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Free Radicals Produced from the Derivatives of Pyrylium Salts in Solution by Photoillumination

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The photoreactions of 2,4,6-triphenyl- (TPP), 2-*t*-butyl-4,6-diphenylpyrylium (2BDPP) and 2,4,6-triphenylthiopyrylium (TPTP) salts in tetrahydrofuran (THF) and/or 1,2-dimethoxyethane were investigated. Photoproducts were identified to be pyranyl radicals on the basis of photochemical behavior and ESR spectra. Quantum yields of one-electron reduction reactions of TPP, 2BDPP, and TPTP were obtained to be 0.21, 0.047, and 0.53, respectively. The hf coupling constants of protons in the radicals were determined by simulation. The photoillumination of TPP in THF at low temperatures revealed that a certain intermediate radical species was involved in this one-electron photoreduction.

Pyrylium salts are present as natural products in pigments named anthocyanin. They have a six-membered ring containing an oxygen atom of the oxonium type. Thus, the ring has a benzenoid structure and has almost the same stability as that of aromatic rings. The compound which has a sulfur atom instead of an oxygen is called a thiopyrylium salt. As the pyrylium ring has a positive charge, it exhibits a high reactivity to nucleophilic reagents. Further, it is expected that the salt can be easily reduced to neutral radical, which may be stable in a rather nonpolar media.

Among several kinds of derivatives of pyrylium and thiopyrylium tetrafluoroborate, 2,4,6-triphenyl- (TPP), 2-*t*-butyl-4,6-diphenylpyrylium (2BDPP) and 2,4,6-triphenylthiopyrylium (TPTP) salts were found to be subject to a one-electron photoreduction with high quantum yields. They can be converted into stable radical species in such nonpolar solvents as tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). Fundamental data concerning a photoreaction by steady light illumination at room temperature, the behavior of radicals produced by a short period of illumination at low temperatures and the results on an ESR spectra analysis of the photoproduct radicals are reported.

Experimental

Materials. All the pyrylium salts used have the form of tetrafluoroborate and were synthesized by the ordinary method.[1] 4,4′-Bi(2,4,6-triphenyl-4*H*-pyran-4-yl) (BTPP) was synthesized by reducing a TPP salt with zinc in a mixture of acetic acid–benzene–water after Panov *et al.*[2] THF and DME as solvents were distilled immediately after a few hours of refluxing on metallic sodium and then stocked on a sodium–potassium alloy in an ampoule connected to a vacuum line. Potassium trisoxalato ferrate (III) for the chemical actinometer was newly synthesized by the usual way before use.

Procedures. The device for illuminating the steady light and following the reaction is the same one as reported previously.[3] The light source was a Toshiba high-pressure mercury lamp USH-100UV with a suitable filter system (Toshiba UV-D36C and SL-1A for 365 nm, and Toshiba C-39B and L-42/Y-43 for 436 nm illumination). The light intensity was measured with a potassium trisoxalato ferrate (III) actinometer at each wavelength.[4] The electronic absorption spectra were taken with a Hitachi 228-type double-beam spectrophotometer. ESR spectra were recorded with a JEOL PE-1X-type ESR spectrometer. The simulation of ESR spectra was performed with the use of an NEC PC-9801 microcomputer and on-line Watanabe WX-4675 plotter. ENDOR spectra were taken with a Varian E-1700 ENDOR spectrometer.

Results and Discussion

General Aspects of Photoreactions and Identification of Photoproducts. The absorption spectrum of a TPP salt in THF is shown in Fig. 1-a. The solution was yellowish green and the absorption maxima were located at 278, 363, and 409 nm. When a solution was illuminated with 436-nm light, the spectrum changed with some isosbestic points and the color changed to pink. The photoproduct (which had absorption maxima at 515 and 555 nm in THF) was found to be a radical species since the solution exhibited a strong ESR signal. When the solution was kept in the dark, the absorption of the starting substance was gradually recovered and at the same time the pink color faded and the ESR signal diminished. By the introduction of air into the pink solution, a quarter of the absorption of the starting substance was recovered. The recovered product was again converted into the pink species and exhibited an ESR signal upon illumination. This indicates that the pyrylium skeleton was retained in the photoproduct molecule. The reactant emitted blue fluorescence[5] in THF and DME but the photoproduct had no emission. The introduction of air into the photoproduct solution caused the emission.

On the basis of the electronic absorption spectrum, the photochemical behavior (mentioned above) and the results of an ESR analysis (see below), the photoproduct of which the electronic spectrum is given by the line (–·–·–) in Fig. 1-a is safely identified to be a neutral radical species, or pyranyl, which was formed by one-electron reduction of the pyrylium salt. The reductant is considered to be the solvent.

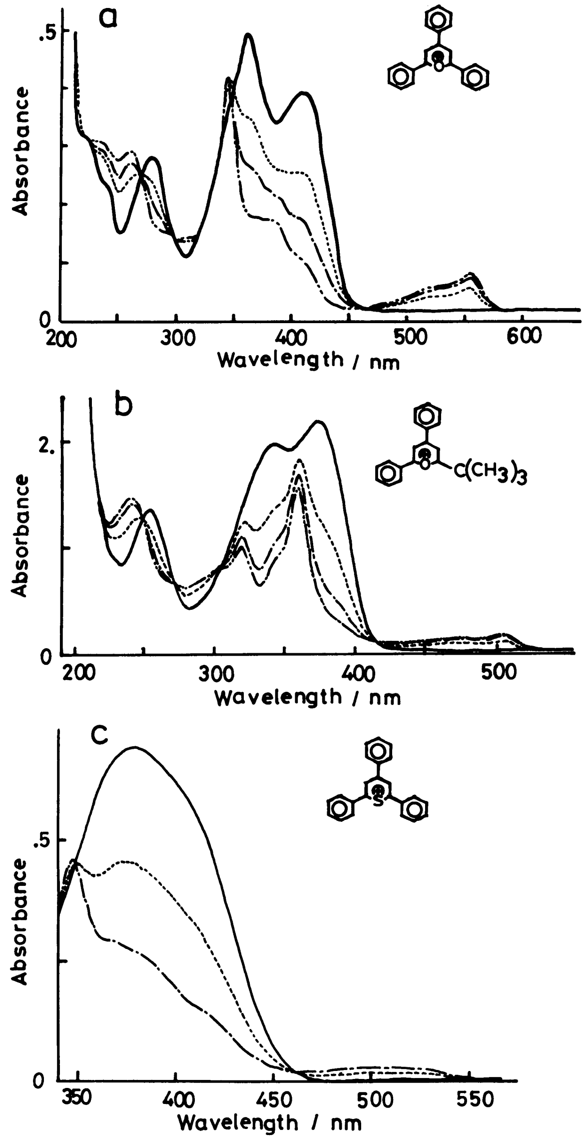


Fig. 1. Absorption spectra in THF and thier change with photoillumination a) of 436 nm light for 0 s(——), 30 s(······), 1 min(– – –) and 3 min(–·–·–), b) of 365 nm light for 0 s(——), 5 min(······), 11 min (– – –) and 20 min(–·–·–) and c) of 436 nm light for 0 s (——), 40 s(······), and 2 min(–·–·–).

The spectral change of 2BDPP and TPTP salts upon illumination is shown in Figs. 1-b and c, respectively. Again, the photoproducts exhibited strong ESR signals, indicating that they were neutral radicals. Their electronic spectra are represented by the line (–·–·–) in Fig. 1-b and the line (–·–·–) in Fig. 1-c, respectively.

Reaction Kinetics by Steady Light Illumination. The quantum yields of the photoreactions of the three salts mentioned above were examined as follows: The solutions were illuminated by an exciting light and the intensities of transmitted light were measured with a phototube-amplifier system. As the reaction rate is considered to be proportional to the amount of absorbed light, equation (1) holds.[3]

$$\ln\left(e^{2.303\varepsilon cd}-1\right) = \mathrm{const} - 2.303\times10^{3}\phi\varepsilon I_0 t \qquad (1)$$

Here, ε, c, d, I_0, and t denote the extinction coefficient of the solute at the observing wavelength, the concentration of the solution, the optical-path length, the incident-light intensity and the time, respectively. ϕ represents the quantum yield of the reaction and is calculated from the slope of the straight line obtained by plotting $\ln(e^{2.303\varepsilon cd}-1)$ against t. ϕ values are listed in Table 1 as well as the ε values used for their calculation. The correction of ϕ for the inner filter effect was carried out in the case that the absorption wavelength of the photoproduct overlapped with that of the excitation wavelength. In Table 1, data on the 4-*t*-butyl-2,6-diphenylpyrylium (4BDPP) salt are added for comparison. The quantum yield for molecules with a higher symmetry tends to be higher. The fact that a higher quantum yield is observed when the ring O atom was replaced by an S atom is in line with the fact that the rate of a one-electron reduction of phenyl(thioxanthone) by Cr^{2+} ion is larger than that of phenyl xanthone.[6]

The effect of the light intensity on the reaction rate was examined about TPP and 4BDPP salts. A linear relation between them was obtained for both salts.

TABLE 1. QUANTUM YIELD OF PHOTOREDUCTION ϕ AND ε VALUE IN THF

Compound		TPP	2BDPP	4BDPP[a]	TPTP
ε[b]	365 nm	24500	20300	13300	23400
	436 nm	7690		830	8560
ϕ	365 nm[c]	0.11[d]	0.047[d]		
	436 nm[c]	0.21[e]		0.23[e]	0.53[d]

a) Irreversible photoreaction. b) In 10^{-3} mol^{-1} cm^2. c) Irradiation wavelength. d) The value obtained by the correction of inner filter effect. e) The reaction rate was proportional to light intensity.

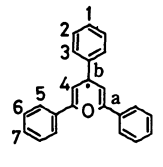
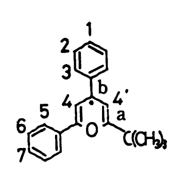
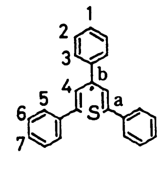
Thus, the photoreaction proceeds with a one-photon process.

An effect of the excitation wavelength on the quantum yield of pyrylium consumption was found to exist in the case of a TPP salt. The quantum yield for 365 nm illumination was about half that for 436 nm illumination, as given in Table 1. The spectral change with 365 nm illumination shows the occurrence of a decomposition reaction of pyrylium ring.

ESR Spectra of Photoproducts. The ESR spectrum of the neutral radical produced by the photoillumination of TPP salts and its temperature dependence are shown in Fig. 2. Simulated spectra are also given in the same figure. All the spectra at different temperatures could be simulated by using a single set of proton hf coupling constants. The spectrum at −10 °C had the smallest linewidth, 48 mG (1 G=10^{-4} T). It increased both at higher and lower temperatures. This implies that the main factor which contributes to the ESR linewidth switches at this temperature. It might represent, for example, a predomination of the spin-rotational interaction (T/η dependence) at the higher-temperature region and of an anisotropy of the Zeeman interaction between the spin and the external magnetic field (η/T dependence) at the lower region. The coupling constants determined by simulation are listed in Table 2 along with those from an ENDOR measurement. The unpaired spin density in the table was calculated using McLachlan's method based on a simple LCAO-MC method. Parameters used in the calculation are also given in the table. From the relation between the hf coupling constants *vs.* the absolute value of the spin densities, 37 G was obtained as McConnell's Q value. Such a large Q value was reported for *o*-semiquinones.[7] Q values for positive ions of aromatic hydrocarbons were also reported to be 36 G.[8] The cited values of the hf coupling constants in the table were those obtained from the radicals produced by zinc powder or other metal reduction in cyclohexane[9,10] and were in good accord with ours.

The ESR spectra of the photochemically produced radical from a 2BDPP salt in THF and their simulation are given in Fig. 3. Although a

Table 2. Coupling constants of pyranyl radicals

Radical and numbering	Position	Number of proton	hf coupling constants (G)				
			ESR			ENDOR	Calculation (Q=37G)
			23—20 °C	a)	b)	−40 °C	c)
	1	1	2.52	2.52	2.40	2.53	2.29
	2	2	0.80	0.84	0.83	0.78	0.85
	3	2	2.10	2.10	2.17	2.24	2.18
	4	2	1.68	1.68	1.66	1.57	1.74
	5	4	1.38	1.26	1.23	1.36	1.29
	6	4	0.42	0.42	0.41	0.41	0.49
	7	2	1.26	1.26	1.26	1.22	1.34
			23 °C	−30 °C	−50 °C	−30 °C	d)
	1	1	2.40	2.40	2.72	2.45	2.60
	2	2	0.84	0.82	0.82	0.84	0.96
	3	2	2.04	1.94	1.64	1.96	2.39
	4	1	3.22	3.08	3.26	2.80	2.74
	4′	1	0.84	0.80	0.82	0.84	0.96
	5	2	1.52	1.62	1.64	1.52	1.53
	6	2	0.50	0.54	0.54	0.50	0.61
	7	1	1.52	1.62	1.64	1.71	1.64
			23 °C	−9 °C	−20 °C	10 °C	e)
	1	1	1.90	1.88	1.88	2.10	1.87
	2	2	0.72	0.70	0.70	0.70	0.71
	3	2	2.52	2.50	2.48	2.46	1.72
	4	2	1.32	1.30	1.28	1.14	1.56
	5	4	0.72	0.72	0.72	0.70	1.17
	6	4	0.44	0.46	0.46	0.36	0.46
	7	2	1.18	1.18	1.18	1.14	1.27

a) *cf.* Ref. 9 (see text). b) *cf.* Ref. 10 (see text). c) $\lambda=1.2$, $\alpha_0=\alpha_c+2.0\beta$, $\beta_a=0.743\beta$ and $\beta_b=0.883\beta$. d) $\lambda=1.2$, $\alpha_0=\alpha_c+2.0\beta$, $\beta_a=0.743\beta$, $\beta_b=0.883\beta$, and $\alpha_2=\alpha_c-0.17\beta$. e) $\lambda=1.2$, $\alpha_s=\alpha_c+1.7\beta$, $\beta_a=0.707\beta$, and $\beta_b=0.766\beta$. Here, α_i is a Coulomb integral of atom i and β is a resonance integral of carbon-carbon bond.

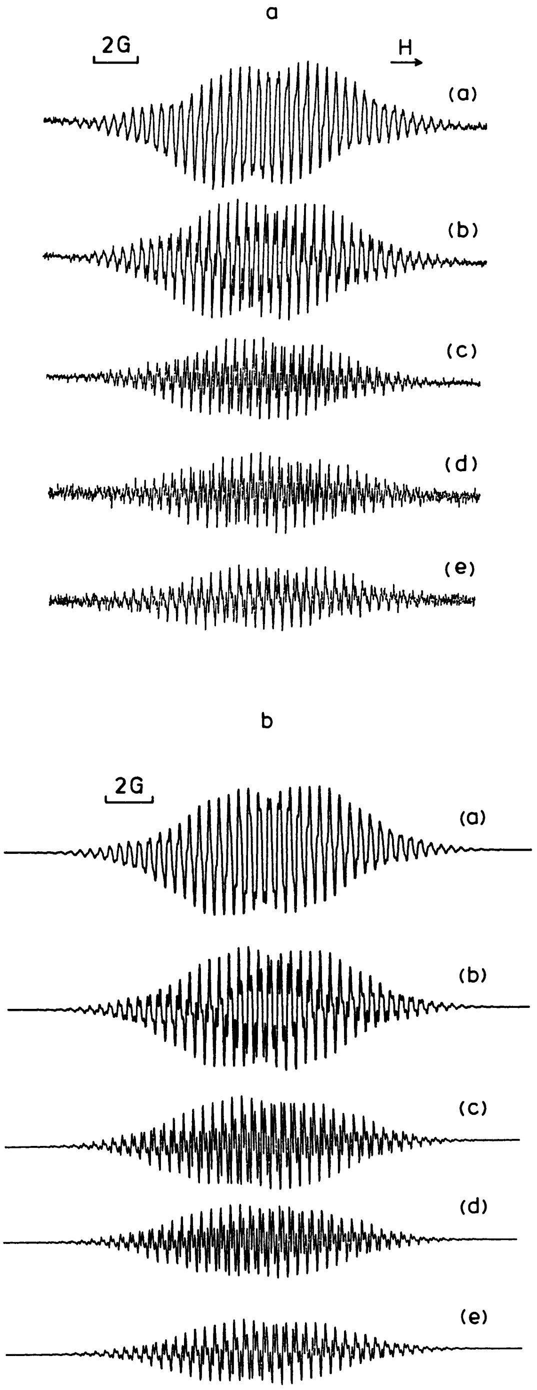


Fig. 2. a: ESR spectra of the radical produced from TPP by the irradiation of 436 nm for 4 min at 23 °C (a) in THF and at 23 °C (b), 0 °C (c), −10 °C (d), and −20 °C (e) in DME. b: Simulated spectra. The linewidths (ΔH_{msl}) used in simulation are 110 mG (a), 80 mG (b), 53 mG (c), 48 mG (d), and 64 mG (e).

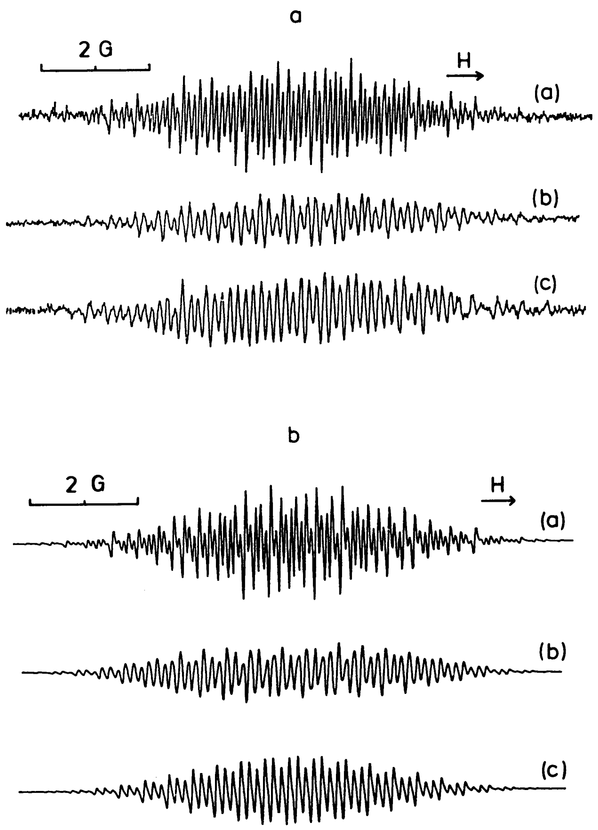


Fig. 3. a: ESR spectra of the radical produced from 2BDPP by the irradiation of 365 nm light for 4 min in THF at 25 °C (a), −30 °C (b), and −50 °C (c). b: Simulated spectra. Marks (a)—(c) correspond to those in ESR spectra.

remarkable change in the spectral shape with temperature change was observed, the simulation parameters were not appreciably different. A slight change in the rotation energy of the *t*-butyl group with temperature may lead to a slight change in the angles between the pyran ring and the two phenyl planes. This may cause a small change in the spin distribution in the molecule.

Figure 4 shows ESR spectra and their simulation for a 2,4,6-triphenyl-4*H*-thiopyran-4-yl radical. A slight variation in the hf coupling constants with temperature may be attributed to a variation in the rotation angle of the three phenyl groups to the thiopyryl ring.

The hf coupling constants of the three radical species were examined by ENDOR. The results coincided with those by the ESR method within the experimental errors and are given in Table 2. Thus, the electronic and steric structures of these radicals were very stable against a temperature change.

The Behavior of Radical at Low Temperatures. The ESR signal intensity of the photochemically produced radical from TPP in THF decreased reversibly with decreasing temperature. This may be due to the occurrence of the following dimerization equilibrium which has been reported for a chemically produced BTPP;[2]

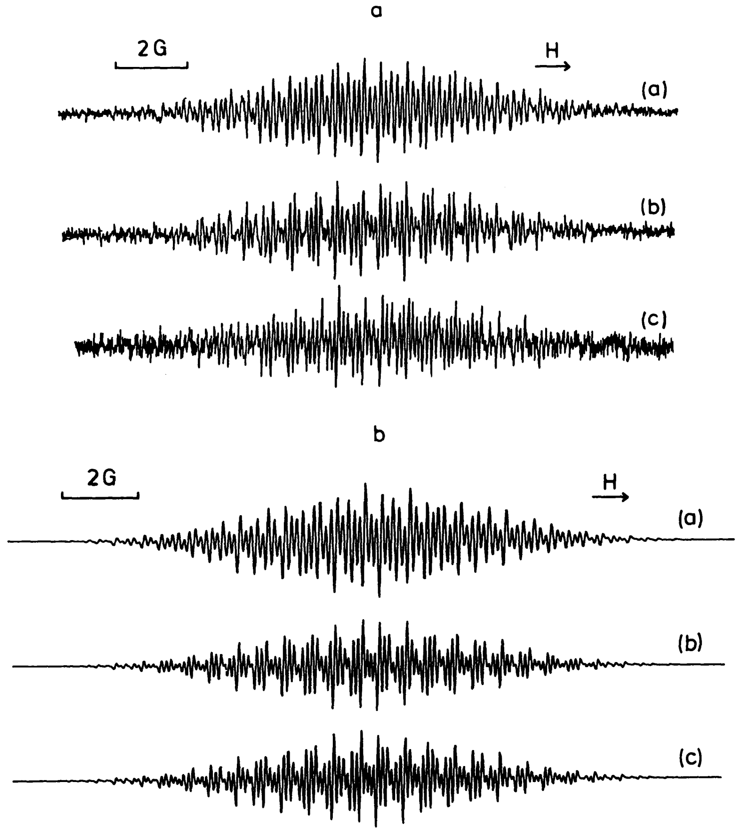
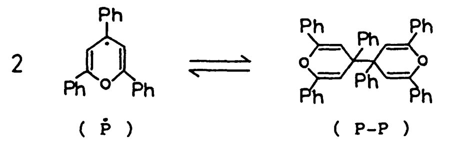


Fig. 4. a: ESR spectra of the radical produced from TPTP by the irradiation of 365 nm light for 4 min in DME at 23 °C (a), −9 °C (b), and −20 °C (c). b: Simulated spectra. Marks (a)—(c) correspond to those in ESR spectra.



(-Ph=phenyl group)

If we estimate the signal intensity at an infinite temperature, I_∞, by extrapolation, the relative dissociation constant, K_d', can be calculated by Eq. 2;

$$K_d' = \frac{I^2}{I_\infty - I} \tag{2}$$

Here I is the signal inteinsity at temperature T. The plot of logalithm of K_d' against the reciprocal of the absolute temperature was found to be linear over a range from 10 to −60 °C, as shown in Fig. 5. From the slope of this straight line, the enthalpy of dissociation was obtained to be 43.1 kJ mol^{-1}. This value is in good atreement with 44.4 kJ mol^{-1} which we also obtained by the electronic absorption method for a system of chemically produced BTPP (P–P) in THF.

It was confirmed that chemically produced BTPP was quite stable against illumination. It is noteworthy that BTPP is partially converted into pyranyl radical only by thermal process.

Photoillumination at Low Temperature. It seems to be interesting to know whether a radical is formed by photoillumination at low temperatures or not. Indeed a radical was formed by a 436-nm illumination of the TPP salt in THF, even at low temperatures (−40——100 °C). With an illumination time as short as three or four seconds, the ESR signal at a fixed magnetic field rose up first abruptly, attained a photostationary state and then started to decay immediately after the illumination terminated. It was difficult to observe the hf structure of its ESR signal even during photoillumination because of line broadening. At temperatures higher than −70 °C, the decay curve approached asymptotically not to zero level but to a constant level. We examined this phenomenon at ten-degree intervals between −30——70 °C. The higher the temperature was, the higher this constant level was. A typical example is shown in Fig. 6. These stable signals showed the same hf pattern as those given in Fig. 2-a at room temperature. The decay rate increased as the temperature rose. The decay curve was successfully analyzed by a first-order reaction-rate equation. On

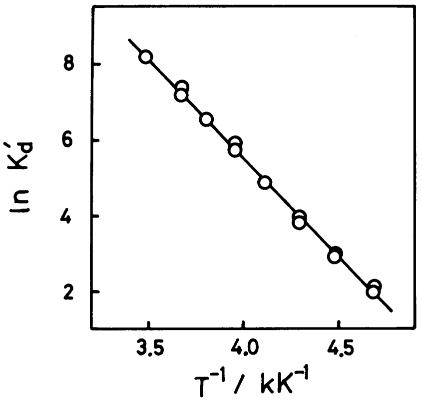


Fig. 5. The temperature dependence of the relative dissociation constant of photochemically produced BTPP in THF.

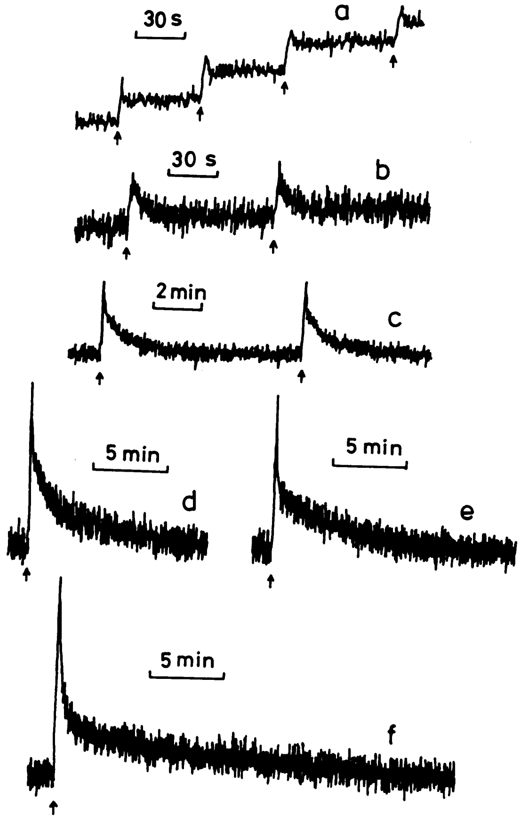
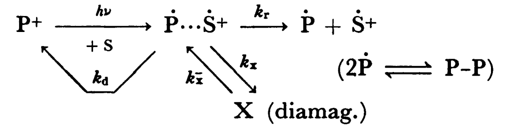


Fig. 6. The time profile of ESR signal intensity at the fixed magnetic field at −30 °C (a), −50 °C (b), −70 °C (c), −80 °C (d), −90 °C (e), and −100 °C (f). 3 to 4 second illumination of 436 nm light was performed at the time point of arrow mark.

the other hand, no permanent formation of the radical was observed at temperatures lower than −70 °C. Between −80—−100 °C, the decay curves were found to comprise two exponential decays, fast and slow ones, as shown in Fig. 6.

This phenomenon may be explained by the following simple scheme;



where P^+ is the TPP cation and S is the solvent molecule, which serves as an electron donor. As no similar reaction was observed in DME, the counter ion, BF_4^-, can not be the electron donor. We propose the very loosely complexed radical pair, $\dot{P}\cdots\dot{S}^+$, as an unstable species which showed a first-order decay at all the temperatures studied. This species may be trapped in a solvent cage with some lifetime. To explain the two-step decay at lower temperatures, a certain diamagnetic species X was postulated to be in equilibrium with the radical pair. It might be a spin-paired complex or a compound between pyrylium cation and THF molecule. Processes k_x and $k_{\bar{x}}$ express the faster decay and processes k_d and k_r the solwer one. At temperatures higher than −70 °C, k_x and $k_{\bar{x}}$ are so large that the faster decay does not appear explicitly. Below −70 °C, k_r becomes practically zero and the $\dot{P}\cdots\dot{S}^+$ species are considered to relax through process k_d into the original P^+ and S.

Since there is no reliable data regarding k_r for an analysis, we hereafter treat only decay at temperatures lower than −70 °C. If we neglect the process k_d at the initial stage of decay, $[\dot{P}\cdots\dot{S}^+]_0=[\dot{P}\cdots\dot{S}^+]+[X]$ holds. Starting with the first-order decay equation, $-d[\dot{P}\cdots\dot{S}^+]/dt=k_x[\dot{P}\cdots\dot{S}^+]-k_{\bar{x}}[X]$, we readily obtain Eq. 3.

$$\ln\left(\frac{[\dot{P}\cdots\dot{S}^+]}{[\dot{P}\cdots\dot{S}^+]_0}-\frac{k_{\bar{x}}}{k_x+k_{\bar{x}}}\right) = -(k_x+k_{\bar{x}})t + \text{const} \tag{3}$$

Here, $[\dot{P}\cdots\dot{S}^+]$ is the radical concentration and $[\dot{P}\cdots\dot{S}^+]_0$ is the same quantity immediately after the light is turned off. In the later stage of a decay, the equilibrium $\dot{P}\cdots\dot{S}^+ \rightleftharpoons X$ is considered to be achieved. Then, the decay curve can be represented by Eq. 4.

$$[\dot{P}\cdots\dot{S}^+] = [\dot{P}\cdots\dot{S}^+]_e \exp(-k_d t) \tag{4}$$

Here, $[\dot{P}\cdots\dot{S}^+]_e$ is the radical concentration just after equilibrium is achieved. Plots of Eqs. 3 and 4 at various temperatures are shown in Fig. 7-a and b where ESR signal intensities, $(SI)_i$, were used instead of radical concentrations, $[\dot{P}\cdots\dot{S}^+]_i$. The equilibrium constant $K_x=k_x/k_{\bar{x}}$ is represented by $[\dot{P}\cdots\dot{S}^+]_e/([\dot{P}\cdots\dot{S}^+]_0-[\dot{P}\cdots\dot{S}^+]_e)$. k_x and $k_{\bar{x}}$ values were calculated separately from the slope of the lines in Fig. 7-a and the K_x values. They are listed in Table 3.

The Arrhenius plots of k_x, $k_{\bar{x}}$, and k_d are given in Fig. 8-a and b. The activation energies for the processes k_x, $k_{\bar{x}}$, and k_d were calculated (from the

TABLE 3. KINETIC PARAMETERS

Temperature	Decay constant (s^{-1})			Equilibrium constant
°C	k_x	$k_{\bar{x}}$	$k_d \times 10^3$	K_x [a]
−80	0.140	0.127	5.00	1.19
−85	0.130	0.095	2.87	1.35
−90	0.109	0.065	3.44	1.69
−95	0.088	0.039	2.00	2.23
−100	0.066	0.021	1.15	3.16

a) $K_x = \dfrac{[\dot{P}\cdots\dot{S}^+]_e}{[\dot{P}\cdots\dot{S}^+]_0 - [\dot{P}\cdots\dot{S}^+]_e}$

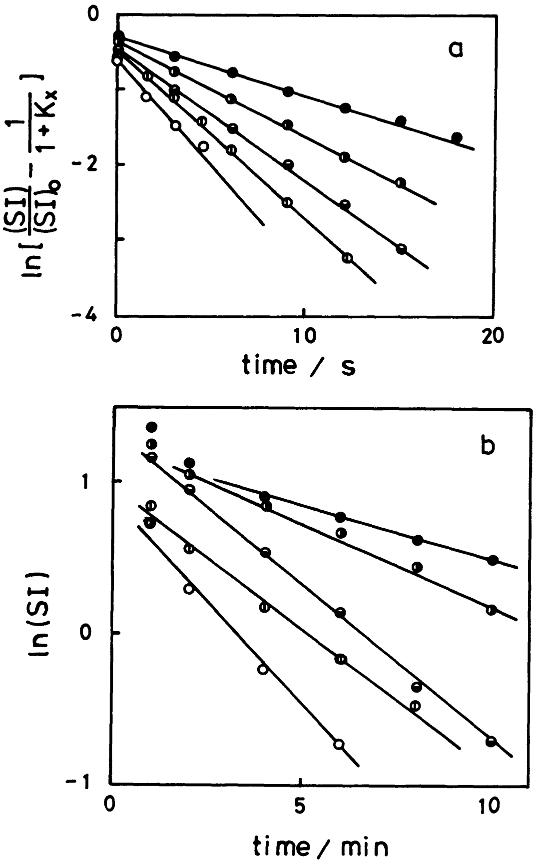


Fig. 7. The analysis of ESR signal decay by the rate equation of the first order reaction at various temperatures.
a: The faster decay, b: The slower decay
○: −80 °C, ⦶: −85 °C, ⊖: −90 °C, ◑: −95 °C, ●: −100 °C

slope of the lines in the figures) to be 12.5, 27.6, and 20.1 kJ mol^{-1}, respectively. The enthalpy change of the reaction $\dot{P}\cdots\dot{S}^+ \rightarrow X$ was calculated to be −15.1 kJ mol^{-1}, the difference between the activation energies for the k_x and $k_{\bar{x}}$ processes. This quantity was also estimated from the temperature dependence of K_x (Table 3) to be −15.5 kJ mol^{-1}. This is in good

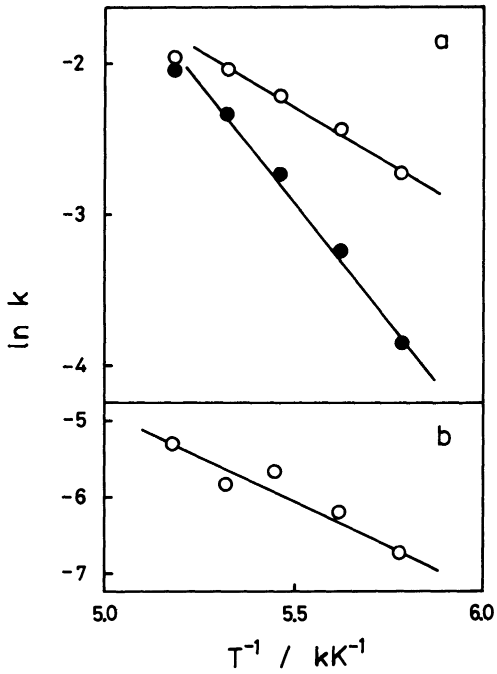


Fig. 8. The Arrhenius plot of k_x (a, ○), $k_{\bar{x}}$ (a, ●), and k_d (b).

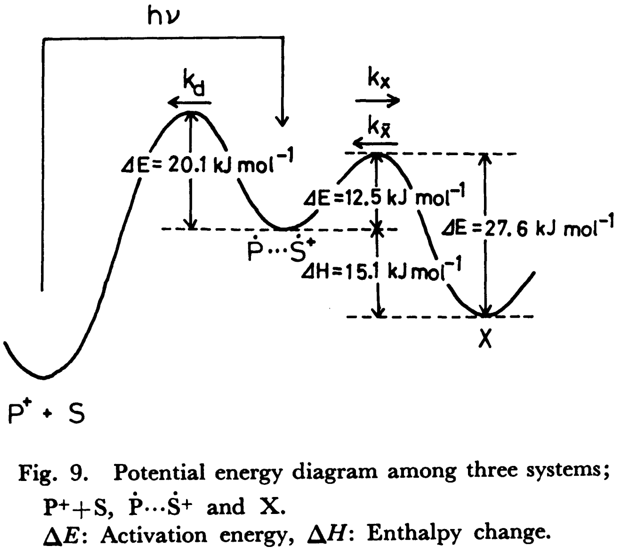


Fig. 9. Potential energy diagram among three systems; $P^+ + S$, $\dot{P}\cdots\dot{S}^+$ and X.
ΔE: Activation energy, ΔH: Enthalpy change.

agreement with the above mentioned value.

A potential-energy diagram concerning the three systems is depicted in Fig. 9. In view of the relatively high activation energy, a certain modification of the molecular structure (for example, the transfer of a hydrogen atom) might be involved in the process k_x. Thus, it is also plausible that the back reaction to the original P^+ and S occurs from $\dot{P}\cdots\dot{S}^+$, which is formed only by an electron transfer.

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