STUDIES ON EFFICIENCIES OF ELECTRO-CHEMILUMINESCENCE OF RUBRENE

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MS received 9 July 1974; after revision 19 August 1974

ABSTRACT

The electrochemiluminescence efficiencies of rubrene system has been obtained by using the transient method in a variety of solvents. The efficiencies are in the range of $0 \cdot 11 \times 10^{-3} - 4 \cdot 1 \times 10^{-2}$. The mixed system efficiencies are less at least by an order of magnitude in all the solvents except in dimethylsulphoxide. The variation in efficiencies of the pure and mixed systems is explained on the basis of mechanistic differences. In the applied magnetic field, the electrochemiluminescence efficiency of the pure system increases by about 7% and of the mixed system by about 18–25%.

INTRODUCTION

WE wish to report in this paper the electrochemiluminescence (ECL) efficiencies of mixed rubrene system [electron transfer reaction involving rubrene (R) anion and cations of amines or R^{+} and anions of quinones] and the pure rubrene system (electron transfer reaction between R^{-} and R^{+}) by the transient method under identical experimental arrangement. The measured efficiencies of the pure and mixed systems are interpreted on the basis of mechanistic differences between the two systems.

Earlier, Maloy and Bard[1] have reported the ECL efficiency of the pure rubrene system using the steady state method of rotating ring disc electrode. Bezman and Faulkner[2,3] later extended a theory for the ECL efficiency and proposed several factors to be considered in the measurement of efficiencies. However, no attempts were made to measure the ECL efficiencies of the mixed systems either by the steady state or transient methods.

EXPERIMENTAL

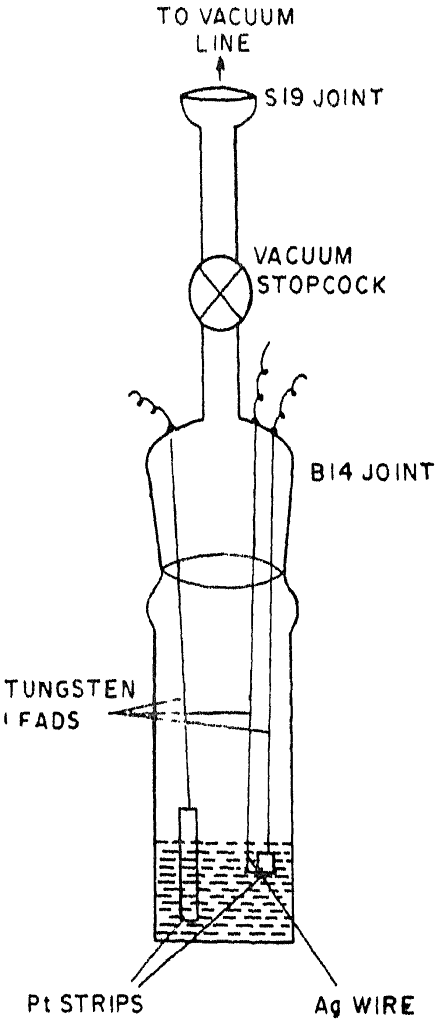
Rubrene was purified by recrystallisation from benzene and stored in a light-proof bottle; *p*-phenylenediamine (PPD) was purified by vacuum sublimation and was stored under vacuum until use. The other samples purified by vacuum sublimation include *o*-phenylenediamine (OPD), *p*-benzoquinone (BQ) and duroquinone (DQ). N, N, N′, N′-Tetramethyl-*p*-phenylenediamine (TMPD) was extracted in ether from TMPD.2HCl after neutralising with NaOH, and later vacuum sublimed. Samples of N, N′-dipheyl-*p*-phenylenediamine (DPPD) and tri-*p*-tolylamine (TPTA) were obtained from Dr. Zachariasse and were used without purification. Polarographic grade tetra-*n*-butyl ammonium perchlorate (TBAP) was vacuum dried and stored in a desiccator.

Solvents were purified by well-established procedures.[4,5] Tetrahydrofuran (THF) was treated with metallic sodium and fractionally distilled over fresh sodium pieces. The distillate is vacuum distilled over $LiAlH_4$ and stored under vacuum over sodium reduced anthracene anions. 1, 2-Dimethoxyethane (DME) was purified in the same way as THF.

N, N′-Dimethylformamide (DMF) was dried over anhydrous $CuSO_4$ overnight and was fractionally distilled under vacuum. The middle fraction is stored in dry argon atmosphere. Reagent grade benzonitrile (BN) was dried over $CaSO_4$ for several days and distilled from fresh $CaSO_4$. The product was distilled under reduced pressure and the middle fraction was stored in argon atmosphere. Dimethylsulfoxide (DMSO) was purified by keeping it over anhydrous Al_2O_3 for over two days and by vacuum distillation under reduced pressure. The middle fraction was stored under dry argon atmosphere.

The cell used in the study is shown in figure 1. Platinum (Pt) strips of areas 3 mm × 2 mm and 2 cm × 3 mm act as test and counter electrodes. A silver wire placed close to the test electrode acts as a quasi reference electrode. The relative positions and orientations of the electrodes have been adjusted such that when placed in the fixed orientation arrangement (to be described later) we have maximum and constant viewing of the test electrode by the photomultiplier tube, and no part of the counter electrode comes in the view of the photomultiplier.

Sample preparations.—Weighed amounts of dry tetra-*n*-butylammonium perchlorate (TBAP) and rubrene (and the amine or quinone) were taken in the ECL cell and dried in vacua. The solvent (THF or DME) was distilled into the cell under vacuum to make up a 2 ml solution. Solutions of DMF, BN and DMSO were prepared by transferring the solvents under dry argon or nitrogen atmosphere. The solutions were degassed by 3-4 freeze-pump-thaw cycles (10^{-4} Torr).



ECL CELL

FIG. 1. Vacuum ECL cell with platinum test electrode and silver reference electrode.

ECL pulses were generated with a double potential step programme by adjusting the potential excursions to go beyond 50–100 mV of the cyclic voltammetric peak potentials. In the present study of comparative ECL efficiencies, the orientation of the ECL cell is fixed with respect to the photomultiplier in a specially designed black box. The clamping arrangements inside the box were such that when the cell is mounted, the test electrode is 5 cm away from the photomultiplier and in line in the sensitive area of the photomultiplier. The constancy of the orientation is checked several times by measuring ECL pulses after repeated remountings.

The photomultiplier (IP21) output under the operating conditions (applied voltage 1000 V) is calibrated in terms of absolute number of photons. This calibration was made with a steady 6·3 V, 2W bulb, fitted with a blue filter, Corning CS-7-59, as the light source whose absolute intensity was determined by potassium ferrioxalate actinometry.

The ECL and fluorescence spectra were recorded with spectrophotofluorimeter built with Hilger-Watts monochromators (D292). RCA IP21 photomultiplier (with a preamplifier) was used as the detector. The magnetic field experiments were conducted with the cell placed between the pole pieces of a magnet (Varian V-4500). The photomultiplier was kept 50 cm away from the magnet and was contained at the end of an aluminium tube.

Cyclic voltammetric curves were recorded with the unit built in our laboratories[6] in combination with Hewlett-Packard *x-y* recorder (135AM). The *iR* effect was found to be negligible in the present arrangement of electrodes and hence no *iR* compensation was given in recording cyclic voltammograms. ECL pulse decay was monitored with a storage oscilloscope HP 181A.

RESULTS

ECL pulses were generated by a double potential step electrolysis method described earlier.[7] The potentials used were selected from an examination of the cyclic voltammetric curves in each of the solvents (table 1). Typical cyclic voltammograms obtained for rubrene in THF and DME are shown

Table 1. *Peak potentials and enthalpy data for rubrene*[a]

Solvent	$R \rightarrow R^+ + e$ E_p V	$R + e \rightarrow R^-$ $-E_p$ V	$-\triangle H^{\circ}$ [b] eV
DME	1·01	1·54	2·39
THF	1·00	1·60	2·44
BN	0·88	1·56	2·28
DMF	0·97	1·48	2·26
DMSO	0·87	1·47	2·18

[a] Potentials are given with respect to saturated calomel electrode. Sweep rate = 50 mV/sec.

[b] The values are calculated with $T\triangle S = 0{\cdot}1$ eV.

For rubrene $E_s = 2{\cdot}30$ eV, $E_T \simeq 1{\cdot}20$ eV,

$-\triangle H^{\circ} = (E_p^{\mathrm{ox}} - E_p^{\mathrm{Red}}) - 0{\cdot}16$ eV.

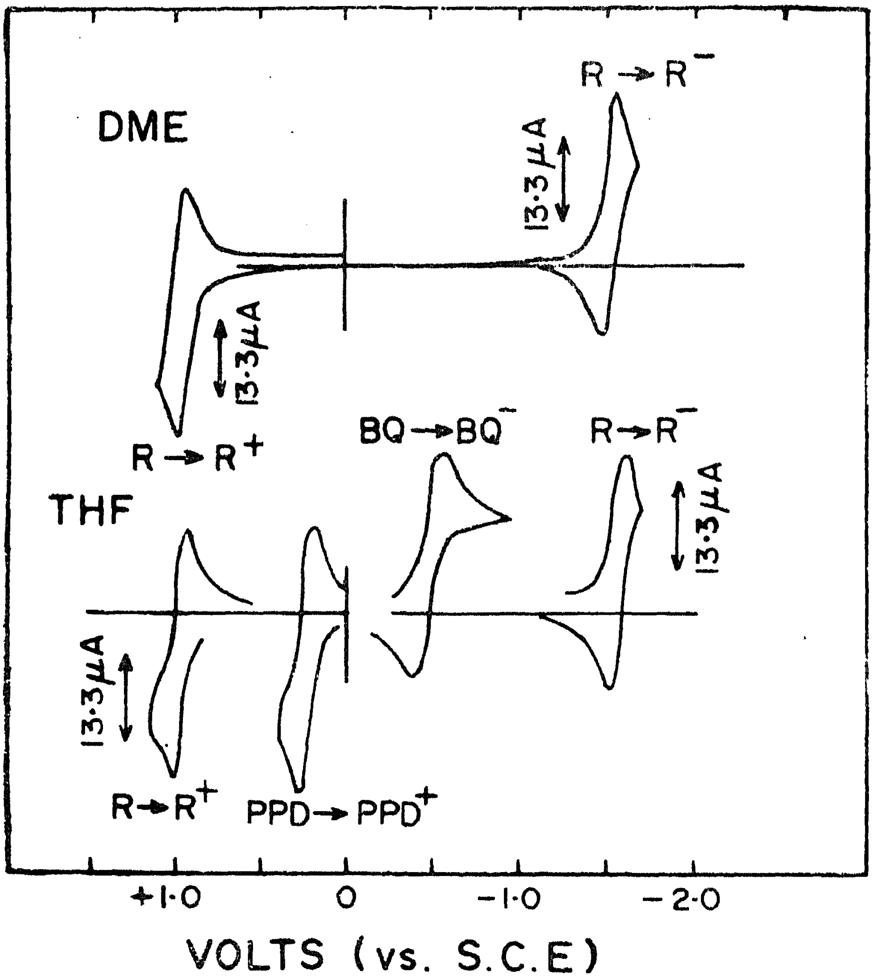


FIG. 2. Cyclic voltammetric curves for rubrene, benzoquinone and *p*-phenylenediamine in THF and DME. Concentrations of the electroactive substances are 1 — 1·1 mM.

in figure 2. Rubrene undergoes reversible 1*e* reduction to form anion radical in these solvents at E_{pc} ranging from — 1·47 to — 1·60 V *vs* SCE. Rubrene undergoes reversible 1*e* oxidation to form radical cation at E_{pa} ranging from 0·87 to 1·0 V *vs* SCE. PPD, TMPD, DPPD and TPTA show reversible 1*e* oxidation peaks and BQ and DQ show 1*e* reduction peaks. Oxidation peak of OPD is reversible only at high sweep rates (1 V/sec). The respective peak potentials in THF are shown in table 2. TPTA oxidation takes place around the same potential where rubrene is oxidised.

The ECL of pure rubrene or mixed system produces an emission with maximum located at 565 nm. This emission is identical with the fluorescence emission of rubrene suggesting that the emission in ECL comes from excited singlet state of rubrene. ECL of rubrene-TMPD and rubrene-TPTA show in addition to the emission with peak around 565 nm another emission at longer wavelength ($>$ 670 nm) which is presumably due to the heteroexcimer emission.

Table 2. *Peak potentials for the mixed systems in THF*[a]

Molecule	$E_p(V)$	$-E_p{}^b(V)$	$-\triangle H^{oc}(eV)$
Rubrene	1·00	1·60	2·44
PPD	0·28	..	1·72
OPD	0·44	..	1·88
DPPD	0·50	..	1·94
TMPD	0·28	..	1·72
TPTA	1·02	..	2·46
BQ	..	0·57	1·41
DQ	..	0·97	1·81

[a] Potentials are with respect to saturated calomel electrode. Peak potentials are for the oxidation of the molecule. Sweep rate = 50 mV/sec.

[b] Peak potentials are for the reduction of the molecule.

[c] Assuming $T\triangle S = 0\cdot 1$ eV. The enthalpy values are for the reaction of rubrene anion or cation and the cations or anions of the molecule indicated in the table $-\triangle H^{c} = (E_p{}^{ox} - E_p{}^{Red}) - 0\cdot 16$ eV.

The calculated enthalpy values for rubrene pure and mixed systems are given in tables 1 and 2 along with the location of the excited singlet and triplet states of rubrene.

The single pulse areas were measured in the fixed orientation arrangement described earlier. In the case of pure system − to + pulse was found to have slightly larger area than the + to − pulse. In the case of mixed systems pulse areas were larger when rubrene radical is generated first. Thus in rubrene-amine systems − to + pulses and in rubrene-quinone systems + to − pulses were considered for Φ_{ECL} calculations. Several pulses were measured for $t_f = 0\cdot 5$ sec (time for generation of the first radical) and the maximum pulse area is considered for the calculations. Table 3 gives the pulse areas measured for rubrene system in different solvents for identical concentration of 1·04 mM. The ECL efficiency Φ_{ECL} is defined as

$$\Phi_{ECL} = \frac{F\int_{t_f}^{\infty} I dt}{\int_{0}^{t_f} i_F dt} \quad (1)$$

Table 3. *Pulse area and ECL efficiency data*

Solvent	Rubrene[a] Pulse area[c] $\times 10^{-10}$	$\Phi \times 10^3$	Rubrene-PPD[b] Pulse area[c] $\times 10^{-10}$	$\Phi \times 10^3$
DME	7·2	41·0	0·49	3·02
THF	6·1	38·3	0·34	2·16
BN	4·6	7·7	0·19	0·35
DMF	2·2	2·5	0·19	0·22
DMSO	0·04	0·11	0·04	0·11

[a] Pulse areas for rubrene concentration of 1·04 mM.

[b] Pulse areas for rubrene (1·04 mM) and PPD (1·1 mM).

[c] Pulse areas in photons.

where F is Faraday, i_F is the faradaic current during t_f, I (photons/sec) is the intensity of ECL emission. The pulse areas (table 3) measured at the fixed orientation arrangement could be related to $\Phi_{ECL} (=\Phi)$ by the following equation (t_f constant)

$$\frac{\Phi_x}{\Phi_y} = \frac{(P.A)_x}{(P.A)_y}\left(\frac{D_y}{D_x}\right)^{\frac{1}{2}} \tag{2}$$

where $(P.A)_x$, $(P.A)_y$ are the pulse areas and D_x, D_y are the diffusion coefficients of rubrene in the two solvents x and y. The diffusion coefficients of rubrene in different solvents are obtained from the cyclic voltammograms. The ratio of Φ_{ECL} in BN and DMF calculated using eq. (1) is 3·1 which is in fair agreement with the value 2·3, reported by Bezman and Faulkner.[3, 8] Hence we chose the value of Φ_{ECL} in DMF[3, 8] as 2·45 Φ 10^{-3} and calculated the Φ_{ECL} in other solvents.

Φ_{ECL} for the mixed system is calculated using eq. (3).

$$\Phi_{\text{mixed}} = \frac{(P.A)_{\text{mixed}}}{(P.A)_{\text{pure}}} \times \Phi_{\text{pure}} \tag{3}$$

Table 3 gives Φ_{ECL} data calculated for rubrene and rubrene-PPD systems in all the solvents. The data indicate that the solvent affects Φ_{ECL}. Secondly, the Φ_{ECL} for a mixed system in a chosen solvent is less by a factor ranging from 11–23 from the pure rubrene system. With DMSO used as solvent, Φ_{ECL} for the pure system equals the mixed system.

With other oxidants used in the electron transfer reaction the trend observed with PPD$^+$ has been maintained (*see* table 4). The mixed system containing rubrene and TPTA gives a higher Φ_{ECL} than the pure or other mixed systems. With this mixed system both rubrene and TPTA are oxidised at about the same potential thus involving both rubrene cation and TPTA$^+$ in the electron transfer reactions with rubrene anion. It is interesting to note that the two quinones employed in ECL has produced contrasting results, BQ anion brings about efficient electron transfer reaction while DQ anion does not (*see* discussion).

Φ_{ECL} in the Applied Magnetic Field.—Magnetic field effect on the ECL of rubrene has been studied earlier.[7, 9] In a previous paper[7] we had reported that external magnetic field increases the ECL intenstiy of the pure system by about 13%. In continuation of these studies we have examined the Φ_{ECL} changes in DME and THF at different magnetic fields. The percentage enhancement of total emission in the magnetic field is plotted in figure 3. Since $\int_0^{t_f} i_F dt$ values do not show a change in the applied magnetic field, the quantity $(I_H - I_0)/I_0$ is essentially equal to $(\Phi_H - \Phi_0)/\Phi_0$. The changes in Φ_{ECL} may be interpreted as due to triplet quenching or triplet-triplet annihilation being altered in the magnetic field. The pure system shows smaller changes in Φ_{ECL} than the mixed systems due to complete triplet formation with latter systems whose encounter produces the excited singlet state. The observation of magnetic field effect on the pure system may be explained as due to production of singlets and triplets or triplets alone in the electron transfer reaction. The differences seen in Φ_{ECL} for the pure and mixed system at zero and higher fields tend to support the formation of both singlets and triplets in the electron transfer reaction.

DISCUSSION

The $-\triangle H^\circ$ values for mixed system electron transfer reaction

$$R^- + A^+ \longrightarrow R + A \qquad (4)$$

given in table 2, where A$^+$ is the oxidant, indicate that the excited singlet state of rubrene is formed *via* triplet-triplet annihilation as $E_s > -\triangle H^\circ > E_T$. With rubrene-TPTA mixed system, the above electron transfer reaction occurs with TPTA$^+$ and R$^+$ as TPTA and rubrene are oxidised at about the same potential. The observation of magnetic field enhancement of luminescence intensity is indicative of intermediate triplet states[7, 9, 10] and such an enhancement is observed with all the systems reported here (table 4).

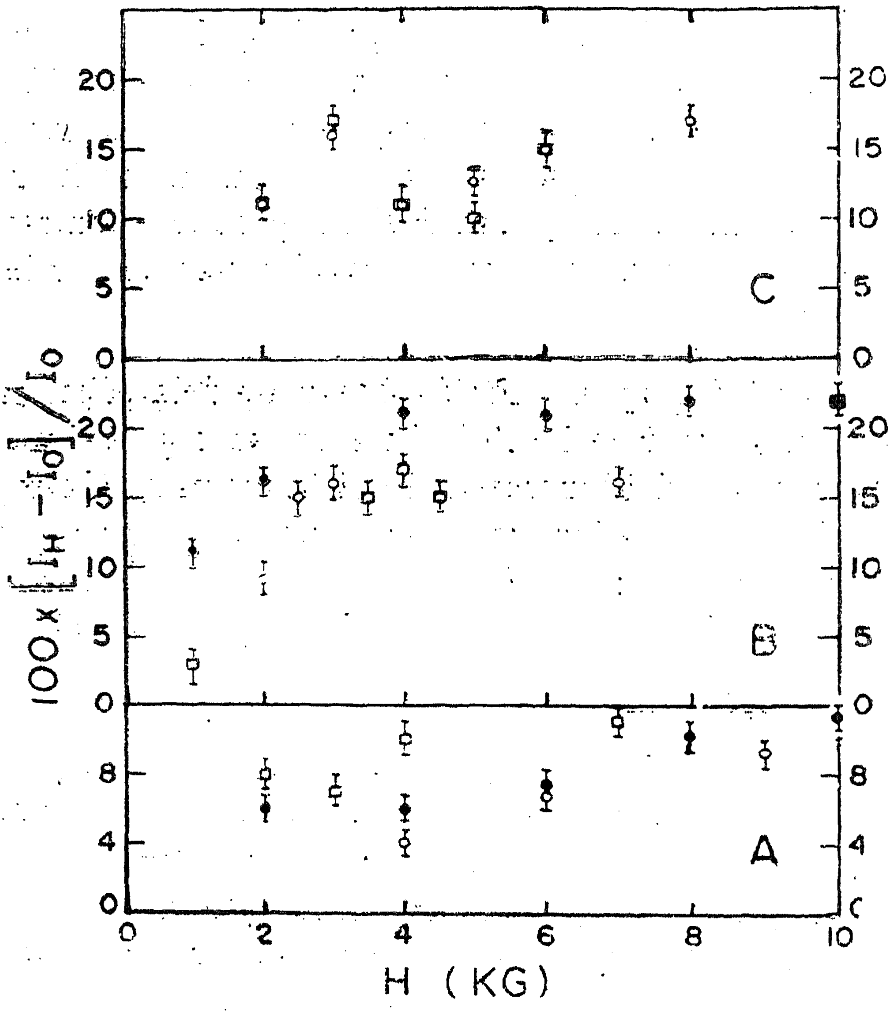


FIG. 3. Magnetic field effects on ECL of rubrene.
A: Rubrene, solvents: DME (○), THF (□) and DMF (●)
B: Rubrene-PPD, solvents: DME (⊙), THF (□) and DMF (●)
C: Rubrene-BQ, solvents: DME (○), THF (□).

The calculated values of $-\Delta H°$ for the pure system (table 1) along with the observation of magnetic field enhancement of luminescence intensity suggests that both singlet and triplet rubrene are formed in the electron transfer reaction

$$R^{-} + R^{+} \begin{cases} \nearrow R^{*} + R \\ \searrow {}^{3}R + R \end{cases} \qquad (5)$$

Part of ECL emission observed from excited singlet state of rubrene can be accounted for as coming *via* triplet-triplet annihilation. Thus the results

Table 4. *Pulse areas and ECL efficiency data for Mixed Systems*[a]

System	Pulse area (photons) $\times 10^{-10}$	$\Phi \times 10^3$	Percentage change in area at 3 KG
$R^- - R^+$	6·1	38·3	7
$R^- -$ PPD$^+$	0·34	2·16	15
$R^- -$ OPD$^+$	0·019	0·12	25
$R^- -$ DPPD$^+$	0·034	0·22	20
$R^- -$ TMPD$^+$	0·48	3·08	20
$R^- -$ TPTA$^+$	7·6	47·5	..
$R^+ -$ BQ$^-$	0·38	2·3	18
$R^+ -$ DQ$^-$	Nil	Nil	..

[a] Solvent THF Concentrations of rubrene is 1·04 mM. Concentration of amine or quinone is 1·05 – 1·1 mM.

presented here have conclusively shown that electron transfer reaction between rubrene cation and rubrene anion is not a singlet route system. In DMSO, the above electron transfer reaction produces presumably only the triplets of rubrene (T-route) due to (*a*) $-\triangle H^\circ < E_S$ and (*b*) lack of sufficient thermal activation to produce the excited singlet state ($kT = 0{\cdot}025$ eV at 20° C).

Relative Efficiencies of Mixed and Pure Systems

The ECL efficiencies of several mixed systems (except rubrene-TPTA) reported here in tables 3 and 4 are less than the pure system by a factor ranging from 11–320. This difference is explained on the basis of mechanistic differences between the pure and mixed systems. In the electron transfer reaction of the pure system excited singlet state is directly accessible since $-\triangle H^\circ > E_S$ (except in DMSO and DMF; *see* subsequent section). In the mixed system the electron transfer reaction produces the triplet state of rubrene which is followed by triplet-triplet annihilation to give excited singlet state of rubrene (except rubrene-TPTA where $-\triangle H^\circ > E_S$). The direct formation of the excited singlet state of rubrene in the electron transfer reaction is excluded on the grounds that the enthalpy of the reaction is very much less than the excited singlet state. Thus with the mixed systems, energy doubling mechanism (triplet-triplet annihilation) and quenching involving the triplet state accounts for the lower Φ_{ECL} values.

Efficiency in DMSO

It is fortuitous that Φ_{ECL} values in DMSO for the mixed and pure systems are equal (table 3). Extending the interpretation proposed in the earlier section, both the mixed and pure systems appear to follow the same mechanistic pathway, *i.e.*, the electron transfer reaction in the pure system does not produce the excited singlet state of rubrene directly, but only through the intermediate triplet state of rubrene. Further support is obtained from the energetics of the electron transfer reaction of the pure system. The reaction enthalpy $-\triangle H^\circ$ for the pure system in DMSO is 2·18 eV which is 0·12 eV less than the energy of the excited singlet state of rubrene ($E_S = 2\cdot30$ eV). Hence the direct formation of excited singlet state of rubrene by electron transfer reaction is unlikely. One considers, then, that the triplet state of rubrene ($E_T = 1\cdot20$ eV) alone is formed in the electron transfer reaction. Thus the pure rubrene system is mechanistically following the same path as the mixed system.

On the basis of the energetics, the $-\triangle H^\circ$ for the electron transfer reaction of the pure system in DMF is $0\cdot04 \pm 0\cdot02$ eV (errors in measurements) less than the E_S of rubrene, but sufficient thermal activation enables the excited singlet state of rubrene directly accessible. As a result, the efficiencies of pure and mixed systems are different in this solvent.

Table 3 shows the variation of Φ_{ECL} with the solvent employed in the ECL experiments. This variation appears to arise from the quenching of the excited singlet or triplet state of rubrene, since Φ_{ECL} decreases with increasing viscosity of the solvent ($\eta_{DME} = 0\cdot43$ cP and $\eta_{DMSO} = 2\cdot003$ cP) and/or solvation differences of the reacting radicals in the different solvents. The greatest solvation of the radical ions is expected to be in solvents like DMF and DMSO.

Efficiency Variation in the Mixed Systems

It is interesting to note that table 2 shows the variation in Φ_{ECL} for different mixed systems with no emission coming from R^+ and DQ^- electron transfer reaction. As no evidence for unusual quenching of fluorescence of rubrene by DQ has been observed in photoluminescence we may conclude that this electron transfer reaction is inefficient to produce the triplet state. The closeness of Φ_{ECL} of $R^- - PPD^+$ ($\Phi_{ECL} = 2{\cdot}2 \times 10^{-3}$) and $R^+ - BQ^-$ ($\phi_{ECL} = 2{\cdot}3 \times 10^{-3}$) points to very little difference existing if the electron is transferred from R^- to PPD^+ or BQ^- to R^+. As a result one is tempted to think that equal amounts of triplets are formed in both the mixed systems with possibly a similar intermediate. The variations in Φ_{ECL} with other oxidants indicate differences in electron transfer efficiencies.

It is interesting to compare the $\Phi_{ECL} = 4{\cdot}8 \times 10^{-2}$ with $TPTA^+$ as oxidant with the value obtained in chemiluminescence,[11] $\Phi_{CL} = 5 \times 10^{-2}$ by actinometric experiments. The chemiluminescence experiments were carried out between R^- and $TPTA^+$ without the presence of extraneous electrolyte. The good agreement seen in the efficiency determined by the two independent methods suggest the absence of significant effect coming from the supporting electrolyte (TBAP). Further the electron transfer efficiencies involving R^- and $TPTA^+$ and R^- and R^+ appear to be nearly equal since ECL experiments employ both R^+ and $TPTA^+$ in the electron transfer reaction.

Quenching of Excited Singlet State by Amines

We have also examined the possibility of quenching of the excited singlet state of rubrene by amines since Rehm and Weller[12, 13] have demonstrated the occurrence of quenching of excited singlet state of aromatic hydrocarbons by amines in photoluminescence. In agreement with the observations of Rehm and Weller[12, 13] we have observed the quenching of the excited single state of rubrene by amines and in particular by PPD. Complete quenching of the excited singlet state of rubrene was observed at a mole ratio of rubrene to PPD of 1 : 50. There is, however, difficulty in extending the quenching factor to ECL experiments as the concentration of the quencher varies with time and distance from the electrode. We, however, estimated the singlet quenching by PPD in ECL by computer simulation procedures to be about 5% in the overall emission zone. This quenching is approximately of the order of accuracy of Φ_{ECL}. Hence, we conclude the quenching of the excited singlet of rubrene by amine in ECL is not dominant in the experimental concentration range.

ACKNOWLEDGEMENT

The authors wish to thank Prof. B. Venkataraman for helpful discussions and Dr. K. Zachariasse for the gift of TPTA and Mrs. S. J. Shah for assistance.

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