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Interaction between Phenothiazine Triplet State with Several Electron Acceptors

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As an extension of the previous paper (This Bulletin, **44**, 341 (1971)) which proposed the formation of a certain charge transfer complex between triplet phenothiazine (PTH^T) and oxygen or dimethylisophthalate, the similar donor-acceptor interaction has been studied between PTH^T and several other acceptors such as dimethylterephthalate (DMTP), nitrobenzene, dinitrobenzene, and terephthalonitrile in deaerated ethanol solutions. In case of DMTP, studies have been made also in cyclohexane. It has been established that all the acceptors except nitrobenzene attack PTH^T with the diffusion controlled rate constant and that in ethanol they give rise to free radical ions and/or solvent shared ion-pair. In cyclohexane, however, no transient species other than triplet has been detected.

Donor and acceptor interaction in the singlet excited state of aromatic compounds has been studied extensively since the discovery of exciplex by Leonhardt and Weller.[1] But very few researches have been reported on the analogous phenomena related with the triplet states of aromatic compounds. As far as we know, Beens and Weller's work[2] on the formation of C-T complex between the triplet state of pyrene and terephthalonitrile, is the only one so far reported. One reason why such investigations are few may be due to the higher ionization potential of the triplet state as compared with that of the singlet excited state, which makes it difficult for such an interaction to occur specifically in the triplet state but not in the ground state. It is expected that for the interaction analogous to the exciplex formation to occur in the triplet state, the ionization potential of donor should be very low or the singlet and triplet energy difference is small. Indeed it has been reported that in some dyestuffs for which S*- and T-levels are close with each other, reactions such as $D^T+D \longrightarrow D^+ + D^-$ or $D^T+O_2 \longrightarrow D^+ \cdots O_2^-$ really occur.[3]

In the previous paper,[4] we have found that the triplet state of phenothiazine (PTH) with a low ionization potential of 6.9 eV[5] interacts with weak electron acceptors such as oxygen and dimethylisophthalate and forms transiently a certain type of C-T complex. In case of oxygen, an ultimate product was a neutral radical of PTH while the initial compounds were recovered in case of dimethylisophthalate. This paper reports the interaction of triplet PTH with several other electron acceptors.

Experimental

Materials. Dimethylterephthalate was recrystallized three times from G. R. grade ethanol. Nitrobenzene of G. R. grade from Wako Junyaku was used without further purification. *p*-Dinitrobenzene was recrystallized twice from G. R. grade ethanol. Terephthalonitrile was recrystallized from methanol and was sublimed *in vacuo*. Cyclohexane of E. P. grade of Wako Junyaku was shaken with the mixture of fuming sulfuric acid and conc. sulfuric acid (1:1) six times, washed with the aqueous solution of potassium permanganate and then shaken with the aqueous NaOH solution three times. After being washed with water five times, it was kept in contact with metallic sodium for one day and then distilled over sodium metal renewed.

Procedures. Apparatus and procedures for the flash experiment are the usual ones employed in our laboratory. A suitable combination of filters (plate glass, Toshiba-glass filters, UVD-25, VB-40, VB-48, PV-43, *etc.*) was used in the flash apparatus in order to excite only phenothiazine.

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[1] H. Leonhardt and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **61**, 791 (1963).

[2] H. Beens and A. Weller, "Molecular Luminescence," Benjamin Inc. (1969), p. 203.

[3] T. Ohno, S. Kato, and M. Koizumi, This Bulletin, **39**, 232 (1966); Y. Usui and M. Koizumi, *ibid.*, **40**, 1041 (1967). L. Lindqvist, *Arkiv Kemi*, **16**, 79 (1960).

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

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

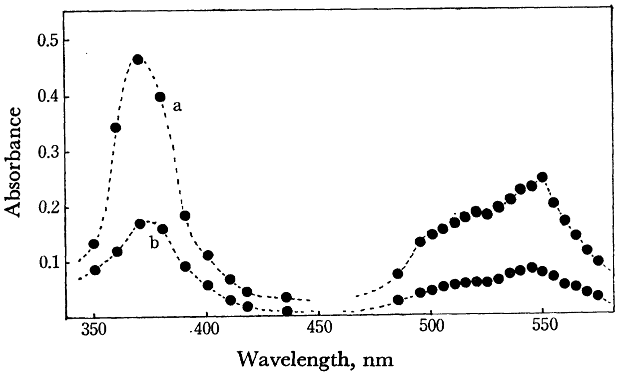

Fig. 1. Transient absorption spectra obtained upon flashing the degassed ethanol solutions of PTH-DMTP;
[PTH]$=8.0\times10^{-5}$M, [DMTP]$=1\times10^{-4}$M
a, immediately after flashing
b, 300 μsec after flashing

Results and Discussion

Interaction between PTH^T and Dimethylterephthalate (DMTP). The electron affinity of DMPT is expected to be a little larger than that of dimethylisophthalate. Figure 1 shows the transient spectrum when the degassed ethanol solution of DMTP (1×10^{-4}M) and PTH (8×10^{-5}M) is flashed. The spectrum resembels that of DMTP radical anion produced when the tetrahydrofuran solution of DMTP is treated with sodium.[6] A little swell in the region 500~520 nm might be due to the PTH cation which should be produced simultaneously. It may be due to the small absorbance that the radical cation is not clearly discerned. The spectrum in Fig. 1 strongly suggests that contrary to dimethylisophthalate, the free radical ion or solvent-shared ion-pair is produced in this system. The decay of the absorbance at 550 nm is of the first order with the same rate constant independent of the DMTP concentration at least when the concentration is lower than 1.0×10^{-5}M. However in case that [DMTP] is 2.5×10^{-5}M or 1.0×10^{-4}M, the early part of the decay is appreciably larger though the latter part decays almost with the same rate constant as that in the lower concentration of DMTP. Table 1 gives the decay constants for the later stage at various DMTP concentrations. Figure 2 shows the change of absorbance with time at different DMTP concentrations. In spite of such situations in the decay curves, the transient spectra in the early and later stages practically coincide, which suggest strongly the coexistence of the free radical ions and the solvent-shared ion-pair. It is reasonable that the latter decays as the first order while the former does in the second order, and the second order decay becomes negligible as the concentration of free ion becomes low.

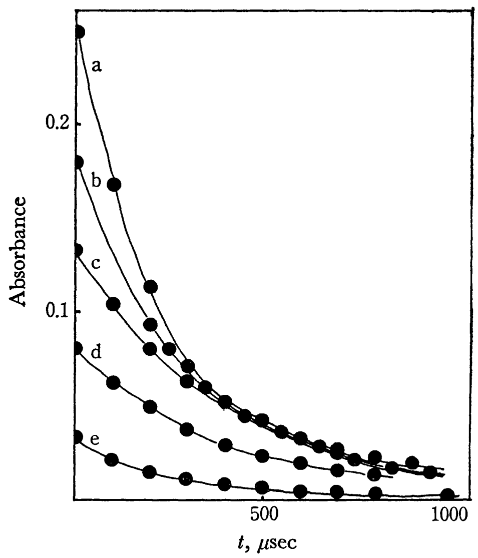

Fig. 2. Change of transient absorption with time at different DMTP concentrations observed at 550 nm.
[PTH]$=8.0\times10^{-5}$M
DMTP concentartion is as follows:
a, 1.0×10^{-4}M b, 2.5×10^{-5}M c, 1.0×10^{-5}M
d, 2.5×10^{-6}M e, 7.5×10^{-7}M

Figure 3 shows the decay of T–T absorption and the rise of absorption at 550 nm. It is clearly seen that these processes occur simultaneously, and this suggests that the 550 nm species is mainly produced from the interaction of triplet PTH and DMTP. Figure 4 gives the decay constant of PTH^T as a function of [DMTP]. From the slope, the rate constant for PTH^T+DMTP $\xrightarrow{k_1}$ is evaluated as 1.4×10^9M^{-1}sec^{-1}. Figure 5 shows the absorbance at 550 nm immediately after flashing, which is the measure of the yield of transient species, plotted against [DMTP].

Assuming the following scheme

$$^3\text{PTH} + \text{DMTP} \xrightarrow{k_r} (\text{PTH}^+\cdots\text{DMTP}^-)$$

Table 1. First order decay constants (at the later stage) of the intermediate at various DMTP concentrations (sec^{-1})

[DMTP]	Wavelength, nm		
	380	555	470
1×10^{-4}	3.1×10^3	2.2×10^3	
2.5×10^{-5}		2.6×10^3	2.9×10^3
1.0×10^{-5}		2.3×10^3	
5.0×10^{-6}	2.6×10^3	2.8×10^3	2.8×10^3
2.5×10^{-6}		2.5×10^3	
7.0×10^{-7}		3.1×10^3	

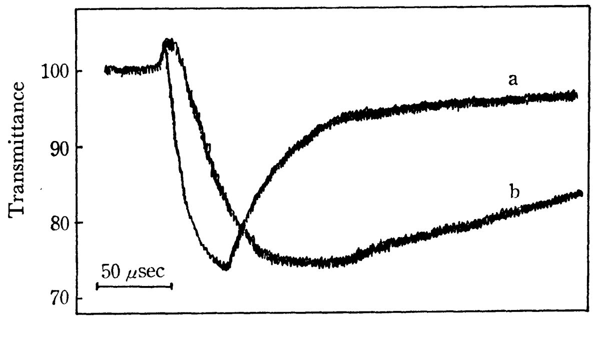

Fig. 3. Change in the transmittance at 470 nm and 550 nm on oscilloscope.
a, 470 nm b, 550 nm

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[6] T. Kowata and M. Koizumi, This Bulletin, **42**, 3352 (1969).

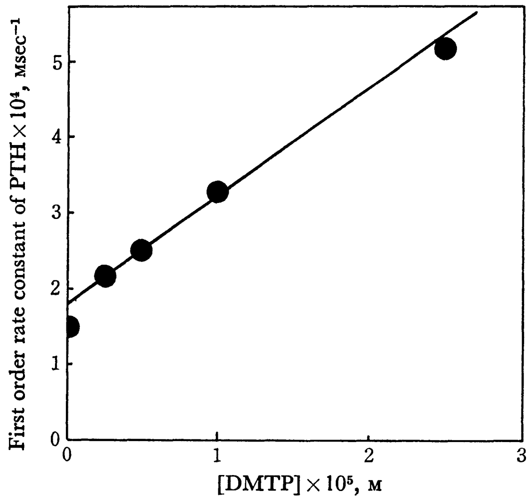

Fig. 4. Dependence of the apparent first order rate constant of phenothiazine triplet state upon the concentration of dimethylterephthalate.
[PTH] = 8.0×10^{-5}M

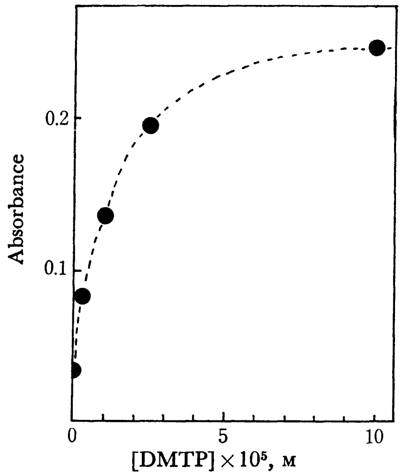

Fig. 5. Plot of the absorbance at 550 nm, immediately after flashing against [DMTP].

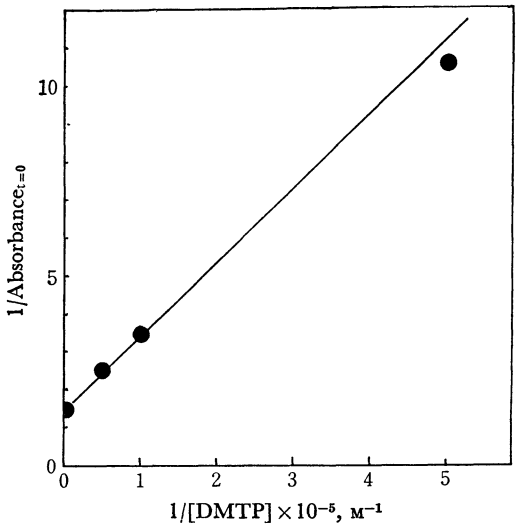

Fig. 6. Plot of 1/Absorbance (at 550nm)$_{t=0}$ against 1/[DMTP]. [PTH] = 8.0×10^{-5}M

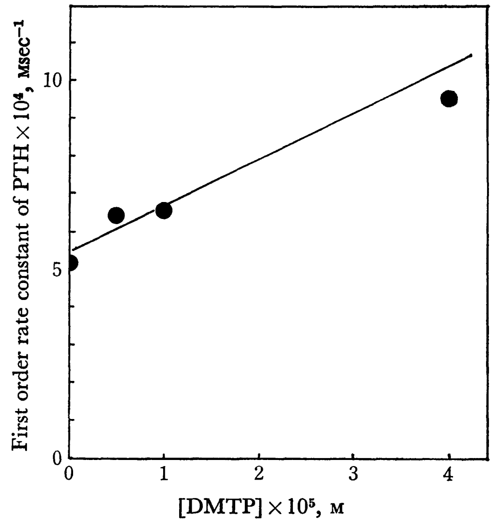

Fig. 7. Dependence of the decay rate of phenothiazine triplet state upon the concentration of dimethylterephthalate in cyclohexane. [PTH] = 8.0×10^{-5}M

$$^3\text{PTH} + \text{DMTP} \xrightarrow{k_q} \text{PTH} + \text{DMTP}$$

$$^3\text{PTH} \xrightarrow{k_d} \text{PTH}$$

and by taking into account the constancy of [PTH] and the flash intensity, the following relation can easily be derived.

$$[\text{PTH}^+\cdots\text{DMTP}^-] = [^3\text{PTH}]\times\frac{k_r[\text{DMTP}]}{k_d+(k_r+k_q)[\text{DMTP}]}$$

If the above scheme holds, the plot $1/[\text{PTH}^+\cdots\text{DMTP}^-]$ *vs.* 1/[DMTP] should be linear. Figure 6 shows that this holds very satisfactorily.

In case of cyclohexane used as a nonpolar solvent, no transient spectrum other than T–T absorption is observable. The decay of T–T absorption increases with the increase in [DMTP] as shown in Fig. 7. From this plot, the rate constant k_1 for ^{3}PTH+DMTP $\xrightarrow[\text{in } C_6H_{12}]{k_1}$ is evaluated as $k_1 = 1.3\times10^9\text{M}^{-1}\text{sec}^{-1}$.

Interaction of Nitrobenzene and p-*Dinitrobenzene with PTH^T*. The addition of 1×10^{-4}M of nitrobenzene (NB) to the deaerated ethanol solution of PTH did not affect the yield of T–T absorption of PTH appreciably. There was no other transient species detected. The decay constant of PTH^T was 4—$5\times10^4\text{M}^{-1}\text{sec}^{-1}$ as compared with 1.5×10^4 in the absence of NB. Hence the rate constant k_1 for PTH^T+NB⟶PTH+NB is estimated to be $\lesssim 10^8\text{M}^{-1}\text{sec}^{-1}$.

In case of 10^{-2}M *p*-dinitrobenzene (DNB), the strongest acceptor in our experiment,[7] no T–T absorption was observed and the transient spectrum perhaps due to radical cation (PTH$^+$) was observed in addition to the absorption of radical anion (DNB$^-$). For 10^{-6}M—10^{-5}M DBN, only the absorption of anion

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[7] Electron affinity of DNB is estimated to be about 1.7 eV according to R. Foster and P. Hanson, *Biochem. Biophys. Acta*, **112**, 482 (1966). Judging from the absorption spectrum, it is plausible that C-T complex is formed already in the ground state.

radical (DNB^-) was obtained as shown in Fig. 8.[8] It decays according to second order from initial to final, which suggests its existence as free radical anion. Figure 9 shows the dependence of triplet decay upon the DNB concentration. The rate constant k_r for $PTH^T + DNB \xrightarrow{k_1}$ was estimated to be $1.7 \times 10^9 M^{-1} sec$. Dependence of the absorption of DNB anion radical at 630 nm on the concentration of triplet PTH clearly showed the formation of the former by the reaction between DNB and PTH^T.

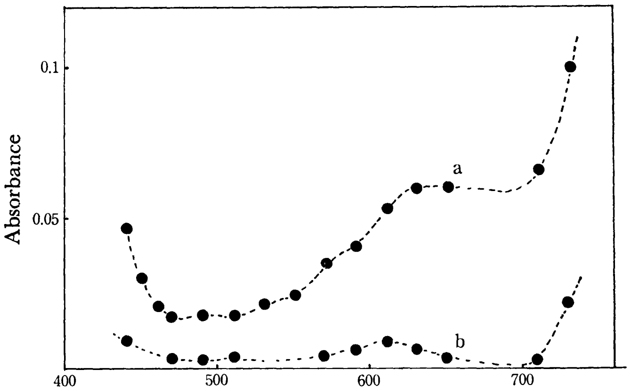

Fig. 8. Transient absorption spectra obtained upon flashing the degassed ethanol solutions of PTH-DNB.
$[PTH] = 8.0 \times 10^{-5} M$, $[DNB] = 3 \times 10^{-5} M$
a, immediately after flashing
b, 8 msec after flashing[7]

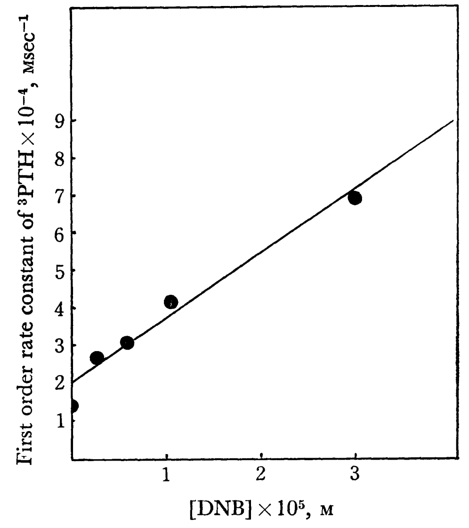

Fig. 9. Dependence of the apparent first order rate constant of phenothiazine triplet state upon the concentration of dinitrobenzene. $[PTH] = 8.0 \times 10^{-5} M$

Interaction of Terephthalonitrile (TPN) with PTH^T. Figure 10 shows the transient spectra of ethanol solutions of $1 \times 10^{-5} M$ PTH containing TPN of two different concentrations. A short-lived absorption at 450—460 nm in Fig. 10a is due without doubt to T–T absorption. In case [TPN] is $1.0 \times 10^{-4} M$, T–T absorption does not appear, as shown in Fig. 10b. Figure 10c is the spectrum of $TPN^{\cdot -}$ in tetrahydrofuran obtained by sodium-treatment, as reported by Ishitani and Nagakura.[9] The relative peak height at 430 nm in Fig. 10b is appreciably larger than in Fig. 10c. This suggests the superposition of another species in this region.[10] It was really found that the decay at

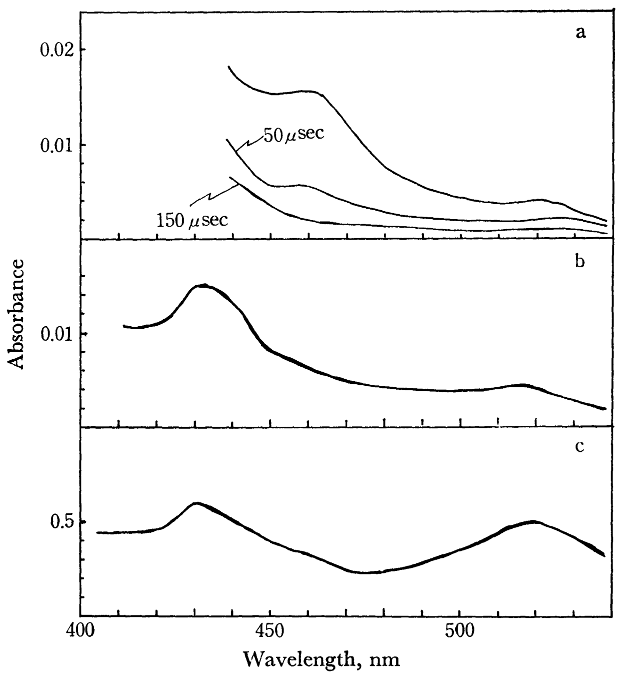

Fig. 10. Transient absorption spectra obtained upon flashing the degassed ethanol solutions of PTH-TPN.
$[PTH] = 8.0 \times 10^{-5} M$
a, $[TPN] = 1.0 \times 10^{-5} M$ b, $[TPN] = 1.0 \times 10^{-4} M$
c, Spectrum of the anion radical of terephthalonitrile in tetrahydrofuran.[9]

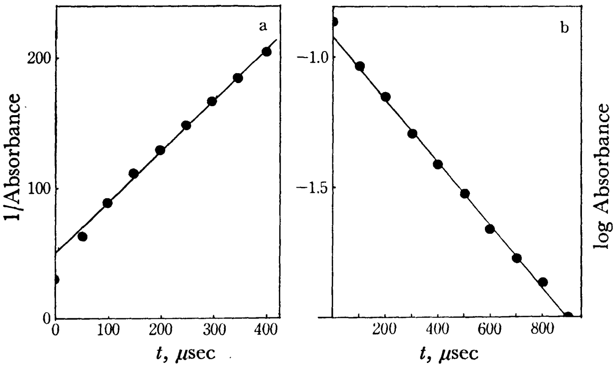

Fig. 11. Second order decay at 520 nm (free TPN^-) and first order decay at 430 nm ($PTH^+ - TPN^-$).
a, 520 nm b, 430 nm

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[8] According to the referee's unpublished result, the absorption spectrum of DNB radical anion has no peak at ~610 nm clearly seen on curve b. In fact there is no sign of its existence on curve a. The 610 nm peak might be due to some unknown by-product produced secondarily from DNB radical anion.

[9] A. Ishitani and S. Nagakura, *Theor. Chim. Acta*, **4**, 236 (1966).

[10] According to the referee, TPN radical anion has no absorption in the wavelength region longer than 500 nm only having a peak at ~430 nm; he attributes the peak at 520 nm reported in Ref. 9 to some unknown by-product. If this is true, the peak in question observed in Fig. 10b may be due to the phenothiazine radical cation.

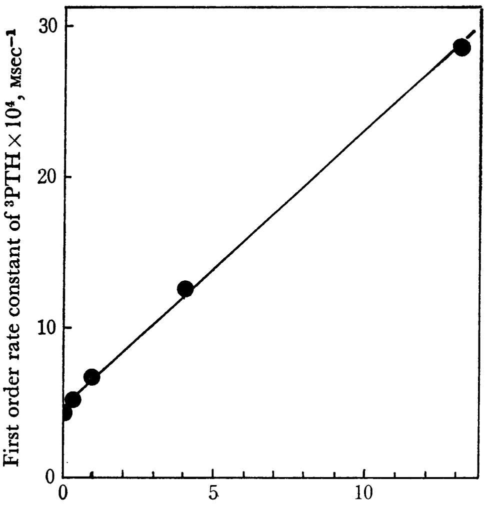

Fig. 12. Dependence of the apparent first order rate constant of phenothiazine triplet state upon the concentration of terephthalonitrile; [PTH] $=8.0\times10^{-5}$M.

520 nm in Fig. 10b is of second order as indicated in Fig. 11a and the peak may be attributed to the free TPN$^-$. The decay at 430 nm on the other hand, obeys the first order as shown in Fig. 11b, and is independent of [TPN]. It is reasonable to consider that free radical ion and the solvent shared ion-pair are produced simultaneously and decay rather independently with each other.

As shown in Fig. 12, the decay of T–T absorption is linearly related with [TPN], and from the slope the rate constant for $\text{PTH}^{\text{T}}+\text{TPN}\longrightarrow$ is evaluated as $2.0\times10^9\text{M}^{-1}\text{sec}^{-1}$.

General Discussion. Although the results of the present investigation are still preliminary, we can draw some conclusions from them. First, the electron acceptors with the values of electron affinity larger than 0.7—0.9 eV quench the triplet PTH with almost the rate constant controlled by diffusion irrespective of the solvent polarity. Secondly, the molecular mechanism for triplet quenching is not the T–T energy transfer, because the T-levels of all the present acceptors are higher than that of PTH. It is due, as verified in the present investigation, to various types of donor-acceptor interaction.

In non-polar solvents no transient species other than triplet are observable. Perhaps transient species produced has too short a life time as to be captured by the ordinary flash technique. In polar solvents formations of C-T complex, ion-pair, and the free ions depend on the electron affinity of the acceptor and on the solvent polarity. However, the detailed feature of these donor-acceptor interaction in the triplet state phenothiazine awaits further systematic studies.

Thanks are due to the referee's presentation of his unpublished absorption spectra of DNB and TPN radical anions.