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Solvent Effect on the Photochemical Oxidation of Phenothiazine with Oxygen

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The photochemical production of neutral radical in the aerated ethanol solution of phenothiazine (PTH) has been studied by means of steady light experiments, flash technique, and ESR measurements.[1] A reaction scheme proposed is 1) $PTH \xrightarrow{h\nu} PTH^*$, 2) $PTH^* \longrightarrow PTH^T$, 3) $PTH^T + O_2 \longrightarrow PTH \cdots O_2$, 4) $PTH \cdots O_2 \longrightarrow PT\cdot + HO_2\cdot$ in which $PTH \cdots O_2$ was presumed to be a certain type of C–T complex with a lifetime $\sim 6 \times 10^{-3}$ sec.

Gilbert,[2] however, has pointed out that the spectrum of the ultimate product resembles that of phenothiazine-5-oxide (5-oxide) and that our transient intermediate might be a radical which gives rise to 5-oxide. In fact our ESR studies were made on 10^{-2}M solutions of PTH while the kinetic studies were chiefly for 10^{-4}M of PTH, so that it might be possible that under the former conditions the main product is radical and under the latter, 5-oxide.

In this note it is demonstrated that the same product, *i.e.* the neutral radical, is produced in the two cases. Further, the solvent effect of the overall reaction and also on the transient intermediate are investigated. The results also support our mechanism.

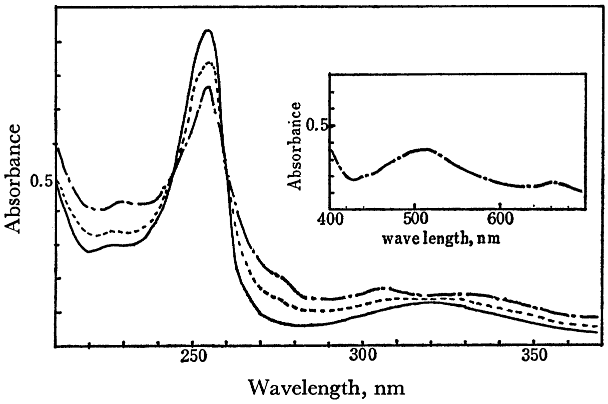

Fig. 1. Spectral change for the ethanol solution of phenothiazine in high concentration (2×10^{-2}M) upon UV illumination. ——; no irradiation ------; 2 hr irradiation —·—; 12 hr irradiation

First it was reconfirmed that the irradiated solutions of PTH, 2×10^{-2}M in ethanol give an ESR spectrum characteristic of neutral radical which remains unaltered after being kept for more than two hours. When diluted 30 times, the irradiated solutions gave UV spectra as shown in Fig. 1. It is seen that the spectral change is similar to that for the dilute solution.[1] The spectrum in the visible region was taken without dilution. The existence of a peak at ~500 nm is consistent with the radical nature of the species.

Table 1. Quantum yields in various solvents

Solvent	DK	Φ
Acetonitrile	37.5	1.4×10^{-3}
Methanol	32.6	8.0×10^{-3}
Ethanol	24.3	6.0×10^{-3}
n-Butanol	17.8	8.0×10^{-3}
Ethyl ether	4.3	2.0×10^{-2}
Cyclohexane	2.0	2.4×10^{-2}

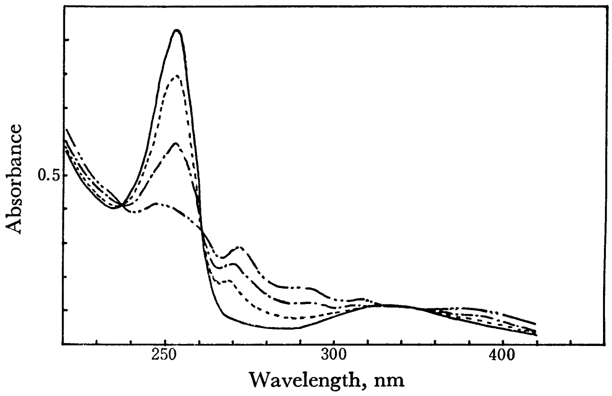

Fig. 2. Spectral change upon illumination (253.7 nm) of phenothiazine solution in the aerated cyclohexane; —— 0 sec, ---- 10 sec, —·— 35 sec, —··— 95 sec, [PTH] = 2.0×10^{-5}M.

Table 1 gives the quantum yields of the reaction in several solvents of different polarity. The spectral change is similar in all the solvents and there is no indication of a drastic change in the reaction scheme such as the formation of radical to that of 5-oxide. As an example, the spectral change in the cyclohexane solution is given in Fig. 2. Although ESR measurements were not made for all the cases, the ESR spectrum in the acetonitrile solution of 2×10^{-2}M PTH confirmed that the product is the neutral radical. From Table 1 it is evident that the values of Φ are one order larger in the weakly polar solvents (DK$<\sim$5) than in the polar solvents (DK$>$15); an approximate parallelism exists between Φ and DK.

This may be interpreted as follows. C–T complex is considered in general to be stabilized more or less by the interaction with the solvent molecules in the solvent sphere, and the more polar the solvent molecules, the greater the interaction is expected to be, resulting in a stronger solvation in more polar solvents. Thus the reorientation of molecules in the solvent sphere might be required for any reaction. In the present system it is likely that a more drastic reorientation is necessary for reaction $PTH \cdots O_2 \longrightarrow PT\cdot + HO_2$ than for the backward reaction $PTH \cdots O_2 \longrightarrow PTH + O_2$. It

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[1] T. Iwaoka, H. Kokubun, and M. Koizumi, This Bulletin, **44**, 341 (1971).

[2] B. G. Gilbert, private communication.

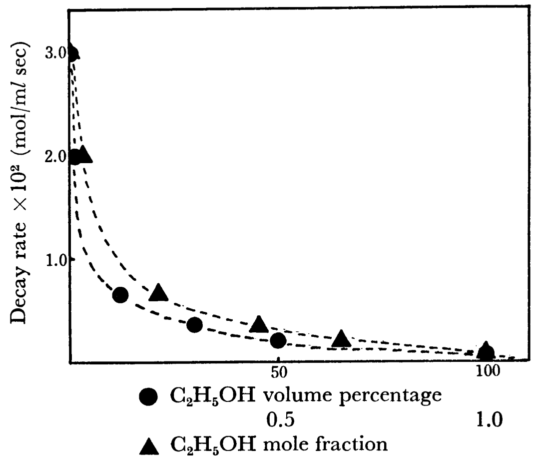

Fig. 3. The rate of disappearance of phenothiazine in the mixed solvent of cyclohexane and ethanol.
[PTH] $=2.0\times10^{-5}$M
light intensity, $I_0=8.7\times10^{-9}$M/sec.cm.

can be expected that the relative ease with which the former reaction occurs becomes smaller in the more polar solvent as was verified by experiment. The change of the decay constant and hence Φ in the mixed solvents of cyclohexane and ethanol given in Fig. 3 can be understood by the above reasoning. Thus a sharp drop in decay rate in the low concentration region of ethanol can be attributed to the selective solvation of the more polar ethanol molecules around PTH, which makes the formation of PT· more difficult.

Table 2 gives the peak positions of the transient spectrum which has been interpreted to be due to C–T complex[1] together with their decay constants. Although it is rather difficult to decide the peak positions accurately due to their low intensity and location at the foot of the original main absorption band, it can be said that in polar solvents (with DK larger than that of pyridine) the peaks are clearly observed around 385—395 nm, while in ethyl acetate, ethyl ether, and cyclohexane they are not observable. This might be due to the blue shift of the peak. The decay constants in these weakly polar solvents were determined from the rise of absorption at 290 nm. It was confirmed that in cases where ~390 nm peaks are observable, their decline and the rise at 290 nm agree well. The decay constants in nonpolar solvents are one order higher than those for polar solvents, indicating that the C–T complex is less stable in these solvents.

Table 2. Solvent effect on the nature of the PTH···O_2 complex

Solvent	DK	Absorption max (nm)	Decay const. (sec^{-1})
Acetonitrile	37.5	385	1.4×10^2
Methanol	32.6	375—385	
Ethanol	24.3	385	1.6×10^2
Acetone	20.7	385	1.5×10^2
n-Butanol	17.8	395	1.2×10^2
Pyridine	12.3	390	7.5×10
Ethyl acetate	6.1	<380	3.9×10^3
Ethyl ether	4.3	<380	$>10^3$
Cyclohexane	2.0	<380	$>10^3$

All the present results support the view that the intermediate is a C–T type complex which yields the neutral radical as a final product. Although simultaneous production of 5-oxide cannot be denied completely, its participation, if it does occur, can be said to be very small. If this were not the case, the spectral change having clear-cut isosbestic points in all the solvents could not be explained.