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The deuterium effect on electrochemiluminescence efficiencies of anthracene and phenanthrene

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Abstract. The effect of deuteration on the electrochemiluminescence (ECL) efficiencies of the mixed systems containing anthracene or phenathrene has been examined using the single light pulse in the double potential programme. Deuteration of anthracene or phenanthrene decreases the ECL efficiencies by factors of 1·2–16·0. This decrease appears to arise from the quenching of the triplets by radical ions in solution. The quenching factors are estimated by using Marcus theory of electron transfer reactions.

Keywards : Deuterim effect; Electrochemi luminescence; electron transfer.

1. Introduction

The electronically excited states of molecules are produced by radical ion annihilation reactions in electrochemiluminescence (ECL) of aromatic hydrocarbons (Hercules 1971, Hoijtink 1968, Bard *et al* 1968). Once formed, the excited molecules behave in a manner identical with those produced by irradiation. Thus both radiative and non-radiative processes occur. Deuterium isotopic substitution in aromatic hydrocarbon alters the non-radiative processes due to changes in the Franck-Condon factor which depends on the square of the vibrational overlap integral; as a result of this the fluorescence efficiencies of anthracene and phenanthrene decrease by deuterium substitution due to increased singlet-triplet intersystem crossing (Birks 1970, Li and Lim 1972).

The present investigation has been undertaken with a view to examine the deuterium effect on ECL efficiencies. For this purpose we have chosen several mixed systems ECL reactions involving anthracene-h_{10} or - d_{10} and phenanthrene-h_{10} or - d_{10}. ECL studies of mixed systems are less complicated than the pure systems due to greater stability of the cations taking part in the electron transfer reactions. The cations of anthracene and phenanthrene have very short lifetimes (Phelps *et al* 1967, Faulkner and Bard 1968, Werner *et al* 1970) in conventional solvents for detailed examination of ECL efficiencies for the deuterium effect studies. The advantages of mixed system ECL reactions under this situation had recently been discussed in earlier publications (Periasamy and Santhanam 1975, Tachikawa and Bard 1973).

2. Experimental

Anthracene - d_{10} (Aldrich Chemical Co.) was purified by vacuum sublimation. Zone refined samples of anthracene - h_{10}, phenanthrene - h_{10} and phenanthrene - d_{10}

were used. Purification of N, N, N′, N′-tetramethyl-*p*-phenylenediamine (TMPD), tri-*p*-tolylamine (TPTA), N, N′-diphenyl-*p*-phenylenediamine (DPPD), tetra-*n*-butyl ammonium perchlorate (TBAP), 1, 2-dimethoxyethane (DME and other experimental details have been described (Periasamy and Santhanam 1974).

The efficiencies were measured by the use of an integrating sphere similar to the one used by Zweig *et al* (1968) and Bezman and Faulkner (1971). The integrating sphere was made out of a spherical flask (5 *l* capacity and i.d. 22 cm). The sphere was provided with two pyrex tubes projecting outwards; one of the tubes (i.d. 2 cms) holds the ECL cell and the other (i.d. 6 mm). situated at 90° to the cell mount, houses the photomultiplier tube. The inner surface of the integrating sphere was spray-coated with MgO dispersed in acetone. A highly stable noncracking coating was obtained and the stability of the coating was checked by manual shock treatment. The outside of the sphere was mirrored with silver and the mirror was protected by a thin coating of lacquer and black tape on top of it.

The conditions necessary for a good integrating sphere are (*a*) constancy of the photomultiplier output for a given light source when placed anywhere inside the sphere except in direct view of the photomultiplier and (*b*) constancy of the photomultiplier output over a period of time during constant illumination. These two conditions were fulfilled largely in the present experimental work.

The photomultiplier output is directly converted into quanta emitted by the source using standard source calibration. The standard source was a tungsten lamp operated at 4 volts and 250 mA. The absolute intensity of the light source was measured by ferrioxalate actinometry. The actinometric value was corrected for the reflectivity losses at the air-solution interface (reflectivity = 1/49).

3. Results

All the efficiency measurements reported in this work were obtained on the single light pulse generated from sequential potential step programme. The details of the experimental techniques have been described earlier (Periasamy and Santhanam 1974, Bard *et al* 1973).

Figure 1 shows the cyclic voltammetric curves of anthracene-h_{10} and anthracene-d_{10}. The cathodic peak potentials for the two systems are identical with $E_{pc} = -2{\cdot}10$ V *vs* SCE. The cathodic peak potential of phenenthrene was situated at $-2{\cdot}58$ V *vs* SCE. The anodic peak potentials, E_{pa}, of the oxidants used in the present ECL investigation are 0·91 V *vs* SCE for TPTA, 0·19 V for TMPD and 0·40 V *vs* SCE for DPPD.

The cyclic voltammetric cathodic peaks of anthracene and phenanthrene exhibited reversibility by the appearance of anodic peak; the anodic peak is slightly displaced towards anodic potentials due to iR effects arising from the use of low dielectric constant solvent. Voltammetric patterns reported here for the oxidants have agreed with the previous reports (Periasamy and Santhanam 1974).

Figure 2 shows the ECL emission spectrum obtained with anthracene-h_{10} and -d_{10} with two different oxidants. These spectra are identical with fluorescence spectra of anthracene -h_{10} and -d_{10}. With $TPTA^+$ used as the oxidant in the ECL experiments, a longer wavelength emission at 540 nm is observed. This

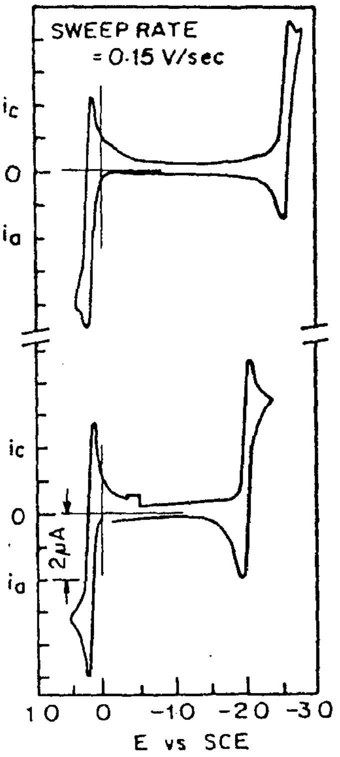


Figure 1. Cyclic voltammogram of 3 mM phenanthrene-TMPD (upper curve) and 3mM anthracene-TMPD (lower curve) at platinum working electrode. The solvent employed is DME.

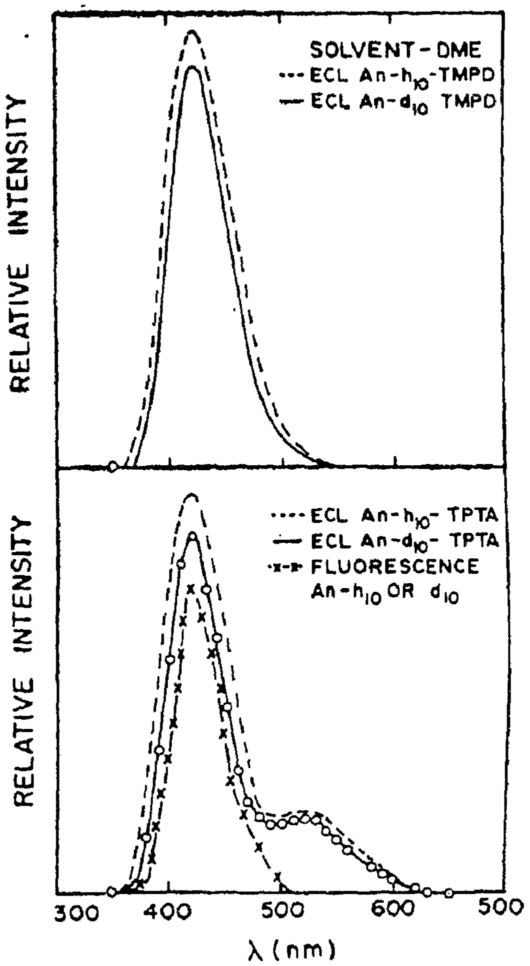


Figure 2. ECL spectra in the reaction between anthracene-h_{10}^- or-d_{10}^- with TMPD$^+$ (upper figure) or TPTA$^+$ (lower figure). The fluorescence spectra of anthracene-h_{10} or anthracene-d_{10} is also indicated for comparison.

emission is assumed to be due to heteroexcimer emission. Excimer formations in ECL experiments of undeuterated molecules is well recognised (Chandross *et al* 1965) and in the present work heteroexcimer emissions are observed with deuterated anthracene and phenanthrene.

The ECL emission spectral regions of the several mixed systems are given in table 1, indicating a common feature at 350–450 nm. This common feature arises due to the emission from the excited singlet state of anthracene or phenanthrene, since the fluorescence emission features are situated at 410 nm and 380 nm for anthracene and phenanthrene respectively. However, the formation of excited singlet state directly in the electron transfer reaction *via*

$$R^- + A^+ \rightarrow R^* + A \tag{1}$$

where R^- is the free radical anion of anthracene or phenanthrene, A^+ is the free radical cation of TMPD, TPTA or DPPD, appears to be unlikely on the grounds of energy considerations. Figure 3 represents the enthalpies of the electron transfer reactions and the location of the excited states. In general the excited singlet state formation of anthracene or phenanthrene appears to be favoured *via* the

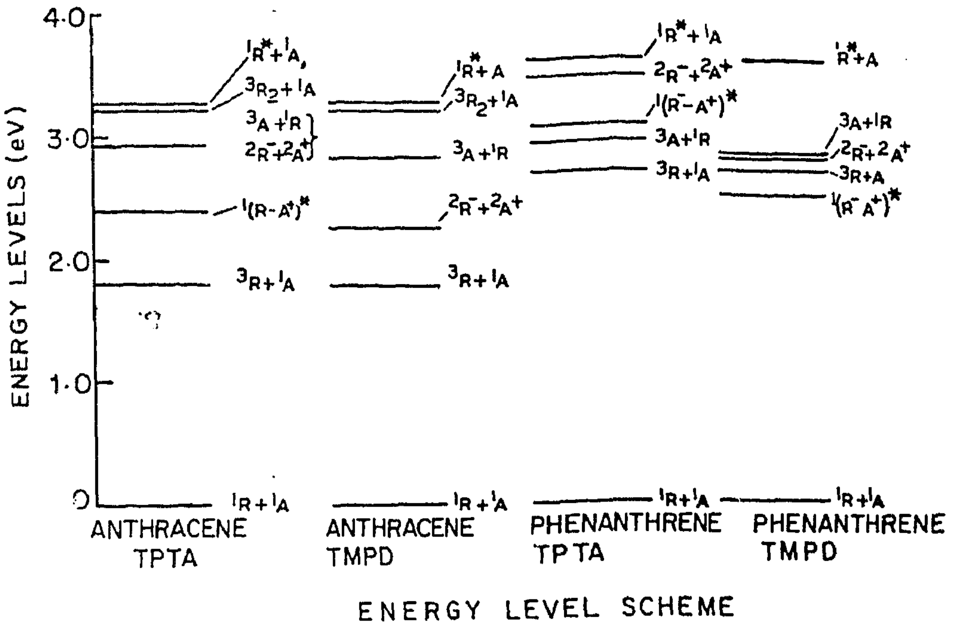


Figure 3. Energy level scheme for the mixed systems. Anthracene or phenanthrene is represented by R and TPTA or TMPD is represented by A. The symbols used in the figure represents, first excited singlet state (${}^1R^*$), the first triplet state (${}^3R$), the second triplet state (${}^3R_2$), the doublet state of the radical (${}^2R^-$), and the heteroexcimer (${}^1(R^- A^+)$). Similar notations apply to A.

triplets; triplet-triplet annihilation possibly leads to the excited singlet state formation *via*

$$R^- + A^+ \longrightarrow {}^3R + A \xrightarrow{{}^3R} R^* + R \qquad (2)$$

it is possible to form the excited singlet state of A in the phenanthrene -TPTA mixed systems, on energetic grounds, but contribution to ECL emission coming from triplet-triplet annihilation of TPTA is less likely due to short lifetime of TPTA (*see* subsequent discussion).

Table 1. Electrochemiluminescence spectral data for the mixed system ECL region

System	350–450 nm	500-550 nm	600 nm
An $(-h_{10})^-$-TPTA$^+$	+	+	—
An $(-d_{10})^-$-TPTA$^+$	+	+	—
An $(-h_{10})^-$-TMPD$^+$	+	—	—
An $(-d_{10})^-$-TMPD$^+$	+	—	—
An $(-h_{10})^-$-DPPD$^+$	+	—	—
An $(-d_{10})^-$-DPPD$^+$	+	—	—
Ph $(-h_{10})^-$-TPTA$^+$	+	+	—
Ph $(-d_{10})^-$-TPTA$^+$	+	+	—
Ph $(-h_{10})^-$-TMPD$^+$	+	—	+
Ph $(-d_{10})^-$-TMPD$^+$	+	—	+
Ph $(-h_{10})^-$-DPPD$^+$	+	—	—
Ph $(-d_{10})^-$-DPPD$^+$	+	—	—

+ Emission observed. — No emission.

The integration of the emission intensity generated by the double potential step programme described by us (Periasamy and Santhanam 1974) provided the pulse areas for different mixed systems, which are employed in the calculation of efficiencies reported in table 3. The efficiencies reported here are the average of ten measurements. The total light output measured in these experiments comprises of contributions from the 350–450 nm and 500–550 nm regions by a choice of TPTA$^+$ oxidant. The contribution coming from the 500–550 nm region is estimated using the isolation filter. The deviations in the pulse areas obtained by the integrating sphere method between any two mesurements are practically negligible (Bezman and Faulkner 1971). The ECL efficiency of pure rubrene system $41\cdot0 \times 10^{-3}$ obtained by this method in DME agrees with the value reported earlier (Periasamy and Santhanam 1974, Bard *et al* 1973).

The efficiencies of anthracene or phenanthrene mixed systems decrease with the oxidant taking part in the ECL reactions in the order TPTA$^+$ > TMPD$^+$ > DPPD$^+$. The decreasing order in efficiency is not changed by generating the cation initially instead of the anion for the ECL reactions.

4. Discussion

The deuterium effect on ECL efficiencies is suggested by the data presented here. The ECL efficiencies of deuterated anthracene or phenanthrene is less than its protonated form by a factor 1·2–16·0. The largest decrease in ϕ_{ECL} is observed with TMPD$^+$ used as the oxidant in the electron transfer reactions; for anthracene the decrease is by a factor of 4 and for phenanthrene it is 16. The observed decrease in ϕ_{ECL} on deuteration is far more than similar decreases of fluorescence efficiencies, ϕ_f, reported in earlier studies. Thus the fluorescence efficiencies of anthracene and phenanthrene decrease by a factor of 1·08 and 1·18 (Berlman 1965).

The ECL efficiency

$$\phi_{\text{ECL}} = \phi_s\, \phi_f. \tag{3}$$

where ϕ_s is the singlet yield in the electron transfer reaction, will decrease on deuteration by the decreasing factor of fluorescence efficiency. However, the expected decrease far surpasses the experimentally determined ϕ_{ECL} suggesting that singlet yields of the deuterated molecules are less than the protonated forms.

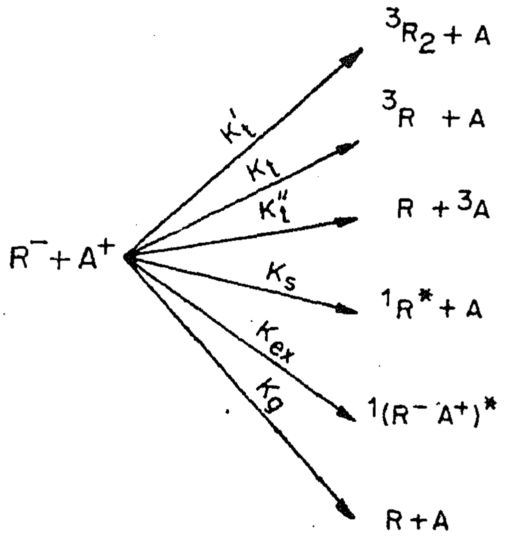
Since the singlet yields in the electron transfer reactions of the mixed systems studied here, comprises of triplet yield, ϕ_t, the triplet-triplet annihilation probability, p, and the quenching factor, θ, of the triplet states by the radical ions in solution, eq. (3) can be modified as

$$\phi_{\text{ECL}} = p\phi_t\, \phi_f\, (1-\theta). \tag{4}$$

Eq. (4) suggests that the lower ϕ_{ECL} values of deuterated molecules arises probably from the alteration of the values of any one of the parameters on the right hand side. The evaluation of these parameters are discussed in the following sections.

Evaluation of ϕ_t

The electron transfer reactions involving small free energy, $\triangle G$, changes can be well understood as adiabatic process involving an activation energy, $\triangle G^*$. Marcus (1965 *a, b*) theory of electron transfer reactions as applied to ECL allows calculation of rate constants in the reaction



(5)

with

$$k = gzk'\rho \exp\left(\frac{-\Delta G^*}{RT}\right) \tag{6}$$

where g is the statistical factor, Z is collisional frequency for uncharged species in solution usually taken at 10^{11} M^{-1} sec^{-1}, k' and ρ are usually taken as close to unity. The free energy of activation is given by

$$\Delta G^* = \left(\frac{\lambda}{4}\right)\left[1 + \frac{\Delta G^\circ}{\lambda}\right]^2 \tag{7}$$

ΔG° is the standard free energy of reaction in any one path in reaction (5) and

$$\lambda = \lambda_0 + \lambda_i \tag{8}$$

which represents the sum of the outer sphere reorganisation free energy, λ_0, and the inner sphere reorganisation free energy, λ_i attributed to structural differences of the reactants in the initial and final electronic states. For the electron transfer processes involving aromatic hydrocarbons or heteroaromatics and their anions, the inner sphere reorganisation free energy is negligible with respect to λ_0 (Hoijtink 1973).

Van Duyne and Fischer (1974) have estimated λ_0 values for several electron transfer reactions involving aromatic hydrocarbons from the homogeneous electron exchange rate constants obtained through ESR studies. The data presented in table 2 are obtained using the λ_0 values reported by them.

The location of various spectroscopic states of anthracene and phenanthrene are shown in figure 3. The rate at which these states are produced in the electron transfer reactions are given in table 2. The triplet yield, ϕ_t, reported in table 3, is obtained as the ratio of the rate constant $k_t + k_t' + k_t''$ to sum of all the rate constants yielding different products. The ϕ_t values are unity for several mixed system ECL reactions except for systems where heteroexcimer is formed directly in the electron transfer reactions (*see* subsequent discussion). The possibility of near unit efficiency of ϕ_t for mixed system electron transfer reactions has been considered by using triplet-interception technique (Freed and Faulkner 1972). For

Table 2. Calculated rates of production of excited states[a]

System[b]	ΔG	Singlet State $^1R^*$			First Triplet State ^3R			Second Triplet State ^3R					Excimer $(R^- A^+)^*$			A^3
		ΔG°	ΔG^*	k_s	ΔG°	ΔG^*	k_t	ΔG°	ΔG^*	k_t'	ΔG°	ΔG^*	k_{ex}	ΔG°	ΔG^*	k_t''
	(eV)	(eV)	(eV)	M^{-1} Sec^{-1}	(eV)	(eV)	M^{-1} Sec^{-1}	(eV)	(eV)	M^{-1} Sec^{-1}	(eV)	(eV)	M^{-1} Sec^{-1}(	eV)	(eV)	M^{-1} Sec^{-1}
Anthracene-TPTA	2·95	0·33	0·44	$2\cdot1 \times 10^4$	−1·13	0·25	$3\cdot4 \times 10_9$	0·27	0·29	$7\cdot5 \times 10^5$	−0·35	0·005	2×10^{10}	0·01	0·11	9×10^8
Anthracene-DPPD	2·44	0·84	0·95	$7\cdot7 \times 10^{-7}$	−0·62	0·016	$3\cdot9 \times 10^{10}$	0·78	0·85	$1\cdot2 \times 10^{-4}$						
Anthracene-TMPD	2·26	1·02	1·21	5×10^{-12}	−0·44	$5\cdot4 \times 10^{-5}$	$7\cdot5 \times 10^{10}$	0·96	1·11	4×10^{-9}				0·77	0·83	$3\cdot5 \times 10^{-1}$
Phenanthrane-TPTA	3·48	0·12	0·18	$1\cdot5 \times 10^7$	−0·79	0·068	5×10^9	0·69	0·73	$1\cdot9 \times 10^{-2}$	−0·38	0·003	$2\cdot2 \times 10^{10}$	−0·52	0·003	$6\cdot5 \times 10^{10}$
Phenanthrane-DPPD	2·97	0·63	0·65	$1\cdot2 \times 10^{-1}$	−0·28	0·016	$3\cdot9 \times 10^{10}$	1·20	1·54	$2\cdot2 \times 10^{-16}$						
Phenanthrene-TMPD	2·79	0·81	0·79	$1\cdot2 \times 10^{-5}$	−0·10	0·068	5×10^9	1·38	1·80	$1\cdot1 \times 10^{-22}$	−0·31	0·01	$1\cdot7 \times 10^{10}$	0·04	0·135	$1\cdot1 \times 10^9$

[a] Solvent reorganisation energy $\lambda_0 = 0\cdot45$ eV in the solvent DME.

[b] For protonated and deuterated molecules.

the mixed system 10-phenyl phenathiozine-fluoranthene the $\phi_t = 0{\cdot}82 \pm 0{\cdot}18$ has been determined experimentally. Extending Marcus theoretical calculations for this situation gives $k_s = 8 \times 10^{-3}$ and $k_t = 6{\cdot}2 \times 10^{10}$ for fluoranthene and $k_t = 6{\cdot}2 \times 10^{9}$ for phenyl phenathiozine ($\lambda_0 = 0{\cdot}32$ eV). These rate constant values yield $\phi_t \approx 0{\cdot}91$ for fluoranthene which is supported by the experimentally determined value.

The formation of ^3A appears to be possible only in the case of TPTA-Anthracene or TPTA-phenanthrene mixed systems due to large enthalpy changes in the electron transfer reactions of these systems. The value given in table 3 includes this factor and the ECL efficiency represents

$$\phi_{\text{ECL}} = \phi_f \phi_t\, p\,(1-\theta) + \phi_f' \phi_t' p' (1-\theta') \tag{9}$$

where primes represent the efficiencies of TPTA. However, the contribution from the second term may be considered negligible due to very short lifetime (n sec) of ^{3}TPTA (Zachariasse 1972). It is assumed that ^{3}TPTA formed in the electron transfer reaction transfers its energy to the aromatic hydrocarbon by favourable disposition of the relative triplet energy levels. Essentially, the contribution to ECL probably arises from the aromatic hydrocarbon.

Evaluation of triplet quenching

The very low ECL efficiencies of the anthracene and phenanthrene mixed systems is explainable on the assumption that triplet or excited singlet state quenching is highly favoured over the triplet-triplet annihilation process. In evaluating the quenching factor, θ, we have considered the possible fluorescence quenching by radical ions. The fluorescence quenching of several aromatic hydrocarbons by TMPD$^+$ has been experimentally observed (Faulkner and Bard 1969, Van Duyne 1973) and the quenching is diffusion controlled with $k \approx 10^{10}$ M^{-1} S^{-1}. This rate constant value, along with the lifetime of the excited singlet state of anthracene 4·9 n sec (Birks 1970) gives the fluorescence efficiency to be reduced to 4/5th of its original value (from Stern-Volmer relationship). However, the fluorescence efficiency of phenanthrene will be reduced to about 2/7th of its original value because of its lifetime of 56 n sec (Birks 1970). This discussion should hold good for both deuterated and protonated forms as the fluorescence lifetimes are seldom affected by deuteration (anthracene-h_{10} = 4·9 n sec; anthracene-d_{10} = 4·9 n sec.).

The probability of two triplets annihilating to give the excited singlet state is estimated as 0·04 for anthracene and 0·025 for phenanthrene (Parker 1970). Inclusion of these values in eq. (4) gives θ, which are given in table 3. These results suggest that a very small fraction of the triplets produced in the ECL experiments is involved in the ultimate formation of the excited singlet state.

On the basis of the above discussion, the deuterium effect on ECL efficiencies can be interpreted as coming from higher quenching factor with deuterated molecules.

The ECL efficiency shows variations with oxidant employed in the electron transfer reactions. In a previous paper (Periasamy and Santhanam 1974), we had reported such variations with rubrene system. We could not propose an explanation for such behaviour earlier, which possibly arises from the differences in extent of quenching by different cations. Evaluation of θ, for phenanthrene and anthra-

Table 3. Efficiencies of mixed systems[a]

System	ϕ_{ECL} $\times 10^4$	ϕ^{E}_{ECL} $\times 10^4$	ϕ_t[b]	ϕ_f	θ[c]
Anthracene-h-$_{10}$-TPTA	2·50	0·90	$4\cdot0\times10^{-2}$	0·24	35·0
Anthracene-h_{10}-TMPD	0·58	..	1·0	0·24	99·40
Anthracene-h_{10}-DPPD	0·014	..	1·0	0·24	99·98
Anthracene-d_{10}-TPTA	2·10	0·90	$4\cdot0\times10^{-2}$	0·22	40·0
Anthracene-d_{10}-TMPD	0·19	..	1·0	0·22	99·79
Anthracene-d_{10}-DPPD	0·009	..	1·0	0·22	99·99
Phenanthrene-h_{10}-TPTA	0·7	2·80	0·76	0·037	90·0
Phenanthrene-h_{10}-TMPD	0·048	0·0025	0·22	0·037	97·5
Phenanthrene-h_{10}-DPPD	0·004	..	1·0	0·037	99·96
Phenanthrene-d_{10}-TPTA	0·33	0·67	0·76	0·031	95·3
Phenanthrene-d_{10}-TMPD	0·003	0·023	0·22	0·031	99·8
Phenanthrene-d_{10}-DPPD	0·0012	..	1·0	0·031	99·98

[a] Efficiencies are measured in DME.

[b] The calculated value of $k_t + k_t' + k_t'' / (k_t + k_s + k_{ox} + k_g + k_t' + k_t'')$; k_g ground state singlet production is negligibly small and is neglected.

[c] Values in per cent.

ϕ^{Ex}_{ECL} = Efficiency of the excimer component.

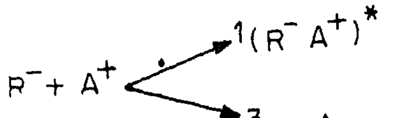
cene, where different oxidants are used in the electron transfer reactions, suggest differences in the magntiude of triplet quenching.

Comparison of ϕ_{ECL} of pure and mixed systems

The efficiency of the pure anthracene—h_{10} system has been reported to yield a value of 6×10^{-5} (Hercules 1971). This value is closer to the mixed system ϕ_{ECL} given in the present work. Evaluation of the relative rates of production of excited singlet and triplet states of anthracene in the electron transfer reaction of the pure system gives $k_s = 7\cdot5 \times 10^7$ and $k_t = 4\cdot5 \times 10^9$. These rate constants give singlet yield in the electron transfer reaction as 0·0164, which would contribute 0·0049 to ϕ_{ECL}; the other contribution to ϕ_{ECL} coming from the triplet route would be small. Hence the lower ϕ_{ECL} value of pure anthracene-h_{10} system appears to arise from factors like the instability of the anthracene cation (Bard *et al* 1968).

Heteroexcimer formation

The mechanism for the formation of heteroexcimer can be assumed as



(10)

competing with the production of ^3R. The mixed triplet interaction has also been considered earlier for the heteroexcimer formation (Zachariasse and Weller 1971). This process is energetically inefficient for the systems reported here as ^3A is not likely to be produced in the electron transfer reactions except with phenanthrene-TPTA systems. However, the absence of magnetic field effect observed with this system suggests that, the percentage of heteroexcimer formed *via* mixed triplet interaction is negligible (Periasamy and Santhanam 1975) with phenanthrene-TPTA system.

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