

STUDIES ON THE PHOTOREACTION OF HETEROCYCLIC N-DIOXIDES: PHOTOCHROMISM OF PHENAZINE N-DIOXIDES IN ORGANIC SOLVENTS

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Summary

The photoreaction of phenazine N-dioxide in various organic solvents has been studied. Photochromism was observed on irradiating with light of wavelength greater than 450 nm. The reaction occurs from the lowest excited singlet state and is an intramolecular process. The quantum yield is 0.075 ± 0.001 in benzene solution at 10 °C. The activation energy of the back reaction in benzene solution is $24.5 \text{ kcal mol}^{-1}$. The photoproduct was assigned to benz[C]-2-azoxy-5-aza-1,6-oxido[10]annulene on the basis of the photoreaction experiment and of the UV, IR and nuclear magnetic resonance spectra.

1. Introduction

The photoreactions of aromatic amine N-oxides are roughly classified into two types: deoxygenation in the excited triplet state and photoisomerization due to intramolecular migration of oxygen in the excited singlet state [1]. The latter reaction occurs via a three-membered oxaziridine intermediate product which, unlike the case of aliphatic nitron photochemistry [2], has not been identified.

It was found that phenazine N-dioxide and its chloroderivatives show photochromism in various organic solvents. This phenomenon has not been observed in other aromatic amine N-oxides. In this study we report the photochemical behavior of phenazine N-dioxides in detail. The photoproducts are different from those of nitrones which are known to be oxaziridines [2].

2. Experimental

Phenazine N-dioxide was synthesized by heating the phenazine in a solution of acetic acid and hydrogen peroxide [3]. The 2,8-dichlorophena-

zine N-dioxide was provided by Professor Tada, Research Institute for Tuberculosis, Leprosy and Cancer. The solvents were purified by appropriate methods. The sample solution was irradiated with light of wavelength greater than 450 nm. (The photoproducts decompose on irradiation at 365 and 253.7 nm.) The exciting light source was an NEC GLG argon ion laser (mainly 488 nm) or a xenon lamp fitted with a 470 nm interference filter. Unless stated otherwise, the experiments were carried out in an air-saturated system. The electronic absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. The measurements of IR spectra were recorded on a Hitachi 285 spectrometer using a cylindrical cell of path length 1.5 cm with KBr windows. Nuclear magnetic resonance (NMR) spectra were obtained using a JEOL FX60 FT spectrometer at -5°C in CDCl_3 containing tetramethylsilane as a standard. The NMR spectra were simulated by a JEOL JEC-6 minicomputer.

3. Results and discussion

The spectral change of the benzene solution of phenazine N-dioxide irradiated with light of wavelength 488 nm is shown in Fig. 1. Isobestic points appear at 319, 452 and 518 nm. The spectrum of N-dioxide is completely recovered when the solution is allowed to stand in the dark at room temperature. A similar reaction was observed in toluene, chloroform, carbon tetrachloride, 1,1,2-trichloro-1,2,2-trifluoroethane, tetrahydrofuran, ether, acetone, methanol, ethanol, carbon disulfide, acetonitrile and acetic acid. In water an irreversible photoreaction proceeds instead of photochromism with much smaller quantum yield. In the monocationic form produced by adding trifluoroacetic acid to the benzene solution neither

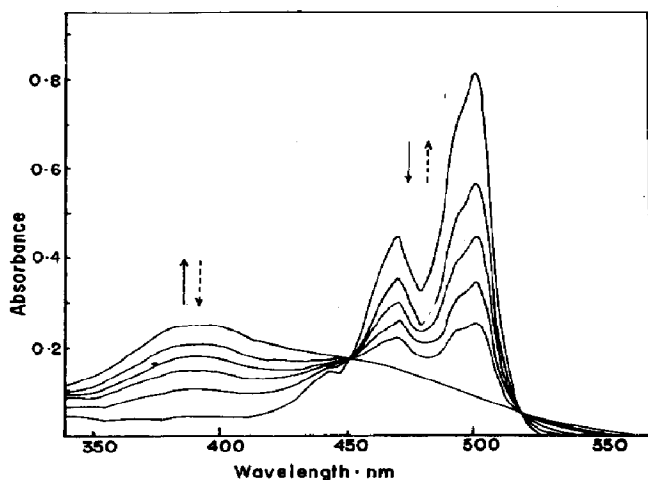


Fig. 1. Change in the absorption spectra of phenazine N-dioxide ($3.0 \times 10^{-5}\text{ M}$) after 488 nm irradiation in benzene solution: \dashrightarrow , with irradiation; \dashleftarrow , in the dark.

photochromism nor an irreversible photoreaction occurs. In a methanol-ethanol mixture (1:1 by volume) at 77 K no photoreaction occurs; this may be due to the activation energy required for the movement of the oxygen atom in the N→O group.

Photochromism occurs even in polyvinyl alcohol film at room temperature. The concentration of phenazine N-dioxide had no effect on the relative quantum yield. Accordingly, the reaction is considered to be intramolecular. When the sample was immersed in liquid nitrogen immediately after irradiation at room temperature, no back reaction was observed; the photoproduct is stable at low temperatures. The back reaction was found to be completely suppressed at temperatures below 10 °C in benzene so that the quantum yield Φ was determined at 10 °C. It was found to be 0.075 ± 0.001 for both aerated and de-aerated solutions by using

$$\begin{aligned} & \ln\{\exp(2.303A) - 1\} - \ln\{\exp(2.303A_0) - 1\} = \\ & = 2.303\Phi I_0 \epsilon_p \left\{ t - \epsilon_x C_0 \int_0^t \frac{1}{A} dt \right\} \times 10^3 \end{aligned} \quad (1)$$

where A is the absorbance at time t , A_0 is the initial absorbance, ϵ_p and ϵ_x are the molar extinction coefficients of phenazine N-dioxide and the photoproduct respectively at 470 nm, C_0 is the initial concentration and I_0 is the incident light intensity ($\text{mol cm}^{-2} \text{s}^{-1}$). Thus, the photoreactive state is the excited singlet state.

Flash photolysis was carried out by observing the absorption at wavelengths longer than 530 nm, where the absorption of the photoproduct does not overlap with that of phenazine N-dioxide. No transient species were detected, however, and the photoproduct was found to be produced within a time far shorter than the FWHM of the exciting light (10 μs). It may be difficult to assign the photoproduct to oxaziridine, because oxaziridine, when produced as an intermediate product in the photoreactions of aromatic amine N-oxides, is believed to have a very short lifetime [1], while the photoproduct in question has a lifetime of about 6 h in benzene and of 10 min in ethanol at 20 °C. Although the reaction is thought to occur via oxaziridine, no evidence of its existence was obtained by the flash technique.

The absorbance $A(t)$ of the solution at time t after the termination of irradiation is given by

$$A(t) = \{(\epsilon_x - \epsilon_p) C_x(t) + \epsilon_p C_0\} d \quad (2)$$

where $C_x(t)$ is the concentration of photoproduct at time t and d is the path length. From eqn. (2), $C_x(t)$ is given by

$$C_x(t) = \frac{\epsilon_p C_0 - A(t)}{\epsilon_p - \epsilon_x} \quad (3)$$

Figure 2 gives the plot of $\ln C_x(t)$ versus t for the benzene solution at 25 °C. From the slope of the straight line in Fig. 2, the first order rate constant was calculated to be $4.40 \times 10^{-5} \text{ s}^{-1}$. The rate constants in various solvents are summarized in Table 1. The rate constant is large in polar solvents. However,

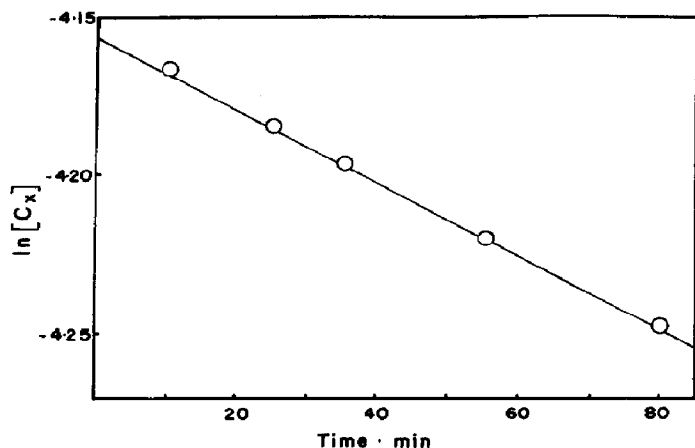


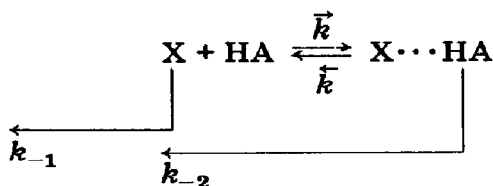
Fig. 2. The plot of $\ln [C_x(t)]$ vs. t .

TABLE 1

Rate constants of back reactions in various solvents

Solvent	Rate constant of back reaction (s^{-1})
Benzene	4.40×10^{-5}
1, 1, 2-Trichloro-1, 2, 2-trifluoroethane	4.41×10^{-5}
1, 1, 2-Trichloro-1, 2, 2-trifluoroethane + ethanol (4.3 M)	4.15×10^{-4}
Acetonitrile	2.33×10^{-4}
Ethanol	1.47×10^{-3}

in the proton-donating solvents, the rate is faster than in the highly polar solvents. The back reaction in acetic acid was too fast to be observed. In order to elucidate the influence of hydrogen bonding, the rate of the back reaction was examined in benzene solutions containing different concentrations of phenol or trifluoroacetic acid. The back reactions from both the non-hydrogen-bonded form X and the hydrogen-bonded form $X \cdots HA$ should be considered as follows:



where HA is phenol or trifluoroacetic acid and $K (= \bar{k}/\tilde{k})$ is the equilibrium constant. The time dependence of the concentration of X is written

$$-\frac{d[X]}{dt} = k_{-1}[X] + \bar{k}[HA][X] - \tilde{k}[X \cdots HA] \quad (4)$$

and the time dependence of the concentration of $X \cdots HA$ is

$$-\frac{d[X \cdots HA]}{dt} = (k_{-2} + \bar{k})[X \cdots HA] - \bar{k}[X][HA] \quad (5)$$

By adding eqns. (4) and (5), eqn. (6) is obtained if it is assumed that $[HA]$ is constant:

$$\ln [X] = -\frac{k_{-1} + k_{-2}[HA]K}{1 + K[HA]} t + \text{const} \quad (6)$$

where $K = [X \cdots HA]/[X][HA]$. $[X]$ is calculated using eqn. (3). The observed rate constant increases linearly with increasing $[HA]$ as shown in Fig. 3. This implies that $K[HA]$ is very much less than 1. From the slope $k_{-2}K$ was determined to be $3.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for phenol and $6.25 \text{ M}^{-1} \text{ s}^{-1}$ for trifluoroacetic acid at 25°C . The effect of hydrogen bonding on the absorption spectrum of the photoproduct is so small that K and k_{-2} cannot be estimated independently. However, it is clear that k_{-2} is much larger than k_{-1} .

The activation energy of the back reaction in the benzene solution was determined from the temperature dependence of the rate constant to be $24.5 \text{ kcal mol}^{-1}$. This value is close to the value of $25.9 \text{ kcal mol}^{-1}$ reported for the photochromism of N-diphenylnitron [2].

The absorption spectrum of the photoproduct has its maximum at 380 - 400 nm depending on the solvent used and its envelope extends to a wavelength longer than that of the original N-dioxide. Thus, the conjugation of π electrons in the photoproduct is considered to be rather long. The blue

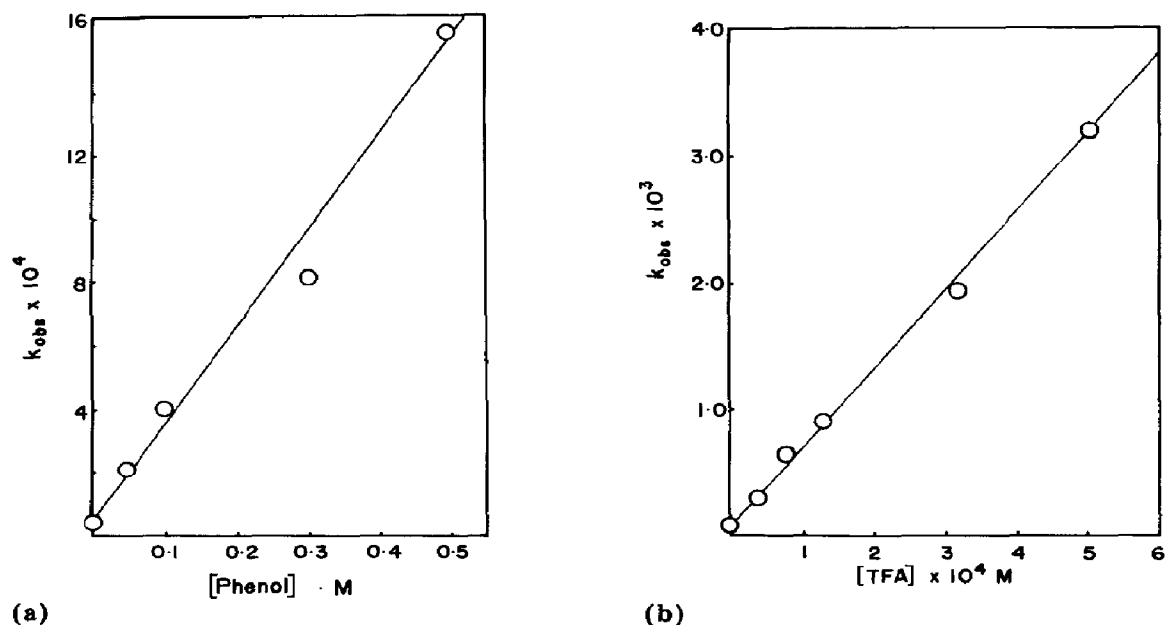


Fig. 3. (a) The plot of k_{obs} vs. concentration of phenol in benzene at 25°C . (b) The plot of k_{obs} vs. concentration of trifluoroacetic acid in benzene at 25°C .

shift of the absorption maximum with the increase in solvent polarity suggests that one of the two N→O groups is left.

Figure 4 shows the IR spectra before and after irradiation in carbon tetrachloride (1500 - 1300 cm^{-1}) and carbon disulfide (1300 - 1000 cm^{-1}). The samples were irradiated with light of wavelength 488 nm at right angles to the direction of IR observation. The strong absorption bands of phenazine N-dioxide at 1090 and 1341 cm^{-1} disappeared and new bands appeared at 1380, 1300 and 1100 - 1260 cm^{-1} . The disappearance of the band at 1090 cm^{-1} and the appearance of several absorption bands in this region suggest that the pyrazine skeleton underwent a structural change. The strong absorption band at 1380 cm^{-1} is assigned to the stretching vibration[†] $\nu_{\text{N}\rightarrow\text{O}}$ of N→O which does not take part in the reaction. This was confirmed by the band shift by about 10 cm^{-1} to a lower wavenumber when a small amount of methanol was added to the irradiated solution [5]. It should be noted that no change in the IR band around 1600 - 1800 cm^{-1} was observed either before or after the irradiation.

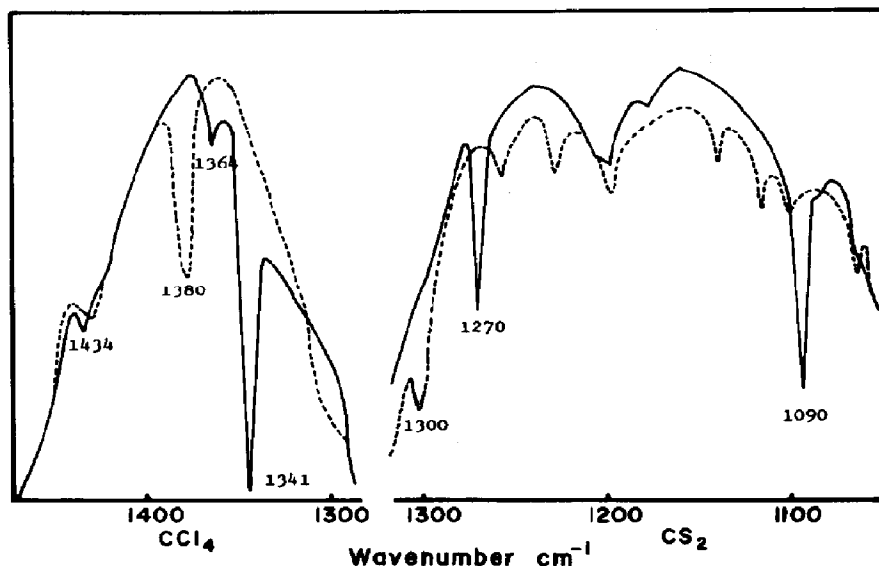
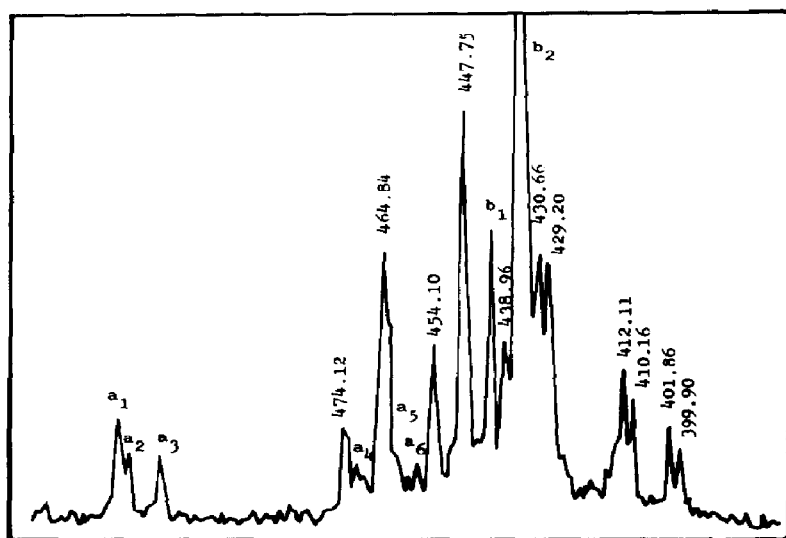


Fig. 4. The IR spectra before and after irradiation in carbon tetrachloride (1500 - 1300 cm^{-1}) and carbon disulfide (1300 - 1000 cm^{-1}): solid curve, before irradiation; broken curve, after irradiation.

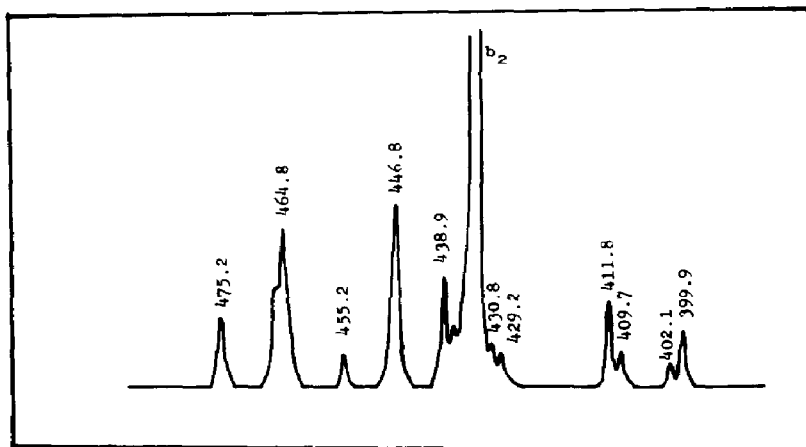
The analysis of the proton NMR spectrum of the photoproduct is quite complicated, whereas that of the photoproduct from 2,8-dichlorophenazine N-dioxide is simpler. 2,8-Dichlorophenazine N-dioxide also exhibits photochromism after irradiation by light of wavelength 488 nm in various organic solvents. The course of the reaction, the change in the UV spectrum and other behaviour are similar to those of its parent compound.

[†]The assignment of $\nu_{\text{N}\rightarrow\text{O}}$ to 1270 cm^{-1} in ref. 4 does not seem to be valid.

We found that the NMR spectrum of the photoproduct of the 2,8-dichloro derivative consists of two kinds of ABC type spectrum. The observed NMR spectrum and the simulated spectrum are shown in Fig. 5. The NMR parameters are listed in Table 2. Although the NMR spectrum of the photoproduct of the non-substituted N-dioxide has not yet been analysed, it should be noted that it might be possible to interpret it using parameters analogous to those of the 2,8-dichloro derivatives, because these compounds show similar patterns and positions of resonance. The τ values of the protons indicate that they are all ring protons [6]. The distance between H₄ (and H_{4'}) and the oxygen atom in N→O should be larger than that in the original



(a)



(b)

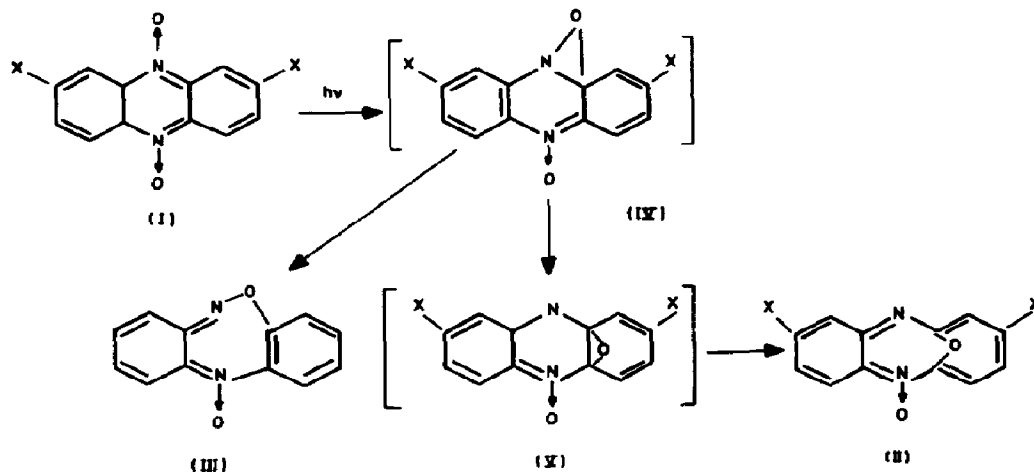
Fig. 5. (a) The NMR spectrum of the photoproduct. The a_i s are attributed to the signals of 2,8-dichlorophenazine N-dioxide and the b_i s are impurity signals. (b) Simulated spectrum of the photoproduct obtained by using the NMR parameters given in Table 2.

TABLE 2

NMR parameters of 2,8-dichlorophenazine N-dioxide and its photoproduct

	2,8-Dichlorophenazine N-dioxide	Photoproduct	
		ABC	A'B'C'
τ_1	1.25	2.23	2.53
τ_3	2.22	3.21	2.73
τ_4	1.33	2.16	2.43
$\Delta\tau_{14}$	-0.08	0.07	0.05
$\Delta\tau_{34}$	+0.89	1.05	0.25
$\Delta\tau_{31}$	+0.97	0.98	0.20
J_{13}	2.05	2.07	1.51
J_{34}	9.64	9.90	8.24
J_{41}	0.58	0.63	0.20

N-dioxide judging from the τ values of the protons at positions 4 and 4' [7]. The positive $\Delta\tau_{14}$ (and $\Delta\tau_{1'4'}$) value implies that the N→O group closest to the chlorine atom is converted. Structures (II) and (III) are possible structures for the photoproduct, since they can explain satisfactorily all the spectroscopic data. The τ shift in the NMR spectrum is interpreted successfully as being due to the distortion of the 10 π annulene-type plane which forces the oxygen in the N→O group out of plane:



where X denotes H or Cl.

In order to determine which structure is correct, the benzene solution containing about 2×10^{-2} M of triphenyl phosphine was irradiated at room temperature. As triphenyl phosphine is known to remove oxygen from oxaziridine or epoxide type compounds [8], phenazine N-monooxide can be obtained by this treatment if the photoproduct contains an —O— bridge structure. The absorption spectrum of N-monooxide was obtained by irradiation. The lifetimes of the intermediate products (structures (IV) and (V))

are short enough to prevent any reaction between them and triphenyl phosphine at this concentration. In contrast, —O— in structure (III) might not react with triphenyl phosphine because non-bonding electrons of this oxygen are involved in π electron conjugation of the molecule. Thus, the structure of the photoproduct was finally assigned to structure (II).

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