BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2951—2953 (1972)

The Photosensitized Reduction of 4-Nitropyridine *N*-Oxides

Isao Ono and Norisuke Hata
Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University
Chitosedai, Setagaya-ku, Tokyo

(Received March 2, 1972)

4-Nitropyridine *N*-oxides are photochemically reduced to afford 4-hydroxylaminopyridine *N*-oxides in ethanol under nitrogen atmosphere.[1] From the measurements of the quantum yields and the flash-spectrophotometric experiments, such a photochemical reduction has been considered to proceed through an intermediate species originating from the excited singlet state of 4-nitropyridine *N*-oxide.[2,3] However, the photochemical reduction of aromatic nitro compounds are generally thought to proceed through the lowest n,π^* triplet state;[4] detailed investigations have been performed on the nitrobenzene,[5] 1-nitronaphthalene,[6] and 4-nitropyridine.[7] Therefore, it seems to be of importance, in elucidating the reaction mechanism, to clarify whether or not the reduction of 4-nitropyridine *N*-oxide can occur from the lowest triplet state. In the present investigation, the biacetyl-sensitized reac-

---

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

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

[3] N. Hata, I. Ono, and T. Tsuchiya, *ibid.*, **45**, 2386 (1972).

[4] H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups," Part 1, ed. by H. Feuer, Interscience Publishers, New York, (1969), Chapter 4.

[5] R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966), *ibid.*, **89**, 6917 (1967).

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

[7] S. Hashimoto, K. Kano, and K. Ueda, *Tetrahedron Lett.*, **1969**, 2733. This Bulletin, **44**, 1102 (1971).

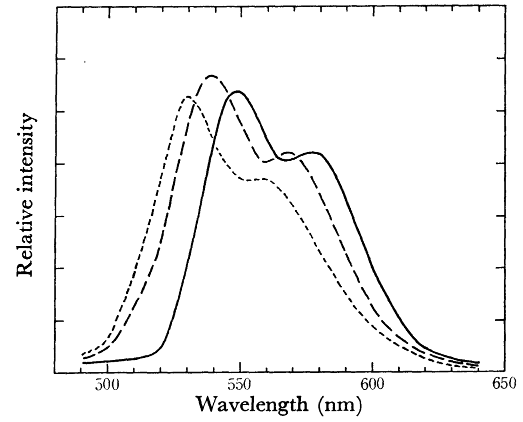


Fig. 1. The phosphorescence spectra of 4-nitropyridine *N*-oxide (——), 3-methyl-4-nitropyridine *N*-oxide (----) and 3,5-dimethyl-4-nitropyridine *N*-oxide (------) in 2-propanol at 77°K.

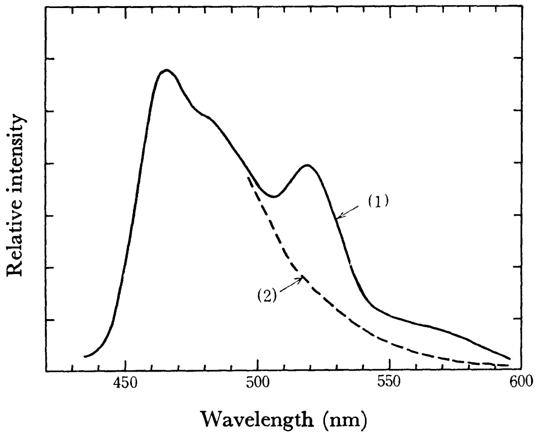


Fig. 2. Quenching of the biacetyl phosphorescence by an addition of 4-nitropyridine *N*-oxide in deaerated 2-propanol at room temperature.

(1) biacetyl alone (5×10^{-2}M)

(2) biacetyl (5×10^{-2}M) and 4-nitropyridine *N*-oxide (1×10^{-3}M)

tions of 4-nitropyridine *N*-oxide (I), 3-methyl-4-nitropyridine *N*-oxide (II), and 3,5-dimethyl-4-nitropyridine *N*-oxide (III) were carried out in deaerated 2-propanol or ethanol.

The lowest triplet state of 4-nitropyridine *N*-oxide has been studied by Kubota *et al.*[8] by means of both its phosphorescence and S–T absorption spectroscopy. As a result, the lowest triplet state of 4-nitropyridine *N*-oxide has been concluded to be a π,π^* state with an excitation energy of about 52 kcal·mol^{-1}. Figure 1 shows the phosphorescence spectra of (I), (II), and (III) in 2-propanol glass at 77°K. Consequently, the biacetyl (E_T=56.3 kcal·mol^{-1}) is expected to be usable as a triplet sensitizer for these *N*-oxides, (I), (II), and (III). As is shown in Fig. 2, the biacetyl phosphorescence in deaerated 2-propanol (5×10^{-2}M) at room temperature was observed to be completely quenched by the addition of the 4-nitropyridine *N*-oxide (1×10^{-3}M). Similar results were also obtained when (II) or (III) was used as a triplet quencher instead of (I). In addition, Fig. 3 shows the progressive spectral change in 4-nitropyridine *N*-oxide in deaerated 2-propanol containing biacetyl when the solution was irradiated with the visible light longer than 400 nm which is absorbed by biacetyl alone; there, it was observed that the absorption spectrum of 4-nitropyridine *N*-oxide decreased progressively in intensity and a new absorption band with its maximum at about 290 nm appeared.

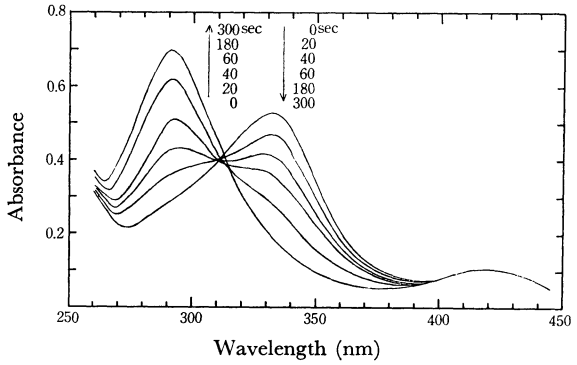


Fig. 3. The progressive spectral change of 4-nitropyridine *N*-oxide (5×10^{-5}M) in deaerated 2-propanol containing 5×10^{-3}M biacetyl on visible light irradiation (>400 nm). Numbers refer to the irradiation time.

Next, the separation and identification of the photoproducts formed in the photosensitized reactions of (I), (II), and (III) were carried out; the procedures will be described below.

An 2-propanol or ethanol solution containing 100 mg of (I) and 200 mg of biacetyl in a quartz cylindrical reaction vessel (5.0 cm in length and 4.5 cm in diameter) was irradiated with a high-pressure mercury lamp (Toshiba H-400 P) equipped with a Hoya L-42 filter for 14 hr while nitrogen was bubbled in. After the removal of the solvent under reduced pressure in an atmosphere of nitrogen, benzene was added to the residue. Then, the undissolved product was collected and washed with a mixture of ethanol and diethyl ether (1: 1). The mp of the photoproduct (Ia) thus obtained was 213—215°C (decomp.), and that of its hydrochlorate, 157—159°C (decomp.). In the same way, the photoproduct (IIa) was also isolated from the irradiated solution of (II): mp 210—213°C (decomp.), and its hydrochlorate, 175—176°C (decomp.). The UV and IR spectra of the two photoproducts, (Ia) and (IIa), were superimposable upon those of 4-hydroxylaminopyridine *N*-oxide or 3-methyl-4-hydroxylaminopyridine *N*-oxide.[9]

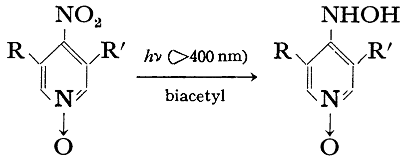
In the case of 3,5-dimethyl 4-nitropyridine *N*-oxide (III), white crystals (IIIa) were isolated by the same procedures as those used for (I) and (II): recrystallized from ethanol in a nitrogen atmosphere, mp 151°C (decomp.), yield 35%, UV $\lambda_{\max}^{\text{EtOH}}$ 296 nm (log ε 4.24), NMR (CF_3COOH, TMS) δ 2.45 ppm (s, 6H, $(CH_3)_2$), 7.94 ppm (s, 2H, aromatic), molecular weight (meas-

---

[8] M. Yamakawa, Y. Mizuno, and T. Kubota, Annual meeting of the Chemical Society of Japan, Tokyo, April, 1970, M. Yamakawa, T. Kubota, and Y. Mizuno, Symposium on the Molecular Structures, Kyoto, October, 1971.

[9] E. Ochiai and H. Mitarashi, *Ann. Rept. ITSUU. Lab.*, **14**, 17 (1965).

ured by freezing-point depression of benzoic acid) 160, Found: C, 54.00; H, 6.48; N, 18.08%. Calcd for $C_7H_{10}N_2O_2$: C, 54.56; H, 6.49; N, 18.18%. On the basis of these analytical data, the photoproduct (IIIa) was assumed to be a 3,5-dimethyl-4-hydroxylaminopyridine *N*-oxide. Further confirmation of the structure (IIIa) was provided by its conversion into 4,4'-azoxy or 4-nitroso derivative in the following way. The treatment of 100 mg of (IIIa) with 5m*l* of 10% aqueous ammonia resulted in a red coloration, which then gradually faded to yellow. After the solution has been allowed to stand for 20 min, extraction with chloroform gave *ca.* 40 mg of yellow crystals (IIIb). The (IIIb) thus obtained was purified by recrystallization from ethanol: mp 265°C (decomp.), UV λ_{max}^{EtOH} 275 nm (log ε 4.21), NMR ($CDCl_3$, TMS) δ 2.22 ppm (s, 6H, $(CH_3)_2$), 2.40 ppm (s, 6H, $(CH_3)_2$), 8.08 ppm (s, 4H, aromatic), Mass (M^+)=288, Found: C, 58.20; H, 5.66; N, 19.25%. Calcd for $C_{14}H_{16}N_4O_3$: C, 58.33; H, 5.56; N, 19.44%. Thus, the product (IIIb) was identified as 4,4'-azoxy-3,5-lutidine 1,1'-dioxide. Similarly, a 100–mg portion of (IIIa) was treated with 5 m*l* of a 10% $FeCl_3$ solution, then, extraction with chloroform gave 70 mg of greenish-yellow crystals (IIIc): mp 203—205°C (decomp.), UV λ_{max}^{EtOH} 253 nm (log ε 3.80), 363 nm (log ε 4.10), NMR ($CDCl_3$, TMS) δ 2.63 ppm (s, 6H, $(CH_3)_2$), 8.05 ppm (s, 2H, aromatic), Mass (M^+)=152, Found: C, 54.54; H, 5.21; N, 17.78%. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.26; N, 18.42%. These analytical data indicate that the product (IIIc) is 3,5-dimethyl-4-nitrosopyridine *N*-oxide



R and R'=H or CH_3

It was revealed by the present experiments that the 4-nitropyridine *N*-oxide and its methyl-substituted derivatives were reduced by a biacetyl sensitization to the corresponding 4-hydroxylamino derivatives; this suggests that the hydrogen abstraction from a solvent molecule can occur from the lowest π,π^* triplet state of 4-nitropyridine *N*-oxide. This is of particular interest because Rosenberg and Servé's mechanism of the hydrogen abstraction by a π,π^* triplet molecule[10] appears to be operative in the photosensitized reduction of 4-nitropyridine *N*-oxide. For this reason, further studies are necessary in order to elucidate the nature of the lowest lying triplet state of 4-nitropyridine *N*-oxide.

---

[10] H. M. Rosenberg and P. Servé, *J. Amer. Chem. Soc.*, **92**, 4746 (1970).