

ELECTROGENERATED CHEMILUMINESCENCE. EFFECT OF SOLVENT AND MAGNETIC FIELD ON ECL OF RUBRENE SYSTEMS

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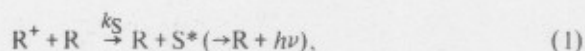
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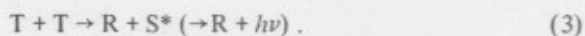
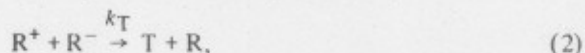
The emission resulting from the electron transfer reaction between radical cations and radical anions of rubrene (5,6,11,12-tetraphenylnaphthacene) generated electrochemically at a platinum electrode (ECL) increases with increasing applied external magnetic field. The extent of this enhancement is greatest for dimethylformamide solutions and for other solvents decreases in the order acetonitrile > benzonitrile > tetrahydrofuran. The results can be interpreted in terms of a model in which the electron transfer reaction produces both triplet and singlet excited states of rubrene (the ST route), with quenching of the triplet states by paramagnetic species (radical ions and/or oxygen). Calculations using the Marcus theory of electron transfer reactions for this system are presented and the possibility of the production of two triplet states upon electron transfer is suggested.

1. Introduction

Although a number of investigations of the electro-generated chemiluminescence (ECL) of rubrene (R) (5,6,11,12-tetraphenylnaphthacene)-containing systems have been reported [1-7], many details in the mechanism of the reaction remain uncertain. One basic question of interest is whether the reaction of the electrogenerated ions ($R^{\cdot-}$ and $R^{\cdot+}$) leads directly and predominantly to the excited singlet state (S^*) (the S route)



or to the triplet state (T), which forms S^* upon triplet-triplet annihilation (the T route)



A third possibility involves the formation of both S^* and T in the radical-ion electron transfer reaction in such amounts that an appreciable fraction of the emitted radiation comes from both paths (the ST route).

The involvement of triplets has been demonstrated by the occurrence of "Feldberg-slopes" [8-10] greater than -1.48 and sometimes near the predicted limit of a pure T route with triplet lifetime controlled by quenching of -2.96 [2, 4]. The magnetic field induced enhancement of rubrene ECL in N,N-dimethylformamide (DMF) solution [5, 7] also demonstrated the occurrence of triplets in the reaction path, since such effects can be explained in terms of variations caused by a magnetic field in both the rate of excited singlet formation by triplet-triplet annihilation and the rate of triplet quenching by paramagnetic species. Independent studies of magnetic field effects on delayed fluorescence in the absence and presence of radical ions [11-13] lend support to this interpretation. The nature and extent of triplet quenching is also of importance in interpreting the ECL results obtained. Triplets may be quenched either by paramagnetic quenchers, P (e.g., $R^{\cdot-}$, $R^{\cdot+}$, O_2) or non-paramagnetic ones, Q:



Such quenching reactions must be invoked to explain the Feldberg-slope results of Chang et al. [2] for benzonitrile (BZN) solutions and of Bezman and Faulkner [4] for both DMF and BZN. The magnetic field enhancements also require the occurrence of the quenching reaction of eq. (4). Visco and Chandross [3] found Feldberg-slopes close to -1.48 for ECL experiments in BZN; this result can only be explained in light of the other results as either the reaction occurring by the T route in the absence of quenching or the reaction occurring by the ST route with strong quenching of the triplets. Moreover, although radical ions are usually invoked as important quenchers of triplets [2,3,5,12,13], especially in explaining previous magnetic field experiments, Bezman and Faulkner [4] suggested that oxygen, generated from residual traces of water, was the paramagnetic quencher, and that the radical ions of rubrene are unimportant as triplet quenchers. Indeed delayed fluorescence measurements have demonstrated a magnetic field effect on quenching of anthracene and pyrene triplets by oxygen in DMF solutions [14], although no effect could be observed for acetonitrile (AN) solutions.

We report here results of magnetic field experiments with rubrene solutions of DMF, AN, BZN and tetrahydrofuran (THF) which contribute to the understanding of the mechanism of ECL in the rubrene system.

2. Experimental

The cells, electrochemical and photometric apparatus have been described previously [5]. Spectroquality acetonitrile (Matheson, Coleman and Bell) was passed through an activated alumina column under a nitrogen atmosphere and drained into a vacuum storage flask. It was distilled into a vessel containing phosphorus pentoxide just before the preparation of the solution to remove water and then it was distilled into a solution preparation vessel. Five freeze-pump-thaw (FPT) cycles were used for de-aeration and the resulting solvent was stored under vacuum.

Spectroquality benzonitrile (Matheson, Coleman and Bell) was purified by two different methods. Either it was passed through an activated alumina column in a dry box before the preparation of the sample, or it was dried by activated molecular sieve

(Linde 4A) before use.

THF (Matheson, Coleman and Bell) was stored under calcium hydride, then distilled into a storage container which contained a sodium mirror. It was allowed to stand for more than 48 hours in contact with the mirror followed by distillation into the cell and de-aeration by several FPT cycles. As supporting electrolyte, polarographic grade tetra-*n*-butylammonium perchlorate (TBAP) was used in all experiments. It was supplied by Southwestern Analytical Chemicals, dried in a vacuum oven at 100°C for 48 hours and stored in a desiccator over anhydrous magnesium perchlorate. It was dried again under vacuum at 100°C for 4–5 hours in some experiments before solvents were distilled into a sample preparation vessel. Rubrene (Aldrich Chemical Co., Inc.) (m.p. $> 300^{\circ}\text{C}$) was purified by double sublimation.

A Varian Model V-3400 electromagnet, with 9-inch pole diameter and 3-inch gap, powered by a Model V-2500 power supply, was employed in all experiments. All solutions were prepared on a vacuum line (10^{-5} torr) and degassed by at least four FPT cycles. The ECL emission was recorded at an applied potential step frequency of 10 Hz (i.e., a step time of 50 msec). The intensity at a given field strength, the average of 10–20 pulses in a train, was divided by the average of zero-field intensity values recorded before and after the measurement to obtain the relative intensity values. A delay of 2 minutes between measurements was employed. Details of these experimental techniques are available [15].

3. Results

A comparison of electrochemical (cyclic voltammetric) data for the oxidation and reduction of rubrene and the reaction enthalpy for the radical ion electron transfer reaction calculated (except for the THF-H₂O mixture) by the equation [5]:

$$-\Delta H^0 = E_p(\text{R/R}^+) - E_p(\text{R/R}^-) - 0.16 \text{ (eV)} \quad (6)$$

is shown in table 1. The singlet energy level, E_S , for rubrene is usually taken as 2.30 eV, although its exact value is not known with certainty [3]. Thus, because of uncertainties in the ΔH^0 and E_S values, it is difficult to judge whether the S route is accessible directly

Table 1
Electrochemical data and reaction enthalpy of rubrene

Solvent ^{a)}	Concentration of rubrene (mM)	Oxidation		Reduction		Reaction enthalpy $-\Delta H^0$ (eV) ^{b)}
		E_p (R/R ⁺) V versus SCE	sweep rate, V/sec	E_p (R/R ⁻) V versus SCE	sweep rate, V/sec	
DMF	1.0	+0.96	0.249	-1.48	0.249	2.28
acetonitrile (AN)	≈0.1	+0.86	0.200	-1.54	0.200	2.24
benzonitrile (BZN)	2.0	+0.87	0.200	-1.53	0.200	2.24
BZN + 36 mM H ₂ O	1.0	+0.89	0.100	-1.52	0.100	2.25
tetrahydrofuran (THF)	0.5	+1.09 ($\Delta E=70$ mV) ^{c)}	0.100	-1.51 ($\Delta E=60$ mV)	0.100	2.44
THF + 40 mM H ₂ O	0.5	+1.12 ($\Delta E=130$ mV)	0.100	-1.55 ($\Delta E=130$ mV)	0.100	2.44

a) The supporting electrolyte was 0.1 M TBAP for all solutions, and a Pt working electrode was employed.

b) Calculated by eq. (5) except for THF-H₂O solution where the equation $-\Delta H^0 = E_{1/2}(R/R^+) - E_{1/2}(R/R^-) - 0.1$ eV was used, where the $E_{1/2}$ values are the average of E_{pa} and E_{pc} .

c) $\Delta E = |E_{pa} - E_{pc}|$.

(i.e., whether the reaction is "energy sufficient"). The location of the triplet level, E_T , is not known from spectroscopic measurements; however, the existence of ECL of rubrene in clearly energy-deficient conditions, e.g., for R⁻/TMPD⁺ (TMPD = N,N,N',N'-tetramethyl-*p*-phenylene diamine) and R⁺/BQ⁻ (BQ = *p*-benzoquinone) [2, 5], as well as ECL emission for the parent, tetracene radical anion, with TMPD⁺ [16] suggests that $2E_T > E_S$, so that E_T is probably near 1.15 eV.

The effect of a magnetic field on the intensity of ECL emission for the rubrene system in the different solvents was investigated; typical results are shown in fig. 1 and the relative ECL intensities at $H = 8$ kG, $I(8\text{kG})/I(0)$, are shown in table 2. The largest magnetic field induced enhancements are observed in the R⁻/TMPD⁺ and R⁺/BQ⁻ systems which also show intensities about two orders of magnitude smaller than the R⁻/R⁺ system in DMF. Bezman and Faulkner [4] showed that the ECL efficiency, ϕ_{ECL} (photons emitted/radical ion electron transfer reaction) was about twice as high for the R⁻/R⁺ system in BZN as it was in DMF.

4. Discussion

The magnetic field results can be explained in terms of either a T or an ST route mechanism. If the mechanism involves a pure T route, it is necessary to

assume a solvent effect on the quenching or triplet-triplet annihilation (TTA) rate constants. We have re-

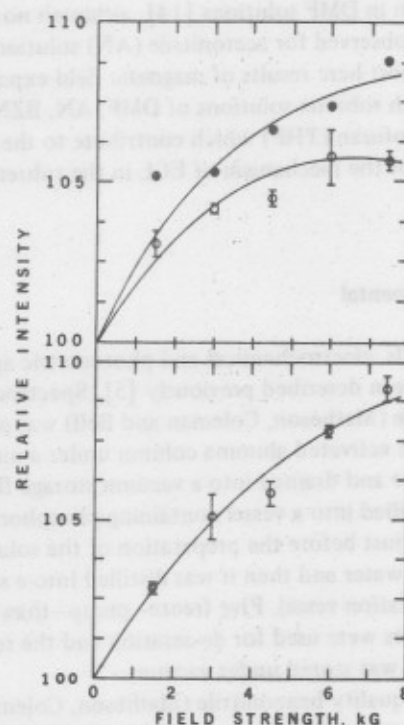


Fig. 1. (a) Magnetic field effects on ECL of (1) 2 mM rubrene, 0.1 M TBAP in benzonitrile (BZN) (2) 1 mM rubrene, 0.1 M TBAP and 36 mM H₂O in BZN. (b) Magnetic field effects on ECL of 0.1 mM rubrene and 0.1 M TBAP in AN.

Table 2
Magnetic field effect and calculated free energies of formation (ΔG^0) and activation (ΔG^*) and rate constants for rubrene ECL

Solvent	System a)	$I(8kG)/I(0)$ %	Free energies of formation (eV) b)		λ c)	Free energies of activation (eV) d)			Rate constants (M ⁻¹ sec ⁻¹)		
			ΔS_G^0	ΔT_G^0		ΔS_G^0	ΔT_G^0	ΔS_G^*	k_S	k_T	k_B
DMF	R ⁻ /TMPD ⁺	28 e)	+0.74	-0.41	0.67	0.741	0.025	0.37	6 × 10 ⁻³	2.8 × 10 ¹⁰	1.4 × 10 ⁴
DMF	R ⁺ /BQ ⁻	15 e)	+0.97	-0.18	0.67	1.00	0.090	0.22	3 × 10 ⁻⁷	2.3 × 10 ⁹	4.8 × 10 ⁶
DMF	R ⁻ /R ⁺	11	+0.02	-1.13	0.67	0.178	0.079	1.09	2.5 × 10 ⁷	3.5 × 10 ⁹	10 ⁻⁸
AN	R ⁻ /R ⁺	9	+0.06	-1.09	0.76	0.221	0.036	0.82	4.8 × 10 ⁶	1.8 × 10 ¹⁰	5 × 10 ⁻⁴
BZN	R ⁻ /R ⁺	6 f)	+0.06	-1.09	0.56	0.161	0.125	1.41	4.9 × 10 ⁷	5.9 × 10 ⁸	10 ⁻¹³
THF	R ⁻ /R ⁺	3 g)	-0.14	-1.29	0.54	0.074	0.261	1.85	1.4 × 10 ⁹	3.0 × 10 ⁶	10 ⁻²⁰
DMF	DPA ⁻ /DPA ⁺	0 e)	-0.04	-1.31	0.67	0.148	0.153	2.35	7.9 × 10 ⁷	2.0 × 10 ⁸	10 ⁻²⁹

a) Abbreviations: R⁻ = rubrene, TMPD = N,N,N',N'-tetramethyl-p-phenylenediamine, BQ = p-benzoquinone.

b) $\Delta S_G^0 = E_p(c) - E_p(a) + 0.06$, $\Delta S_G^0 = \Delta S_G^0 + (E_S + 0.2)$, $\Delta T_G^0 = \Delta S_G^0 + (E_T + 0.10)$; $E_S = 2.30$ eV, $E_T = 1.15$ eV.

c) See table 3.

d) Calculated with eq. (10).

e) $I(8kG)/I(0)$ for system + 36 mM H₂O was 9%.

f) $I(8kG)/I(0)$ for system + 40 mM H₂O was 3%.

e) Ref. [5].

g) $I(8kG)/I(0)$ for system + 40 mM H₂O was 3%.

cently proposed the following equation for magnetic field effects in delayed fluorescence and ECL [13]:

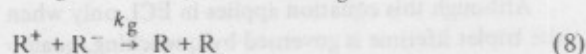
$$\frac{I(H)}{I(0)} = r_\gamma(H) \left[\frac{D+q}{r_D(H)D+q} \right] \quad (7)$$

where $r_\gamma(H) = \gamma(H)/\gamma(0)$, is the ratio of TTA rate constants at field H and at zero field, $r_D = k_D(H)/k_D(0)$, is the ratio of the rate constants for quenching by a paramagnetic species at field H and zero field, D is the concentration of the paramagnetic species, and $q = k_Q Q/k_D(0)$ (k_Q is the rate constant for (5), Q is the concentration of non-paramagnetic quencher, $k_D(0)$ is the rate constant for (4) at zero field).

Although this equation applies in ECL only when the triplet lifetime is governed by quenching, qualitative conclusions about the variation of $I(H)/I(0)$ with solvent drawn from (7) are valid. Thus a decrease in $I(H)/I(0)$ could be explained by a decrease in $r_\gamma(H)$ or D , or an increase in q or $r_D(H)$. Although a small difference in $r_\gamma(H)$ was observed for anthracene delayed fluorescence in DMF and CH₂Cl₂ [11, 12], this change was much too small to explain the observed trend with solvent. Since triplet lifetimes are sometimes larger in DMF than in THF, it is possible that Q is somewhat larger in THF. This leaves changes in parameters concerned with (4), quenching by paramagnetic species, as those responsible for the observed trend. If these species are the radical ions, then D would be essentially the same in all of the solvents under the conditions of the same applied signal to the electrodes. A change of $r_D(H)$ or $k_D(0)$ is possible, but again the magnitude of the change required to explain the results appears too large. If the paramagnetic quencher is oxygen (generated by oxidation of traces of water during the anodic step) as suggested by Bezman and Faulkner [4], then a decrease in the water present as an impurity from DMF to THF could explain the results. Indeed increasing the H₂O concentration in the experiment with BZN increased the observed magnetic field effect, although no such increase was observed for THF with added water (table 2). Moreover, we did not observe a magnetic field effect for oxygen quenching on anthracene triplets in AN [14] and the differences between the field effects in the R⁻/TMPD⁺ and R⁺/BQ⁻ systems and that of R⁻/R⁺, all in DMF, suggest that at least for the former cases, radical ion quenching is significant. Unfortunately, these possibilities cannot be tested

by direct experiments using photoexcitation, because neither direct nor sensitized delayed fluorescence of rubrene has been observed.

An alternate explanation involves assumption of an ST route with the relative number of singlets produced on electron transfer increasing in the order of THF > BZN > AN > DMF. We have previously invoked such an increase in S route character to explain the change in ECL efficiency and field effect with solvent and electrolyte concentration in another ECL system [17]. Such a trend is consistent with the Marcus theory of electron transfer reactions as applied to ECL [18, 19]. Briefly, this theory allows calculation of k_S , eq. (1), k_T , eq. (2), or k_g ,



by the equation

$$k = pZ\kappa\rho \exp(-\Delta G^*/RT), \quad (9)$$

where ΔG^* is the energy of activation, and is given by $\Delta^{\ddagger}G^*$, $\Delta^{\dagger}G^*$, and $\Delta^{\S}G^*$ for production of rubrene in the ground (k_g), excited singlet (k_S), or triplet (k_T) state; κ and ρ are usually taken as close to unity, Z is the collision frequency for uncharged species in solution, usually taken at $10^{11} \text{ M}^{-1} \text{ sec}^{-1}$, and p is a statistical factor equal to 1/4 for the singlet reactions (1) and (8) and 3/4 for the triplet reaction (2). The free energy of activation is given by

$$\Delta G^* = (\lambda/4) [1 + (\Delta G^0/\lambda)]^2 \quad (10)$$

when work terms are neglected. ΔG^0 is the standard free energy of reaction (1), (2), or (8), and λ is a reorganizational energy term composed of λ_i , attributed to structural differences of the reactants in the initial and final electronic states, and λ_0 , attributed to solvent (outer shell) orientation polarization differences. While λ_0 depends upon size and shape of the reactants, for spherical particles and a dielectric continuum assumption, it is given by the equation

$$\lambda_0 = \frac{1}{2} e^2 \left[\frac{1}{r_+} + \frac{1}{r_-} - \frac{2}{a} \right] \left[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right] \quad (11)$$

where e is the electronic charge, r_+ and r_- are the radii of the reactants, R^+ and R^- , respectively, $a = r_+ + r_-$,

Table 3

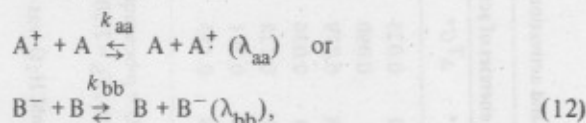
Dielectric constants and refractive indexes of solvents and λ_0 value for rubrene electron transfer in each solvent ^{a)}

Solvent	Dielectric constant (ϵ_s)	Refractive index (n_0)	ϵ_{op}^{-1}	ϵ_s^{-1}	λ_0 ^{b)} (eV)
DMF	36.71 (25°C)	1.428 (25°C)	0.463	0.67	0.67
AN	37.50 (20°C)	1.344 (25°C)	0.528	0.76	0.76
BZN	25.50 (25°C)	1.526 (25.5°C)	0.391	0.56	0.56
THF	7.58 (25°C)	1.405 (25°C)	0.378	0.54	0.54

^{a)} Assuming $r_+ = r_- = 5 \text{ \AA}$ and $a = 10 \text{ \AA}$.

^{b)} Calculated by eq. (11).

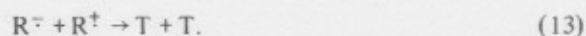
ϵ_{op} is the square of the refractive index and ϵ_s is the static dielectric constant. Values of λ_0 for the solvents under consideration here, assuming $r_+ = r_- = 5 \text{ \AA}$ are given in table 3. The value of λ can be obtained experimentally from the rate constant of the electron transfer reaction, such as



where the work terms and ΔG^0 are zero, using (9) and (10). For a number of radical ion systems k_{aa} and k_{bb} lie between 10^8 and $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ (see, e.g. ref. [20]), so that λ_{aa} and λ_{bb} lie between 0.5 and 0.7 eV. Since $\lambda_{ab} = (\lambda_{aa} + \lambda_{bb})/2$, the λ values for the electron transfer reactions are in the range of the calculated λ_0 values. The values of ΔG^* and the rate constants for the production of ground and excited state singlets and triplets based on the λ values of table 3 and the free energy data are given in table 2. For comparison, similar calculated results for 9,10-diphenylanthracene (DPA) in DMF, thought to be an S route system, are included in table 2. Since only about 1% of the triplets formed will ultimately yield an emitted photon because of triplet quenching and the excited singlet state efficiency of the TTA reaction [4, 13], a reaction will be "T route" when $k_T \geq 10^2 k_S$ and will be "S route" when $k_S \geq 10^{-2} k_T$. By these criteria, the reactions $R^-/\text{TMPD}^{\ddagger}$ and R^{\ddagger}/BQ^- in DMF are clearly T route, while rubrene alone in DMF and AN are T route reactions with perhaps some contribution from directly produced excited singlets. By these calculations, rubrene in BZN is an ST route system and rubrene in THF an S route system. The calculated values

in table 2 can only be considered suggestive because of uncertainties in λ and the neglect of the work terms. (Note also that the calculated rate constants should be based on the viscosity-dependent Z value in each solvent [20]; however, the choice of Z obviously does not affect the relative values in a given solvent.) However, the observed magnetic field effect trends, assuming triplet quenching by radical ions and/or oxygen, follows the expected decrease with increasing S route character.

One more reaction must be considered for the special case of rubrene, the formation of two triplets on electron transfer [19]



Since $2E_T \approx E_S$, the rate of this reaction will be of the order of k_S . The formation of two triplets close to one another would probably lead to more efficient TTA and hence relatively less quenching, but would show a magnetic field effect under energy-sufficient conditions. This "TT route" could be of importance in BZN and especially in THF.

The results given here demonstrate the important effect of solvent on the path of the ECL reaction. The general trend appears to be that a decrease in the dielectric constant will increase the value of ΔG^0 for the electron transfer reaction because of decreasing solvation of the radical ions, and will lead to a decrease of λ_0 . Both of these effects will favor the formation of excited states over ground states and for many cases, depending upon the value of $E_S - E_T$, favor the formation of excited singlets over triplets. Another factor which must be considered, however, is the increase of ion pairing between the radical ions and supporting electrolyte ions, with decreasing solvent dielectric constant. This ion pairing would decrease ΔG^0 for the $R^{\cdot+}/R^{\cdot-}$ reaction. While this effect may not be of importance for the bulky radical ions of rubrene, it was invoked to explain the effect of supporting electrolyte concentration on the 9,10-dimethylanthracene(-)/tris-*p*-tolylamine(+) ECL in THF solutions [17].

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