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Mechanistic Studies on the Photochemical Oxidation of Phenothiazine with Oxygen in Ethanol

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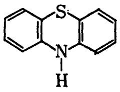
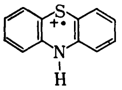
It has been established that phenothiazine (PTH) undergoes photooxidation, $PTH+O_2 \xrightarrow{h\nu} PT\cdot+HO_2$ in the aerated ethanol (dehydrated!) yielding a neutral radical as a stable product. The reaction is a one photon process and the reactive state is triplet PTH. It has further been established that the reaction occurs *via* a molecular complex (PTH-O_2) most likely of C-T type, which has the absorption at ~385 nm and decays with the first order rate constant of $1.6\times10^2\,sec^{-1}$. A similar transient C-T complex has been found to be produced from triplet PTH and dimethylisophthalate (weak electron acceptor) (absorption ~385 nm, decay constant $2\times10^3\,sec^{-1}$) with almost the diffusion controlled rate constant, although the eventual reaction does not occur. Thus in case of (PTH-O_2), reaction $(PTH\text{-}O_2)\rightarrow PT\cdot+HO_2$ occurs while in case of (PTH-DMIP), the analogous reaction does not. Behavior of radical species (containing radical cation and (PTH-O_2)) produced in the rigid aerated ethanol at 77°K has also been studied. The present C-T complex is interesting in the point that it is produced *via* triplet state of donor and has a rather long lifetime.

The oxidation reaction of phenothiazine has long been attracting much attention owing to the interest in the pharmacological properties of its substituted derivatives. As Lhoste *et al.* have pointed out,[1] this compound having π-electrons in number differing from $4n+2$ as a result of two heteroatoms in the central ring, is very liable to be oxidized photochemically as well as chemically. It is seen in literature that phenothiazine (PTH) (I) converts by one step oxidation to radical cation (II) or neutral radical (III) according to the experimental conditions, and by the additional oxidation to diamagnetic phenazothionium ion (IV).


(I)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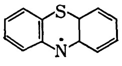
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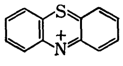
(IV)

Shine and Mach[2] who have made systematic studies on the related compounds, observed that I in the aqueous acetic acid transforms to II photochemically but they proposed on the ground of the difference in ESR signals that in 95% aqueous ethanol, III instead of II is produced photochemically. Gilbert *et al.*[3] reported on the other hand, that by oxidation with perchlorate in acetonitrile, II is produced as a perchlorate salt, and in the reaction of II with water in acetonitrile, III is produced as a primay product. According to them, III is also obtained from II by treating it with triethylamine or D_2O. Although it is possible to capture IV electrochemically, for instance by anodic oxidation of I in acetonitrile,[4] II and III are extremely stable under the ordinary conditions. However, reactions of these species have been reported in some systems, for instance, III produced in DMSO-Ac_2O mixture (deaerated) gradually converts to two types of dimer and certain higher polymers.[5] Even at liquid nitrogen temperature, PTH is photooxidized rather easily. For instance, Kasha[6] reported that upon irradiation of PTH in EPA (perhaps aerated), a new absorption peak at 19300 cm^{-1} with another weak band ~22900 cm^{-1} appeared, indicating the formation of II. In addition, ESR studies on II were reported by Odiot and Tonnard,[7] and those of II and III by Shine *et al.*[2] and also by Gilbert *et al.*[3]

In spite of all these observations, there is still no detailed kinetic work made on this photooxidation reaction as far as we know. The purpose of the present investigation is to confirm that the photochemical

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[1] J. M. Lhoste, C. Helene, and M. Ptak in Proceedings of the International Symposium of Triplet States, Beirut, 1967 (Cambridge Univ. Press, New York, 1967).

[2] H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1964).

[3] B. C. Gilbert, P. Hanson, R. O. C. Norman, and B. J. Sutcliffe, *Chem. Commun.*, **1966** (6), 161.

[4] J. P. Billon, *Bull. Soc. Chim. Fr.*, **1960**, 1784.

[5] Y. Tsujino, *Tetrahedron Lett.*, **38**, 4111 (1968).

[6] B. R. Henry and M. Kasha, *J. Chem. Phys.*, **47**, 3319 (1967).

[7] S. Odiot and F. Tonnard, *J. Chim. Phys.*, **61**, 382 (1964).

oxidation of phenothiazine with oxygen yields III in *pure ethanol* and to elucidate the detailed mechanism of the reaction, by the steady light experiment and by the flash technique. ESR studies on the radical species produced at 77°K have also been made.

Experimental

Materials. Phenothiazine of Tokyo Kasei E.P. grade was recrystallized two times from ethanol. Ethanol of Wako Junyaku G.R. grade was used without further purification unless otherwise described. DMIP of Tokyo Kasei E.P. grade was purified by recrystallization from ethanol, carbon tetrachloride and finally from G.R. grade ethanol. It was then dried *in vacuo* for one day.

Procedures and Apparatus. The 253.7 nm irradiation was made using a Toshiba 6 W low pressure germicidal lamp and the 313 nm irradiation by a Toshiba 100W high pressure mercury lamp using, as a filter, potassium chromate 1×10^{-3} M, 0.05 N NaOH in a quartz cell of 5 mm thickness. The reaction was followed by a Hitachi EPS-3T spectrophotometer. A JEOL P-10-type ESR spectrometer (X-band, 100 kc modulation) was used for the ESR measurement. Apparatus and procedures for the flash experiment are the usual ones employed in our laboratory.

Results and Discussion

Steady Light Experiments. General Feature of the Steady Light Photooxidation: When the aerated solution of PTH in ethanol was irradiated by 253.7 nm or 313 nm, photoreaction of a simple type occurred as shown in Fig. 1. Isosbestic points are observed clearly at 241 and 263 nm. The spectrum obtained ultimately kept its shape for a few days. When the solution was degassed, practically no reaction occurred; irradiation for more than an hour caused the decrease of only 0.5% or so in optical density. It was checked that there is no essential spectral difference between the deaerated and aerated solution. The photoproduct was identified as a neutral radical by taking its ESR spectrum; thus the spectrum obtained was almost the same as that of a neutral radical reported by Gilbert *et al.*[3] and was quite different from that of radical cation which for the purpose of comparison, was produced in the concentrated sulfuric acid. It was ascertained further, that the hfs constants obtained by a simulation method agrees aproximately with those reported by Gilbert *et al.*[3] Thus our results have reconfirmed Shine and Mach's statement[2] and that reaction,

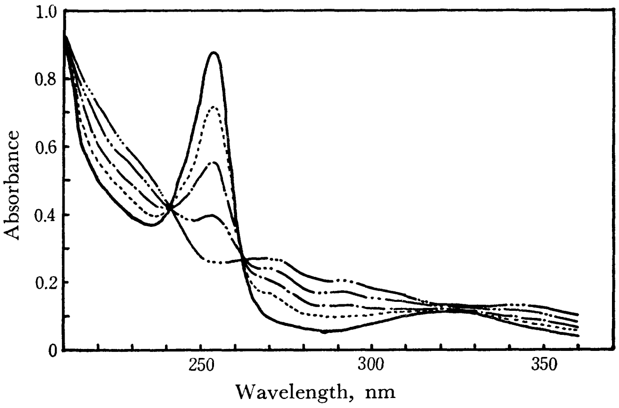

Fig. 1. Spectral change upon illumination (253.7 nm) of the phenothiazine solution in the aerated ethanol; —— 0 sec, ---- 75 sec, —·— 184 sec, —··— 340 sec, —···— 700 sec.
$[\mathrm{PTH}]=2.6\times10^{-5}$ M

$$\mathrm{PTH} + \mathrm{O_2} \xrightarrow{h\nu} \mathrm{PT\cdot} + \mathrm{HO_2} \qquad (1)$$

occurs in ethanol. We thought however, that it is necessary to examine the effect of the presence of a small quantity of water in view of the experimental conditions employed by the previous workers. For instance, Shine and Mech[2] used 95% aqueous ethanol while Gilbert *et al.*[3] prepared a neutral radical by treating a radical cation (obtained by oxidizing PTH with perchloric acid in acetonitrile) with the buffered aqueous solution of pH 7. We therefore purified ethanol and removed a trace of water with much care and repeated the experiment with the so purified ethanol. The result was essentially the same, except that the kinetic feature of the reaction became a bit simpler (see below) and the quantum yield became a little larger. This may be due to the removal of impurities of aldehyde type, and the possibility of the scheme

$$\left.\begin{array}{l}\mathrm{PTH} + \mathrm{O_2} \rightarrow \mathrm{PTH\cdot^+} + \mathrm{O_2^-}\\ \mathrm{PTH\cdot^+} + \mathrm{H_2O} \rightarrow \mathrm{PT\cdot} + \mathrm{H_3O^+}\end{array}\right\} \qquad (2)$$

is rejected.

Effect of Light Intensity: The runs for reaction were satisfactorily reproduced by linear $\ln(e^{\alpha cd}-1)$ *vs.* t plots when the inner-filter effect of photoproduct was taken into account.[8] It is to be noted that purification of ethanol does not alter the feature of the run except a little better linearity of the plot with a little larger slope. As is shown in Fig. 2, the rate of disappearance of PTH (evaluated from the initial slope of the run) is proportional to the light intensity. Thus the main reaction is a one photon process.

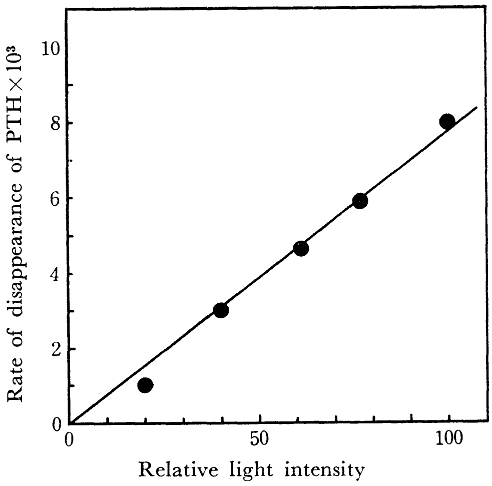

Fig. 2. Dependence of the rate of disappearance of phenothiazine on the light intensity; relative light intensity 100 corresponds to 8.8×10^{-9} M/cm² sec.

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[8] T. Iwaoka, S. Niizuma, and M. Koizumi, This Bulletin, **43**, 2786 (1970).

The Effect of Oxygen Concentration on the Rate: The overall reaction having been established (except for the reactions induced by HO_2) as

$$PTH + O_2 \rightarrow PT\cdot + HO_2 \qquad (1)$$

the effect of oxygen concentration on the rate was examined in order to know the reactive state of PTH. For the system containing $\sim 10^{-6}$ M of oxygen, the rate decreased gradually but recovered by redissolving the oxygen through shaking the sample cell. It is to be added that a slight recovery of absorption was observed when the irradiation was stopped. This suggests the existence of very long lived intermediate (see below). Figure 3 gives the plot of quantum yield *vs.* the oxygen concentration. Although a little larger values were obtained at lower concentrations of oxygen, the reason for which is unknown, the quantum yields were almost constant when the concentration of oxygen was larger than 10^{-4} M. This strongly suggests that the triplet state is a reactive one.

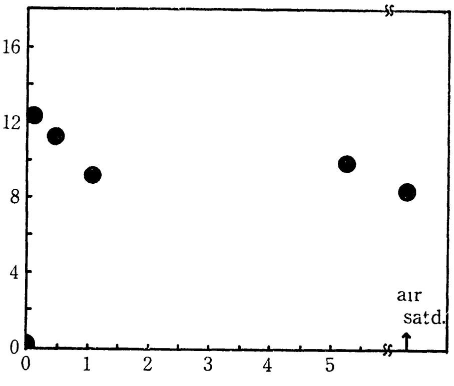

Fig. 3. Effect of oxygen concentration on the quantum yield of phenothiazine disappearance in ethanol; $[PTH]=3\times10^{-5}$ M.

The Effect of PTH Concentration on the Quantum Yield: Table 1 gives the quantum yields at various PTH concentrations. Since there is no concentration effect, we may conclude that the participation of the ground state PTH in the later stage of reaction does not occur in any sense.

Table 1. The effect of PTH concentration on the quantum yield, Φ

[PTH]	$\Phi\times10^3$
$1.2_3\times10^{-5}$	6.6
$1.8_1\times10^{-5}$ a)	6.9
$2.6_0\times10^{-5}$ b)	8.6
$3.7_6\times10^{-5}$	6.4
$2.2_3\times10^{-4}$	6.4
$3.6_9\times10^{-4}$	6.2

a) G.R. grade ethanol was used.
b) Sample solution was prepared in the dried box, immediatetly after the purification of ethanol.
Other data were for the ethanol purified previously.

Studies on the Reaction Mechanism by the Flash Technique. Now that the overall reaction has been established to be very simple, the next problem is to make clear whether the reaction occurs as a real simple reaction or a complex one, and in the latter case to know the composing processes, in particular the primary one. Reasonable schemes other than a simple reaction are

$$\left.\begin{array}{l} PTH + O_2 \rightarrow PTH\cdot^{+} + O_2^{-} \ \text{(electron transfer)} \\ PTH\cdot^{+} + O_2^{-} \rightarrow PT\cdot + HO_2 \end{array}\right\} \quad (3)$$

$$\left.\begin{array}{l} PTH + O_2 \rightarrow (PTH\text{-}O_2) \ \text{(formation of molecular complex)} \\ (PTH\text{-}O_2) \rightarrow PT\cdot + HO_2 \end{array}\right\} \quad (4)$$

To solve the problem, the behaviors of transient species have been studied by the flash technique.

The Behaviors of Transient Species Produced in a PTH-O_2 System. Figure 4 shows the transient spectra for degassed PTH solutions in ethanol. These are assigned as T–T absorption on the ground that the peak (465

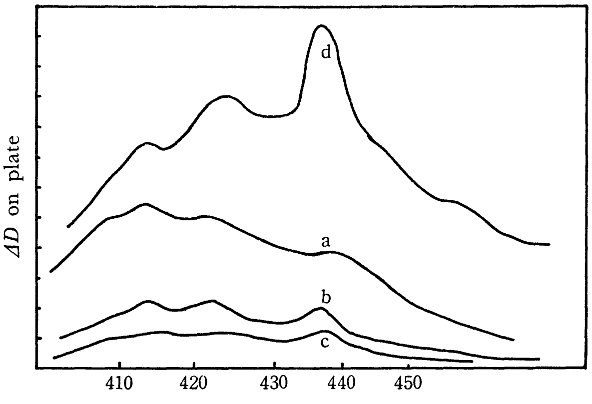

Fig. 4. Transient absorption spectra obtained by the flash photolysis of the degassed phenothiazine solution in ethanol (plate, orthochromatic): $[PTH]=2.2\times10^{-4}$ M.
a: 82 μsec, b: 150 μsec, c: 780 μsec after flashing. d is a transient absorption at 82 μsec taken with a panchromatic plate.

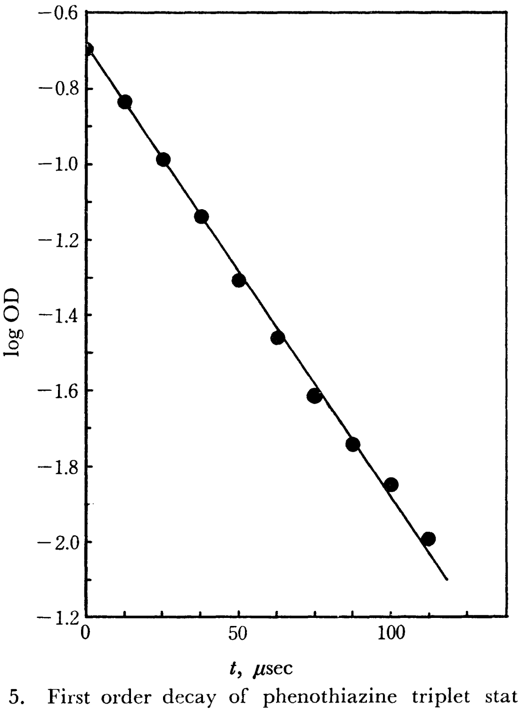

Fig. 5. First order decay of phenothiazine triplet state in deaerated ethanol (470 nm); $[PTH]=1.1\times10^{-4}$ M.

nm) agrees with the peak of T–T absorption (467 nm) (77°K, EPA) reported by Kasha and Henry[6] and that the decay is first order with the rate constant of $1.5 \pm 0.4 \times 10^4$ sec^{-1}. This is shown in Fig. 5. The decay curve suggests the existence of a small amount of another long lived species ($\tau_{1/2}$ a few sec) which might be a PTH$\cdot^+$ the reason for which will be described later.

In the aerated solutions, the T–T absorption did not appear at all and a new absorption band of small intensity was observed near 385 nm. A principal photoproduct obtained after several flashings was identified as a neutral PT$\cdot$, because the spectral shape was similar to that obtained by the steady light irradiation. A slight difference might be due to the reaction product originating from radical cation. This band (hereafter designated as a X-band and a species giving rise to this band as X-species) decays as a first order process with the rate constant of 1.6×10^2 sec^{-1}. Figure 6 gives the spectrum drawn from the decay curves at different wavelengths. In parallel with the decay at 385 nm, the absorption increased at 290 nm where the absorption of both photoproduct and the initial PTH exist. This indicates that X-intermediate converts to PT$\cdot$ or reconverts to PTH. When 0.1 N HCl was added to the solution, X-band did not appear and a new band was observed near 510 nm (perhaps radical cation, see below). Thus there is no doubt that X-intermediate is a precursor of reaction $\mathrm{PTH} + \mathrm{O_2} \rightarrow \mathrm{PT\cdot} + \mathrm{HO_2}$.

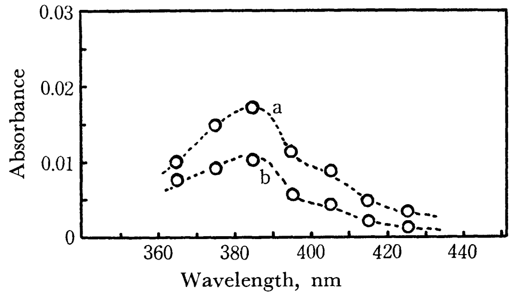

Fig. 6. Absorption of X-species in the aerated ethanol solution of phenothiazine; $[\mathrm{PTR}] = 1.9 \times 10^{-5}$ M.
a, immediately after flashing
b, 5 msec after flashing

Experiment using DMIP as an Electron Acceptor. We have now reached to the step to elucidate the nature of X-species. To confirm more definitely that it is a molecular complex with oxygen, we have studied the transient species when DMIP instead of oxygen was used as an acceptor. DMIP is a weak electron acceptor[9] and it was expected to act just like oxygen as far as electron transfer is concerned, but not to produce a stable neutral radical because reaction $(\mathrm{PTH^+\text{-}DMIP^-}) \rightarrow \mathrm{PT\cdot} + \mathrm{DMIPH\cdot}$ is not likely to occur. Another reason for performing such an experiment was that the intensity of X-band in the case of oxygen was considered to be too weak to make accurate quantitative studies. This way of attacking the problem has proved to be very successful.

The transient spectra were measured varying the concentrations of DMIP from 10^{-6} to 10^{-2} M at a fixed PTH concentration of 1.14×10^{-4} M. It was established that the eventual reaction does not occur by a number of flashing. As Fig. 7 shows, the transient spectrum is very much like X-band in the case of oxygen. The decay is first order and the rate constant obtained is 1.7×10^3 sec^{-1} independent of wavelengths. When the concentration of DMIP was lower than 5×10^{-5} M, T–T absorption of PTH was observed at 420—470 nm. The triplet PTH decayed faster with the increasing DMIP concentration. Figure 8 gives the plot of the apparent first order decay constant against [DMIP]. From the slope, the second order rate constant for the disappearance reaction of PTH$^\mathrm{T}$, $\mathrm{PTH^T} + \mathrm{DMIP} \rightarrow$ was evaluated as 1.9×10^9 M^{-1}sec^{-1}. The yield of X-intermediate increases with the increases in [DMIP]. Assuming that the interaction between triplet PTH

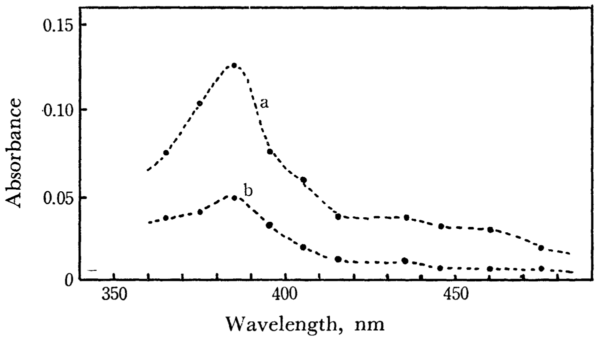

Fig. 7. Transient absorption spectra obtained upon flashing the degassed ethanol solutions of PTH-DMIP; $[\mathrm{PTH}] = 1.1 \times 10^{-4}$ M, $[\mathrm{DMIP}] = 1 \times 10^{-2}$ M.
a, immediately after flashing
b, 5 msec after flashing

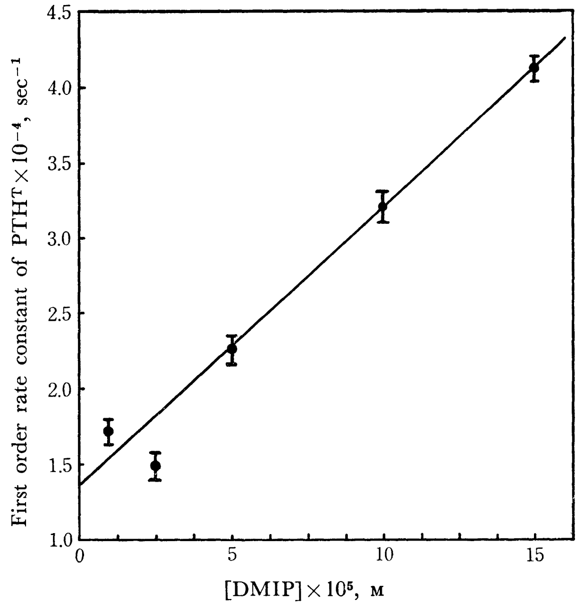

Fig. 8. Dependence of the apparent first order rate constant of phenothiazine triplet state upon the concentration of dimethylisophthalate; $[\mathrm{PTH}] = 1.1 \times 10^{-4}$ M.

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[9] M. Koizumi and H. Yamashita, *Z. Physik. Chem. N. F.*, **57**, 103 (1968); H. Yamashita, H. Kokubun, and M. Koizumi, This Bulletin, **41**, 2312 (1968).

and DMIP consists only of reaction $PTH^T + A \xrightarrow{k_r} X$ (A stands for DMIP), the following equation can easily be derived.

$$[OD_{PTH^T}]_0/[OD_X]_\infty = (\varepsilon_{PTH^T}/\varepsilon_X)(1+k_d/k_r[A]) \qquad (5)$$

where $[OD_{PTH^T}]_0$, optical density of triplet PTH immediately after flashing, $[OD_X]_\infty$, optical density of X immediately after disappearance of PTH^T, and k_d, the decay constant of triplet PTH.

As shown in Fig. 9 the plot of $[OD_{PTH^T}]_0/[OD_X]_\infty$ against 1/[DMIP] gives a straight line as is expected from (5). The rate constant k_r as evaluated from the slope and the intercept, is $1.3\times10^9\,\text{M}^{-1}\text{sec}^{-1}$. Thus it has been verified that the reaction between triplet PTH and DMIP occurs with an almost diffusion controlled rate and produces intermediate X.

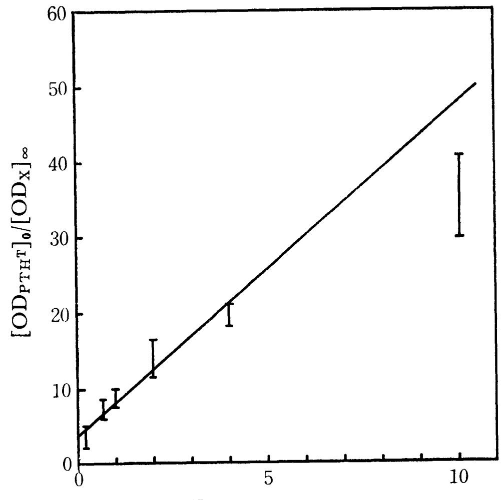

Fig. 9. Plot of $[OD_{PTH^T}]_0/[OD_X]_\infty$ against 1/[DMIP], as obtained at 470 nm; $[PTH]=1.1\times10^{-4}\,\text{M}$.

Intermediate X in the present system also decays as first order independent of the concentration of DMIP. Table 2 gives the results. It is to be added that a small quantity of a very long lived species ($\tau\sim$sec) is suspected to exist from the decay feature of X. This species appears to decay as second order and may perhaps be a radical cation.

Figure 10 shows the transient spectrum for the PTH solution in the degassed acidic ethanol (0.1 N HCl) containing $2.5\times10^{-6}\,\text{M}$ of DMIP. This agrees with the spectrum of cation radical obtained in *s*-butylchloride by γ-radiolysis[10] and that in H_2SO_4 reported by Shine and Mach.[2] There is no sign of X-band. The decay is second order with the rate constant of $k/\varepsilon=2.8\times10^5$. Thus in an acidic medium intermediate X is not produced and only the formation of radical cation occurs.

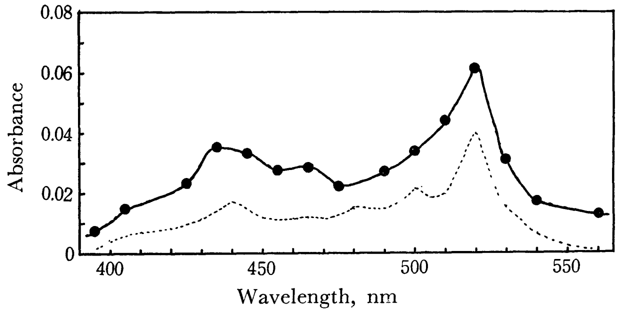

Fig. 10. Transient absorption spectrum immediately after flashing the solution of phenothiazine in the degassed acidic ethanol (0.1 N HCl) containing $2.5\times10^{-6}\,\text{M}$ DMIP; $[PTH]=1.1\times10^{-4}\,\text{M}$.
----: cation radical produced by γ-radiolysis in *s*-butylchloride[10] at 77°K (1/20 of the measured absorbance)

We may now conclude that X-species is a molecular compound most likely of C–T character. Although there is a possibility that this is a triplet exciplex, it may perhaps be a C–T complex in the ground state which is unstable as compared with the two separated components. If this is true, the peak position of X-band should be well related with those of other stable complexes. It is well known that the wave number of C–T absorption is linearly related with the electron affinity of the acceptor. Phenothiazine with very low ionization potential of 6.96 eV,[11] forms stable

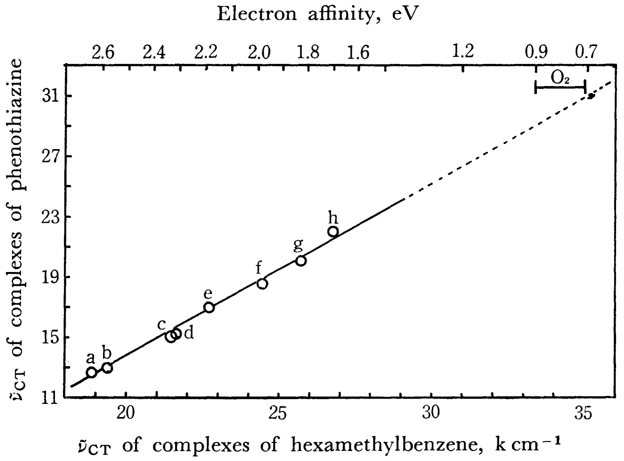

Fig. 11. Plots of $\tilde{\nu}$ for complexes of phenothiazine with various acceptors against $\tilde{\nu}$ for the corresponding hexamethylbenzene complexes; Acceptor; a: bromanil, b: chloranil, c: 2,6-dichloro-*p*-benzoquinone, d: 2,5-dichloro-*p*-benzoquinone, e: monochloro-*p*-benzoquinone, f: *p*-benzoquinone, g: 1,3,5-trinitrobenzene, h: 2,4,6-trinitrotoluene, cited from Ref. 12. Electron affinity scales were added by the authors.

TABLE 2. DECAY CONSTANT OF X

[DMIP]	1.0×10^{-6}	2.5×10^{-6}	5×10^{-6}	1.0×10^{-5}	1.5×10^{-5}	5.0×10^{-5}	1.0×10^{-4}	1×10^{-2}
Rate const. $\times10^{-3}$	2.1	2.3	1.8	2.0	2.3	2.7	2.2	1.7

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[10] We are grateful to Dr. T. Shida of Inst. of Phys. and Chem. Res. Tokyo for presenting this spectrum.

[11] A. Fulton and L. E. Lyons, *Aust. J. Chem.*, **21**, 873 (1968).

C–T complexes with a large number of electron acceptors. According to Foster and Hanson,[12] a good linear relation exists between $\tilde{\nu}_{CT}$ and the electron affinity of acceptor. This is shown in Fig. 11. The electron affinity of oxygen is 0.7—0.9 eV and that of DMIP is considered to be a little less than 1.5 eV (the value for phthalic anhydride). The peak position of 385 nm for oxygen and DMIP does not appear to deviate so much from the linear relation of Foster and Hanson as shown in Fig. 11.

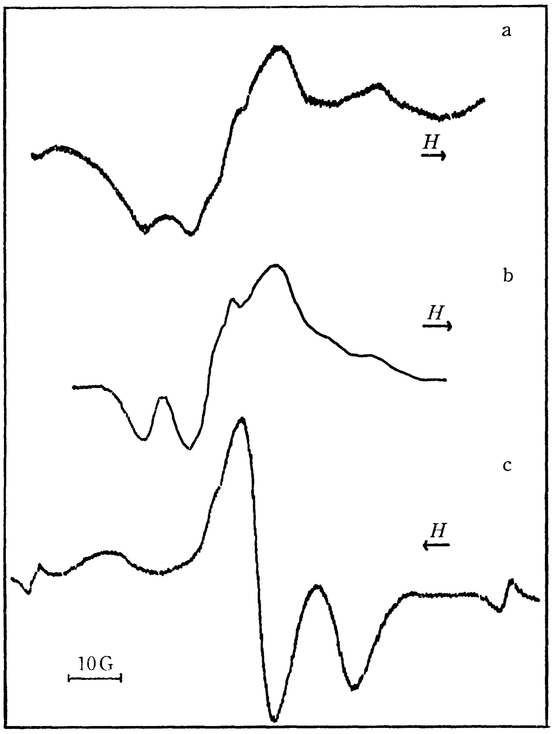

Fig. 12. ESR spectra at 77°K for a) photoproduct obtained upon illumination of the aerated ethanol solution of phenothiazine, b) phenothiazine radical cation in concentrated H_2SO_4, and c) phenothiazine neutral radical produced at room temperature.

Behavior of the Radical Species Produced when the Aerated Solution of PTH in Ethanol was Irradiated at 77°K. To get further information on the radical species related to the present reaction, ESR studies have been made on the photoproduct obtained by irradiation at 77°K. Upon irradiation of the PTH solution in ethanol at 77°K by the light 250—400 or >340 nm, the solution gradually colored from yellow to light brown and the absorption spectrum of the resultant rigid solution displayed peaks at 385 and ~520 nm. This implies that both X-intermediate and the radical cation are formed at 77°K. The ESR spectra observed were of a simple shape independent of the exciting wavelength. Figure 12 shows the ESR spectra for a) the photoproduct, b) the radical cation produced in a concentrated sulfuric acid solution and c) the neutral radical produced at room temperature, all measured at 77°K. The agreement of a) and b) leads to the conclusion that the main radical species produced at 77°K is the radical cation. The colors of the solution for a) and b) were both light brown while that for c) colored pink with a tint of violet. This also supports the above assignment. The formation of the radical cation at 77°K agrees with the observation of Henry and Kasha[6] in EPA. From the above findings, we may conclude that X-intermediate is diamagnetic and reaction $(PTH^{+}\text{-}O_2^{-}) \rightarrow PT\cdot + HO_2$ does not occur photochemically.

It is to be added that in the degassed medium, 313 or 365 nm irradiation produces mainly ethanol radical which could be identified by comparing the ESR signals with those reported by Niizuma and Koizumi.[13]

Next, the sample irradiated at 77°K was brought to room temperature. The ESR spectrum showed a complicated structure and was quite different from that of the neutral radical. This sample upon cooling to 77°K, showed the ESR spectrum which clearly showed the coexistence of the neutral and cation radicals. This is very natural since X-species converts quickly to the neutral radical at room temperature. An interesting conclusion which we can draw from this experiment is that the radical cation is rather stable and can coexist with the neutral radical, because it took more than an hour to carry through the above experiment. The radical cation once formed does not seem to transform to the neutral radical so easily.

The results obtained by further irradiation are also interesting. Irradiation by 395 nm for more than two hours at 77°K caused very little formation of the neutral radical. This again indicates the stability of X-species against irradiation. When the radical cation obtained at 77°K was brought to room temperature and was irradiated by the $\lambda > 395$ nm light, then the color turned from light brown to pink violet. The ESR spectrum at room temperature clearly showed three peaks due to ^{14}N and at 77°K it consisted mainly of the neutral radical (with a very small contribution of the radical cation). We may conclude that the radical cation when excited, transforms to the neutral radical while the neutral radical is rather stable against irradiation.

General Discussion and Some Future Problems. The present work has established that the final photoproduct for the aerated PTH solution in ethanol at room temperature, is the neutral radical III. On the other hand, a large quantity of radical cation II was produced in the rigid ethanol at 77°K. The reason for this difference may be as follows. The formation of C–T type X-species may require the reorientation of the solvent molecules surrounding donor and acceptor to a higher extent, which is easy to occur at room temperature but not at 77°K. For radical cation II to be formed on the other hand, a pair of radical ions produced, must diffuse apart from each other utilizing the excess energy as the kinetic one of the two components prior to its dissipation to the surrounding medium. This may be more feasible in the rigid medium. The formation of II or III may also depend upon the solvent polarity and also on the acidity and basicity of the medium. For instance, the formation of II may be fovored by the high polarity of the solvent.

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12) R. Foster and P. Hanson, *Biochem. Biophys. Acta*, **112**, 482 (1966).

13) S. Niizuma and M. Koizumi, This Bulletin, **41**, 1090 (1968).

As to the stability of radical species, it is easy to understand that III is stable, because the HO_2 radical produced by reaction, $PTH+O_2 \rightarrow PT\cdot + HO_2$ may quickly disappear in the succeeding reactions leaving only PT·. But the finding that radical cation II produced at 77°K can coexist with III for more than an hour, seems somewhat curious; O_2^- produced by reaction, $PTH+O_2 \rightarrow PTH\cdot^+ + O_2^-$ is expected to react according to $PTH\cdot^+ + O_2^- \rightarrow PT\cdot + HO_2$, if HO_2 is more stable than O_2^- in pure ethanol. That II remains stable might be due to reaction $O_2^- + H_3O^+ \rightarrow HO_2 + H_2O$, because the experiment was not performed in the purified ethanol.

Turning to the mechanism for the formation of III, it has been established on the basis of the experiments on $PTH\text{-}O_2$ and PTH-DMIP systems that intermediate X of C–T type is a precursor of the reaction. Further it has been concluded that X reacts as follows in the aerated solution,

$$(PTH^+\text{-}O_2^-) \left\langle \begin{array}{l} \nearrow PTH + O_2 \\ \searrow PT\cdot + HO_2 \end{array} \right.$$

HO_2 disappearing in the succeeding reactions and thus leaving PT· as a stable radical. The reason why DMIP does not give the neutral radical is that reaction

$$(PTH^+\text{-}DMIP^-) \rightarrow PT\cdot + DMIPH\cdot$$

does not eventually occur, because even if it occurs the backward reaction $PT\cdot + DMIPH\cdot \rightarrow PTH + DMIP$ will soon ensue. The effect of environmental medium on the stability of this complex is again an interesting problem. By the analogy of exciplex, the stability may perhaps increase from nonpolar to weakly polar solvents and further, the molecular compound might gradually turn into the ion pair and finally to the separated ions as the solvent becomes from medium to highly polar. In this respect, we have made some preliminary experiments using acetonitrile and cyclohexane as solvents. In these solvents the photooxidation of PTH with oxygen occurred in the same way as in ethanol, $PTH+O_2 \rightarrow PT\cdot + HO_2$, and the transient spectra observed were very much like that of X in ethanol. Table 3 gives the comparison of the quantum yields of reaction (Φ) and the first order rate constant for the disappearance of X-spesies (k) in the three solvents. The results are understandable from the general nature of C–T complex. Thus in moderately polar solvents the complex becomes more stable than in nonpolar solvents. In addition, reaction $(PTH^+\text{-}O_2^-) \rightarrow PT\cdot + HO_2$ may occur more easily in nonpolar solvents. This causes the increase in Φ and may contribute to the increase in the k-value for cyclohexane.

TABLE 3.

	DK	Φ	k
Ethanol	24.3	6.5×10^{-3}	1.6×10^{2}
Acetonitrile	37.5	1.4×10^{-3}	1.4×10^{2}
Cyclohexane	2.02	2.4×10^{-2}	too fast to be measured

Studies on the solvent effects in the wider scope are desirable.

Studies on the present C–T type molecular complex from various view points will be interesting. Although X-species is most likely a C–T complex in the ground state, still a possibility of triplet exciplex may not be excluded altogether. It is desirable to develop the similar studies using acceptors of various strength including those constituting stable C–T complexes and to investigate their absorption and emission spectra (if any).

Admitting that the present C–T complex is an unstable ground state one, it can be said that it is a very novel type of reaction intermediate. A few years ago we proposed the formation of a somewhat similar molecular complex between eosine and oxygen in the aqueous solution,[14] but it was considered to be a solvent-shared ion pair $(D^+\cdots O_2^-)$ having almost the same absorption band as that of free D^+. The present complex is produced in moderately polar solvents and has a quite different absorption band from that of free cation. Moreover, it has quite a long lifetime of more than msec. We believe that this is the first example of a molecular complex in the points that it is produced *via* triplet donor and acceptor and has such significant characteristics. It will be instructive to investigate the general nature of the intermediate of this type.

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[14] Y. Usui and M. Koizumi, This Bulletin, **40**, 440 (1967); Y. Usui, C. Iwanaga, and M. Koizumi, *ibid.*, **42**, 1231 (1969).