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The Photoreduction of 2-Nitronaphthalene in 2-Propanol

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The photoreduction of 2-nitronaphthalene in 2-propanol has been studied at 313 nm. The photoreduction is suppressed in the presence of dissolved oxygen or a triplet quencher such as 1,3-cyclohexadiene. The results are consistent with the triplet state of 2-nitronaphthalene being the reactive species. 2-Naphthylhydroxylamine is formed as the reaction product. The quantum yield for the disappearance of 2-nitronaphthalene is estimated to be 0.037. The low quantum yield results from the slow reaction rate of hydrogen abstraction by the $\pi\pi^*$ triplet state of 2-nitronaphthalene.

The photoreduction of simple aromatic nitrocompounds has been the subject of several recent publications.[1] Whereas the photoreduction occurs with good efficiency in the presence of protons[2,3] or such reducing agents as tri-*n*-butylstannane,[4] the reduction in alcoholic solvents is much less efficient. The photoreduction of nitrobenzene in 2-propanol[5] has been reported to occur with a low quantum yield ($\Phi \sim 0.01$). While several groups have studied the photoreduction of 1-nitronaphthalene,[3,6] no concordant conclusion has yet been obtained.

It has generally been agreed that the photoreduction of the aromatic nitrocompounds should take place through their triplet state in accordance with the aromatic carbonyl compounds, of which very extensive researches have been established rather conclusively that the $n\pi^*$ triplet state as the reacting state.[7] However, much less agreement exists as to the nature ($n\pi^*$ or $\pi\pi^*$) of the reacting triplet state of aromatic nitrocompounds.

The phosphorescence study[8] has suggested that the lowest triplet states of nitrobenzene are $n\pi^*$ and that those of 1- and 2-nitronaphthalenes are $\pi\pi^*$ states. The hydrogen abstraction reaction of the $n\pi^*$ triplet state has been widely understood, whereas generally that of the $\pi\pi^*$ triplet has not been observed or occurs at significantly lower reaction rates.

In this paper, we wish to report on the photoreduction of 2-nitronaphthalene in 2-propanol and to discuss the hydrogen abstraction reaction by the $\pi\pi^*$ triplet state of 2-nitronaphthalene.

Experimental

Chemicals. 2-Nitronaphthalene was obtained from K & K, Ltd., and was purified by recrystallization from hexane. Spectral-grade 2-propanol was obtained from Merck and was used as received.

Procedures. Unless otherwise specified, all the samples were thoroughly degassed on a high-vacuum line by freeze-pump-thaw cycles. A medium-pressure mercury lamp (Toshiba H-400P) was used as the 313 nm radiation source; it was equipped with a combination filter of a nickel sulfate solution and a Toshiba UV-31 filter, while a high-pressure mercury lamp (Toshiba SHL-1200) with a Pyrex filter was used for the ESR studies. The light intensity was measured with a potassium ferroxalate actinometer.

The disappearance of 2-nitronaphthalene was determined spectrophotometrically. The ultraviolet absorption spectra were taken with Hitachi 124 and EPS-2 spectrophotometers. The ESR spectra were measured by means of a JEOL JES-3BS-X.

Results and Discussion

The spectrum of the 2-propanol solution of 2-nitronaphthalene changed upon irradiation with 313 nm light, as shown in Fig. 1. The absorption bands of 2-nitronaphthalene at 254, 261, and 305 nm decreased, and new bands with maxima at 244 and *ca.* 280 nm appeared, as the irradiation time increased, with isosbestic points at 250, 270, and 288 nm and probably also at 330 and 340 nm. If the irradiated solution was allowed to stand for several days in contact with air,

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[1] H. A. Morrison "The chemistry of the nitro and nitroso groups" Part 1, Wiley, New York (1969), p. 165.

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

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

[4] W. Trotter and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 7044 (1968).

[5] R. Hurley and A. C. Testa, *ibid.*, **88**, 4330 (1966).

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

[7] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York (1966), p. 528.

[8] R. Rusakowicz and A. C. Testa, *Spectrochim. Acta.* **27A**, 787 (1970).

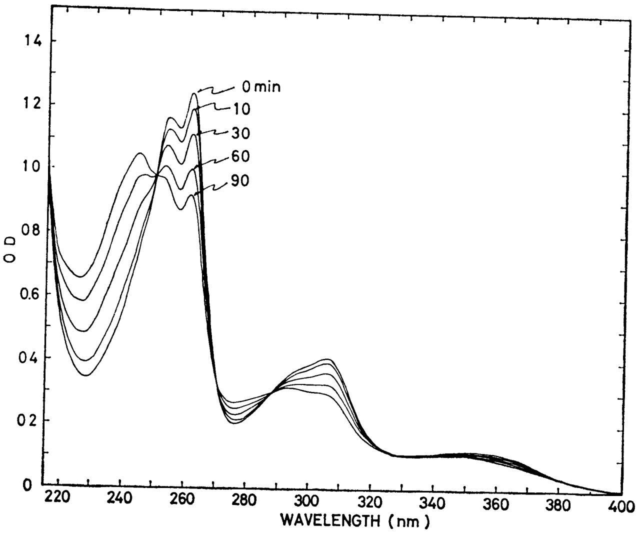

Fig. 1. Spectral change of 2-propanol solution of 2-nitronaphthalene on 313 nm irradiation.

the band of the products at 244 nm disappeared and a broad new band appeared around 520 nm assignable to the azoxy compound. By adding a small amount of hydrochloric acid to the irradiated solution, the absorption peak of the products disappeared and a new peak appeared at 233 nm, which corresponded to 2-naphthylamine hydrochloride. It has been established that N-aromatic-hydroxylamines are autoxidized to the corresponding azoxy compounds in contact with air,[9] and also undergo a reaction to give the corresponding amines when a small amount of hydrochloric acid is added.[10] Thus, a possible candidate for the products is thought to be 2-naphthylhydroxylamine. In the photolysis of 2-propanol solutions of nitrobenzene[5,10] and 1-nitronaphthalene,[6] the nitro-compounds are photoreduced to phenylhydroxylamine and 1-naphthylhydroxylamine respectively. The similar reaction is also observed in the photolysis of 4-nitropyridine-1-oxide.[11] Therefore, it is reasonable to consider the reaction product of 2-nitronaphthalene to be 2-naphthylhydroxylamine.

The quantum yields of the disappearance of 2-nitronaphthalene were measured. The yields decreased slightly with the irradiation time; the results are shown in Fig. 2. The small decline must come from the internal filter effects of the produdts. The initial quantum yield (Φ_0) of the disappearance of 2-nitronaphthalene was obtained by extrapolating it to the zero irradiation time. The 2-nitronaphthalene concentration did not affect the quantum yield, which was 0.037, as is shown in Fig. 3. In order to study the effects of the dissolved oxygen, the aerated solution was photolyzed. The results, however, showed no spectra change after a 120-min irradiation.

Quenching experiments with 1,3-cyclohexadiene were also carried out; the results are shown in Fig. 4.

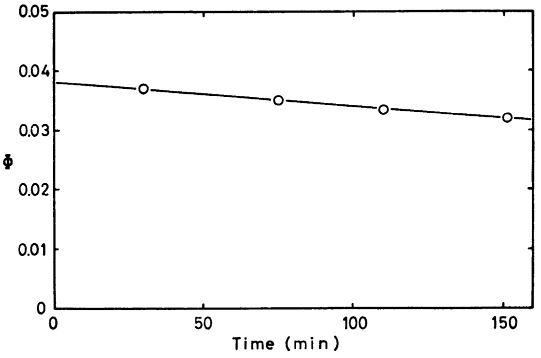

Fig. 2. Dependence of apparent disappearance quantum yields on irradiation time with 7.0×10^{-5} M 2-nitronaphthalene.

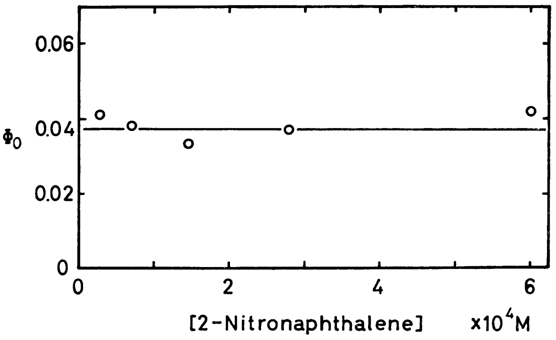

Fig. 3. Dependence of disappearance quantum yields on 2-nitronaphthalene concentration.

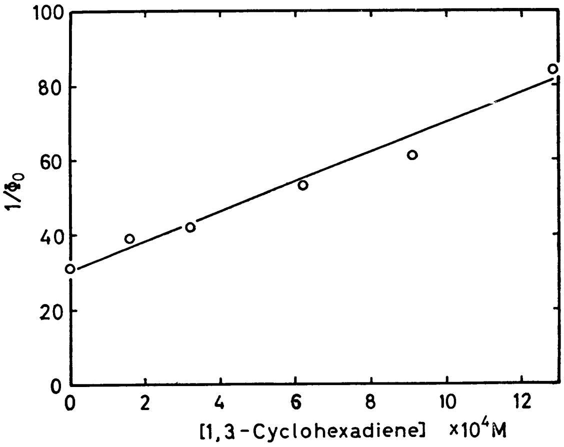

Fig. 4. Reciprocal of disappearence quantum yields *vs.* 1,3-cyclohexadiene concentration with 1.6×10^{-4} M 2-nitronaphthalene.

Since the triplet energy of 1,3-cyclohexadiene[12] (E_T=54 kcal) is lower than that of 2-nitronaphthalene[8] (E_T=56.8 kcal), this compound is effective as a triplet quencher. The linear Stern-Volmer plots shown in Fig. 4 indicate that the triplet state of 2-nitronaphthalene plays an important role in the photoreduction. The absence of any product formation by the photochemical reaction in the aerated solution also supports the triplet mechanism.

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[9] Y. Ogata, M. Tsuchida and Y. Takagi, *J. Amer. Chem. Soc.*, **79**, 3397 (1957).

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

[11] N. Hata, E. Okutsu and I. Tanaka, *ibid.*, **41**, 1769 (1968).

[12] N. J. Turro, "Energy Transfer and Organic Photochemistry" Wiley, New York (1969), p. 133.

According to the above discussion, the following reaction scheme is obtained:

$$S_0 + h\nu \longrightarrow S_1 \quad (1)$$
$$S_1 \longrightarrow S_0 \quad (2)$$
$$S_1 \longrightarrow T_1 \quad (3)$$
$$T_1 \longrightarrow S_0 \quad (4)$$
$$T_1 + \text{IPA} \longrightarrow \text{products} \quad (5)$$
$$T_1 + Q \longrightarrow S_0 + {}^3Q \quad (6)$$

where S_0, S_1, and T_1 are the ground state, the excited singlet state,[13] and the lowest triplet state of 2-nitronaphthalene respectively, IPA is 2-propanol, and Q is 1,3-cyclohexadiene. This scheme leads to the following equation:

$$\frac{1}{\Phi_0} = \frac{1}{\Phi_T}\left\{1 + \frac{k_4 + k_6[Q]}{k_5[\text{IPA}]}\right\}$$

where Φ_T is the quantum yield of the 2-nitronaphthalene triplet. Using the value of $\Phi_T = 0.83$ given by Rusakowicz and Testa,[8] the following values are obtained:

$$k_4/k_5[\text{IPA}] = 24.3 \text{ and } k_6/k_5[\text{IPA}] = 3.19 \times 10^4\,\text{M}^{-1}$$

Since the flash photolysis of 2-nitronaphthalene in 2-propanol at room temperature showed no triplet-triplet absorption, the lifetime of the triplet state is probably less than 20 μ sec; that is, $\tau_T^{-1} = k_4 + k_5 \times [\text{IPA}] > 5 \times 10^4\,\text{s}^{-1}$. On the other hand, the 1,3-cyclohexadiene quenching of the triplet is thought to be diffusion-controlled at the most; $k_6 \leq 3 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$. Using these relations, the following limits are obtained:

$$5 \times 10^4 < k_4 < 2 \times 10^6\,\text{s}^{-1}$$
$$2 \times 10^3 < k_5[\text{IPA}] < 8 \times 10^4\,\text{s}^{-1}$$
$$6 \times 10^7 < k_6 < 3 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$$

The radiationless decay rate of the triplet 2-nitronaphthalene is roughly of the same order as that of benzophenone[14] ($5.3 \times 10^5\,\text{s}^{-1}$), while it is significantly slower than that of nitrobenzene[15] ($\sim 10^9\,\text{s}^{-1}$). On the other hand, the rate of Reaction (5), which is the hydrogen abstraction reaction, is much slower than those of benzophenone[16] ($k_5[\text{IPA}] = 1.3 \times 10^7\,\text{s}^{-1}$) and of nitrobenzene ($k_5[\text{IPA}] \simeq 1.7 \times 10^7\,\text{s}^{-1}$), which is estimated from the triplet yield[15] (0.67), the radiationless decay rate[15] ($\sim 10^9\,\text{s}^{-1}$), and the disappearance quantum yield[5] in 2-propanol (0.011) of nitrobenzene. Therefore, the slower abstraction rate of 2-nitronaphthalene results in the disappearance quantum yield of 2-nitronaphthalene being lower than that of benzophenone ($\Phi = 1$).

In order to study the reaction mechanism in more detail, the ESR spectrum of the reaction intermediates were measured at −110 °C. The spectrum observed at short irradiation time consists of three broad absorption lines and is shown in Fig. 5. The formation of this intermediate was saturated within about a 20-s irradiation, while no 2-propanol radicals were observed in this period. Since no radical was formed in the carbon tetrachloride solution of 2-nitronaphthalene at −110 °C, this radical is probably formed by the interaction between excited 2-nitronaphthalene and 2-propanol and would be the precursor of 2-naphthylhydroxylamine. Since the observed ESR spectrum did not give a hyperfine structure at −110 °C, it was difficult to identify the intermediate.

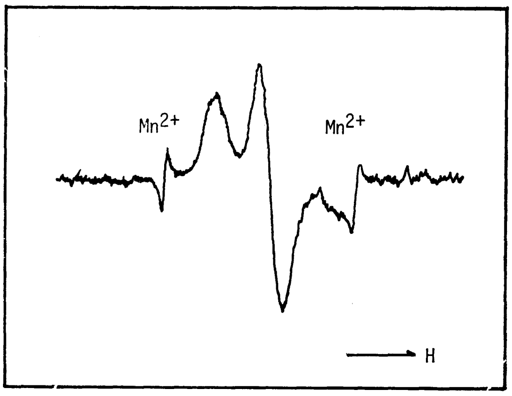
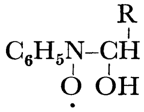
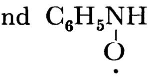
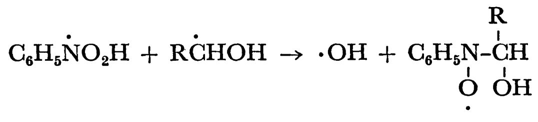


Fig. 5. ESR spectra obtained during the photolysis of 2-nitronaphthalene at −110 °C with 3.5×10^{-4} M 2-nitronaphthalene.

In the photolysis of nitrobenzene in alcohols at room temperature,  $C_6H_5\underset{\dot{O}}{N}\text{-}\underset{OH}{\overset{R}{C}H}$ and  $C_6H_5\underset{\dot{O}}{N}H$ radicals have been observed in the primary and secondary alcohols respectively, while no alcohol radicals have been observed by means of the ESR technique.[17,18] The following reaction scheme is proposed.[18]

$$C_6H_5NO_2 + h\nu \longrightarrow C_6H_5NO_2^* \quad (7)$$

$$C_6H_5NO_2^* + RCH_2OH \rightarrow C_6H_5\dot{N}O_2H + R\dot{C}HOH \quad (8)$$



$$C_6H_5\dot{N}O_2H + R\dot{C}HOH \rightarrow \cdot OH + C_6H_5\underset{\dot{O}}{N}\text{-}\underset{OH}{\overset{R}{C}H} \quad (9)$$

and if the alcohol is secondary, $C_6H_5\dot{N}OH$ radicals are formed. As no alcohol radicals appeared in the photolysis of nitrobenzene and 2-nitronaphthalene in 2-propanol, it seems reasonable to expect that similar reaction mechanisms are operative in the two systems. Therefore, the absence of 2-propanol radicals, which should be formed by the abstraction reaction, indicates their consumption by some secondary reactions similar to Reaction (9). However, the detailed reaction mechanism has not yet been determined.

Whereas the lowest triplet state of 2-nitronaphtha-

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[13] As the 313 nm absorption belongs to the second absorption band of 2-nitronaphthalene, S_1 does not mean the lowest excited singlet state.

[14] H. L. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

[15] R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 1949 (1968).

[16] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

[17] P. B. Ayscough, R. C. Sealy, and D. E. Woods, *J. Phys. Chem.*, **75**, 3454 (1971).

[18] C. Chachaty and A. Forchioni, *Tetrahedron Lett.*, **3**, 307 (1968).

lene has been identified as $\pi\pi^*$ by the phosphorescence study,[8] the hydrogen abstraction reaction from 2-propanol occurs with a higher quantum yield (0.037) than that (0.01) for nitrobenzene, the lowest triplet state of which[15] is $n\pi^*$. The reaction rate of the hydrogen abstraction by 2-nitronaphthalene seems likely to be slower than those by such $n\pi^*$ triplet states as benzophenone and nitrobenzene. However, the longer triplet lifetime would compensate for the slower reaction rate and may result in the relatively high quantum yield.