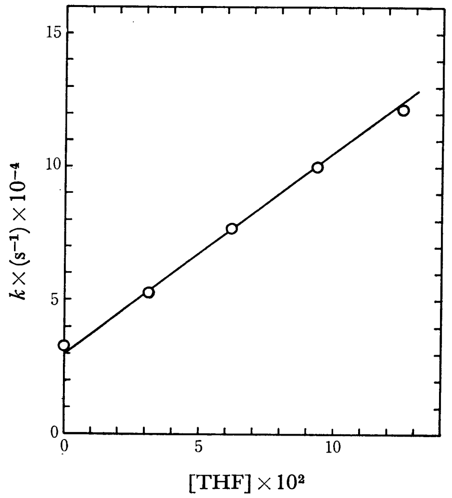

Fig. 6. The effect of THF on the decay rate of the intermediate X in deaerated water at room temperature (concentration of 4-nitropyridine *N*-oxide: 7.0×10^{-5} M).

Although the transient spectrum in water (Fig. 3) is closely similar in appearance to that in alcohol (Figs. 1 and 2 in Ref. 1), the nature of the intermediate species involved seems to be different in each case, for a reason to be presented below. In the case of an alcoholic solution,[1] the decay of the transient absorption (~550 nm) appeared immediately after the flash had been clearly observed to be followed by the appearance of the 380 nm absorption. Moreover, these absorption spectra have been obtained even in an oxygen-saturated solution, indicating that all the intermediate involved originated from the excited singlet state of 4-nitropyridine *N*-oxide. In the case of an aqueous solution, however, apparently the two absorption systems (Fig. 3) appeared simultaneously within the time of the flash (10 μs), although they were located in the same spectral region as in the case of an alcoholic solution. In addition, they were completely quenched by the dissolved oxygen, suggesting that the intermediates involved is due to a triplet and related species. It is remarkable that, whereas the decay rate (k_Y) of the intermediate Y was independent of [RH], the absorption intensity was observed to decrease with an increase in [RH]. As an example, Fig. 7 shows the decrease in the absorption intensity of the intermediate Y with an increased concentration of 2-propanol. This can possibly be interpreted by assuming the following pathways, (i) and (ii), for the decay of the intermediate X:

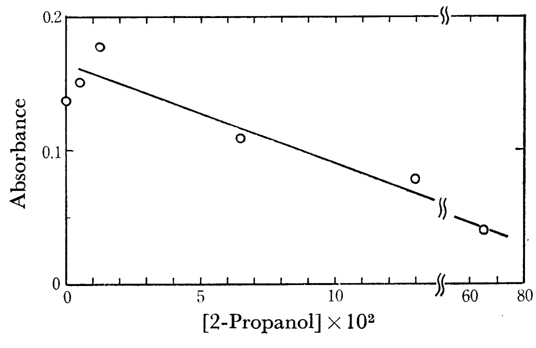

Fig. 7. The effect of the concentration of 2-propanol on the absorption intensity of the intermediate Y in deaerated water at room temperature (concentration of 4-nitropyridine *N*-oxide: 7.0×10^{-5} M).

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[5] In this case, the decay rate (k_Z) of the intermediate Z was observed to decrease initially with an increased concentration of 2-propanol, although the reason was quite ambiguous at present.

$$\begin{tikzcd} & \text{Hydrogen-atom abstraction} \quad \text{(i)} \\ \text{Intermediate X} \arrow[ru, "+\text{RH}"] \arrow[rd] & \\ & \text{Intermediate Y} \quad \text{(ii)} \end{tikzcd}$$

That is, as the concentration of the hydrogen-donor increases, the hydrogen-atom abstraction (i) would become much more important than the formation of the intermediate Y (ii), leading to a decrease in the absorption intensity of the intermediate Y. The fact that the absorption intensity at 350 nm was observed to increase slightly with the lapse of time (Fig. 5) seems to support the idea that the intermediate Y[6] could be produced from the intermediate X. Judging from these facts, it appears reasonable to assign the intermediate X to the lowest triplet state (T_1) of 4-nitropyridine *N*-oxide.[7] Accordingly, the following reaction scheme can be obtained.

	Rate
$S_0 + h\nu \longrightarrow S_1$	I_a
$S_1 \longrightarrow S_0$	$k_1[S_1]$
$S_1 \longrightarrow T_1$	$k_2[S_1]$
$T_1 + RH \longrightarrow$ Hydrogen-atom abstraction	$k_3[T_1][RH]$
$T_1 \longrightarrow Y$	$k_4[T_1]$
$T_1 \longrightarrow S_0$	$k_5[T_1]$

where the intermediate Z is not involved because of the ambiguous nature.

Assuming the photostationary state conditions, the quantum yield of the 4-nitropyridine *N*-oxide disappearance is given by the following equation:

$$1/\Phi = 1/\Phi_{isc} + (k_4+k_5)/\Phi_{isc}k_3[RH] \tag{1}$$

where Φ_{isc} represents the efficiency of the S_1–T_1 intersystem crossing as follows:

$$\Phi_{isc} = k_2/(k_1+k_2) \tag{2}$$

Thus, if Processes I and II, both of which proceed from the S_1 state,[1] can be neglected in an aqueous solution, a linear relationship should be expected to exist between the reciprocals of Φ and [RH]. The experimental results shown in Fig. 2 gave a straight line, in accordance with Eq. (1), and thus supporting the proposed reaction scheme. The values of Φ_{isc} and $(k_4+k_5)/\Phi_{isc}k_3$ were estimated from the slope and intercept of the straight-line respectively. Meanwhile, according to the reaction scheme presented above, the decay rate (k_X) of the intermediate X, or the triplet species, may be given by the following equation:

$$k_X = k_4 + k_5 + k_3[RH] \tag{3}$$

As has been described before, it was seen that the decay rate (k_X) of the intermediate X was directly proportional to the concentration of 2-propanol or THF; this was consistent with Eq. (3). Therefore, k_3 was evaluated from the slope of the straight line, while k_4+k_5 was estimated by extrapolating [RH] to zero. The value of Φ_{isc}, k_3 and k_4+k_5 thus obtained are listed in Table 1. The values of $(k_4+k_5)/k_3$ determined from both the steady-light and flash spectroscopic experiments are also given in Table 1; these values agree approximately with each other. This also supports the proposed reaction scheme.

TABLE 1. OBSERVED VALUES OF Φ_{isc}, k_3 AND k_4+k_5 IN AN AQUEOUS SOLUTION CONTAINING A HYDROGEN-DONOR AT ROOM TEMPERATURE

Hydrogen-donor	Φ_{isc}[a]	k_3[b] (l mol^{-1} s^{-1})	k_4+k_5[b] (s^{-1})	$(k_4+k_5)/k_3$
THF	0.20	7.5×10^5	3.0×10^4	0.016[a], 0.040[b]
2-Propanol	0.19	7.1×10^5	3.0×10^4	0.021[a], 0.042[b]

a) Represents the value determined from the steady-light experiment (Fig. 2).

b) Represents the value determined from the flash spectroscopic experiment (Figs. 6 and 7).

The following conclusions can be drawn from the experimental results described above. The photochemical reduction of 4-nitropyridine *N*-oxide in deaerated water proceeds through the lowest triplet state (probably, π,π^*),[8] whereas in an alcoholic solution the intermediate species resulting from the S_1 state is responsible for the photoreduction. Also, in an aqueous solution, approximately 20% of the 4-nitropyridine *N*-oxide in the S_1 state undergoes an intersystem crossing into the T_1 state responsible for the hydrogen-atom abstraction, but the intermediate A (and therefore B as well) and A′ are scarcely formed at all; thus, Process I does not occur. In the case of an alcoholic solution, on the other hand, the formation of the intermediate species A (and therefore, of B) and A′ from the S_1 state is considered to become much more predominant than the S_1–T_1 intersystem crossing; thus, both Processes I and II proceed. These conclusions are of particular interest in relation to the effect of the solvent on a dynamic behavior of the excited singlet state of 4-nitropyridine *N*-oxide. Further studies of these points are now in progress.

In conclusion, the authors wish to thank Professor Shiro Matsumoto for his permission to use the flash-photolysis apparatus.

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[6] The intermediate Y does not undergo chemical changes but it seems to be converted to the 4-nitropyridine *N*-oxide (S_0), although the structure is not clear at present.

[7] Exactly, a comparison of the decay time of the transient absorption with that of the phosphorescence of 4-nitropyridine *N*-oxide in a deaerated water at 77 K must be made to identify the intermediate X to the lowest triplet state of *N*-oxide, but it was experimentally too difficult under such conditions.

[8] I. Ono and N. Hata, This Bulletin, **45**, 2951 (1972).