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ARTICLES

Excited Singlet State Reactions of Thiopyrylium with Electron Donors: Electron Transfer, Induction of Triplet by Internal and External Heavy Atom Effect, and Comparison of Pyrylium and Thiopyrylium Reactions

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The free energy dependence on the fluorescence quenching of 2,4,6-triphenylthiopyrylium tetrafluoroborate (TPTP) by a variety of halogenated benzenes, toluenes, and anisoles were studied in acetonitrile. The k_q values calculated using $\Delta G^{\ddagger}$ from the Levine expression and the k_d value of 5.4×10^{10} M^{-1} s^{-1} from the Smoluchowski expression are in good agreement with the experimental k_q values. The observation of the $TPTP^{\bullet}$ signal at 550 nm and the correlation of k_q with ΔG_{et} expound the possibility of an electron-transfer mechanism. The radical yield and intersystem-crossing rate constants are evaluated using flash photolysis techniques. The influence of sulfur atom in the triplet induction is reflected in the intersystem-crossing rate constant and radical yield values. The recombination rate constants k_b obtained from the radical yield values are compared with the k_b values calculated using the semiclassical expression.

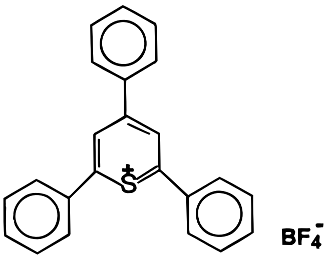
Introduction

Photoinduced electron-transfer reaction is a subject of prime importance due to its ubiquity in various emerging fields.[1] In the last few decades, considerable and continuing progress has been made in the theoretical and experimental treatment of electron-transfer reactions.[2] Since 1970, fluorescence quenching due to the exciplex formation[3] and electron transfer[4] was expounded explicitly. Lewitza[5] et al. rationalized the concomitant occurrence of energy and electron transfer during the fluorescence quenching of perylene.

The formation of free radical in the photoinduced electron-transfer process is a subject of immeasurable importance due to its utility in polymerization,[6] organic synthesis,[7] and cosensitization.[8] A bell-shaped energy gap dependence was observed for the charge recombination rate constants obtained from the radical yield values for a number of systems.[9] The effect of driving force and molecular dimension,[10a] molecular charge,[10b] isotopic substitution,[10c] separation distance,[10d] stoichiometry,[10e] external pressure,[10f] and steric effect on the radical yield[11] have been studied. The Marcus inverted behavior is also observed for the recombination of the triplet-based geminate radical pair of thionine.[12] In our present investigation, we dealt with the role played by sulfur (S) atom in the triplet induction, radical yield, and recombination reactions.

The systematic investigations of external heavy atom effect were reported [13] by Kasha and co-workers. Heavy atom effect on the radical and triplet yields was described by Kikuchi and others.[14] The fluorescence quenching of oxanine and selenine were carried out in the presence of halogenated quenchers, and the intersystem-crossing efficiency was determined.[15] The positional dependent heavy atom effect in triplet quenching of thionine by electron donors was rationalized by Steiner et al.[16] Miranda et al.[7] reviewed thoroughly the reactions of the oxygen analogue of thiopyrylium, i.e., 2,4,6-triphenylpyrylium, in 1994. The present investigation is taken as a complement to our studies carried out for 2,4,6-triphenylpyrylium (TPP) in acetonitrile,[17] and the role of S atom in the recombination and the intersystem-crossing rate constants is established.

TPTP is a well-known sensitizer, and the practical applications of TPTP are quite significant. TPTP can be used in the preparation of photosensitive compounds for electrophotographic photoconductors and optical recording materials.[18] They can especially be used in the preparation of photoresists, printing plates, and photosensitive compounds for laser imaging.[19] Thiopyrylium salts can also find a place in medicine and biology.[20] All the chalcogen pyrylium dyes can act as a photosensitizer for photodynamic therapy, a technique developed recently for the treatment of cancer.[21] The important photophysical parameters of TPTP that are necessary for the present investigation are represented below.



$E_{o,o}$ = 2.88 eV [22b]
$E_{1/2(red)}$ = -0.21 V(*vs* SCE)[22]
E_T = 2.28 eV
τ_s = 3.1 ns[23]
ϕ_{isc} = 0.50[23]

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

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Experimental Methods

The 2,4,6-triphenylthiopyrylium tetrafluoroborate was prepared using 2,4,6-triphenylpyrylium tetrafluoroborate and sodium sulfide with the aid of an earlier reported procedure[24] and was recrystallized before use. All the quenchers were purified as mentioned in the literature,[25] and the acetonitrile (spectroscopic grade solvent) was used as received.

The absorption and fluorescence spectra were recorded using Hitachi-320 and Hewlett-Packard 8452A diode array Spectrophotometers and a Perkin-Elmer LS5B fluorimeter, respectively. The TPTP concentration was adjusted to have an absorbance of 0.1 and the quenchers concentrations used are in the range of 10^{-3}−0.1 M.

The microprocessor-based Tacussel Polaroprocessor, which works in association with an EGMA polarographic stand, was used for the indirect determination of diffusion coefficient values from the diffusion current using a rotating disk electrode (RDE). The diffusion current is measured as a function of angular speed, and the slope of the Levich plot gives the diffusion coefficient value. The rotating disk electrode used in this investigation was made up of platinum, and 0.1 M tetrabutylammonium perchlorate was used as the supporting electrolyte. The reference electrode used in this investigation was Ag/AgCl, and the solution was degassed completely using argon for 25 min.

The free radical yield was measured as reported in the literature[26] from the absorbance and the molar extinction coefficient of the radical. While the radical yield was determined, the concentration of the quencher was adjusted in such a way to bring about 100% fluorescence quenching (around 0.5 M), and the solution was degassed for 20 min. Since the absorbance of other species at 550 nm is nil, the absorbance of TPTP radical is proportional to its concentration. The absorbance of $TPTP^{\bullet}$ was measured at 550 nm using an Applied Photophysics KN-020 conventional flash photolysis spectrometer consisting of a 100 W tungsten halogen lamp as the monitoring source and a LR-16 Inotech flash lamp as the excitation source. The light obtained from the flash has been filtered using acetone present in the outer jacket of the cell. Hamamatzu R-928 PMT was used as the detector, and a 20 MHz digital storage oscilloscope was used as the storage device. The radical absorbance was obtained from the intercept of the plot of log A_t vs time of the transient decay. The molar extinction coefficient of the $TPTP^{\bullet}$ was measured after generating the radical by the chemical reduction of thiopyrylium in acetonitrile using zinc dust by following the literature reported procedure,[22a] and the value obtained at 550 nm is around 620 ± 50 M^{-1} cm^{-1}.

The intersystem-crossing efficiency of the sensitizer in the absence of the quencher was already known,[23] and the intersystem-crossing efficiency in the presence of the quencher was measured directly from the triplet absorbance of TPTP at 480 nm using nanosecond laser flash photolysis. For laser excitation at 355 nm, an 8 ns pulse width Quanta ray GCR-2 Nd:YAG laser was used in a right angle geometry and a 1 cm path length cell was used in this investigation. The signals were detected using a 250 W pulsed xenon lamp, Czerny Turner monochromator, and R-928 PMT. The signals were captured in a Hewlett-Packard 54201A digital storage oscilloscope. The experiments were carried out under an argon atmosphere by degassing the solution for 25 min. Kinetic analysis were carried out using the software described elsewhere.[27]

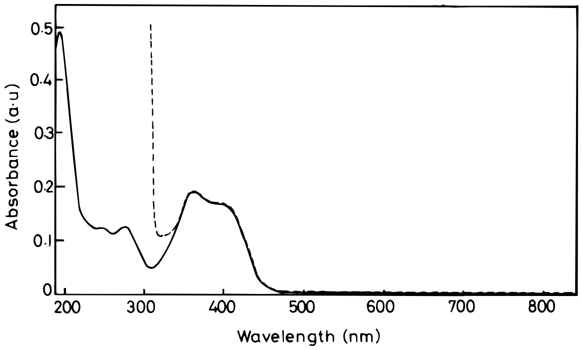

Figure 1. Absorption spectrum of TPTP ([TPTP] = 9.6×10^{-5} M) in the absence (—) and the presence (---) of iodoanisole ([iodoanisole] = 0.5 M).

Results and Discussion

Fluorescence of TPTP was quenched effectively by a variety of halogenated benzene derivatives, and the unaltered absorption spectrum of the fluorescer in the presence of the quencher precludes the possibility of ground-state complex formation. We already discussed[17] the absence of any ground-state complexation for the TPP molecule in the presence of the same quenchers. Wintgens et al.[28] already reported the charge-transfer (CT) complex absorption for the TPP in the presence of anthracene in the region of 570 nm with the ϵ value of 2000 M^{-1} cm^{-1}. The unsubstituted thiopyrylium salt also forms CT complexes with olefins and aromatic hydrocarbons with a characteristic absorption band for the CT absorption.[29,30] Since the oxidation potential of the quenchers used in our investigation ranges from 1.35 to 2.56 eV, the CT absorption should appear at the tail end of the spectrum. The absence of any characteristic CT absorption in the presence of all the quenchers confirms the absence of ground-state complexation (Figure 1). The naive Stern−Volmer relationship is used in the determination of the quenching constant (k_q), and the plots are quite linear up to high concentrations of the quencher (0.1 M).

The thermodynamic feasibility of the excited singlet state electron-transfer reaction is calculated by employing the well-known Rehm−Weller[31] expression.

$$\Delta G_{et} = E_{1/2(oxid)} - E_{1/2(red)} - E_{0,0} + C \qquad (1)$$

where $E_{1/2(oxid)}$ is the oxidation potential of the donor and is obtained from the ionization potential as mentioned in the literature.[32] $E_{1/2(red)}$ is the reduction potential of the acceptor, and C is the Coulombic term. Since the thiopyranyl radical species is neutral and the solvent used is polar, the Coulombic term in the above expression is negligible. The propensity of k_q to increase with increasing exothermicity of ΔG_{et} and the observation of $TPTP^{\bullet}$ absorbance at 550 nm are the incontrovertible proof for the electron-transfer mechanism, and based on this, the following scheme (Scheme 1) is conceivable

SCHEME 1

where k_d and k_{-d} are the rate constants of diffusion and dissociation of the encounter complex, respectively. k_{et} and k_{-et} are the activation controlled rate constants of electron transfer, and k_{esc} is the rate constant for the separation of the radicals.

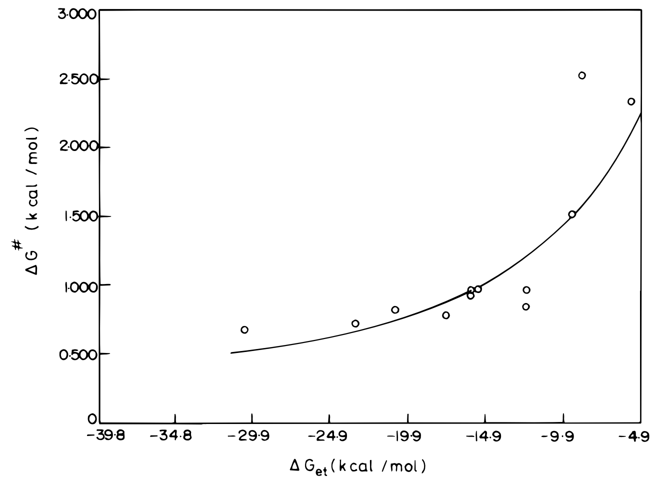

Figure 2. Plot of free energy of activation ($\Delta G^{\ddagger}$) vs free energy change of the reaction (ΔG_{et}): (○) experimental $\Delta G^{\ddagger}$ values; (—) $\Delta G^{\ddagger}$ values calculated using the Levine expression ($\Delta G^{\ddagger}$ in kcal/mol).

$k_{\text{isc(S)}}$ and $k_{\text{isc(I)}}$ are the rate constants of spontaneous and induced triplet formation, respectively. k_f is the radiative rate constant, and k_b is the rate constant for the recombination of the radical pair. k_R is the rate constant for the decay of the TPTP radical.

Using steady-state approximation, the overall quenching constant k_q of the above reaction is given by

$$k_q = \frac{k_d}{1 + \frac{k_d}{K_D \cdot A}\left[\exp\left(\frac{\Delta G^{\ddagger}}{RT}\right) + \exp\left(\frac{\Delta G_{\text{et}}}{RT}\right)\right]} \qquad (2)$$

where $K_D = k_d/k_{-d}$[33] and A is the preexponential factor or frequency factor; normally the A value of 10^{11}−10^{14} s^{-1} is used in the calculation[34] of k_q. The k_q values calculated using the A value of 10^{11} s^{-1} are in good agreement with the observed k_q values. $\Delta G^{\ddagger}$ is the free energy of activation, and ΔG_{et} is the free energy change of the reaction.

The free energy of activation ($\Delta G^{\ddagger}$) can be estimated using Marcus,[35] Rehm−Weller,[4] and Levine[36] treatments provided the free energy of activation at $\Delta G_{\text{(et)}} = 0$ ($\Delta G_0^{\ddagger}$) is known. The $\Delta G_0^{\ddagger}$ is usually evaluated by the fitting procedure.[1a] The $\Delta G^{\ddagger}$ values derived from the experimental quenching constants are correlated with the $\Delta G^{\ddagger}$ values calculated using the Levine expression by varying the $\Delta G_0^{\ddagger}$ values. The better fitting is observed between experimental and calculated $\Delta G^{\ddagger}$ values for the $\Delta G_0^{\ddagger}$ value of 4 k cal/mol (0.17 eV) and is represented in Figure 2. The overall quenching constant k_q is calculated using $\Delta G^{\ddagger}$ from all the three above treatments and the k_d value from the Smoluchowski[37] expression

$$k_d = 4\pi N(D_f + D_q)a \qquad (3)$$

where D_f and D_q are the diffusion coefficients of the fluorescer and quencher, respectively. The encounter distance a used in the above calculation is of the order of 7 Å. The D_f value is obtained from the rotating disk electrode (RDE) experiment by employing the Levich equation[38]

$$i = 0.62\, nFACD^{2/3}\, \nu^{-1/2}\, \omega^{-16} \qquad (4)$$

where i, n and F are the diffusion current, number of electrons exchanged, and Faraday constant, respectively. A is the area of the electrode and is equal to 0.01 cm^2, D is the diffusion coefficient, and C is the concentration of TPTP, which is of the order of 10^{-3} M. ω is the angular speed of the disk ($\omega = 2\pi N$, where N is the rotational speed), and ν is the kinematic viscosity obtained from the viscosity and density of the solution. The D_f value obtained using the above expression is 8.3×10^{-5} cm^2 s^{-1}. Since the quenchers used in this investigation are benzene derivatives, the D_q value reported for the benzene derivatives as 2.2×10^{-5} cm^2 s^{-1} was taken from the literature.[7] The k_d value calculated using the above D values is of the order of $(5.4 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}.

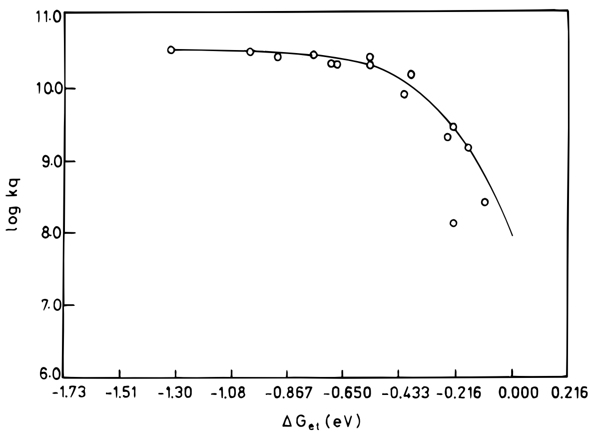

Figure 3. Plot of log k_q vs $\Delta G_{\text{(et)}}$: (○) experimental k_q values; (—) k_q values calculated using $\Delta G^{\ddagger}$ from the Levine expression and $k_d = 5.4 \times 10^{10}$ M^{-1} s^{-1} from the Smoluchowski expression.

The k_q values calculated using the above k_d value and $\Delta G^{\ddagger}$ from the Levine expression given below

$$\Delta G^{\ddagger} = \Delta G_{\text{et}} + \frac{\Delta G_0^{\ddagger}}{\ln 2} \ln\left[1 + \exp\left(\frac{-\Delta G_{\text{et}} \ln 2}{\Delta G_0^{\ddagger}}\right)\right] \qquad (5)$$

are in good agreement with the experimental k_q values. However, the k_q values calculated using this k_d and $\Delta G^{\ddagger}$ from the empirical Rehm−Weller and Marcus relationships are not in good agreement with the observed k_q values, and this could be due to the ineptitude of the expression to account for the changes in the thermodynamic properties during the course of the electron-transfer reaction. Since the $\Delta G^{\ddagger}$ calculated using Levine[36,39] expression accounts for the change in entropy and enthalpy during the course of electron transfer, this is a preferable expression. The plot of log k_q vs ΔG_{et} is represented in Figure 3, and the values are collated in Table 1.

Radical Yield and Intersystem Crossing. The radical pair produced due to electron-transfer undergoes recombination, separation, and intersystem crossing to the triplet state (provided the radical pair energies are higher than that of the triplet). The recombination rate constants are obtained from the quantum yield of the radicals and are evaluated using the absorbance and molar extinction coefficient of the radical. The separated radical lives up to seconds under argon atmosphere, and the decay of radical follows first-order kinetics; the rate constants are depicted in Table 2. The first-order decay reveals the lack of dimerization at room temperature as already evidenced by Wintgens et al.,[22a] and the equilibrium constant for the dimerization was reported as 4.5. Hence the decay of the radical may be due to the disintegration of the radical into products. The transient absorption spectrum for the TPTP radical is depicted in Figure 4.

TABLE 1: Comparison of Quenching Constants Calculated Using Marcus, Rehm−Weller, and Levine Treatments Assuming $k_d = 5.4 \times 10^{10}$ M^{-1} s^{-1} with Experimentally Observed Fluorescence-Quenching Constants[a]

					k_q calcd $\times 10^{-10}$, M^{-1} s^{-1} ($\pm 0.3 \times 10^{-10}$)		
no.	quencher	$E_{1/2(oxid)}$, eV	ΔG_{et}, eV	k_q exptl $\times 10^{-10}$, M^{-1} s^{-1} (log k_q)	Marcus	Rehm−Weller	Levine
1	DMB	1.34	−1.32	3.19 (10.50)	0.4	2.2	3.3
2	*p*-iodoanisole	1.65	−1.01	2.99 (10.48)	1.5	1.9	3.1
3	*o*-bromoanisole	1.75	−0.90	2.71 (10.43)	2.5	1.5	3.0
4	anisole	1.90	−0.76	2.51 (10.40)	3.3	1.7	2.7
5	*p*-bromotoluene	1.97	−0.69	2.09 (10.32)	3.3	1.3	2.5
6	*p*-chlorotoluene	1.99	−0.67	1.98 (10.30)	3.3	1.3	2.5
7	toluene	2.12	−0.54	1.99 (10.30)	2.9	1.0	1.9
8	iodobenzene	2.12	−0.54	2.45 (10.39)	2.9	1.0	1.9
9	bromobenzene	2.28	−0.38	1.42 (10.15)	1.6	0.6	1.0
10	chlorobenzene	2.42	−0.24	0.19 (9.28)	0.4	0.2	0.3
11	benzene	2.44	−0.22	0.27 (9.42)	0.5	0.2	0.3
12	cyclohexanone	2.44	−0.22	0.03 (8.40)	0.5	0.2	0.3
13	fluorobenzene	2.50	−0.15	0.12 (9.08)	0.1	0.1	0.1
14	cyclopentanone	2.56	−0.09	0.02 (8.36)	0.1	0.1	0.04

[a] k_q values are determined within the error limits 1%. $E_{1/2(oxid)} = \mathrm{IP} - 6.7$. DMB = 1,4 dimethoxybenzene.

TABLE 2: Free Energy Change of the Radical Pair and Back Electron Transfer, Radical Yield, Back Electron Transfer, Intersystem-Crossing, and Decay Rate Constants of the Radical

no.	quencher	ΔG_{RP},[a] eV	ϕ_r	ΔG_b, eV	$k_b \times 10^{-9}$, s^{-1}	α	$k_{isc(I)} \times 10^{-9}$, s^{-1}	k_R, s^{-1}
1	DMB	1.55		−1.55				
2	*p*-iodoanisole	1.86		−1.86				
3	*o*-bromoanisole	1.97		−1.97				
4	anisole	2.11		−2.11				
5	*p*-bromotoluene	2.18	0.03 ± 0.003	−2.18	16.33			0.236
6	*p*-chlorotoluene	2.20	0.03 ± 0.002	−2.20	15.68			0.073
7	toluene	2.33	0.06 ± 0.002	−2.33	7.211	0.152	1.38	0.149
8	iodobenzene	2.33		−2.33		0.454		
9	bromobenzene	2.49	0.02 ± 0.002	−2.49	18.21	0.364	10.7	0.044
10	chlorobenzene	2.63	0.07 ± 0.002	−2.63	5.406	0.185	1.34	0.121
11	benzene	2.65	0.08 ± 0.001	−2.65	4.993	0.132	0.835	0.224
12	cyclohexanone	2.65	0.09 ± 0.003	−2.65	4.024	0.200	1.276	1.210
13	fluorobenzene	2.71	0.08 ± 0.003	−2.71	4.837	0.144	0.687	0.252
14	cyclopentanone	2.77	0.09 ± 0.003	−2.77	3.848	0.200	1.086	0.310

[a] $\Delta G_{(RP)} = E_{1/2(oxid)} - E_{1/2(red)}$.

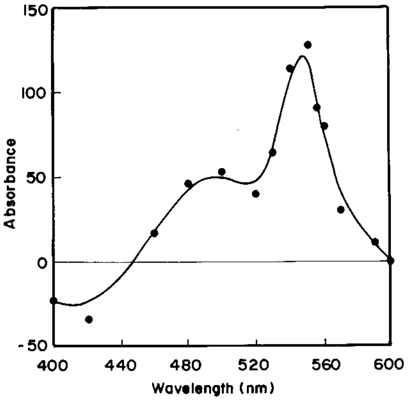

Figure 4. Transient absorption spectrum recorded 1 s after flash for a deaerated solution containing 1×10^{-5} M TPTP and 1×10^{-2} M toluene.

Based on Scheme 1, the quantum yield of the radical[40] is given by

$$\phi_r = \phi_{gem} \frac{k_{esc}}{k_{esc} + k_b} \tag{6}$$

for systems whose radical pair energies are lower than the triplet energy (2.28 eV) of the fluorescer, and the radical pair energies (ΔG_{RP}) are listed in Table 2, where ϕ_{gem} is the fraction of singlet molecules quenched to form the geminate radical pair and is given by

$$\phi_{gem} = \frac{k_q[D]}{k_o + k_q[D]} \tag{7}$$

The concentration of the quencher is adjusted in such a way to bring about 100% quenching, and, normally, the concentration of the quencher used is of the order of 0.5 M. In this concentration range of the quencher, the k_o value ($k_f + k_{isc(s)}$) is negligible compared to k_q[D] and hence the value of ϕ_{gem} can be approximated to 1, and the above expression is simplified to

$$\phi_r = \frac{k_{esc}}{(k_{esc} + k_b)} \tag{8}$$

When the triplet energy of the fluorescer is lower than the energy of the radical pair, we can expect the population of the triplet from the radical pair and is represented in Scheme 1. The radical yield is then given by

$$\phi_r = \frac{k_{esc}}{(k_{esc} + k_b + k_{isc(I)})} \tag{9}$$

where k_{esc} is the rate constant for the separation of the geminate radical pair and is taken as 5×10^8 s^{-1}. This value is obtained by Weller[41] from magnetic field measurements for the ion−pair in acetonitrile, and it is in good agreement with the value obtained using the following empirical relationship

$$k_{\mathrm{esc}} = \frac{2.3 \times 10^{9}}{\eta} \exp\left(-\frac{e^{2}}{4\pi\epsilon_{0}\epsilon KT(r_{\mathrm{grp}} - r_{\mathrm{ec}})}\right) \qquad (10)$$

where η is the viscosity in cP, ϵ is the dielectric constant of the solvent, k is the Boltzmann constant, and r_{ec} and r_{grp} are the separation distances for the encounter complex and the geminate radical pair, respectively. Generally, one would expect higher a k_{esc} value in the case of the charge-shift type of reactions due to the larger separation of the radical pair compared to the ion pair. In polar solvents such as acetonitrile, the Coulombic force of attraction is very small, around 0.06 eV, and the ions in the ion-pair are well-separated. The influence of greater separation distance (due to the lack of Coulombic force of attraction) on the k_{esc} value will be smaller compared to the influence of the dielectric constant of the solvent. Hence the same k_{esc} value can be extended for the charge-shift type of systems that have no Coulombic force of attraction.

The induced intersystem-crossing rate constant ($k_{\mathrm{isc(I)}}$) is evaluated from the total intersystem-crossing efficiency (spontaneous and induced), which in turn is directly related to the triplet−triplet absorbance of the molecule

$$\phi_{\mathrm{isc}} = \phi^{\circ}{}_{\mathrm{isc}}\left(\frac{A}{A^{\circ}}\right) \qquad (11)$$

where A and A^{o} are the triplet absorbance of TPTP in the presence and absence of the quencher, respectively. On the basis of Scheme 1, the intersystem-crossing efficiency can be directly related to the intersystem-crossing rate constant[42]

$$\phi_{\mathrm{isc}} = \frac{k_{\mathrm{isc(s)}}}{k_{\mathrm{o}} + k_{\mathrm{q}}[\mathrm{D}]} + \frac{k_{\mathrm{q}}[\mathrm{D}]}{k_{\mathrm{o}} + k_{\mathrm{q}}[\mathrm{D}]}\alpha \qquad (12)$$

where k_{o} is the rate constant for the decay of the singlet state of TPTP ($k_{\mathrm{o}} = k_{\mathrm{f}} + k_{\mathrm{isc(S)}}$) and α is the efficiency of triplet formed during the decay of the radical pair and is given by

$$\alpha = \frac{k_{\mathrm{isc(I)}}}{k_{\mathrm{isc(I)}} + k_{\mathrm{b}} + k_{\mathrm{esc}}} \qquad (13)$$

By substituting the values of ϕ_{isc}, $\phi^{\circ}_{\mathrm{isc}}$, k_{o}, $k_{\mathrm{isc(S)}}$, k_{q}, and the concentration of donor (D), the value of α can be evaluated.

Finally, the $k_{\mathrm{isc(I)}}$ value is obtained from the ratio of α and ϕ_{r}

$$\frac{\alpha}{\phi_{\mathrm{r}}} = \frac{k_{\mathrm{isc(I)}}}{k_{\mathrm{esc}}} \qquad (14)$$

after substituting for the k_{esc} value, and the $k_{\mathrm{isc(I)}}$ values obtained are collated in Table 2. In the case of the TPTP−iodobenzene system, due to the absence of measurable amount of radical absorbance, the separation of the radical pair seems to be almost negligible, and hence only the ratio between k_{b} and $k_{\mathrm{isc(I)}}$ can be evaluated from the α value.

The triplet absorbance of TPTP increases with increasing concentration of the quenchers for systems with radical pair energies higher than that of the triplet energy of the sensitizer and is represented in parts a and b of Figure 5 for systems with heavy atom (iodobenzene) and without heavy atom (toluene), respectively.

This enhancement in the triplet absorbance of TPTP in the presence of quenchers with respect to the triplet absorbance of TPTP in the absence of the quencher is rationalized on the basis of the heavy atom effect. In the presence of heavy atom substituted quenchers, both the external[17,43] and internal heavy atom effects (due to the presence of S atom in the TPTP) are responsible for the increase in the triplet absorbance, whereas for other quenchers without the heavy atom, the internal heavy atom effect alone is responsible for the enhancement in the triplet absorbance.

The role of heavy atom can be justified by comparing $k_{\mathrm{isc(I)}}$ values for the systems of similar energy gap between the radical pair and the triplet. Due to the nonavailability of the $k_{\mathrm{isc(I)}}$ value in the case of TPTP−iodobenzene system, the α value is used for the comparison instead of $k_{\mathrm{isc(I)}}$. The TPTP−iodobenzene and TPTP−toluene systems have similar energy gaps, and the higher α value observed in the presence of iodobenzene compared to toluene is due to the spin−orbit coupling of iodine present in the system. The α value increases with the increasing size of the halogen atom in the benzene series and Figure 6 reveals explicitly the role played by heavy atom substituent in the triplet induction. This was further evidenced by comparing the α values of halogenated benzenes with the spin−orbit coupling constants. The α value in the case of benzene series increases with the increasing spin−orbit coupling constant[44] of Cl (587) < Br (2460) < I (5060 cm^{-1}). In the case of heavy atom substituted anisoles and toluenes, the radical pair energies are lower than the triplet energy of the sensitizer and this in turn leads to negligible triplet induction.

The k_{b} values are estimated from the radical yield values after substituting for the $k_{\mathrm{isc(I)}}$ and k_{esc} values. In the case of 1,4 dimethoxybenzene, iodoanisole, anisole, and bromoanisole quenchers, it is not possible to evaluate the k_{b} values due to the absence of a measurable amount of the radical absorbance. The observed k_{b} values are compared with the k_{b} values calculated using the semiclassical expression[45] and are given by

$$k_{\mathrm{b}} = \left(\frac{\pi}{h^{2}\lambda_{\mathrm{s}}k_{\mathrm{B}}T}\right)^{1/2} |V|^{2} \sum_{w=0}^{w=\infty} \frac{e^{-s}S^{w}}{w!} \exp\left\{-\frac{(\lambda_{\mathrm{s}} + \Delta G_{\mathrm{b}} + wh\nu)^{2}}{4\lambda_{\mathrm{s}}k_{\mathrm{B}}T}\right\} \qquad (15)$$

where V is the electronic coupling matrix element and generally describes the coupling of electronic states of the initial state with those of the final state, $h\nu$ is the average energy of active vibrational mode, S is the electronic vibrational coupling constant and is related to λ_{i} and $h\nu$ by $S = \lambda_{\mathrm{i}}/h\nu$, and λ_{s} and λ_{i} are the solvent and vibrational reorganization energy. ΔG_{b} is the free energy change for the back electron transfer reaction and is given by

$$\Delta G_{\mathrm{b}} = E_{1/2(\mathrm{red})} - E_{1/2(\mathrm{oxid})} \qquad (16)$$

The curve-fitting procedure adopted to find the best fit values was innocuous.[46,10d] The λ_{s}, λ_{i}, and V are varied in order to obtain good correlation between the calculated and experimental k_{b} values. The λ_{s} and λ_{i} values are varied for every ±0.05 eV, keeping the value of V constant. The k_{b} values calculated using the following parameters, $V = 2.5 \times 10^{-3}$ eV, $\lambda_{\mathrm{i}} = 0.5$ eV, $\lambda_{\mathrm{s}} = 1.3$ eV, and $h\nu = 0.1363$ eV, are consistent with the data obtained.

The plot of log k_{b} vs ΔG_{b} represented in Figure 7 does not show a clear Marcus inverted region in the case of thiopyrylium in comparison with the TPP system. This is due to the lack of the number of experimental points in the inverted region because of the poor quenching ability of quenchers with an oxidation potential greater than 2.6 eV.

Thiopyrylium vs Pyrylium. The reactivity of thiopyrylium is different from that of pyrylium because of the presence of S

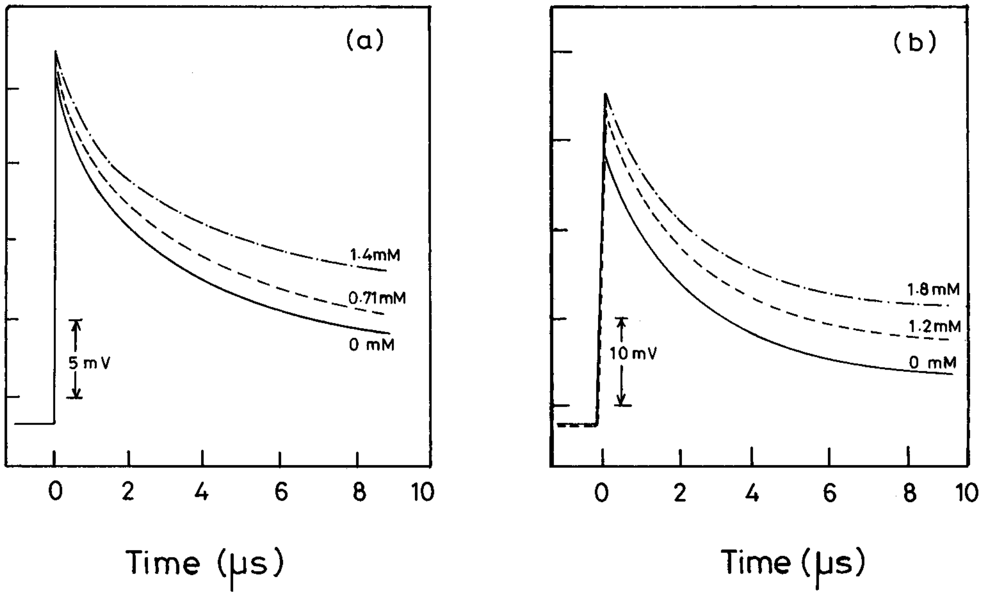

Figure 5. Transient absorption decay at 480 nm with different concentrations of **(a)** iodobenzene and **(b)** toluene.

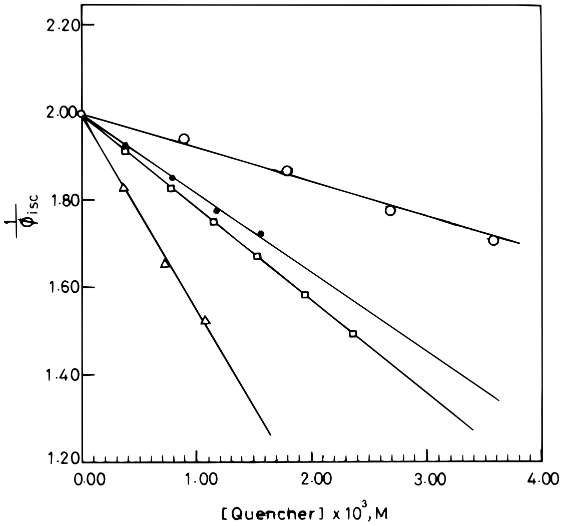

Figure 6. Plot of $1/\phi_{\mathrm{isc}}$ vs concentration of quenchers: iodobenzene (△), bromobenzene (□), chlorobenzene (●), and benzene (○).

atom with the vacant d orbital. This has been observed in various stages of the investigation such as diffusion, induction, radical yield, and recombination of the radical pair.

Diffusion. The k_d value in the case of thiopyrylium (5.4×10^{10} M^{-1} s^{-1}) is higher than that of pyrylium[17] (3.7×10^{10} M^{-1} s^{-1}) and is justified on the basis of the mobility of ions. The mobility of the ions depends on the diffusion coefficient of the ions,[47] which in turn relies on the solvated radii rather than on the ionic radii of the molecule. Generally, the smaller ion and localized charge gets solvated to a larger extent compared to bigger ions. In the case of thiopyrylium, the charge on the sulfur atom (around 0.28) is delocalized over the vacant d orbital and hence solvated to a lesser extent compared to the TPP molecule where the charge is completely localized on the oxygen atom (0.44).[48] This reduced solvation of the TPTP molecule is reflected in the higher diffusion rate constant. This was further evidenced by looking into the mobilities of the alkali metal ions in polar solvents where the Cs$^+$ moves faster compared to Li$^+$ ions.[49]

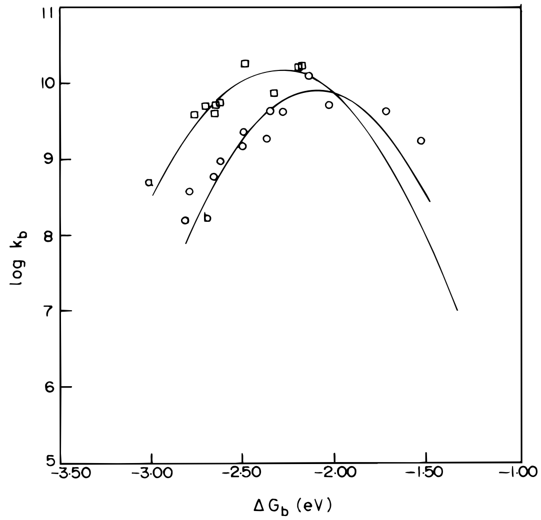

Figure 7. Plot of log k_b versus ΔG_b. The curve was drawn using k_b values calculated on the basis of eq 15 with the following fitting parameters: (a) For TPTP in acetonitrile $\lambda_\mathrm{i} = 0.5$ eV, $V = 2.5 \times 10^{-3}$ eV (20 cm^{-1}), $\lambda_\mathrm{s} = 1.3$ eV, $h\nu = 0.1363$ eV, and (□) represents experimental points. (b) For TPP in acetonitrile $\lambda_\mathrm{i} = 0.5$ eV, $V = 1.8 \times 10^{-3}$ eV (14 cm^{-1}), $\lambda_\mathrm{s} = 1.1$ eV, $h\nu = 0.1363$ eV, and (○) represents experimental points.

Radical Yield and Triplet Induction. The role played by S atom in the radical yield and intersystem-crossing rate constants are evidenced from the values represented in Table 2. The observed radical yield of TPTP is 10-fold smaller compared to TPP in acetonitrile, and it is due to the enhanced recombination and intersystem crossing in the radical pair; the reason for the enhancement can be explained as follows.

In the case of pyrylium,[17] the triplet induction is observed only in the presence of heavy atom substituted quenchers (due to the spin−orbit coupling effect). Since the triplet enhancement due to hyperfine coupling is negligible (in the case of charge-shift type of systems), there is no triplet induction for systems with no heavy atom, despite their radical pair energies being higher than the triplet energy of the sensitizer.[50] In the case of thiopyrylium, however, the internal heavy atom effect of sulfur results in triplet induction irrespective of the quenchers for all the systems with a radical pair energy higher than that of the triplet energy of the sensitizer. The presence of S atom in the thiopyrylium is the reason for the enhancement in the intersystem-crossing rate constant. The increase in spin−orbit coupling due to the substitution of a skeletal atom of the system by S is known as homocyclic heavy atom spin−orbit coupling,[51] and the influence of S atom in the enhancement of spontaneous triplet formation is already known.[52]

Radical Pair Recombination. The recombination rate constants are influenced by the solvent reorganization energy (λ_s), electronic coupling matrix element (V), and the free energy change for the recombination of the radical pair. The solvent reorganization energy (λ_s) and the electronic coupling matrix element (V) for the thiopyrylium radical pair are higher than that of pyrylium, and the reason for this can be rationalized as follows. The λ_s value for the radical pair is higher in the case of thiopyrylium by 0.2 eV. Since the λ_s value shows dependence on the separation distance, the increase in λ_s can be explained on the basis of the separation distance (r_{12}), and the r_{12} values are evaluated using the solvent dielectric continuum model for both forward and backward electron-transfer reaction

$$\lambda_s = \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}}\right]\left(\frac{1}{\epsilon_{OP}} - \frac{1}{\epsilon_s}\right) \qquad (17)$$

where r_1 and r_2 are the molecular radii of the thiopyrylium and quencher and are of the order of 6.5 and 3 Å, respectively. r_{12} is the separation distance between the fluorescer and quencher and ϵ_{OP} and ϵ_s are the optical and the static dielectric constants of the solvent. The r_{12} value for the encounter complex and the geminate radical pair is evaluated from λ_s for the forward electron transfer ($4\Delta G_0^{\ddagger} = \lambda_s = 0.69$ eV) and from the fitted λ_s for recombination in the radical pair, and the values obtained are on the order of 8.1 and 21 Å, respectively.

In the case of pyrylium,[17] the separation distance is around 13 Å for the radical pair and 7 Å for the encounter complex from the above model. The larger separation distance in turn is reflected in the larger λ_s value for the thiopyrylium system. The reason for the larger separation in the case of TPTP is due to the smaller charge density on the sulfur atom compared to that on the oxygen atom.

Normally, the V value decreases with increasing separation distance. Despite the larger separation distance, the V value is higher in the case of TPTP (2.5×10^{-3} eV) compared to TPP (1.8×10^{-3} eV). This is due to the presence of a vacant d orbital in the S atom, which results in the enhanced overlap of the orbitals compared to the TPP system. Generally, the magnitude of the electronic coupling matrix element V is determined by the overlap of the wave functions of the initial and final states.[53]

Despite the larger reorganization energy, the k_b values of thiopyrylium are higher than those of pyrylium.[17] This is due to the overwhelming role played by the free energy change of the reaction (i.e., free energy change is more favorable), and it results in the smaller activation energy for the recombination of the thiopyrylium radical pair compared to the pyrylium system. The plot of log k_b vs ΔG_b is shifted toward more negative region in the case of thiopyrylium (−2.40 eV) compared to that of pyrylium (−2.00 eV) and as depicted in Figure 7 accounts for the higher λ_s value.

Conclusion

The electron-transfer mechanism was proposed for the fluorescence quenching of TPTP by a variety of halogenated benzenes in acetonitrile, and it was established using the flash photolysis technique. The k_q values calculated using $\Delta G^{\ddagger}$ from the Levine treatment and the k_d value of 5.4×10^{10} M^{-1} s^{-1} are in good agreement with the experimental k_q values. The higher diffusion rate constant k_d in the case of thiopyrylium compared to that of TPP is because of the reduced solvation due to the smaller charge density on the S atom. The presence of S atom in the thiopyrylium increases the recombination and induction due to its vacant d orbital (internal heavy atom effect). The comparison of results of thiopyrylium with the pyrylium salt reveals clearly the indirect role played by S atom in enhancing the diffusion, induction of triplet, and recombination of the radical pair.

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