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Photoreduction of Phenazine in Alcohols and by EDTA in the Aqueous Solution

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By the combined use of the steady-light experiment and a flash technique, photoreduction of phenazine in methanol, ethanol, isopropanol and by EDTA in the aqueous solution and also the related elementary processes have been studied. The photoproduct has been identified as dihydrophenazine of which the absorption spectrum has been measured for the first time. It has been concluded that the lowest triplet, $T(\pi\text{–}\pi^*)$ is not a reactive state. Most probably the reactive state is a higher $T(n\text{–}\pi^*)$. The quantum yields of photoreduction in methanol, ethanol, and isopropanol are respectively 0.023, 0.037 and 0.050. Singlet-Triplet transition probability (Φ_{ST}) has been found to be >0.33 in the aqueous solution. Semiquinone produced in alcohols disappears by disproportionation reaction with almost the diffusion controlled rate constant while in the aqueous solution the disproportionation is much slower and at high EDTA concentrations, semiquinone is further reduced by EDTA. The absorption due to a molecular compound consisting of phenazine and dihydrophenazine has been detected in the visible region. It has been suggested that a certain equilibrium exists between three compounds and that a rather stable radical species, the existence of which has been proved by an ESR spectroscopy, participates in this equilibrium.

This paper is an extension of our photochemical investigation of acridine[1–5] and reports the general feature of the photoreduction of phenazine in alcohols and by EDTA in the aqueous solution all dearated which was elucidated by the steady light experiment and by flash photolysis.[6] At the time when we commenced this work, there was no work on the photoreduction of phenazine other than that of Toromanoff.[7] He reported that the deaerated 2-propanol solutions of phenazine (ϕ), when exposed to sunlight, yield two types of molecular compound, 3 phenazine-1 dihydrophenazine (violet) and 1 phenazine-1 dihydrophenazine (blue) but the final product obtained by the prolonged irradiation is dihydrophenazine (ϕH_2) (colourless). The interrelation of the molecular compound with the eventual photoreduction was unknown and even the electronic spectrum of dihydrophenazine was not found in literature.

A little later after we have finished the present work, a report by Bailey *et al.*[8] appeared. They studied mainly in acidic methanol and concluded that the photoproduct in weakly acidic solutions is dihydrophenazine while in strong acidic solutions the final product is a radical cation, ϕH_2^+. They also proposed that a reactive state is the excited singlet (n-π^*) state. But unambigous evidence for the formation of molecular complex was not given and the product in the weakly acidic solution, *i.e.* dihydrophenazine was not identified in any way.

We have investigated the photoreduction in pure methanol, ethanol and isopropanol and by EDTA in the aqueous solution. The results obtained agree with Bailey's in some points but not in others. This is natural partially because the experimental conditions are different. Firstly, we have demonstrated unequivocally, that the photoproduct is dihydrophenazine by comparing its absorption spectrum with that of chemically prepared dihydrophenazine. Secondly, strong evidence has been obtained for the view that a molecular complex consisting of ϕ and ϕH_2 is produced in solution in equilibrium with ϕ and

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[2] A. Kira and M. Koizumi, *ibid.*, **40**, 2486 (1967).

[3] M. Koizumi, Y. Ikeda and H. Yamashita, *ibid.*, **41**, 1056 (1968).

[4] S. Niizuma and M. Koizumi, *ibid.*, **41**, 1090 (1968).

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[6] It has already been reported previously that the photoreduction of phenazine by EDTA in the aqueous solution occurs most likely in a higher $T(n\text{–}\pi^*)$ state. M. Koizumi, Y. Ikeda and T. Iwaoka, *J. Chem. Phys.*, **48**, 1869 (1968).

[7] C. Dufraisse, A. Etienne and E. Toromanoff, *Compt. Rend.*, **232**, 2379 (1951); **235**, 759 (1952); E. Toromanoff, *Ann. Chim.*, **1**, 115 (1956).

[8] D. N. Bailey, D. K. Roe and D. M. Hercules, *J. Amer. Chem. Soc.*, **90**, 6291 (1968).

ϕH_2. A radical cation reported by Bailey *et al.* has also been detected by ESR in pure methanol but in a very small quantity. Thirdly, it has been concluded that our kinetic results cannot be consistently interpreted unless a higher $T(n\text{–}\pi^*)$ is a reactive state.

Before entering the experimental part, it will be convenient to write down the reaction scheme in alcohol (RH_2) which we would like to propose. The processes underlined are the main ones.

$$\underline{\phi \xrightarrow{h\nu} {}^1\phi^*} \tag{1}$$

$$\underline{{}^1\phi^* \longrightarrow {}^3\phi(n\text{-}\pi^*)} \tag{2}$$

$${}^3\phi(n\text{-}\pi^*) \longrightarrow {}^3\phi(\pi\text{-}\pi^*) \tag{3}$$

$$\underline{{}^3\phi(n\text{-}\pi^*) + RH_2 \longrightarrow \phi H\cdot + RH\cdot} \tag{4}$$

$${}^3\phi(n\text{-}\pi^*) + O_2 \longrightarrow \phi + O_2 \tag{5}$$

$${}^3\phi(n\text{-}\pi^*) + \phi \longrightarrow 2\phi \tag{6}$$

$${}^3\phi(\pi\text{-}\pi^*) + \phi \longrightarrow 2\phi \tag{7}$$

$${}^3\phi(\pi\text{-}\pi^*) + RH_2 \not\longrightarrow \tag{8}$$

$$\underline{2\phi H\cdot \longrightarrow \phi H_2 + \phi} \tag{9}$$

$$\phi H_2 + \phi \longrightarrow (\phi H_2\cdots\phi) \tag{10}$$

In the case of the aqueous solution, (4) and (9) are replaced by

$${}^3\phi(n\text{-}\pi^*) + \text{EDTA} \longrightarrow \phi H\cdot + \text{EDTA}' \tag{4}$$

$$2\phi H\cdot \longrightarrow \phi H_2 + \phi \tag{9}$$

$$\phi H\cdot + \text{EDTA} \longrightarrow \phi H_2 + \text{EDTA}' \tag{9'}$$

Experimental

Materials and Procedures. Phenazine rom Tokyo Kasei was purified by recrystallization from ethanol two times. Methanol, ethanol, isopropanol and tetrahydrofuran used as solvents were of Wako Junyaku and were distilled before use. Disodium ethylenediaminetetraacetate (EDTA) of Wako Junyaku G. R. grade was used without further purification. Palladium charcoal was kindly supplied by Professor Nakanishi.

An apparatus for the steady-light illumination and a flash apparatus are the ordinary ones used in our laboratory. The exciting light for the steady-light experiments was 365 nm from a Toshiba SHL-100UV mercury lamp monochromatized with suitable filters. The reaction temperature was always 25°C.

Results from the Steady-light Experiments

Photoreduction in Alcohols. Figures 1a, b, c, d give the spectral changes when the solutions of phenazine in methanol, ethanol, isopropanol and tetrahydrofuran were irradiated by 365 nm. Broadly speaking, they are similar in that the 362 nm peaks of phenazine decline monotonously with more or less shift to shorter wavelengths and with isosbestic points around 340 nm. The ultimate absorption spectra obtained by prolonged illumination are different from solvent to solvent; the peak positions are 345 nm (methanol), 358 nm (ethanol), 360 nm (isopropanol) and 320 nm (tetrahydrofuran). At first sight, these results led us to suspect that the photoproduct might not be dihydrophenazine, because dihydro compounds with the similar type of structure such as acridan in general, have no absorption in this wavelength region. Hence the hydrogenation of phenazine by two other methods were attempted. One is the reduction by treating the ethanol solution of

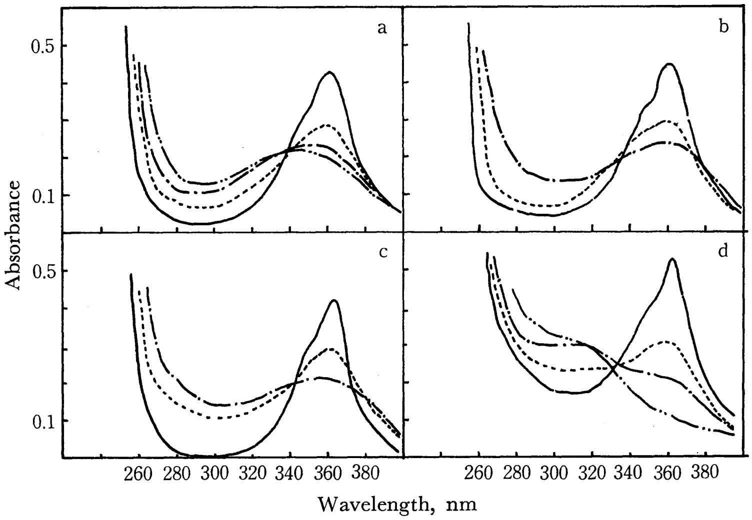

Fig. 1. Spectral change of phenazine in the deaerated solutions.
a: Methanol $[\phi]=3.3\times10^{-5}$ M. ——, 0 sec; - - -, 9 min; —·—, 27 min; —··—, 115 min
b: Ethanol $[\phi]=3.4\times10^{-5}$ M. ——, 0 sec; - - -, 7 min; —·—, 87 min
c: Isopropanol $[\phi]=3.9\times10^{-5}$ M. ——, 0 sec; - - -, 10 min; —·—, 24 min
d: Tetrahydrofuran $[\phi]=3.1\times10^{-5}$ M. ——, 0 sec; - - -, 2.5 min; —·—, 7 min; —··—, 60 min

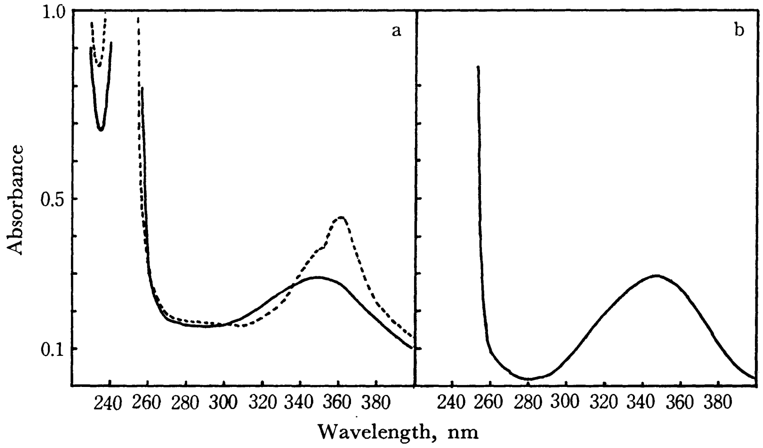

Fig. 2. Ultraviolet spectra of the chemically prepared dihydrophenazine.
a: By reduction with amalgamated sodium *in vacuo*. - - -, after air introduction.
b: By catalytic hydrogenation.

phenazine with amalgamated sodium *in vacuo*, and the other is the catalytic hydrogenation using palladium charcoal as a catalyst. As seen from Figs. 2a, and 2b, the absorption spectra of both products dissolved in ethanol agree with that of the photoproduct except for the lack of a slight absorption around ~280 nm. The difference may be due to the presence of aldehyde or some other photoproduct resulting from alcohol in the irradiated sample. Upon introduction of air, the chemically prepared dihydrophenazine was oxidized quantitatively to phenazine as shown in Fig. 2a, while the photoproduct gave some unknown substance in addition to phenazine, as judged from a slight shift of the absorption peak to the longer wavelength. Apart from these minor points, the agreement between the photoproduct and chemically prepared dihydrophenazine verifies that the photoproduct is dihydrophenazine and that it gives the absorption band near 340 nm. This may be due to the participation of lone pairs on nitrogen atoms in the π-electron system of the molecule.

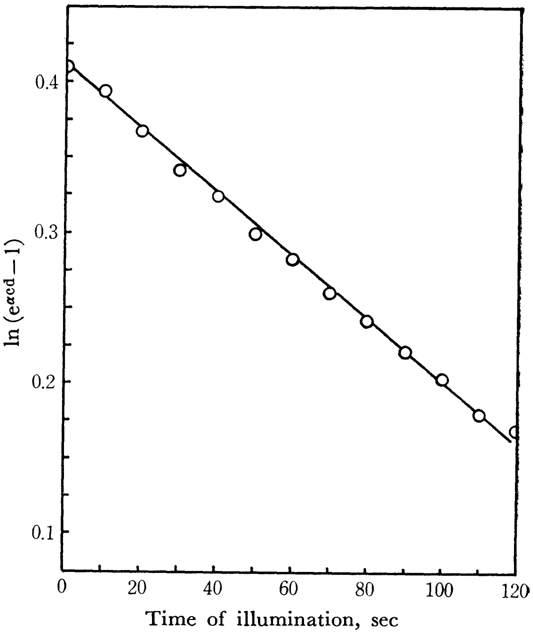

Fig. 3. Photobleaching curve of phenazine in the deaerated methanol solution.
$[\phi]=3.3\times10^{-5}$ M. α, absorption coefficient.
c, phenazine concentration
d, optical path length.

Quantum Yields of Photoreduction in Alcohols. Figure 3 gives a typical example for photobleaching curves, which indicates that the photoreduction rate is simply proportional to the absorption of light. But in order to get the correct values of quantum yield, a certain correction should be made because the photoproduct absorbs the exciting 365 nm light to some extent. By assuming that the photoproduct merely acts as an inner filter, the following relation can easily be derived,

$$\ln(\mathrm{e}^{2.303\mathrm{A}}-1)-\ln(\mathrm{e}^{2.303\mathrm{A}_0}-1)$$

$$=2.303\Phi I_0\varepsilon\left\{t-\varepsilon'\mathrm{C}_0\int_0^t(1/A)\mathrm{d}t\right\}\times10^3 \qquad (1)$$

where I_0, ε and ε' are respectively the incident light intensity (mol/cm^2 sec), molar extinction coefficients of phenazine and of the photoproduct (both at 365 nm). The evaluation of the correction terms $\varepsilon'\mathrm{C}_0\int_0^t(1/A)\mathrm{d}t$ is a simple matter, and these corrections made on the time axis for the similar plots as in Fig. 3 give the corrected values of quantum yield. The quantum yields for the four solvents, corrected and uncorrected are given in Table 1. The quantum yield increases in the order, methanol<ethanol<isopropanol; this is the same as the order of easiness with which α-hydrogen is detached from alcohols.

TABLE 1. QUANTUM YIELD (Φ) OF PHOTOREDUCTION

	Concn. of phenazine (M)	Φ, uncorrected	Φ, corrected
CH_3OH	3.3×10^{-5}	0.0094	0.023
C_2H_5OH	3.4×10^{-5}	0.016	0.037
$(CH_3)_2CHOH$	3.1×10^{-5}	0.020	0.050
Tetrahydrofuran	3.7×10^{-5}	0.031	0.062

Retarding Effect of Oxygen on the Photoreduction of Phenazine in Methanol and Ethanol. Since dihydrophenazine is sensitive to oxygen, the photoreduction does not occur in the aerated solutions. This is in sharp contrast to acridine which is reduced to acridan by a molecular mechanism even in the presence of oxygen. When the aerated solutions of phenazine in methanol or in ethanol are irradiated by 365 nm for a long time, the original peak of phenazine at 362 nm gradually shifts to red and attains to 370 nm and 375 nm in the case of methanol and ethanol respectively. These shifts may perhaps be due to some oxidation reaction which yields, for instance, phenazine oxide. Along with these shifts, a new small band appeared at about 510 nm, the assignment of which is still unknown. The above spectral changes, however, proceed at very slow rates and no appreciable spectral change was observed by several minutes' irradiation. In such a short time illumination, oxygen is considered as a mere quencher on the photoreduction and the retarding effect of a small quantity of oxygen is expected to afford the information about the intermediate which is attacked by oxygen. From such a viewpoint, the photoreduction of phenazine in methanol and ethanol containing oxygen in the order of 10^{-5} M were investigated. It was really found that the spectral change is not essentially different from that of the completely deaerated solution. Some typical photobeaching curves are shown in Fig. 4. The plots are somewhat similar to those obtained in the case of acridine[3)] in the point that the bleaching occurs at much slow rate in the initial stage and after a certain time interval the rate increases rather rapidly to the final value which is 70—90% of the rate in the deaerated solution. These results imply that in the initial stage oxygen prevents the photoreduction by attacking some intermediate, and that the final rate is attained after oxygen is consumed by the reaction, for instance, with semiquinone. Figure 5 shows the dependence of Φ (obtained from the initial slopes in Fig. 4) on the oxygen concentration. Presuming tentatively that oxygen[*1] attacks $^3\phi$-(n-π^*), the data can be treated simply by the following equation,

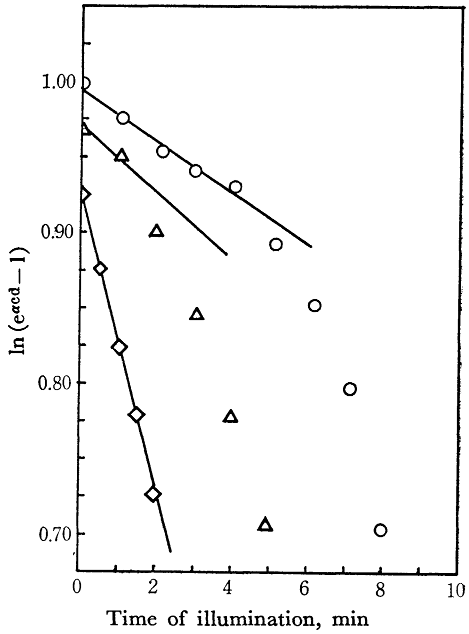

Fig. 4. Photobleaching curve of phenazine methanol solution, dissolving a small amount of oxygen. ○: $[O_2]=2.05\times10^{-5}$ M, △: 1.38×10^{-5} M, ◇: $[O_2]=0$ M

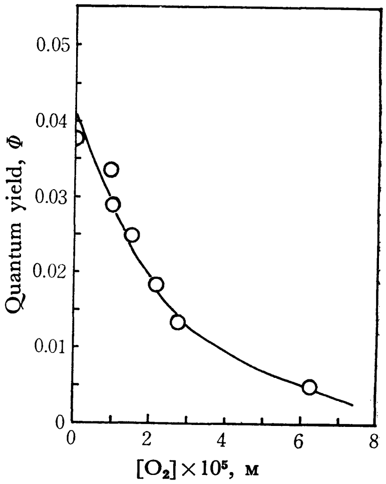

Fig. 5. Dependence of the quantum yields on the oxygen concentration in ethanol solution. $[\phi]=3—6\times10^{-5}$ M

$$1/\Phi = (1/\Phi_0)\times(1+k_5[O_2]/k_3) \qquad (2)$$

where Φ_0 and Φ are the quantum yields in the absence and in the presence of oxygen respectively. Assuming that the quenching process is diffusion controlled, and putting $k_5=10^{10}$ M^{-1} sec^{-1}, the estimated lifetime of the intermediate in methanol and ethanol was 8×10^{-6} and 5×10^{-6} sec respectively.

[*1] It will be demonstrated later that this intermediate is neither semiquinone nor the excited singlet state. (See Discussion.)

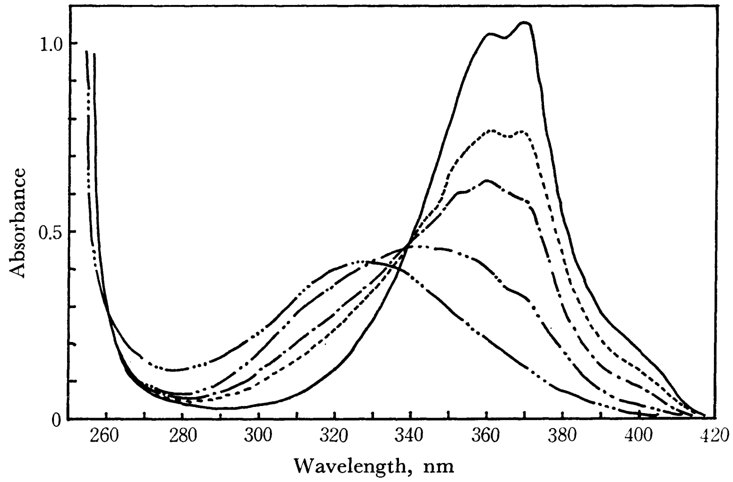

Fig. 6. Spectral change of phenazine in the aqueous solution involving EDTA.
$[\phi]=8.4\times10^{-5}$ M. $[\text{EDTA}]=7.9\times10^{-3}$ M.
Time of illumination,
—— before illumination, - - - 40 sec, —·— 80 sec, —··— 270 sec,
—···— 165 min

Photoreduction of Phenazine by EDTA in the Aqueous Solution. To get a better insight into the mechanism of the photoreduction in question, the reaction with a reducing agent (EDTA) dissolved as a solute in an inert solvent (H_2O) was investigated. pH of the solution containing EDTA is *ca.* 6. A typical example of the spectral change caused by 365 nm irradiation is shown in Fig. 6. It is seen that the reaction proceeds in a simple way with a higher rate than in organic solvents. The spectrum for 165 min irradiation shows a slight deviation from the isosbestic point, perhaps due to the decomposition of dihydrophenazine. In contrast to alcoholic solutions, there is no sign of the superposition of the absorption band due to some other photoproduct. Upon introduction of air, phenazine was recovered almost quantitatively unless the illumination period was not so long.

Dependence of the Quantum Yield on the Concentration of Phenazine and of EDTA in the Aqueous Solution. The phenazine concentration effect was investigated because it is well known that the triplet states of some substances are often quenched by the same substances in the ground state. Fixing the concentration of EDTA at 7.9×10^{-3} M, the concentration of phenazine was changed from 3×10^{-5} to 1×10^{-4} M. The results are shown in Fig. 7. It is to be added that a small absorption becomes observable at 450 nm at higher concentrations of phenazine; this may be

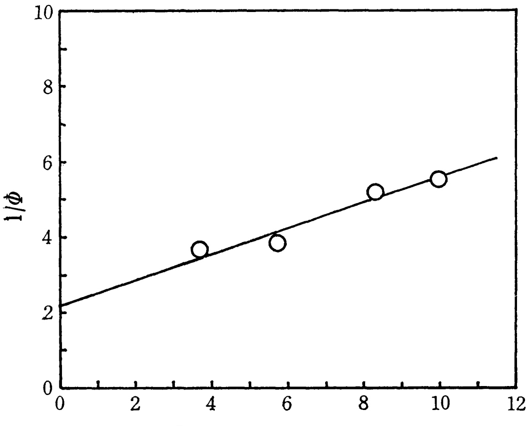

Fig. 7. Dependence of the quantum yield on the phenazine concentration in the aqueous solution involving EDTA as a reducing agent.
$[\text{EDTA}]=7.9\times10^{-3}$ M

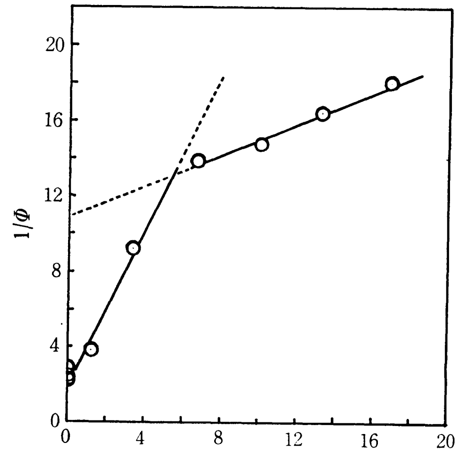

Fig. 8. Dependence of the quantum yield on the concentration of EDTA in the aqueous solution.
$[\phi]=5.0\times10^{-5}$ M

attributed to the formation of a certain molecular complex as will be described later. Since the absorption spectrum is not essentially affected by the above change in the phenazine concentration, decrease in the quantum yield with increasing phenazine concentrations is due to deactivation of a certain reactive state by phenazine in the ground state.

The quantum yield increases with the increase of EDTA concentration but becomes practically constant above 3×10^{-2} M. Figure 8 gives the plot of $1/\Phi$ against 1/[EDTA]. It is apparent that the plot consists of two linear portions. This is due to the processes (9) and (9′) as will be more fully established later. Assuming that the entire reaction consists of (1), (2), (3), (4), (6), (9) and (9′), the lower limit of the intersystem crossing probability, Φ_{ST} was evaluated from the intercept of the plot in Fig. 8 as 0.33. If this is a true value for Φ_{ST}, the values of k_6/k_4 and k_3/k_4 are calculated from the slope of the plot in Fig. 7 and the slope/intercept of the plot in Fig. 8 as follows,

$$k_4/k_3 = 2.7\times10^{2}\,\mathrm{M}^{-1}$$

$$k_4/k_6 = 1.3\times10^{-2}$$

Investigation by a Flash Technique

Transient Spectra in Various Media. Figure 9 shows the transient spectra in various media and at various time points after flashing. Since

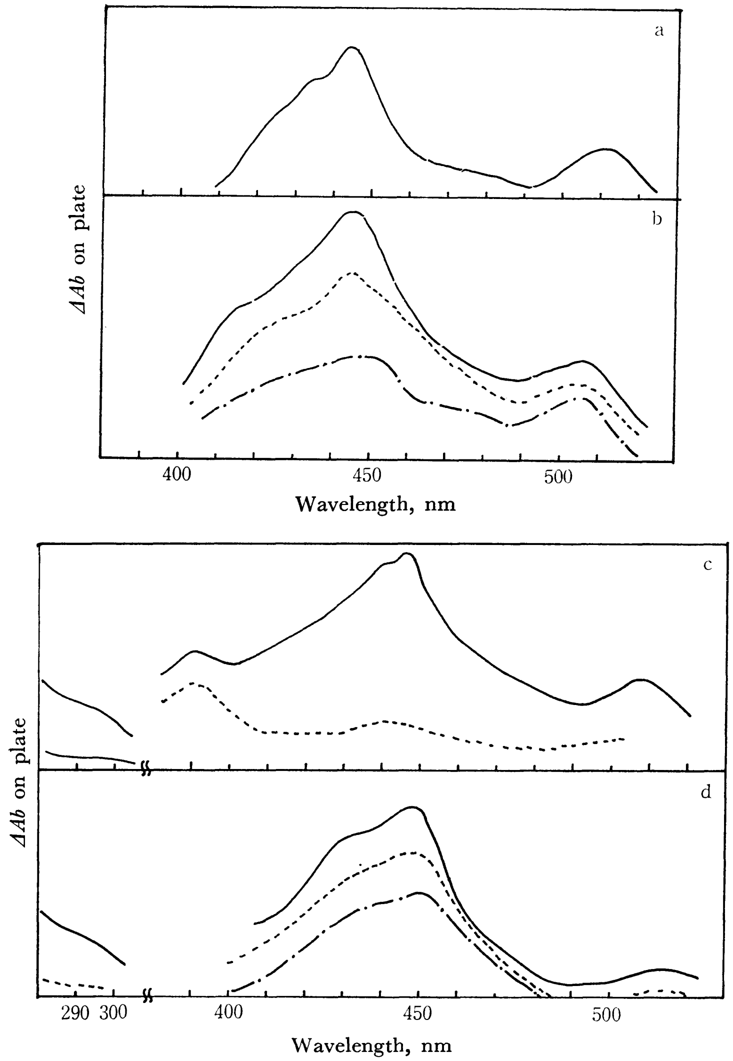

Fig. 9. Transient absorption spectra in the deaerated various solutions of phenazine.
a: Cyclohexane, —— 30 μsec after flashing.
b: Water, —— during photolysis; - - - after 17 μsec; —·— 30 μsec.
c: Methanol, —— 65 μsec after flashing; - - - 365 μsec.
d: Water involving EDTA, [EDTA]$=3.2\times10^{-2}$ M; —— during photolysis; - - - 17 μsec after flashing; —·— 1200 μsec

photoreduction does not occur in the plain aqueous solution, the transient spectra observed in these cases are safely assigned as $T(\pi\text{-}\pi^*)$. In the case of the reactive media on the other hand, two transient species can be discriminated, short lived and relatively long lived ones. The comparison with the results for inert media leads to the assignment that the former is $T(\pi\text{-}\pi^*)$ and the latter is most likely semiquinone. These assignments will be further substantiated by the findings described later. The characteristic bands for $T(\pi\text{-}\pi^*)$ are

490—525 nm (510), 410—470 nm (∼445), <300 nm

and are essentially the same in different solvents. The numbers in parentheses are for the peak positions. The results are consistent with those of Bailey *et al.*[8)]

The absorption of semiquinone in the aqueous solution was investigated in some details. From Fig. 9d it is evident that there is a prominent absorption in the 400—480 nm (∼450 nm) region in agreement with the spectrum given by Bailey *et al.*[8)] The assignment of this band to semiquinone is supported by the fact that the absorbance at 320 nm due to dihydrophenazine increases in a parallel way with the decrease in absorbance at 445 nm. The transient increase in absorbance occurs in the neighborhood of 360 nm and this means that the gain in absorption by semiquinone supersedes the loss due to the disappearance of phenazine. At 340 nm *i.e.* at the isosbestic point of the steady light reaction, the opposite phenomenon is observable. Although the exact measurement of the absorption spectrum of semiquinone was not attempted, the tentative values of extinction coefficient at some selected wavelengths were determined in the following way. Assuming that dihydrophenazine is exclusively produced by disproportionation of semiquinone in methanol and that in the aqueous solution, semiquinone is further reduced by EDTA (when its concentration is high) (see below), the yield of the semiquinone was estimated from the decrease in the phenazine concentration by one flash. The ε-values thus obtained are given in Table 2. Although these values are not very reliable but may be used for the semiquantitative discussion on the kinetic data.

TABLE 2. ε-VALUES OF SEMIQUINONE

	390 nm	400 nm	430 nm	450 nm
in methanol	2.1×10^4	1.2×10^4	1.4×10^4	1.7×10^4
in water	$(6.0\pm1)\times10^3$ at 445 nm			

Kinetics for the Elementary Reactions. The decay of semiquinone in methanol was measured at 390 nm where the absorption of other species does not exist. As shown in Fig. 10, the decay was found to be satisfactorily reproduced by the second order plot throughout the entire stage beginning from the end of flashing. This is one of the strongest evidences that $T(\pi\text{-}\pi^*)$ still surviving after flashing, does not participate in

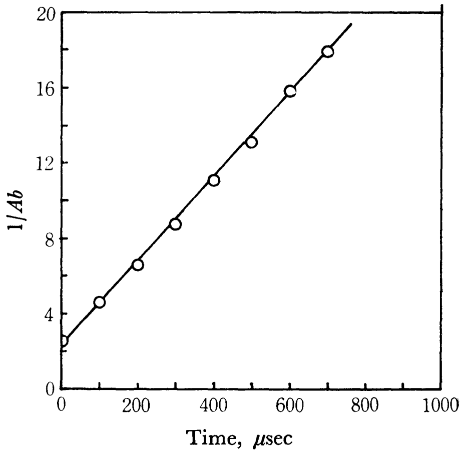

Fig. 10. Second order decay of phenazine semiquinone in the deaerated methanol solution observed at 390 nm.

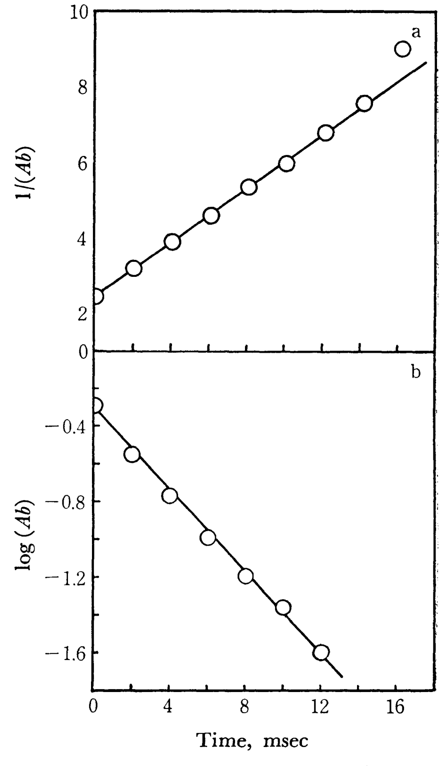

Fig. 11. Decays of phenazine semiquinone in the aqueous solutions involving EDTA as a reducing agent, observed at 445 nm.

a: Second order decay at low EDTA concentration, [EDTA] = 7.9×10^{-3} M

b: First order decay at high EDTA concentration, [EDTA] = 7.7×10^{-2} M the reaction. It can also be concluded that the semiquinone does not react with alcohol nor with alcoholic radical produced in the preceeding process. The analysis was also made at 445 nm where the triplet absorption superposes, by making use of the data in the later stage. The results obtained are moderately satisfactory and the ultimate value for the disproportionation rate constant is $(3.0\pm 0.5)\times 10^9\ \text{M}^{-1}\,\text{sec}^{-1}$. The semiquinone in the aqueous solution survives a longer time than in alcohol. This made it possible to measure the decay rate at 445 nm. It has been found that the decay consists of two processes, disproportionation reaction and the reaction with EDTA. Of course the former prevails in low concentrations of EDTA while the latter is predominant in the opposite condition. This is shown in Fig. 11. In general the decay can be treated by the following equation which takes into account the above two processes.

$$-\mathrm{d}[\phi\mathrm{H}]/\mathrm{d}t = 2k_9[\phi\mathrm{H}]^2 + k_{9'}[\phi\mathrm{H}][\mathrm{EDTA}] \tag{3}$$

From this equation the following relation can easily be derived.

$$\log A - \log(A + k_{9'}[\mathrm{EDTA}]\varepsilon\cdot d/2k_9) = -k_{9'}[\mathrm{EDTA}]t/2.303 \tag{4}$$

This relation fits the decay curve quite satisfactorily. By making experiments at various EDTA concentrations, the ultimate values of k_9 and $k_{9'}$ were evaluated as follows.

$$k_9/\varepsilon d = (1.8\pm 0.2)\times 10^2, \quad k_9 = 1.1\times 10^7\ \text{M}^{-1}\,\text{sec}^{-1},$$
$$k_{9'} = \sim 3\times 10^3\ \text{M}^{-1}\,\text{sec}^{-1}$$

These values are not so much reliable, particularly so for the disproportionation reaction because of the uncertainty of the ε-value.

The decay of $T(\pi\text{-}\pi^*)$ in methanol was measured at 280 nm, where the absorption of semiquinone is small, though not negligible. The decay is neither first order nor second order. Assuming that $T(\pi\text{-}\pi^*)$ is not a reactive state, the analysis was made by the following formula

$$\ln(A - A(\phi\mathrm{H})) = -kt + \text{const} \tag{5}$$

where $A(\phi\mathrm{H})$ is the absorbance of semiquinone and can be evaluated from the extrapolation of the later stage of the $1/A$ - t plot in case of methanol. In the aqueous media the similar procedure was allowed for low EDTA concentrations but the $\log A$ - t plot must be used for high EDTA concentrations. The first order rate constant obtained for methanol is $\sim 10^4\ \text{sec}^{-1}$. Figure 12 gives the dependence of the decay rate on the concentration of EDTA in the aqueous solution. Figure 12 definitely shows that the addition of EDTA does never increase the decay constant of $T(\pi\text{-}\pi^*)$. The effect is rather opposite and may be due to the difference in physical properties of the solutions such as pH or ionic strength. The dependence of the decay rate on the phenazine concentration was similarly investigated, in order to know whether the triplet state $T(\pi\text{-}\pi^*)$ is deactivated by the ground state molecule or not. The result as shown in Fig. 3, clearly demonstrates the occurrence of such a process. The k_7-value was estimated to be $\sim 4\times 10^7\ \text{M}^{-1}\,\text{sec}^{-1}$.

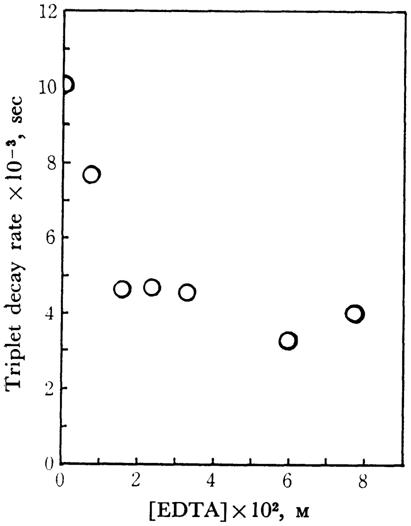

Fig. 12. Dependence of the decay rate of phenazine triplet, $T(\pi\text{-}\pi^*)$ on the concentration of EDTA in the aqueous solution.
$[\phi]=5\times 10^{-5}\ \text{M}$

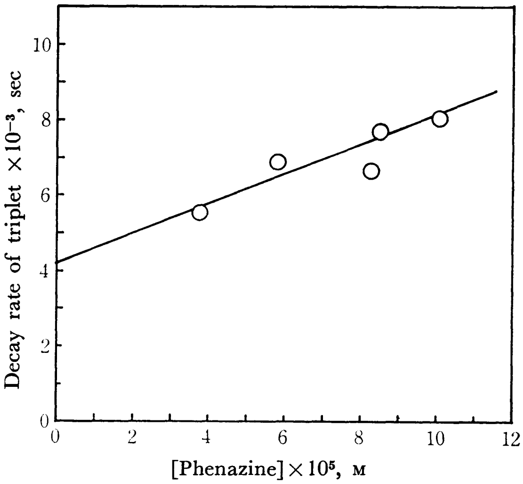

Fig. 13. Dependence of the apparent first order decay constant of phenazine triplet, $T(\pi\text{-}\pi^*)$ on the phenazine concentration.
$[\mathrm{EDTA}]=7.9\times 10^{-3}\ \text{M}$

The Formation of Molecular Complex and a Radical Species related with it

In the course of the steady light experiment, a remarkable fact was found that in the illuminated solutions of rather high phenazine concentrations (from 10^{-4} to $10^{-2}\ \text{M}$), a new small absorption band appears in the ~450 nm region, as shown in

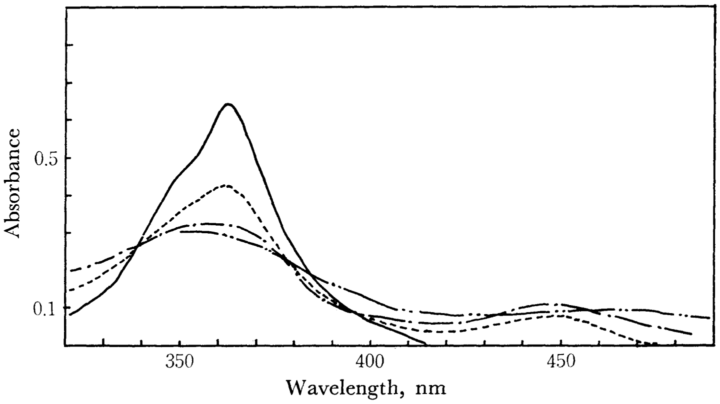

Fig. 14. Spectral change of the deaerated methanol solution in the high phenazine concentration. $[\phi]=1.7\times10^{-4}$ M. —— 0 min, - - - 6 min, —·— 12 min, —··— 199 min

Fig. 14. This band with a peak at 450 nm gradually grows with the time of illumination and in about 30 minutes attains its maximum and then declines slowly accompanied with a shift to the longer wavelength. The ultimate position of the peak is usually about 500 nm. The quantum yields of the photoreduction in the case that the above band was observed, were not essentially different and the spectral changes from 300 to 400 nm region was the same as that in other cases. All these facts are understandable if one assumes that the visible absorption is due to the complex formation occuring between phenazine and dihydrophenazine and the equilibrium exists between them with a rather small equilibrium constant for the complex formation.

Since the complex consisting of 3 phenazine-1 dihydrophenazine and 1 phenazine-1 dihydrophenazine has been reported by Toromanoff *et al.*,7) the molecular weight of the photoproduct was examined by mass spectrometry. Thus the deaerated ethanol solution of phenazine was illuminated for about three hours, and then the solid mixture obtained by distilling off the solvent, was submitted to mass spectrometry. A fragment with a molecular weight about two times that of phenazine was really detected but most of the fragments are of the molecular weight near that of phenazine. No fragment of larger molecular weight was not detected. The solid mixture consisting of the complex, phenazine and dihydrophenazine was found to display the ESR signal. When the degassed methanol solution of phenazine 1×10^{-3} M was illuminated in a capillary cell for ESR with a light of 365 nm, the signal was clearly detected and it increased in intensity with the time of irradiation. The signal intensity was found to remain constant for a long time after the irradiation was stopped. Hence the signal is due to a certain stable paramagnetic species different from neutral semiquinone radical which is not so stable. The complex itself may be paramagnetic, but some other radical species might be formed in the equilibrium system $\phi+\phi H_2 \rightleftarrows (\phi\cdots\phi H_2)$ in solutions. In the former case a molecular complex may be of a charge transfer type or the dimer of the semiquinone radical. However, we have some evidence for identifying the paramagnetic species as the radical cation reported by Bailey *et al.*,8) though it is not clear how it is formed. Further studies are now in progress.

General Discussion

As to the reactive state of phenazine, the results obtained exclude definitely the possibility of the lowest $T(\pi\text{-}\pi^*)$ being a reactive state. Evidence in addition to the one already described are as follows. Firstly, in alcohols the decay constant of $T(\pi\text{-}\pi^*)$, $k\lesssim10^4\,\text{sec}^{-1}$ is too small for considering it as a reactive state because this value cannot compete with the quenching action of $\sim10^{-5}$ M oxygen. If the reactive state were $T(\pi\text{-}\pi^*)$, the reaction would have to be retarded by oxygen far more efficiently than was observed. Secondly, in the aqueous solution, the decay rate of $T(\pi\text{-}\pi^*)$ does not increase by the addition of EDTA in the amount which is enough to make the steady reaction to occur.[*2] Thus the remaining possible states are certain higher $T(n\text{-}\pi^*)$ or the singlet excited state. But the latter is not likely in view of the result that the quantum yield becomes constant at and above the EDTA concentration of $\sim3\times10^{-2}$ M. Furthermore, the inhibiting action of oxygen of 10^{-5} M in methanol cannot be understandable if the reactive state is the excited singlet.

The view that a $T(n\text{-}\pi^*)$ is a reactive state is

[*2] Baiely *et al.* concluded from somewhat similar argument as above, that the lowest $T(\pi\text{-}\pi^*)$ is not a reactive state. But their argument does not seem to be strong enough to support the excited singlet mechanism and to reject the $T(n\text{-}\pi^*)$ state.

further supported by the following consideration about the intermediates attacked by oxygen. At first sight it seems reasonable to consider that oxygen attacks only semiquinone in addition to the final product, ϕH_2. But this is highly improbable because semiquinone would have a much longer lifetime than 5—8×10^{-6} sec (the value of lifetime estimated for the intermediate attacked by oxygen). One must therefore consider another shorter-lived intermediate attacked by oxygen and there is no other state conceivable than a certain higher $T(n\text{-}\pi^*)$. The exact lifetime of $T(n\text{-}\pi^*)$ however, cannot be evaluated, since the deactivation process of $T(n\text{-}\pi^*)$ by oxygen is superposed by the reaction between semiquinone and oxygen. Hence the above value 5—8×10^{-6} sec is an overestimation. The real value may be $\lesssim 1\times10^{-6}$ sec.

The result that the quantum yield is much less in alcohols than the Φ_{ST} value obtained for the aqueous solution, 0.33 (lower limit) can be attributed to the difference of reactivity of alcohol molecules and EDTA. The exact value of Φ_{ST} will be determined in near future.

As for the semiquinone, it disappears in methanol only by disproportionation and its rate constant approximates the diffusion controlled value. This differs from Bailey's result in acidic medium where the disproportionation is rather slow. In the aqueous solution on the other hand, the reaction with EDTA occurs in addition to the disproportionation. The rate constant for the former is $\sim 3\times10^3\ \text{M}^{-1}\,\text{sec}^{-1}$ and for the latter $\sim 1\times10^7\ \text{M}^{-1}\,\text{sec}^{-1}$. The result that the $1/\Phi$ - $1/[\text{EDTA}]$ plot consists of two linear portions is related with these two reactions. Thus the overall quantum yield when the semiquinone disappears by disproportionation is expected to be half that when it is reduced to dihydrophenazine by EDTA. The result in Fig. 8 is qualitatively consistent with this expectation. Much smaller rate constant of disproportionation in the aqueous solution may be due to the liquid state.*3 If one assumes that the lifetime of $T(n\text{-}\pi^*)$ in the aqueous solution, is the same as that in alcohol, then the rate constants k_4 and k_6 in the aqueous solutions are evaluated as $k_4=3\times10^8\ \text{M}^{-1}\,\text{sec}^{-1}$, $k_6=2\times10^{10}\ \text{M}^{-1}\,\text{sec}^{-1}$, from the values of $k_4/k_3=2.7\times10^2\ \text{M}^{-1}$ and $k_4/k_6=1.3\times10^{-2}$ obtained by the steady light experiments. The value of k_6 is compared with the rate constant, $4\times10^7\ \text{M}^{-1}\,\text{sec}^{-1}$ for the reaction $T(\pi\text{-}\pi^*)+\phi\rightarrow2\phi$.

The determination of the exact Φ_{ST} value, the dependence of the stability of semiquinone on the solvent property, especially the dependence on pH, and more decisive evidence for $T(n\text{-}\pi^*)$ as a reactive state by means of the triplet energy transfer await further studies. In particular, further investigations on the molecular complex and the radical species related with it will be most interesting.

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*3 It is well comprehended that Bailey's result in acidic media is rather similar to the present one in the aqueous solutions.