

ELECTROGENERATED CHEMILUMINESCENCE. XV. ON THE FORMATION OF EXCIMERS AND EXCIPLEXES IN ECL

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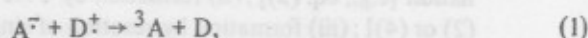
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The emission resulting from the reaction of electrogenerated radical anions ($A^{\cdot-}$) and cations ($D^{\cdot+}$) (ECL) for four systems which provide evidence for the intermediacy of excimers or exciplexes is described. The effect of solvent and supporting electrolyte concentration and the energetics of the radical ion reaction on the nature of the emission is discussed and the results are compared with previous chemiluminescence studies of Weller and Zachariasse. For one system involving *trans*-stilbene radical anion and tri-*p*-tolylamine radical cation, only radiation attributable to an exciplex formed in the initial cation-anion encounter, is observed.

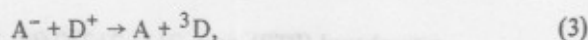
1. Introduction

Several previous investigations involving electrogenerated chemiluminescence (ECL) or radical ion recombination chemiluminescence (CL) have dealt with the appearance of emission bands which could be ascribed to dimeric emitting species, either excimers or exciplexes (heteroexcimers). Chandross et al. [1] proposed the direct formation of excimers upon reaction of radical anion ($A^{\cdot-}$) and radical cation ($A^{\cdot+}$) of anthracene in *N,N*-dimethylformamide (DMF). The long wavelength emission in this case, however, was later shown to be attributable to emission from a decomposition product of the anthracene radical cation [2]. This possibility of secondary product formation from radical ion decomposition and luminescence from this species is always present in ECL studies, especially in single component systems (i.e., systems where both radical anion and cation are produced from the same species) where one electrogenerated species is usually not stable. Excimer emission was observed by Parker and Short [3] for 9,10-dimethylanthracene and ascribed by them to formation of excimer by direct radical ion reaction. Maloy and Bard [4] observed excimer formation in the ECL of electrogenerated tetraphenylpyrene (TPP)

radical anion ($A^{\cdot-}$) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) cation radical ($D^{\cdot+}$) in DMF solutions. In this case the excimer was shown to be formed upon triplet-triplet annihilation (TTA) in the reaction sequence



Weller and Zachariasse [5-8] reported the CL of a number of "mixed systems" (systems where the radical anions and cations are produced from different species) in low dielectric constant solvents, such as dimethoxyethane and tetrahydrofuran (THF), and demonstrated formation of excimers by TTA, as well as exciplexes by either mixed TTA, reactions (1), (3) and (4);



or directly, (5)



The mode of formation of exciplex depended primarily upon the energetics of the radical ion recombination process. We have also previously suggested the possible

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Table 1
 Electrochemical and spectroscopic data

Compound	$E_{1/2}^a)$ (V versus Ag R.E.)	$E_S^c)$ (eV)	Ref.	$E_T^c)$ (eV)	Ref.
	(R/R ⁻)				
(A) 2,5-diphenyloxazole (PPO)	-2.26 ^{b)}	3.61	[11]		
<i>p</i> -terphenyl (PTP)	-2.75	3.97	[11]	2.55	[8]
<i>trans</i> -stilbene (<i>t</i> -St)	-2.22	3.80	[6]	2.20	[6]
	(R/R ⁺)				
(D) thianthrene (TH)	+1.22	2.86	[9]	2.60	[9]
tri- <i>p</i> -tolylamine (TPTA)	+0.90 ^{b)}	3.51	[7]	2.96	[7]

a) $E_{1/2}$ data taken at platinum electrode versus a shielded Ag wire reference electrode; see fig. 1 for the specific conditions of measurement (solvent, supporting electrolyte conc., solute conc.).

b) Values quoted are those measured in the PPO(-)/TH(+) and the PTP(-)/TPTA(+) and *t*-St(-)/TPTA(+) systems, respectively; in the PPO(-)/TPTA(+) system the measured potentials were 0.25 V more positive for both PPO-reduction and TPTA-oxidation.

c) E_S = energy level of first excited singlet state; E_T = energy level of lowest triplet state.

formation of exciplexes in the ECL of the thianthrene (TH)-2,5-diphenyl-1,3,4-oxadiazole (PPD) system in acetonitrile (ACN) [9].

There are thus three possible paths to dimeric emitters in ECL: (i) direct formation on radical ion combination [e.g., eq. (5)]; (ii) formation by TTA [e.g., eqs. (2) or (4)]; (iii) formation by reaction of singlet excited state with ground state species. We report here a study of ECL in four systems showing longer wavelength emission and evidence of dimeric emitters. Two systems have been previously studied by CL [5-8] and we include these to compare their behavior under ECL conditions with those in CL (see ref. [10] for a discussion of the effects of solvent and supporting electrolyte in ECL versus CL studies).

2. Experimental

p-terphenyl (PTP), m.p. 211-212°C (lit. 211-212°C), and 2,5-diphenyloxazole (PPO), m.p. 70.5-72.5°C (lit. 70-72°C), both scintillation grade, were obtained from Nuclear Equipment Chemical Corporation. *Trans*-stilbene (*t*-ST), m.p. 124-125°C (lit. 124-125°C), scintillation grade, was obtained from Matheson Coleman and Bell. Thianthrene (TH), m.p. 154.5-156.5°C (lit. 154-156°C) was obtained from

Aldrich Chemical Co. The scintillation grade compounds showed no fluorescent or electro-active impurities, and were used as received; we have previously [9] assessed the purity of our TH sample. Other chemicals employed in these studies, tri-*p*-tolylamine (TPTA), tetra-*n*-butylammoniumperchlorate (TBAP) and the solvents, as well as instrumentation and experimental procedures, have been described in a previous communication [10].

3. Results and discussion

The electrochemical and spectroscopic properties of the compounds under consideration are given in table 1. In table 2 are listed the four systems considered; in all cases the ECL was observed by continuous alternate pulsing at a platinum electrode to the first reduction and first oxidation wave so that the electron transfer reaction occurs between the indicated radical ions. The ECL emission spectra (uncorrected for photomultiplier response) are shown in fig. 1 and assignments of emitting species are given in table 2. A more detailed description of each system is given below.

PPO(-)/TH(+). Both the radical anion of PPO and the radical cation of TH are stable in ACN solutions. The ECL emission spectrum (fig. 1a) shows a peak attribut-

Table 2
ECL systems and reaction enthalpies

System A(-)/D(+)	Solvent - supporting electrolyte	$-\Delta H_r^0$ (eV)	ECL emitters
PPO(-)/TH(+)	ACN - 0.1 M TBAP	3.38	$^1A^*$; $^1D^*$; $(A_2)^*(?)$; $(AD)^*(?)$
PTP(-)/TPTA(+)	THF - 50 mM TBAP	3.55	$^1A^*$; $^1D^*$; $(A^-D^+)^*$
PPO(-)/TPTA(+)	THF - 50 mM TBAP	3.06	$^1A^*$; $(A_2)^*$; $(A^-D^+)^*$
<i>t</i> -St(-)/TPTA(+)	THF - 50 mM TBAP	3.02	$(A^-D^+)^*$

able to PPO singlet near 380 nm, one for TH singlet near 430 nm, and longer wavelength emission. Since the enthalpy of the radical ion reaction is 3.38 eV, the reaction is energy sufficient with respect to singlet TH, but energy deficient with respect to singlet PPO. Hence, $^1A^*$ must arise from a TTA reaction with triplet PPO formed in the radical ion reaction. This TTA may also produce PPO excimers which are responsible for the long wavelength emission. Since PPO has a high fluorescence efficiency [11], delayed fluorescence has not been observed with PPO. Possibly the long wavelength emission is caused by an exciplex of PPO and TH form-

ed directly in the radical ion reaction (see below). The general behavior of this system closely follows that of the PPD(-)/TH(+) system studied earlier [9].

PTP(-)/TPTA(+). This system is energy deficient with respect to the singlet excited states of PTP and barely sufficient for TPTA. The ECL spectrum (fig.1b), as noted in the CL spectrum by Zachariasse [8], corresponds to $^1A^*$, $^1D^*$, and longer wavelength emission ascribed to exciplex. Zachariasse favored a mechanism involving initial formation of an exciplex $^1(A^-D^+)^*$ followed by dissociation to form either $^3A^*$ (which

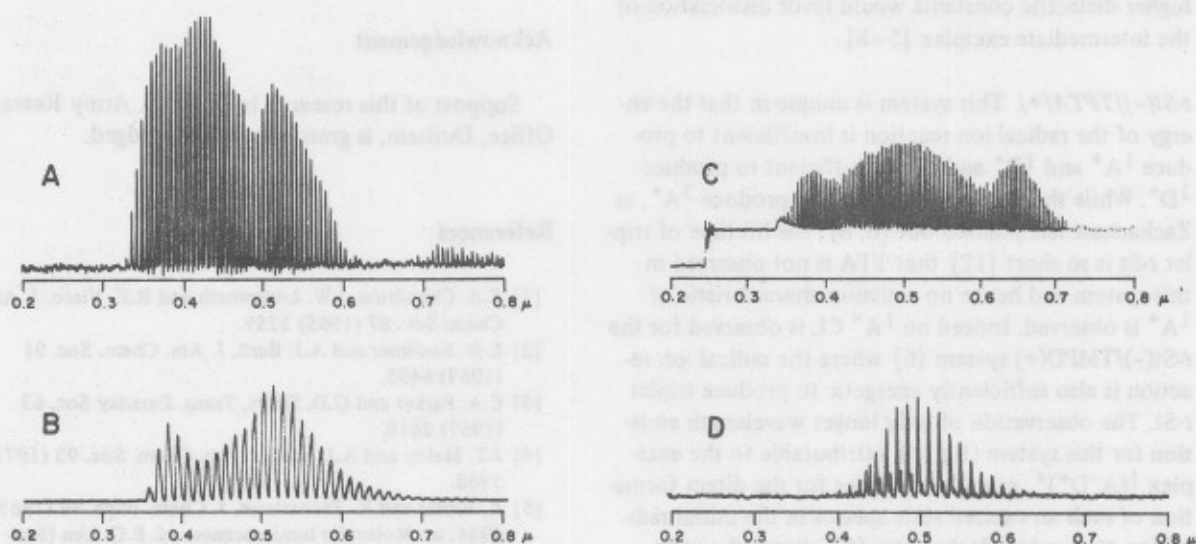


Fig. 1. Spectral distribution of the ECL emission in four mixed systems. (a) PPO/TH in ACN-0.1 M TBAP. Potential steps between -2.38 V and +1.30 V versus Ag R.E. at 1 Hz; concentration of the solute species was 2 mM each; (b) PTP/TPTA in THF-50.0 mM TBAP. Potential steps between -2.90 and +0.95 V versus Ag R.E. at 0.5 Hz; the concentration of solutes was 4.00 mM each; (c) PPO/TPTA in THF-50.0 mM TBAP. Potential steps between -2.10 and +1.30 V versus Ag R.E. at 0.5 Hz; concentration of solutes was 4.00 mM each; (d) *t*-St/TPTA in THF-50.0 mM TBAP. Potential steps between -2.35 and +0.95 V versus Ag R.E.; the *t*-St concentration was 0.200 mM and that of TPTA was 0.100 mM. All spectra are uncorrected for the response of the S-20 photomultiplier tube (Hamamatsu R456).

then produces $^1A^*$ by TTA) or $^1D^*$. Formation of 3D , followed by TTA annihilation to form $^1D^*$, is energetically possible in this case, but the lack of correlation of $^1D^*$ emission for reaction of solid $TPTA^+ClO_4^-$ and a series of radical anion solutions with reduction potential as well as the very short triplet lifetime of TPTA, led Zachariasse to the mechanism involving thermal dissociation of $^1(A-D^+)^*$. Note that the results shown in fig. 1b were obtained with 50 mM supporting electrolyte (TBAP). At TBAP concentrations of 100 mM or more the emission intensity is greatly reduced, paralleling the behavior observed in the dimethylantracene-TPTA system [10].

PPO(-)/TPTA(+). Both radical ions are stable in the solvents THF, ACN, or propylene carbonate (PC). The radical ion reaction is energy deficient with respect to $^1A^*$ and $^1D^*$; the energy is also barely sufficient to produce $^3D^*$. The observed species in THF (fig. 1c and table 2) can be ascribed to initial formation of $(A-D^+)^*$ which can form $^3A^*$ and then $^1A^*$ and $^1(A_2)^*$ via TTA or can lead to exciplex emission from the $^1(A-D^+)^*$ state. The long wavelength component is virtually absent in ACN or PC, as expected, since their higher dielectric constants would favor dissociation of the intermediate exciplex [5-8].

t-St(-)/TPTA(+). This system is unique in that the energy of the radical ion reaction is insufficient to produce $^1A^*$ and $^1D^*$ and barely sufficient to produce $^3D^*$. While the energy is sufficient to produce $^3A^*$, as Zachariasse has pointed out [6, 8], the lifetime of triplet *t-St* is so short [12] that TTA is not observed in this system and hence no emission characteristic of $^1A^*$ is observed. Indeed no $^1A^*$ CL is observed for the *t-St(-)/TMPD(+)* system [6] where the radical ion reaction is also sufficiently energetic to produce triplet *t-St*. The observation of only longer wavelength emission for this system (fig. 1d), attributable to the exciplex $^1(A-D^+)^*$, provides evidence for the direct formation of such an excited state species in the initial radical ion encounter. Zachariasse [8] observed a very small amount of emission from $^1D^*$ in the *t-St(-)/TPTA(+)* system in dimethoxyethane in his CL studies and ascribed it to the thermal dissociation of the exciplex to $^1D^*$. However, in the CL studies the electrolyte concentration was very small ($\approx 10^{-4}M$), which in our ECL study the TBAP concentration was 5.0 mM, so

that the radical ion reaction in CL studies occurred in a somewhat different environment [10]. Indeed, when ECL studies of this system were carried out in THF containing 0.1 M TBAP or in ACN or PC (0.1 M TBAP) no emission at all is observed.

The results taken together demonstrate the existence of dimeric intermediates in the radical ion annihilation process in ECL as well as the importance of solvent and supporting electrolyte in the formation of exciplexes, as predicted by Weller and Zachariasse [7]. The direct formation of a dimeric intermediate by the radical ions (encounter complex, solvent separated or tight ion pair or exciplex) may also have some bearing on the efficiency of these processes. In cases where these form, radiationless processes leading to deactivation of the exciplex will decrease the overall ECL efficiency (photons emitted per radical ion annihilation). When such intermediates cannot form, for example, because of steric effects, then direct paths to excited states are possible. The relatively high efficiency of ECL in the sterically-hindered 9,10-diphenylanthracene and rubrene systems may be examples of systems which do not form dimeric intermediates.

Acknowledgement

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