Excited Singlet State Reactions of Triphenylpyrylium Ion with Electron Donors: Evidence for Electron Transfer and the Observation of Marcus Inverted Region for the Charge Shift in the Radical Pair

S. S. Jayanthi and P. Ramamurthy*

Department of Inorganic Chemistry, School of Chemistry, University of Madras, Guindy Campus, Madras 600 025, India

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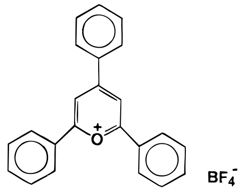
The excited singlet state of 2,4,6-triphenylpyrylium ion reacts with benzene derivatives by the electron transfer mechanism, and the radical yield was measured using the flash photolysis technique. A poor correlation is observed between experimental and theoretical k_q values calculated using k_d from the Debye expression. The observed quenching constants are in good agreement with the k_q values calculated using $k_d = 3.7 \times 10^{10}$ M^{-1} s^{-1}, which is obtained from Smoluchowski expression and $\Delta G^{\ddagger}$ from the Rehm−Weller expression. The back electron transfer rate constant is determined from the quantum yield of the radical. Marcus inverted region is observed for the back electron transfer rate constants in the highly exothermic region of ΔG_b.

Introduction

Photoinduced electron transfer has been an area of immense research for more than 30 years. Considerable efforts have been made by several groups to explain the mechanism of fluorescence quenching.[1] Fluorescence quenching through electron transfer was explained by Rehm−Weller in 1970.[2] Weller explained the quenching through the formation of exciplex.[3] Fluorescence quenching of aromatic hydrocarbons by unsaturated hydrocarbon was studied by Murov *et al*. in 1968.[4] The presence of exciplex during the fluorescence quenching of naphthalenes by tertiary amines was explained by Van *et al.*[5] Induced triplet formation from the radical pair produced during the fluorescence quenching of pyrene was described clearly by Weller and co-workers.[6] Heavy atom effect on fluorescence quenching and triplet and radical yields were explained by Kikuchi and others.[7] The role of n and π donors during quenching was investigated thoroughly by Gohneim *et al.*,[8] and the steric effect of bulky substituents on quenching and radical yield was explained by Gould *et al*. in 1993.[9] The role of inner sphere reorganization energy in photoinduced electron transfer reactions was studied very recently by Maruyama.[10] Closs *et al.*[11] first experimentally observed the Marcus inverted region in the distance dependent intramolecular electron transfer of organic radical anions. Bell-shaped energy gap dependence of the charge recombination reaction of the geminate radical pair produced during the luminescence quenching was established very well.[12] The back electron transfer rate constant is normally obtained from the quantum yield of the radicals. Steiner *et al.* explained two absolute methods for the estimation of the quantum yield of the radicals.[13] The Marcus inverted region is observed in the back electron transfer rate constants obtained from the quantum yield of the radicals for a number of systems,[14,15] and the Marcus inverted behavior is observed only for a few systems in the case of the charge-shift type of reactions. Gould *et al.*[15c] reported Marcus inverted behavior for the recombination of the geminate radical pair produced by *N*-methylacridine and alkylbenzenes. Grampp *et al.* observed Marcus inversion in the recombination of the triplet-based geminate radical pair of thionine.[15d] The major aim of our investigation is to understand the mechanism of fluorescence quenching of 2,4,6-triphenylpyrylium (TPP) by electron donors and to explain the cause for the deviation between experimental and theoretical quenching constants. The second part of the work deals with the verification of the presence of the Marcus inverted region in the charge-shift process within the geminate radical pair, and here, we report for the first time the *Marcus inverted behavior* for the charge shift in the radical pair along with the presence of triplet induction.

The 2,4,6-triphenylpyrylium tetrafluoroborate used in this investigation is a well-known sensitizer and an excellent oxidizing agent.[16] The important photophysical parameters that are necessary for the present investigation are given below



$E_{½(red)} = -0.38$ eV[17]

$E_{o,o} = 2.80$ eV[18]

$E_T = 2.30$ eV [19]

$\tau_s = 4.2$ ns[20]

$\Phi_{isc} = 0.42$[21]

$\Phi_f = 0.55$

Experimental Methods

The 2,4,6-triphenylpyrylium tetrafluoroborate obtained from Aldrich was recrystallized before use, and all the quenchers (halogenated benzenes, anisoles, toluenes) were purified as mentioned in the literature.[22] Acetonitrile (spectroscopic grade solvent) was used as received.

Absorption spectra were recorded using a Hitachi-320 spectrophotometer. Fluorescence quenching experiments were carried out using a Perkin-Elmer LS5B spectrofluorimeter. For all the quenching experiments, the pyrylium concentration was adjusted to have an absorbance of 0.1, and the concentration of the quencher was normally of the order of 10^{-3}−0.1 M. In this concentration range, up to 70% of TPP fluorescence was quenched.

The diffusion coefficient of TPP was determined indirectly from the measured diffusion current value using the microprocessor-based Tacussel polaroprocessor which works in association with an EGMA polarographic stand. 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 current value was measured with

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varying rotational speed of the electrode, and an argon-purged solution was used.

Free radical yield was measured as reported in the literature[23] from the absorbance and the calculated molar extinction coefficient of the TPP radical. While the radical yield was being determined, the concentration of the quencher was adjusted in such a way to bring about 100% singlet quenching. The absorbance of $TPP^\bullet$ was measured at 550 nm using an Applied Photophysics KN-020 conventional flash photolysis spectrometer comprising a 100 W tungsten halogen lamp as the monitoring source and an LR-16 Inotech flash lamp as the excitation source, and light obtained from the flash lamp was filtered using acetone present in the outer jacket of the cell. A Hamamatzu R-928 PMT was used as the detector, and a 25 MHz digital storage oscilloscope was used as the storage device. The radical absorbance at zero time was obtained from the intercept of the plot of $1/\Delta A$ *vs* time of the transient decay. The molar extinction coefficient of $TPP^\bullet$ was measured after generating the radical by the chemical reduction of TPP by following the literature-reported procedure,[17] and the value obtained is 2790 ± 48 M^{-1} cm^{-1}. The dimerization of $TPP^\bullet$ occurs only at 15 °C, and the radical is the predominant species at room temperature (25 °C). This was further confirmed by carrying out the experiment at 30 °C, which revealed no change in the absorbance of the radical when compared to room temperature experiments.

Intersystem crossing efficiency in the presence of the quencher was measured directly from triplet absorption of TPP at 480 nm using a nanosecond laser flash photolysis apparatus. The triplet absorption of TPP varies with the concentration of the quencher. For laser excitation at 355 nm, an 8 ns pulse width Quanta Ray GCR-2 Nd-YAG laser was used in right angled geometry and a 1 cm path length cell was used. The signals were detected using a 250 W pulsed xenon lamp, Czerny Turner monochromator, and R-928 PMT. The signals were captured in an Hewlett-Packard 54201A digital storage oscilloscope. Kinetic analyses were carried out using the software described elsewhere.[24] Deaerated solutions were used for the determination of ϕ_r and ϕ_{isc}.

Results and Discussion

Quenching Constants and Mechanisms. Fluorescence quenching of triphenylpyrylium by a variety of benzene derivatives was carried out in acetonitrile, and the absence of any new peak and the fact that the absorption spectrum of TPP was unaltered in the presence of the quencher eliminate the possibility of ground state complexation. Wintgens *et al.*[25] 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 oxidation potential of the quenchers used in our case ranges from 1.2 to 2.38 eV, and if there is any ground state charge transfer complex formation, a new absorption should appear from the tail end of the TPP absorption spectrum. This absorption shall be blue-shifted when compared to the literature-reported charge transfer complexes due to the higher oxidation potential of the quenchers. The absence of any such absorption in that region represented in Figure 1 for the TPP and 1,4-dimethoxybenzene system eludes the formation of ground state complex. The concentration of dimethoxybenzene used is high enough to quench more than 70% of the fluorescence of TPP. The absence of CT complex was already confirmed by Jacques *et al.*[26] and Akaba *et al.*[21] for the quenching of TPP by aromatic hydrocarbons in acetonitrile and dichloromethane, respectively. The quenching constant k_q is determined using the Stern−Volmer relationship, and the plots are quite linear when up to 70% of TPP fluorescence is quenched.[27]

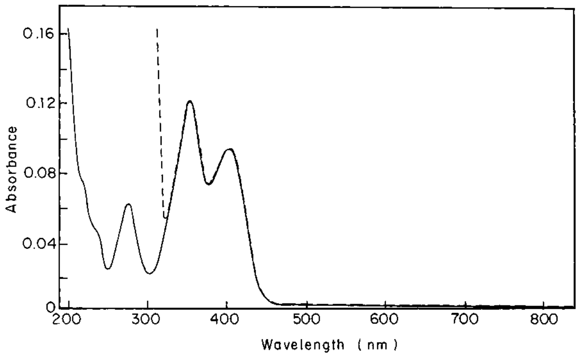
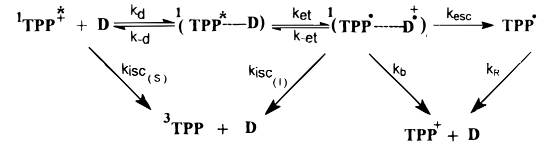


Figure 1. Absorption spectrum of TPP in the presence of 1,4-dimethoxybenzene (concentration of DMB = 0.02 M).

SCHEME 1



$$\frac{I_0}{I} = 1 + k_q\tau[Q] \qquad (1)$$

where I_0 and I are the intensities of the fluorescer in the absence and the presence of the quencher, respectively. [Q] is the concentration of the quencher, and τ is the fluorescence lifetime of the TPP in the absence of the quencher.

The quenching constant (k_q) can be correlated with the free energy change for electron transfer, ΔG_{et}, and is given by the well-known Rehm−Weller expression.[2]

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

where $E_{1/2(oxid)}$ is the oxidation potential of the donor and is obtained from the ionization potential as mentioned in the literature.[28]

$$E_{1/2(oxid\ vs\ SCE)} = IP - 6.7 \pm 0.1\ V \qquad (3)$$

$E_{1/2(red.)}$ is the reduction potential of the acceptor, $E_{0,0}$ is the singlet state energy of the sensitizer, and C is the Coulombic term. Since one of the species is neutral and the solvent used is polar, the Coulombic term in the above expression is neglected.[29] Good correlation of log k_q with ΔG_{et} is evidence for quenching through electron transfer. The observation of the characteristic signal of $TPP^\bullet$ at 550 nm in the millisecond time scale is the direct proof for electron transfer quenching,[17] and Scheme 1 is proposed for electron transfer reaction in solution.

In Scheme 1, k_d and k_{-d} are the rate constants of diffusion and dissociation of the encounter complex, respectively. k_{et} is the rate constant for the formation of the ion pair, and k_{-et} is the rate constant for the recombination. $k_{isc(S)}$ is the spontaneous intersystem crossing rate constant, and k_R is the rate constant for the recombination of the separated radical pair. k_{esc} is the rate constant for the separation of the radical pair, and k_b is the rate constant for the charge recombination reaction producing the acceptor molecule in the ground state. For some of the quenchers, the radical pair energy is higher than the triplet energy of the TPP molecule. There may be an induced triplet formation from the radical pair, and it is represented by $k_{isc(I)}$.

TABLE 1: Comparison of Quenching Constants Calculated Using Marcus, Rehm−Weller, and Levine Treatments Assuming $k_d = 2 \times 10^{10}$ M^{-1} s^{-1} with Experimentally Observed Fluorescence Quenching Constants

				k_q calcd $\times 10^{-10}$, M^{-1} s^{-1}		
no.	quencher	ΔG_{et}, eV	k_q exptl $\times 10^{-10}$, M^{-1} s^{-1} (log k_q)	Marcus	R−W	Levine
1	HMB	−1.27	2.27 (10.36)	a[b]	1.48	1.60
2	DMB	−1.08	2.39 (10.38)	b[b]	1.46	1.60
3	iodoanisole	−0.77	2.51 (10.40)	0.33	1.40	1.59
4	anisole	−0.66	2.20 (10.34)	0.94	1.37	1.58
5	*o*-bromoanisole	−0.52	1.94 (10.29)	1.51	1.29	1.54
6	*p*-bromotoluene	−0.45	1.54 (10.19)	1.58	1.24	1.50
7	*p*-chlorotoluene	−0.43	1.52 (10.18)	1.59	1.22	1.48
8	toluene	−0.30	1.62 (10.21)	1.49	1.05	1.31
9	iodobenzene	−0.30	1.90 (10.28)	1.49	1.05	1.31
10	DCB	−0.18	0.76 (9.88)	1.05	0.769	0.92
11	bromobenzene	−0.14	1.07 (10.03)	0.814	0.631	0.73
12	chlorobenzene	0.00	0.17 (9.24)	0.130	0.127	0.13
13	dioxane	0.02	0.18 (9.26)	0.089	0.086	0.086
14	benzene	0.02	0.12 (9.08)	0.089	0.086	0.086

[a] HMB = hexamethylbenzene, DMB =1,4-dimethoxybenzene, DCB = *p*-dichlorobenzene. [b] The values are too low. a = 3.61×10^3, b = 2.68×10^6.

Using steady state approximation, the overall quenching constant is given by

$$k_q = \frac{k_d}{1 + \dfrac{k_d}{K_D A}\exp\left[\dfrac{\Delta G^{\ddagger}}{RT} + \dfrac{\Delta G_{et}}{RT}\right]} \tag{4}$$

where K_D is the equilibrium diffusion constant[30] and A is the frequency factor or preexponential factor, and normally the A value of $10^{11}-10^{14}$ s^{-1} is employed in the calculation of k_q. The k_q values calculated using the A values of 10^{12}, 10^{13}, and 10^{14} s^{-1} are incongruous, and hence the value of 10^{11} s^{-1} is used in the calculation[31] of k_q and $\Delta G^{\ddagger}$ is the free energy of activation for electron transfer. In order to calculate the effective quenching constant, the proper relationship between $\Delta G^{\ddagger}$ and ΔG_{et} is important. Free energy of activation can be related to the free energy change for electron transfer by Marcus,[32] Rehm−Weller,[2] and Levine[33] relationships.

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_0\left(1 + \frac{\Delta G_{et}}{4\Delta G^{\ddagger}_0}\right)^2 \tag{5}$$

$$\Delta G^{\ddagger} = \frac{\Delta G_{et}}{2} + \left[\left(\frac{\Delta G_{et}}{2}\right)^2 + (\Delta G^{\ddagger}_0)^2\right]^{1/2} \tag{6}$$

$$\Delta G^{\ddagger} = \Delta G_{et} + \frac{\Delta G^{\ddagger}_0}{\ln 2}\ln\left[1 + \exp\left(\frac{-\Delta G_{et}\ln 2}{\Delta G^{\ddagger}_0}\right)\right] \tag{7}$$

The unexplained term in the above expressions is $\Delta G^{\ddagger}_0$, which is nothing but free energy of activation when there is no driving force for the reaction,[34] *i.e.* $\Delta G^{\ddagger} = \Delta G^{\ddagger}_0$ at $\Delta G_{et} = 0$. For the present investigation, the $\Delta G^{\ddagger}_0$ value is obtained from the conventional way of plotting $\Delta G^{\ddagger}$ *vs* ΔG_{et} and is of the order of 2.4 kcal/mol (0.1 eV). The overall theoretical quenching constants k_q calculated using $\Delta G^{\ddagger}$ from all three expressions and $k_d = 2 \times 10^{10}$ M^{-1} s^{-1} obtained from the Debye expression[35]

$$k_d = 8RT/3000\eta \tag{8}$$

are collated in Table 1. The calculated k_q values are quite lower than the experimentally observed k_q (Figure 2) values in the whole region of ΔG_{et} ($-1.27 < \Delta G_{et} < 0.02$). In the literature,[36] the deviation of experimental k_q values from the theoretically calculated k_q values is used as a tool to identify the mechanism. The deviation is explained as due to either of the following: (i) simultaneous participation of energy and electron transfer or (ii) the presence of exciplex.

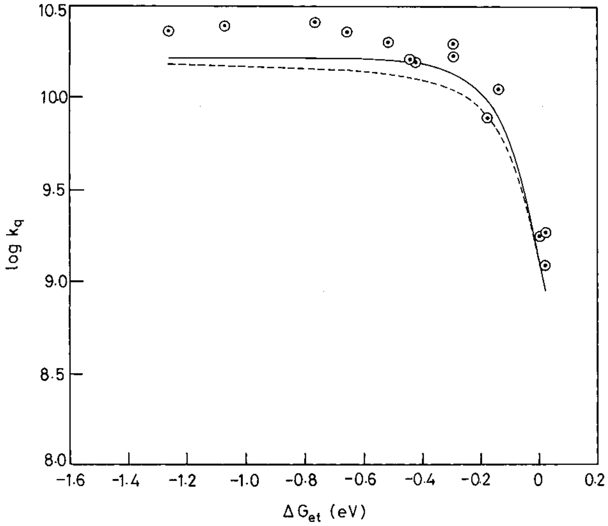


Figure 2. Plot of log k_q *vs* ΔG_{et}. k_q values were calculated using $k_d = 2 \times 10^{10}$ M^{-1} s^{-1} from the Debye expression, and $\Delta G^{\ddagger}$ was calculated from the Levine (—) and Rehm−Weller (- - -) expressions.

(i) Lewitza and Löhmannsröben[36] explained the deviation with the simultaneous participation of singlet−triplet energy transfer and electron transfer. Energy transfer takes place provided the singlet or the triplet energy of the quenchers are lower than the singlet energy of the sensitizer. Since the singlet and triplet energies of the quenchers used in this investigation are higher than the singlet energy of the sensitizer (TPP), the energy transfer possibility is completely ruled out.

(ii) The deviation between experimental and theoretical quenching constants is explained as due to the formation of exciplex in number of systems.[37] In compounds similar to TPP such as oxanine and acridizinium, the fluorescence quenching by halogenated benzenes was explained through the formation of exciplex.[28,38] If the reaction proceeds through the exciplex formation, the radical yields are expected to be low. The observation of high radical yield in the case of TPP eludes the possibility of exciplex formation.

Diffusion Rate Constants. The approximations used in the calculation of k_q are A and k_d. The reason for using the A value of 10^{11} s^{-1} is already evidenced in the earlier discussion. The other main cause for the deviation could be due to the

TABLE 2: Comparison of Quenching Constants Calculated Using Marcus, Rehm−Weller, and Levine Treatments Employing $k_d = 3.7 \times 10^{10}$ M^{-1} s^{-1} with Experimentally Observed Fluorescence Quenching Constants[a]

				k_q calcd × 10^{-10}, M^{-1} s^{-1}		
no.	quencher	ΔG_{et}, eV	k_q exptl × 10^{-10}, M^{-1} s^{-1} (log k_q)	Marcus	R−W	Levine
1	HMB	−1.27	2.27 (10.36)	a[b]	2.32	2.59
2	DMB	−1.08	2.39 (10.38)	b[b]	2.27	2.59
3	iodoanisole	−0.77	2.51 (10.40)	0.415	2.14	2.56
4	anisole	−0.66	2.20 (10.34)	1.26	2.06	2.54
5	*o*-bromoanisole	−0.52	1.94 (10.29)	2.39	1.91	2.44
6	*p*-bromotoluene	−0.45	1.54 (10.19)	2.57	1.81	2.36
7	*p*-chlorotoluene	−0.43	1.52 (10.18)	2.59	1.77	2.32
8	toluene	−0.30	1.62 (10.21)	2.33	1.47	1.95
9	iodobenzene	−0.30	1.90 (10.28)	2.33	1.47	1.95
10	DCB	−0.18	0.76 (9.88)	1.43	0.991	1.23
11	bromobenzene	−0.14	1.07 (10.03)	1.14	0.786	1.01
12	chlorobenzene	0.00	0.17 (9.24)	0.141	0.142	0.144
13	dioxane	0.02	0.18 (9.26)	0.095	0.097	0.044
14	benzene	0.02	0.12 (9.08)	0.095	0.097	0.044

[a] k_q values are determined within the error limits of 1%. [b] The values are too low. a = 3.61 × 10^3, b = 2.68 × 10^6.

approximation of the k_d value in the evaluation of k_q. The Debye expression used for the calculation of k_d includes temperature and viscosity parameters and is applicable only to molecules of size comparable with the solvent molecule.[35] Since TPP is a charged species and larger in size, the k_d value has to be determined only from the diffusion coefficient values, which in turn account for the radius of the molecule. Hence Smoluchowski's expression is used for the determination of k_d[39]

$$k_d = 4\pi N(D_f + D_q)a \tag{9}$$

where D_f and D_q are the diffusion coefficients of the fluorescer and quencher, respectively, and a is the encounter distance. The encounter distance of 7 Å is used in the above calculation of k_d.[2] The diffusion coefficient of the TPP molecule is calculated using the Levich equation[40]

$$i = 0.62nFACD^{2/3}\nu^{-1/6}\omega^{1/2} \tag{10}$$

where i is the diffusion current in milliamperes, n is the number of electrons exchanged, F is the Faraday constant, A is the area of the electrode and is equal to 0.01 cm^2, C is the concentration of TPP which is of the order of 1 × 10^{-3} M, D is the diffusion coefficient in cm^2 s^{-1}, 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 diffusion coefficient obtained from the above expression is 5.6 × 10^{-5} cm^2 s^{-1}, and the diffusion coefficient of benzene derivatives obtained from the literature[36] is of the order of 2.2 × 10^{-5} cm^2 s^{-1}. The k_d value calculated using these diffusion coefficients is of the order of 3.7 × 10^{10} M^{-1} s^{-1}. The k_q values calculated using the k_d value from Smoluchowski's expression and $\Delta G^{\ddagger}$ from all three treatments are listed in Table 2, and the experimental k_q values are in fairly good agreement with the k_q values obtained from the Rehm−Weller and Levine expression. Figure 3 represents the plot of log k_q *vs* ΔG_{et}. The singlet quenching of TPP using aromatics and alkenes was studied by Wintgens *et al.*[25] and by Jacques *et al.*[26] recently. They calculated the theoretical quenching constant assuming the k_d value as 5 × 10^{10} M^{-1} s^{-1} in order to fit the experimental quenching constants, and the assumption of a higher value is attributed to the polarization of the charged TPP molecule.

Marcus Inverted Region and Radical and Intersystem Crossing Yields. The diffusion-controlled nature of the forward electron transfer reaction prevents the occurrence of Marcus inverted region in the highly exothermic region of ΔG_{et}. The lack of Marcus inverted region in the charge separation reaction was already explained beyond doubt.[41] Marcus inverted region has been observed experimentally for charge recombination, charge shift, or intramolecular distance dependent electron transfer reactions.[15] In order to explore the presence of the Marcus inverted region, the back electron transfer rate constant is determined from the quantum yield of the radicals.[42]

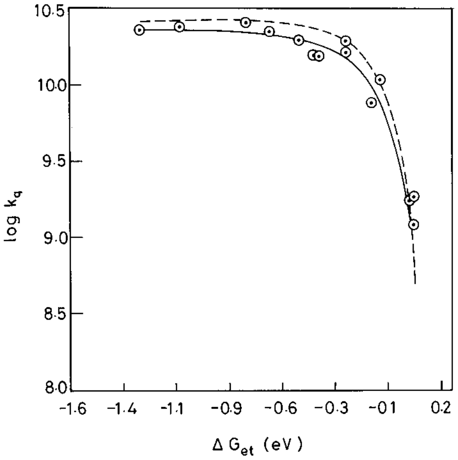


Figure 3. Plot of log k_q *vs* ΔG_{et}. k_q values were calculated using k_d = 3.7 × 10^{10} M^{-1} s^{-1} from Smoluchowski's expression, and $\Delta G^{\ddagger}$ was calculated from the Levine (- - -) and Rehm−Weller (—) expressions.

The quantum yield of the radical is given by eq 11 for systems whose radical pair energies (ΔG_{RP}) are lower than the triplet energy (2.30 eV) of the fluorescer,[43] and the radical pair energies calculated are collated in Table 3.

$$\phi_r = f\left(\frac{k_{esc}}{k_{esc} + k_b}\right) \tag{11}$$

where f is the fraction of the quenched singlet molecules. Since the contribution of k_{-d} is small compared to k_d, the formation of the radical pair from the encounter complex is taken almost as unity (f = 1), which implies that the k_{-d} is negligible in front of k_d and eq 11 can be written as

$$\phi_r = \frac{k_{esc}}{k_{esc} + k_b} \tag{12}$$

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

TABLE 3: Free Energy Change of the Radical Pair, Radical Yields, Back Electron Transfer, Intersystem Crossing, and Recombination of Separated Radicals Rate Constants

no.	quencher	$\Delta G_{(RP)}$,[a] eV	ϕ_r	ΔG_b, eV	$k_b \times 10^{-9}$, s^{-1}	$k_{isc(I)} \times 10^{-8}$, s^{-1}	$k_R \times 10^{-5}$, M^{-1} s^{-1}
1	HMB	1.53	0.23 ± 0.07	−1.53	1.72		1.53
2	DMB	1.72	0.10 ± 0.01	−1.72	4.37		1.53
3	iodoanisole	2.03	0.08 ± 0.01	−2.03	5.41		1.07
4	anisole	2.14	0.04 ± 0.01	−2.14	12.5		1.63
5	*o*-bromoanisole	2.28	0.10 ± 0.01	−2.28	4.29		1.60
6	*p*-bromotoluene	2.35	0.10 ± 0.01	−2.35	4.42	0.84	1.76
7	*p*-chlorotoluene	2.37	0.21 ± 0.03	−2.37	1.88		1.90
8	toluene	2.50	0.25 ± 0.04	−2.50	1.50		1.73
9	iodobenzene	2.50	0.10 ± 0.02	−2.50	2.34	23.59	1.63
10	dcb	2.63	0.34 ± 0.04	−2.63	0.96		1.53
11	bromobenzene	2.66	0.33 ± 0.04	−2.66	0.61	4.29	1.57
12	chlorobenzene	2.80	0.56 ± 0.05	−2.80	0.39		1.46
13	benzene	2.82	0.75 ± 0.1	−2.82	0.16		1.51
14.	dioxane	2.82		−2.82			

[a] $\Delta G_{(RP)} = E_{1/2(oxid)} - E_{1/2(red.)}$.[29]

$$\phi_r = \frac{k_{esc}}{k_{esc} + k_b + k_{isc(I)}} \qquad (13)$$

This equation is applicable for systems with $\Delta G_{RP} > 2.30$ eV, where k_{esc} is the rate constant for the separation of the geminate radical pair and is taken as 5×10^8 s^{-1}, which has been determined by Weller 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.[44]

$$k_{esc} = \frac{2.3 \times 10^9}{\eta} \exp\left(-\frac{e^2}{4\pi\epsilon_0 \epsilon k T (r_{grp} - r_{ec})}\right) \qquad (14)$$

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 separation distances for the encounter complex and geminate radical pair, respectively. Normally, one would expect a higher 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.[45] The influence of greater separation distance (due to the lack of Coulombic force of attraction) on the k_{esc} value when compared to ϵ of the solvent will be smaller in acetonitrile medium. In the later part of the discussion, this was further substantiated by calculating the k_{esc} value using the separation distance obtained from the continuum model. Hence the same k_{esc} value can be extended for the charge-shift type of system which has no Coulombic force of attraction. Due to the similarity in the quencher structures, the same k_{esc} value can be extended for all the quenchers. k_b and $k_{isc(I)}$ are the rate constants of the spin-allowed back electron transfer of the geminate radical pair and intersystem crossing for the induced triplet formation, respectively.

The intersystem crossing rate constants are obtained from the intersystem crossing efficiency[46a] which is estimated from the triplet absorbance of the TPP molecule.

$$\phi_{isc} = \phi^0_{isc}\left(\frac{A}{A^0}\right) \qquad (15)$$

where A and A^0 are the triplet absorbances of TPP in the presence and absence of the quencher, respectively. According to Scheme 1, the quantum efficiency for the triplet can be represented as follows.

$$\phi_{isc} = \frac{k_{isc(s)}}{k_0 + k_q[D]} + \frac{k_q[D]}{k_0 + k_q[D]} \times \alpha \qquad (16)$$

where ϕ_{isc} is the intersystem crossing efficiency in the presence of the quencher and k_q is the quenching constant. k_0 and $k_{isc(s)}$ are the rate constants for the decay of the singlet state of TPP and spontaneous intersystem crossing, respectively. α is the efficiency of the triplet formed during the decay of the radical pair, and it can be derived from the scheme as given below, applying the approximation that k_{-d} and k_{-et} are negligible in front of k_d and k_{et}, respectively.[46b]

$$\alpha = \frac{k_{isc(I)}}{k_{isc(I)} + k_b + k_{esc}} \qquad (17)$$

By substituting the experimentally determined values of k_q, ϕ_{isc}, $k_{isc(s)}$, and k_0, the value of α can be evaluated. The ratio between α and ϕ_r gives the value of $k_{isc(I)}$ after substituting for the k_{esc} value. The $k_{isc(I)}$ values are collated in Table 3.

$$\frac{\alpha}{\phi_r} = \frac{k_{isc(I)}}{k_{esc}} \qquad (18)$$

The triplet induction is observed only for heavy atom substituted quenchers such as iodobenzene, bromobenzene, and bromotoluene due to the spin−orbit coupling of the heavy atom present in the quencher, and the α value obtained is of the order of 0.45, 0.27, and 0.016 (iodobenzene > bromobenzene > bromotoluene), respectively. In spite of the presence of induction in the above mentioned three cases, the triplet absorbance increases only with increasing concentration of the iodobenzene and the triplet absorbance rather decreases with the increasing concentration of bromobenzene and bromotoluene. The reason for this can be rationalized as follows. The triplet absorption is a measure of total concentration of triplet formed from both spontaneous and induced triplet formation. Generally, with increasing the concentration of the quencher, the singlet reaction competes with the spontaneous triplet formation and in turn leads to the decrease in the spontaneous triplet absorption. This decrease is compensated by the triplet induction in the case of iodobenzene due to its efficient external heavy atom effect. In the case of bromobenzene and bromotoluene, the induction may be less than the decrease in the spontaneous triplet concentration due to the singlet reaction. Since the triplet energy of TPP is higher than the radical pair energy of TPP−iodoanisole and −bromoanisole systems, no such triplet induction is observed.

The observed $k_{isc(I)}$ values gave explicit information about the role of the heavy atom based on the energy gap between ^{3}TPP and the singlet radical pair of the systems. The extent of heavy atom effect is clearly evidenced on comparing the $k_{isc(I)}$ values of similar energy gap systems along with the presence

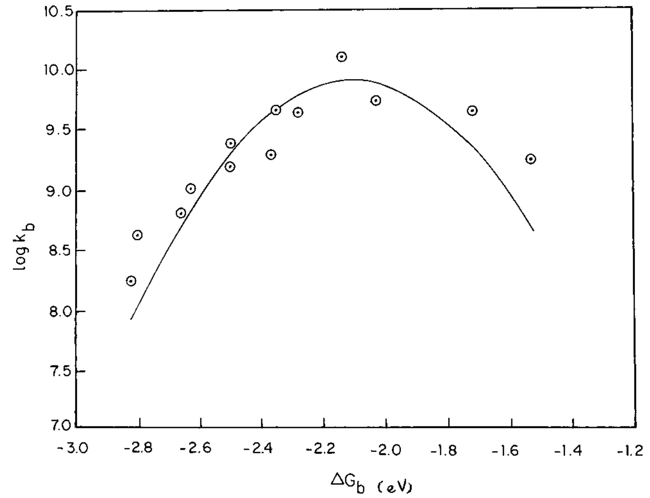


Figure 4. Plot of log k_b *vs* ΔG_b. The curve was drawn using k_b values calculated on the basis of eq 20 with the following fitting parameters: $\lambda_i = 0.5$ eV, $V = 1.8 \times 10^{-3}$ eV (14 cm^{-1}), $\lambda_s = 1.1$ eV, $h\nu = 0.1363$ eV.

of heavy atom in one of the systems. The energy gap between ^{3}TPP and the radical pair of TPP−iodobenzene and TPP−toluene is of the order of 0.2 eV, and the triplet induction is observed only in the case of the iodobenzene system.

Generally, the $k_{isc(I)}$ value increases with decreasing energy gap between the radical pair and triplet state of the sensitizer. In our case, the $k_{isc(I)}$ value for TPP−bromotoluene system with the energy gap of 0.05 eV (403 cm^{-1}) is lower than that of the TPP−bromobenzene system with the energy gap of 0.36 eV, and the reason for this can be rationalized as follows. The smaller energy gap leads to thermal equilibrium between the triplet and the radical pair states and in turn results in the back intersystem crossing to the radical pair state, which clearly influences the $k_{isc(I)}$ value. The back intersystem crossing at room temperature due to the smaller energy gap was already known in the case of aromatic thione systems.[46c]

k_b values obtained from eqs 12 and 13 after substituting for the $k_{isc(I)}$ and k_{esc} are listed in Table 3, and Figure 4 represents the plot of log k_b *vs* ΔG_b, where ΔG_b is the free energy change for back electron transfer and is given by

$$\Delta G_b = E_{1/2(\text{red.})} - E_{1/2(\text{oxid})} \tag{19}$$

The experimental k_b value increases with increasing exothermicity of ΔG_b in the downhill region, and the k_b values are close to the diffusion limit in the middle region. In the region of $\Delta G_b < -2.00$ eV, the k_b value begins to decrease and shows Marcus inverted behavior.

A well-known semiclassical expression is used for the calculation of the back electron transfer rate constant.[47] Generally, the back electron transfer rate constant is derived from the product of V^2 and Franck−Condon weighed density of states. The Franck−Condon term shows dependence on the exothermicity of ΔG_b.

$$k_b = \left(\frac{\pi}{h^2\lambda_s k_B T}\right)^{1/2} |V|^2 \sum_{w=0}^{w=\infty} \frac{e^{-S} S^w}{w!} \exp\left\{-\frac{(\lambda_s + \Delta G_b + wh\nu)^2}{4\lambda_s k_B T}\right\} \tag{20}$$

where V is the electronic coupling matrix element and generally describes the coupling of electronic states of the reactants with those of the products and is normally of the order of 2×10^{-3} eV for aromatic compounds, and $h\nu$ is the average energy of the active vibrational mode. In the case of aromatic compounds, the mean vibrational frequency, ν, is commonly chosen between 1000 and 1500 cm^{-1} which is the typical value for in-plane C−C skeletal vibration. S is the electronic vibrational coupling constant, and it is related to λ_i and $h\nu$ by $S = \lambda_i/h\nu$, and λ_s and λ_i are the solvent and vibrational reorganization energies, respectively.

The curve-fitting procedure was adopted to find the best fit values. The three parameters λ_s, λ_i, and V were varied in order to obtain a good correlation between the calculated and experimental k_b values. The values of λ_s and λ_i are varied for every ±0.05 eV, keeping the value of V constant. The k_b values calculated on the basis of eq 20 using the following fitting parameters, $V = 1.8 \times 10^{-3}$ eV, $\lambda_i = 0.5$ eV, and $\lambda_s = 1.1$ eV, and $h\nu = 0.1363$ eV are consistent with the data obtained.

The fitted λ_s value can be used to calculate the separation distance using the dielectric continuum model,[32] which in turn justifies the k_{esc} value judiciously used in the evaluation of k_b

$$\lambda_s = \frac{e^2}{(4\pi\epsilon_0)}\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}}\right)\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_s}\right) \tag{21}$$

where r_1 and r_2 are the molecular radii of the fluorescer and quencher and is of the order of 6.5 and 3 Å, respectively. r_{12} is the distance between the fluorescer and the quencher; ϵ_0 and ϵ_s are the optical and the static dielectric constants of the solvent. The same expression is employed in the determination of r_{12} for both the geminate radical pair and encounter complex from the fitted λ_s and λ_s from the forward electron transfer reaction (0.4 eV), and the values obtained are of the order of 13.2 and 7 Å, respectively. Since the electron is removed from the π cloud of the quencher, the uncertainty involved in the substitution of ionic radii by molecular radii is subtle during the estimation of r_{12} for the geminate radical pair. On the basis of the r_{12} values obtained from the above expression, the k_{esc} calculated using eq 14 is of the order of 5.4×10^8 s^{-1} and is consistent with the 5×10^8 s^{-1} value used in the calculation of k_b. The higher reorganization energy in the case of back electron transfer within the geminate radical pair compared to the forward electron transfer reaction can be justified on the basis of the separation distance. The apparent increase in λ_s with increasing separation distance was already observed for variety of systems.[48] The increase in λ_s was substantiated by calculating the difference in λ_s using the following expression, and the value obtained is around 0.5 eV.

$$\Delta\lambda = 7.36\left(\frac{1}{R_{ec}} - \frac{1}{R_{grp}}\right) \tag{22}$$

The higher reorganization energy in the case of back electron transfer is attributed to the existence of the enhanced activation barrier in forming the ground state molecules from the radical pair.[48]

The smaller V value can also be explained using orbital overlap and the radical pair separation distance. The diffused molecular orbitals due to the larger size of the TPP molecule and the delocalization of electrons in all the benzene rings lead to reduced orbital overlap and in turn are reflected in the smaller V value of 1.8×10^{-3} eV (14 cm^{-1}) compared to those of aromatic compounds.[42] The influence of separation distance on the V value was already explained beyond scepticism by Miller *et al.*[49] and Gould *et al.*[15c] The earlier results reveal the variation of V value from 10 to 160 cm^{-1} as the separation distance varies from 11 to 6 Å.[50]

The plot of log k_b *vs* ΔG_b is very helpful to select the system for the process of cosensitization.[42] The concept of cosensitization was already explained by Gould *et al*., and the implication of this process is quite significant in the photooxygenation of olefins.[51a,b]

The $PhI^{\bullet +}$ is a well-known photoinitiator for cationic polymerization,[51c] and the combined system of TPP−iodobenzene could not function as a photoinitiator due to the higher homogeneous recombination and intersystem crossing of the radical pair rather than separation. From the radical yield values represented in Table 3, it is obvious that the TPP−benzene system produces a high radical yield and can act as cosensitizer for increasing the radical yield of iodobenzene.

Conclusion

Fluorescence quenching of TPP by benzene derivatives (halogenated benzenes, anisoles, and toluenes) were carried out in acetonitrile, and the presence of the electron transfer mechanism was established by flash photolysis technique. Rehm−Weller behavior is observed in the plot of log k_q *vs* ΔG_{et} which confirms the presence of the electron transfer mechanism. It is a usual practice to calculate the k_q values by taking the k_d value from the Debye expression, and the deviation between the calculated and observed k_q values is used to establish the mechanism of the electron transfer process. Here it is demonstrated that sometimes inaccurate estimates from the Debye expression may lead to misjudgment of the mechanism, and hence the calculation of the k_d value using Smoluchowski's expression is stressed using the experimentally determined diffusion coefficients. Marcus inverted region is observed in the back electron transfer rate constant in the region of $\Delta G_b < -2.03$ eV.

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