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Photochromic Reaction of *N*-Nitroso-*N*-alkylaniline in the Aqueous Solution—A Contribution to the Photochemistry of Nitrosamine

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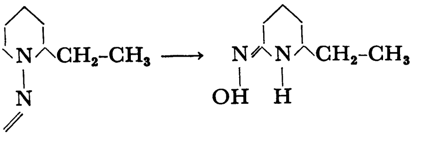
It has been found that the aqueous solution of *N*-nitroso-*N*-methylaniline when irradiated by 253.7 nm shows photochromism. The unstable photoproduct reconverts to the original compound photochemically as well as thermally. The quantum yields for the forward and backward reaction are respectively 0.23 and 0.58. *N*-Nitroso-*N*-ethylaniline also reacts in the similar way. In the alcoholic solutions, different types of reaction occurred; in the absence of oxygen the reaction is mainly the formation of *N*-methylaniline. It has been suggested that the present photochromism is due to the *cis-trans* isomerization.

Photochemical reactions of nitrosamines have attracted much attention in recent years because of various and interesting types of reaction. One type is a splitting of nitrous oxide, an example of which is $(CH_3)_2N-NO \rightarrow (CH_3)_2N\cdot + NO$ studied by Banford in the gaseous state.[1] Another type of reaction is a photoaddition of *N*-nitrosodialkylamine to olefines followed by the C–C double bond cleavage.[2] The third is an intramolecular rearrangement of the following type studied extensively by Chow,[3–5] and by others,[6,7] from the organic viewpoint,



Chow in one of his papers, mentioned the non-reactivity of *N*-nitroso-*N*-methylaniline (NMA) even in the acidic mixture of water and alcohol. We have found, however, that this compound shows an interesting type of photochromism in the aqueous solution although the eventual reaction does not occur. The present paper reports on this newly discovered photochromism and some observations related with it.

Experimental

Materials. NMA was prepared by a usual method from *N*-methylaniline and nitrous acid and purified by vacuum distillation.

Procedures. A light source is a 6 W germicidal mercurs lamp. The absorption spectrum was measured by a Hitachi EPS-3T spectrophotometer. The gradual change of the optical density with time was followed at several fixed wavelengths on the same instrument.

Results

Photochromism and the UV Spectrum of the Product. When the aqueous solution of 1.32×10^{-4} M NMA was irradiated by 253.7 nm for about five minutes, the UV spectrum displayed a change as shown in Fig. 1. Further it was found that the original spectrum was almost completely recovered by keeping the irradiated solution in dark for thirty minutes. This photochromism was observed in quite the same way in the degassed solution indicating the non-participation of oxygen in the reaction. When one plots the decrease

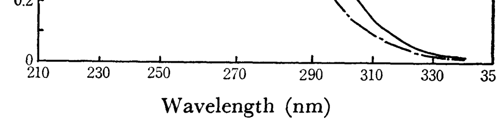


Fig. 1. Spectral change.
—— Spectrum of NMA in the aqueous solution(a)
—·— after irradiation at 253.7 nm for 5 min(b)
····· after being kept in dark for 30 min

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[1] C. H. Banford, *J. Chem. Soc.*, **1939**, 12.
[2] Y. L. Chow, *J. Amer. Chem. Soc.*, **87**, 4642 (1965).
[3] Y. L. Chow, *Can. J. Chem.*, **45**, 53 (1967).
[4] Y. L. Chow, *Tetrahedron Lett.*, **1964**, 2333.
[5] Y. L. Chow, *ibid.*, **1964**, 2473.
[6] E. M. Burgass and J. M. Lavanish, *ibid.*, **1964**, 1221.
[7] T. Axenrod and G. W. A. Milne, *ibid.*, **1967**, 4443.

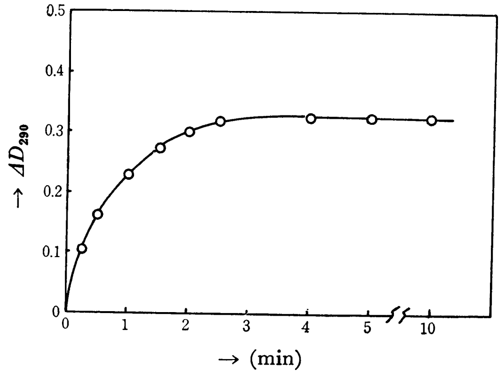


Fig. 2. Change of D (at 253.7nm) with time of irradiation.

in the optical density, ΔD at 290 nm against the time of irradiation, ΔD reaches a certain limiting value in about four minutes as shown in Fig. 2. This indicates that the photoproduct which absorbs the exciting light (see below) is not transformed photochemically to any other compound than NMA and that the photostationary state holds between the forward and backward reaction.

The absorption spectrum of the photoproduct was obtained in the following way. The ratios of the optical density of the absorption spectrum a and b in Fig. 1 were evaluated at various wavelengths and were found to be constant beyond 290 nm. This means that the photoproduct has no absorption in this region. On the basis of this assumption, the absorption of the photoproduct can easily be obtained. The result is shown in Fig. 3.

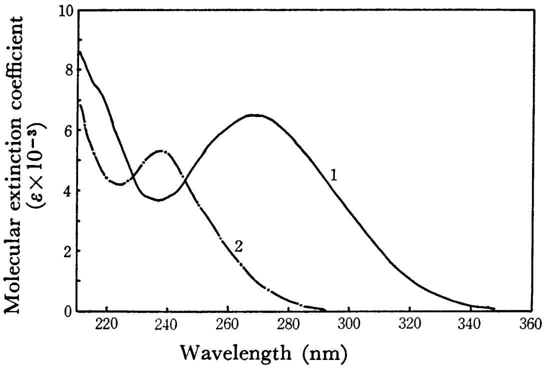


Fig. 3. Spectrum of the photoproduct.
——— Spectrum of NMA
—·— unstable photoproduct in the aqueous solution

Kinetics of the Recovery Reaction. As shown in Fig. 4, the recovery of the initial spectrum proceeds in a simple manner with isosbestic points at 320 nm and 243 nm.

The reaction is interpreted by the following most simplest scheme,

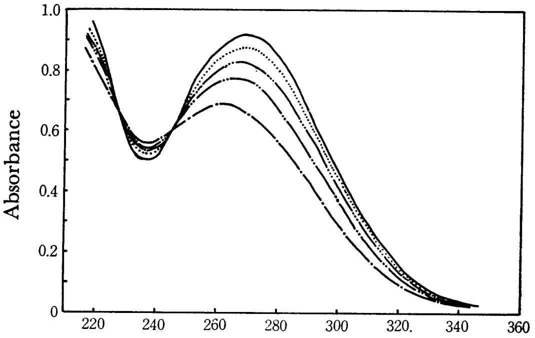


Fig. 4. Thermal recovery of spectrum.
——— before irradiation
—·—· after irradiation for 5 min
—··— kept in dark for 2 min
—···— kept in dark for 4 min
········ kept in dark for 10 min

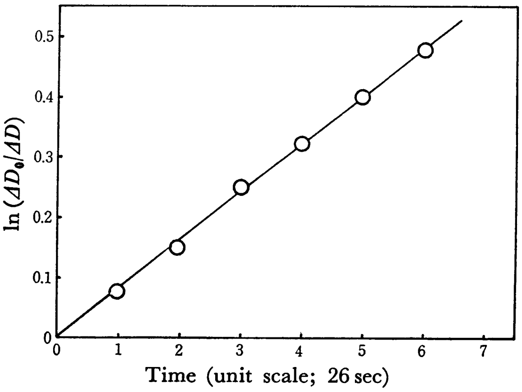


Fig. 5. Plot of ln ($\Delta D_0/\Delta D$) (at 290 nm) against time of irradiation.

$$B \longrightarrow A$$

where B is the photoproduct and A is the original compound. From the above scheme the following equations hold,

$$D = \varepsilon_A C_A + \varepsilon_B C_B$$

$$\Delta D = \varepsilon_A C_A{}^0 - (\varepsilon_A C_A + \varepsilon_B C_B) = (\varepsilon_A - \varepsilon_B) C_B$$

$$-\frac{d\Delta D}{dt} = k\Delta D$$

where D is the optical density of the sample at time t, $\Delta D = D_0 - D$ and $C_A{}^0$ is the original concentration of NMA. The other notations are the usual ones. Figure 5 gives the plot of ln(ΔD_0/ΔD) against time. From the slope of the plot one obtains the value of the rate constant at 17°C as 3.08×10^{-3} sec^{-1}. Thus the lifetime of the photoproduct at this temperature is about 5.5 min.

The Effect of Light Intensity on the Steady State and the Evaluation of the Quantum Yields for the Two Opposed Reactions. Since the backward reaction in photochromism often proceeds photochemically, the dependence of the steady state on the light intensity was examined.

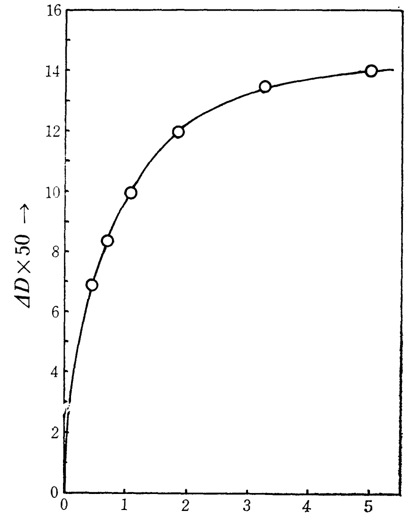
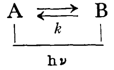


Fig. 6. Dependence of ΔD_∞ (at 290 nm) on light intensity.

As seen from Fig. 6, the limiting value of ΔD_∞ at 290 nm increases appreciably with the increase in light intensity when it is low but gradually tends to a constant value which is only a fraction of the original optical density. This indicates that the backward reaction involves the photochemical reaction in addition to the thermal one.

On the basis of the following scheme,



$$\underset{\lfloor\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\lrcorner}{A \underset{k}{\overset{h\nu}{\rightleftarrows}} B}\atop h\nu$$

the result given in Fig. 6 was analysed in the following way. The rate of the forward reaction is

$$\frac{dC_B}{dt} = \Phi_{AB} I_0 (1 - e^{-2.303D})\left(\frac{D_A - \alpha D_B}{D}\right) - kC_B$$

where D, D_A and D_B are the optical densities of the sample, A- and B- species at time t and Φ_{AB} and $\alpha\Phi_{AB}=\Phi_{BA}$ are respectively the quantum yields for the forward and backward reactions. In the photostationary state, the relation

$$\Phi_{AB} I_0 (1 - e^{-2.303D}) \frac{D_A - \alpha D_B}{D} = kC_B$$

holds, and this equation can be rewritten as follows.

$$\Phi_{AB}(1-(D_B/D_A)\alpha) = (1/I_0)(1/1-e^{-2.303D})(D/D_A)kC_B$$
$$(=\Gamma)$$

Since all the quantities involved on the right hand term are known experimentally, the values of Γ at various light intensities can easily be obtained. Then the Γ *vs.* (D_B/D_A) plot should be linear with an intercept Φ_{AB} and the slope $\Phi_{AB}\alpha=\Phi_{BA}$. Figure 7 shows the result obtained when the light intensities were changed at the constant concentration of NMA, 1.56×10^{-4} M, at 17°C. It was checked that the rate of the thermal backward reaction always remained constant. The values of quantum yield for the forward and backward reactions thus obtained are

$$\Phi_{AB} = 0.23, \qquad \Phi_{BA} = 0.58$$

The intercept of the abscissa which corresponds to the infinite light intensity gaves the values of Φ_{AB}/Φ_{BA}, because the relation $\Phi_{AB}D_A=\Phi_{BA}D_B$ holds under this condition. The value of Φ_{AB}/Φ_{BA} evaluated by this method is 0.4 in complete agreement with 0.39_4 calculated from the values of Φ_{AB} and Φ_{BA} obtained above.

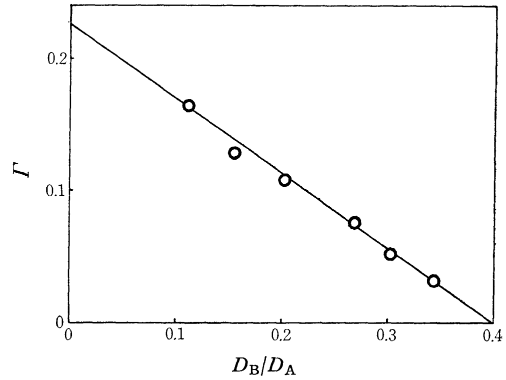


Fig. 7. Plots of Γ *vs.* D_B/D_A.
$\Gamma=(1/I_0)(1/1-e^{-2.303D})(D/D_A)kC_B$

Photoreaction of Other Related Nitrosamines in the Aqueous Solution. Some other nitroso-compounds were investigated in order to know whether they show the similar photochromism or not. It was found that *N*-nitroso-*N*-ethylaniline (NEA) displays quite the same photochromism as shown in Fig. 8. On the other hand, *N*-nitrosodiethylamine 10^{-3} M in the aqueous solution decomposed photochemically without any sign of pnotochromism. *N*-nitrosodiphenylamine 5.3×10^{-5} M in the aqueous solution also did not

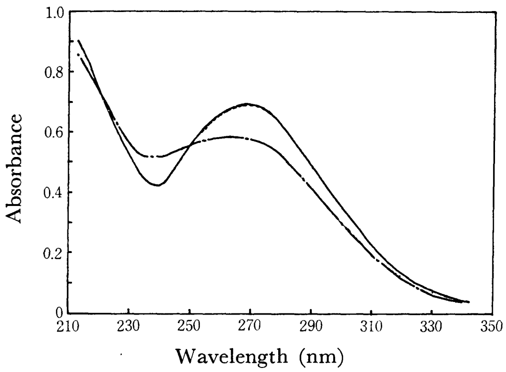


Fig. 8. Spectral change of NEA in the aqueous solution.
—— Spectrum of NEA
—·— after 5 min irradiation (at 253.7 nm).

show photochromism and only the formation of carbazole was observed.

Reaction in Ethanol. In order to know whether the similar photochromism occurs in other solvents, the reaction of NMA and NEA in alcohols were investigated preliminarily. When the degassed ethanol solution of 1.08×10^{-4} M of NMA was irradiated by 253.7 nm, the absorption spectrum changed quite rapidly with two distinct isosbestic points, as shown in Fig. 9. But in this case the final product was found to be stable. It was identified as *N*-methylaniline for the following reason. Firstly, NMA in ethanol gives no emission, while the sample irradiated for 25 minutes gives the fluorescence spectrum with two peaks at 345 nm and 430 nm, and the measurement of the excitation spectra clearly showed that these two peaks belong to the two different emitting species. The excitation spectrum for the 345 nm peak agrees with that of *N*-methylaniline, and moreover, the fluorescence spectrum of this compound coincides almost exactly with the shorter wavelength part of the spectrum of the irradiated sample (Fig. 10). The absorption spectrum also supports this identification.

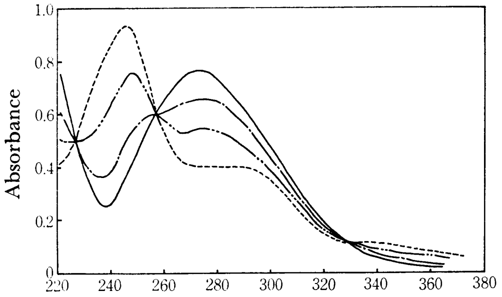


Fig. 9. Spectral change of NEA in degassed ethanol solution.
——— before irradiation
—·—· 4 min irradiation
—··— 8 min irradiation
········· 12 min irradiation

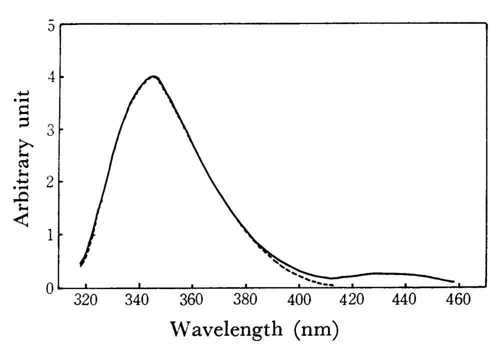


Fig. 10. Fluorescence spectrum of the photoproduct when the degassed ethanol solution of NMA was irradiated at 253.7 nm for 12 min.
—— solid line
- - - *N*-Methylaniline in ethanol

On the other hand, the aerated ethanol solution when irradiated, gave a quite different absorption spectrum, which is shown in Fig. 11. The photoproduct in this case has not yet been identified although there is no doubt that it is not *p*-nitroso-*N*-methylaniline. Somewhat similar spectral change was also observed upon irradiation of the aerated ethanol and cyclohexane solutions of *N*-nitroso-*N*-ethylaniline.

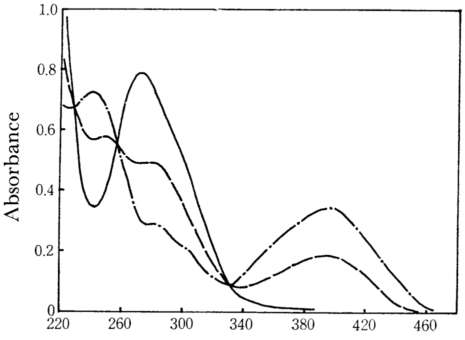
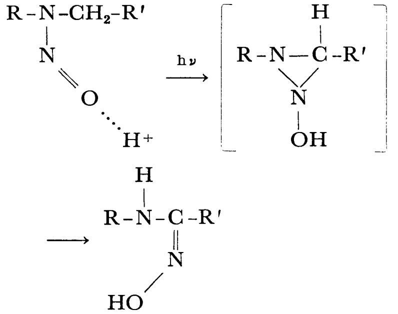


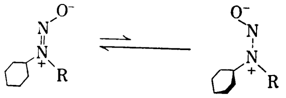
Fig. 11. Spectral change of NEA in the aerated ethanol on the irradiation at 253.7 nm.
——— before irradiation
— — after 6 min
—·— after 12 min

Discussion

The unstable photoproduct produced in the present photochromism has not yet been fully identified. Here, a plausible interpretation will be given by taking into consideration the results reported in literature. Chow in his study on photochemical isomerization reaction of nitrosamines, presumes the formation of a ring of the –N–C– type, as follows,



If one considers as a possible interpretation, that the present photoproduct has such an annular structure, then the C–N bond instead of the N–N bond should be broken for the present photochromism to occur. This, however, is not reasonable in view of the bond strength of C–N and N–N. As another possibility, *cis-trans* isomerization is conceivable and this is very plausible. Karabatsos *et al.*[8] in their studies on the structure of *N*-nitroso-*N*-alkylamines by means of NMR, proposed the existence of the following *cis-trans* isomerization in *N*-nitroso-*N*-alkylamines,



According to them, only the *cis*-form exists in case that *R* is methyl, while in ethyl and isopropyl, *trans-form* can also be existent in equilibrium with the *cis-form*. They proposed that the absorption of the *trans-form* is located in the shorter wavelength than that of the *cis-form*. In view of these results it is very likely that the present photochromism is the *cis* to *trans* isomerization. The non-occurrence of photochromism in alcoholic solution may be due to the preponderance of other types of reaction.

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8) G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, **86**, 4373 (1964).