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ELECTROGENERATED CHEMILUMINESCENCE

PART XLIII. AROMATIC HYDROCARBON / PEROXYDISULFATE SYSTEMS IN ACETONITRILE–BENZENE SOLUTIONS

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ABSTRACT

Electrogenerated chemiluminescence (ECL) has been observed during the reduction of peroxydisulfate ($S_2O_8^{2-}$) by electrogenerated radical anions of several aromatic compounds ($\mathrm{Ar}^{\cdot -}$) in 2:1 CH_3CN–benzene solutions. The ECL spectra that arise at the Ar reduction wave agree with the fluorescence spectra of the corresponding aromatic compound. The cyclic voltammetric Ar reduction waves in the presence of $S_2O_8^{2-}$ were generally of the catalytic type, with Ar regenerated by the following chemical reaction with peroxydisulfate. Formation of Ar* with the resulting ECL was primarily caused by the $\mathrm{Ar}^{\cdot -}/\mathrm{Ar}^{\cdot +}$ reaction, with $\mathrm{Ar}^{\cdot +}$ generated via oxidation of Ar by $SO_4^{\cdot -}$ (a product of the reduction of $S_2O_8^{2-}$). The relative ECL efficiencies qualitatively depend upon the stability of the hydrocarbon radical cations, with rubrene producing the most intense ECL. A tertiary reactant system in which thianthrene fluorescence was observed during the catalyzed reduction of $S_2O_8^{2-}$ by the radical anion 2,5-diphenyl-1,3,4-oxadizole was also studied.

INTRODUCTION

The earliest systems for the production of electrogenerated chemiluminescence (ECL) involved the annihilation of oppositely charged radical ions of aromatic compounds in an aprotic medium [1,2]. The luminescence mechanism involved sequential oxidation and reduction at an electrode to form sufficiently energetic species, which produced an excited state of one of the precursors upon the electron transfer reaction.

$$\mathrm{A} + e^- \rightarrow \mathrm{A}^{\cdot -} \tag{1}$$

$$\mathrm{D} \rightarrow \mathrm{D}^{\cdot +} + e \tag{2}$$

$$\mathrm{A}^{\cdot -} + \mathrm{D}^{\cdot +} \rightarrow \mathrm{A}^* + \mathrm{D} \text{ or } \mathrm{A} + \mathrm{D}^* \tag{3}$$

The reagents A and D can be, but are not necessarily, the same compound. ECL has been observed for a wide variety of organic and organometallic compounds. The nature of the excited state produced (eqn. (3)) depends upon the energetics of the

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electron transfer reaction. When the reaction enthalpy is sufficiently large, the singlet excited state of A or D is produced. In less energetic reactions, triplet states are produced (^3A or ^3D), with the emitting singlet state produced by a triplet–triplet annihilation process, e.g.,

$$^3A + {}^3A \rightarrow {}^1A^* + A \tag{4}$$

In all of these systems, alternating negative and positive potential steps at the electrode were employed to generate the reacting precursors. More recently, reports from this laboratory and other have been concerned with ECL which results from a single potential step with mixtures of a luminescent compound and a suitable coreactant (e.g., $C_2O_4^{2-}$ or $S_2O_8^{2-}$), which can form an energetic reductant or oxidant upon bond cleavage. For example, in the previously studied $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ (where bpy is 2,2′-bipyridine [3]) a single cathodic potential step produces ECL by the reaction sequence:

$$Ru(bpy)_3^{2+} + e \rightarrow Ru(bpy)_3^{+} \tag{5}$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + S_2O_8^{3-\cdot} \tag{6}$$

$$S_2O_8^{3-\cdot} \rightarrow SO_4^{2-} + SO_4^{-\cdot} \tag{7}$$

$$Ru(bpy)_3^{+} + SO_4^{-\cdot} \rightarrow Ru(bpy)_3^{2+*} + SO_4^{2-} \tag{8}$$

$$Ru(bpy)_3^{2+} + SO_4^{-\cdot} \rightarrow Ru(bpy)_3^{3+} + SO_4^{2-} \tag{9}$$

$$Ru(bpy)_3^{+} + Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{2+*} + Ru(bpy)_3^{2+} \tag{10}$$

Although quantitative considerations of the ECL transient suggested that reactions (9) and (10) were more important in excited state formation than the reaction in eqn. (8), definitive evidence for the occurrence of this latter reaction was not obtained. The present study was undertaken to extend this $S_2O_8^{2-}$-based "reductive oxidation" sytem, with organic radical anions playing the role of the reductant and luminescence precursor, and to obtain a better understanding of the ECL reaction mechanism.

EXPERIMENTAL

Tetra-n-butylammonium peroxydisulfate ($(TBA)_2S_2O_8$) was prepared from analytical grade tetra-n-butylammonium hydroxide (TBAOH, Southwestern Analytical Chemicals, Austin, TX) and $(NH_4)_2S_2O_8$ (recrystallized from MCB, reagent grade). Excess $(NH_4)_2S_2O_8$ was added to a stirred aqueous solution containing TBAOH in a fume hood. The resultant by-product, NH_3, was removed from solution by nitrogen flushing until the odor of ammonia could no longer be detected. The reaction mixture was extracted three times with CH_2Cl_2 and the organic fraction was treated with activated charcoal and dried over anhydrous $MgSO_4$. After filtration, the CH_2Cl_2 was removed under vacuum. To prevent thermal decomposition, care was taken to avoid heating of the $(TBA)_2S_2O_8$ during preparation and storage.

Rubrene (RUB), 9,10-diphenylanthracene (DPA), anthracene (ANT), fluoranthene (FLU), 2,5-diphenyl-1,3,4-oxadiazole (PPD) and thianthrene (TH) were purchased commercially (Aldrich) and purified either by recrystallization from ethanol/benzene or sublimation. 1,3,6,8-tetraphenylpyrene (TPP, Pfaltz and Bauer) was purified by sublimation and 9,10-dicyanoanthracene (DCA, Eastman Kodak) was recrystallized from benzene. The acetonitrile and benzene (MCB omnisolv distilled in glass) were dried over super I Woelm alumina N (thermally activated under vacuum) for one week prior to use [4]. The supporting electrolyte was tetra-n-butylammonium tetrafluoroborate ($TBABF_4$, Southwestern Analytical Chemicals, Austin, TX) which was recrystallized from ethyl acetate and dried under vacuum. Electrochemical and ECL experiments were performed with either a Princeton Applied Research (PAR) model 175 universal programmer, model 173 potentiostat/galvanostat and model 179 digital coulometer, or an IBM model EC 225 voltammetric analyzer. Photoabsorption and photoluminescence spectra were recorded using an Aminco–Bowman spectrophotofluorometer as a polychromator, adapted with a PAR model 1215–1216 optical multichannel analyzer incorporating a model 1254 SIT Vidicon detector. An ISA holographic grating optimized at 500 nm (147) lines/mm) was used to disperse the emission spectra. The emission spectra shown are uncorrected for Vidicon tube spectral response.

ECL intensity vs. time curves were measured through the bottom of the electrochemical cell by either an EG&G model 550-1 radiometer/photometer or Hamamatsu model R928 photomultiplier tube. The data were recorded and the areas under the curves were integrated with a Bascom–Turner Instruments model 8110C electronic recorder.

The ECL cell and general procedures followed previous practice [1–3]. The platinum disk working electrode had an area of 0.0282 cm^2.

RESULTS

Cyclic voltammetry

Cyclic voltammetric measurements of the different organic compounds in the absence and presence of $S_2O_8^{2-}$ were performed at a platinum disk electrode in 2 : 1 (v/v) CH_3CN–benzene that was thoroughly degassed by solvent saturated N_2 (Table 1). Note that while previous studies with the $S_2O_8^{2-}$ system could be carried out in partially aqueous CH_3CN systems [3], solubility requirements for the organic species made the CH_3CN–benzene system more useful in this work. A representative voltammogram for RUB is shown in Fig. 1b. Addition of $(TBA)_2S_2O_8$ (20 m*M*) to a solution containing 1 m*M* RUB/0.1 *M* $TBABF_4$ resulted in a drastic change in the shape of the RUB cyclic voltammetric wave (Fig. 2b). The electrochemical reduction of RUB in the presence of $S_2O_8^{2-}$ showed an irreversible wave with a peak current (i_{pc}) 18 times larger than in the absence of $S_2O_8^{2-}$. The RUB reduction peak potential was scan rate dependent, shifting to more negative values with increasing scan rate (v), while $i_{pc}v^{-1/2}$ decreased with increasing scan rate. For example, at 10

TABLE I

Experimental results from $S_2O_8^{2-}$ catalyzed reductions

	$E^{\circ\prime}(R/R^{+\cdot})$[a]/V	$E^{\circ\prime}(R/R^{-\cdot})$[a]/V	E_{00}[b]/eV	i_c/i_d[c]	I_{ecl}[d]
RUB	+0.89	−1.47	2.28	18.0	10.2
DPA	+1.28	−1.88	3.04	20.0	0.16
TPP	+1.19	−1.83	3.00	24.8	0.14
ANT	+1.2[e]	−1.96	3.21	16.0	0.03
FLU	+1.6[e]	−1.77	3.01	15.8	0.10
DCA	–	−0.87	2.88	1.4	–
		−1.58		–	trace
PPD[f]	–	−2.13	4.00	12.5	trace
TH[f]	+1.29	–	3.31	–	–

[a] $E^{\circ\prime}$ = average of peak potential of the cathodic and anodic waves measured at a Pt disk vs. SCE in 2:1 CH_3CN–benzene containing 0.1 *M* TBA(BF_4). $v = 50$ mV s^{-1}.

[b] Energy of the lowest singlet excited state measured from the overlap of the photoabsorption and photoemission spectra.

[c] Peak catalytic reduction current from solutions containing 20 m*M* $S_2O_8^{2-}$ and 1 m*M* fluorphore divided by peak diffusional current without $S_2O_8^{2-}$.

[d] Relative integrated intensity for a 15 s negative step to 100 mV negative of the peak potential.

[e] Onset of irreversible anodic wave.

[f] Values measured in CH_3CN.

mV s^{-1} $i_{pc}v^{-1/2} = 23.3$ μA $(mV/s)^{-1/2}$ and $E_p = -1.50$ V while at 100 mV s^{-1}, $i_{pc}v^{-1/2} = 12.5$ μA $(mV/s)^{-1/2}$ and $E_p = -1.57$ V. Background voltammograms (Fig. 2a) show that the direct reduction of $S_2O_8^{2-}$ gave a broad, drawn-out wave

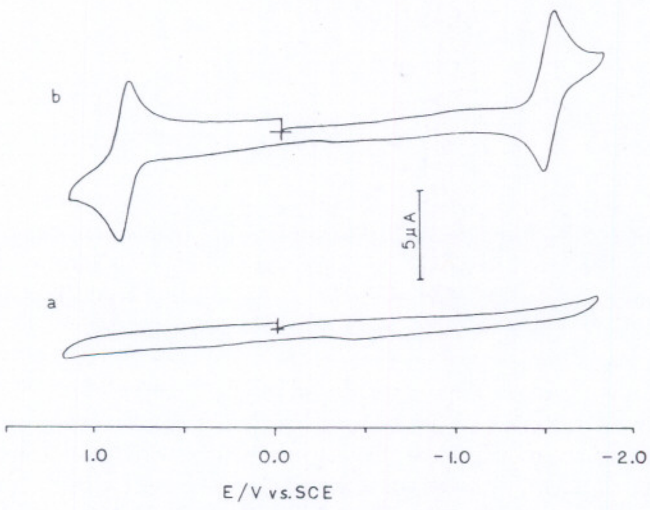

Fig. 1. Cyclic voltammograms (0.1 V s^{-1}) at a Pt disk electrode in 2:1 CH_3CN–benzene (v/v) containing: (a) supporting electrolyte (0.1 *M* $TBABF_4$), (b) 1.0 m*M* RUB and 0.1 *M* $TBABF_4$.

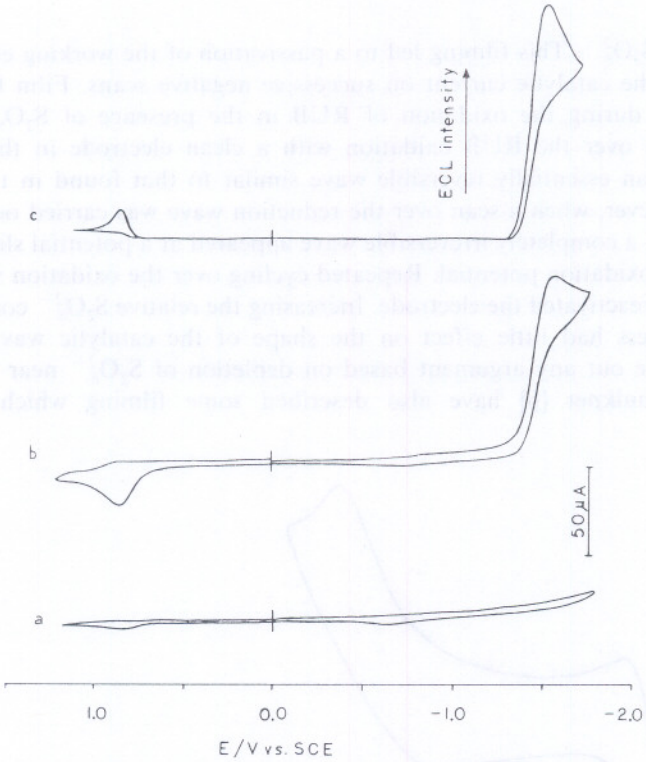

Fig. 2. cyclic voltammograms (0.1 V s^{-1}) at a Pt disk electrode in 2:1 CH_3CN–benzene (v/v) containing: (a) 0.1 *M* $TBABF_4$ and 20 m*M* $(TBA)_2S_2O_8$, (b) solution (a) with 1.0 m*M* RUB, (c) relative ECL intensity vs. potential for solution (b).

beginning at about −0.3 V [3a]. The current measured from this process was negligible at the current sensitivities employed under catalytic conditions. This behavior in the presence of rubrene is generally characteristic of a catalytic (E_rC_i') process with a fast following irreversible reaction [5]:

$$\mathrm{Ar} + e \rightarrow \mathrm{Ar}^{\overline{\cdot}} \tag{11}$$

$$2\,\mathrm{Ar}^{\overline{\cdot}} + \mathrm{S_2O_8^{2-}} \xrightarrow{k} 2\,\mathrm{Ar} + \mathrm{SO_4^{2-}} \quad \text{(in several steps)} \tag{12}$$

However, the behavior deviates somewhat from the limiting case expected for large values of k/v where an S-shaped curve with a limiting current that is independent of v is expected. While no reverse anodic wave was observed with v up to 10 V s^{-1}, the current did not retrace upon scan reversal, even at much lower scan rates, and $i_p/v^{1/2}$ was dependent on v. The deviations from strict E_rC_i' behavior can be attributed to complexities in the overall reaction sequence (eqn. (12)) and also to an apparent electrode filming that occurs in this solvent during reduction of RUB in the presence of $S_2O_8^{2-}$. This filming led to a passivation of the working electrode and a decrease in the catalytic current on successive negative scans. Film formation was also evident during the oxidation of RUB in the presence of $S_2O_8^{2-}$. An initial positive scan over the RUB oxidation with a clean electrode in the presence of $S_2O_8^{2-}$ gave an essentially reversible wave similar to that found in the absence of $S_2O_8^{2-}$. However, when a scan over the reduction wave was carried out prior to the positive scan, a completely irreversible wave appeared at a potential slightly negative of the RUB oxidation potential. Repeated cycling over the oxidation wave removed the film and reactivated the electrode. Increasing the relative $S_2O_8^{2-}$ concentration to a 100:1 excess had little effect on the shape of the catalytic wave and would, therefore, rule out any argument based on depletion of $S_2O_8^{2-}$ near the electrode. Kim and Faulkner [6] have also described some filming which occurred in

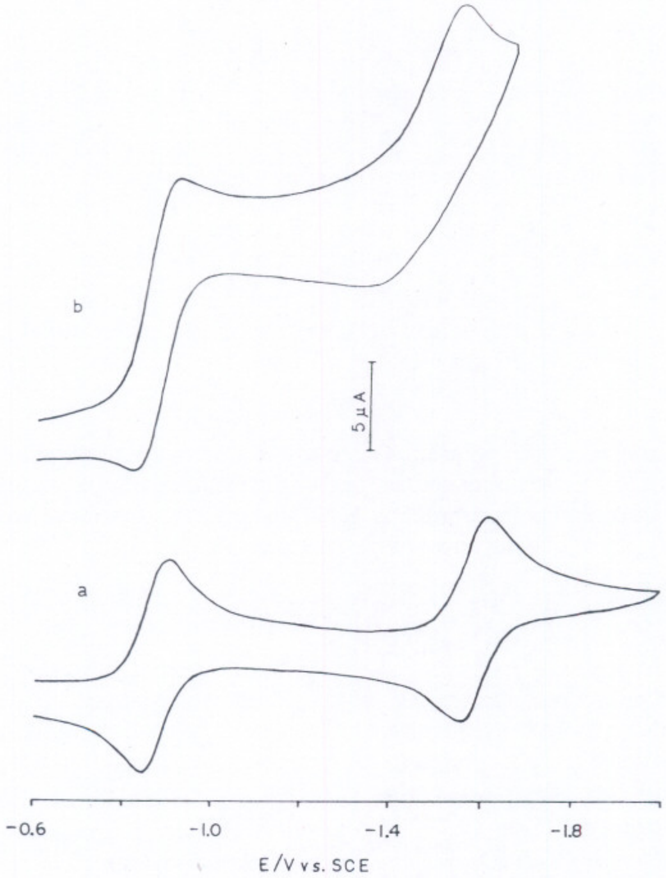

Fig. 3. Cyclic voltammograms (0.05 V s^{-1}) at a Pt disk electrode in 2:1 CH_3CN–benzene (v/v) containing: (a) 0.1 *M* $TBABF_4$ and 1.0 m*M* DCA, (b) solution (a) with 20 m*M* $(TBA)_2S_2O_8$.

CH_3CN/TBA solutions during voltammetric studies of RUB and FLU.

The reductions of DPA, TPP, ANT, FLU and PPD in the presence of $S_2O_8^{2-}$ all showed cathodic waves and electrochemical behavior similar to that of RUB. The catalytic currents for these reductions are listed in Table 1. In all cases film formation and electrode passivation occurred to varying degrees during the catalyzed reduction.

The behavior of DCA was different, however. In the absence of $S_2O_8^{2-}$ the cyclic voltammogram of DCA consisted of two reversible waves at -0.87 and -1.57 V vs. SCE (Fig. 3a). Electrochemical oxidation of DCA was not observed within the positive solvent limit. Addition of a 20 : 1 excess of $S_2O_8^{2-}$ gave a cyclic voltammogram for the first DCA reduction ($v = 0.1$ V s^{-1}) that showed some increase in i_{pc} and decrease in i_{pa} (Fig. 3b). At a scan rate of 5 mV s^{-1} an S-shaped wave which retraced itself upon scan reversal was obtained. At 1 V s^{-1} a reversible wave essentially the same as that found in the absence of $S_2O_8^{2-}$ was observed. The ratio of the maximum current (catalytic to diffusional, i_c/i_d) for a 50 mV s^{-1} scan rate indicated that the pseudo first-order rate constant for reaction of $DCA^{\overline{\cdot}}$ with $S_2O_8^{2-}$ was 0.58 s^{-1} [5]. The second reduction wave of DCA did not show a significant catalytic cathodic current upon addition of $S_2O_8^{2-}$. Instead, the cyclic voltammogram was highly irreversible even at scan rates in excess of 5 V s^{-1}. This suggests that a rapid nonregenerative reaction between DCA^{2-} and $S_2O_8^{2-}$ effectively competes with the possible catalyzed reduction mechanism.

ECL of organic fluorophores

Electrogenerated chemiluminescence was observed from RUB, DPA, TPP, ANT and FLU upon electrochemical reduction of the corresponding fluorophore in the presence of a 20 : 1 excess of $S_2O_8^{2-}$. In all cases the ECL spectra agreed well with fluorescence spectra obtained by photoexcitation (see, e.g., Fig. 4). Discrepancies in the short wavelength portion of the ECL spectra can be attributed to some reabsorption of emitted light in the fluorophore solution located between the electrode surface and the photodetector. Studies of ECL intensity as a function of applied potential (Fig. 2c) demonstrated that ECL was initiated by the electrochemical reduction or organic fluorophore. Luminescence was not observed at potentials before the fluorophore wave where only the small amount of direct reduction of $S_2O_8^{2-}$ appears. Furthermore, the similarity between the ECL intensity profile (Fig. 2c) and the voltammogram (Fig. 2b), suggested that the ECL mechanism is intimately associated with the electroreduction of the fluorophore. The mechanism follows closely that previously proposed for the $Ru(bpy)_3^{2+}$ system [3a]:

$$Ar^{\overline{\cdot}} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\overline{\cdot}} + Ar \quad (13)$$

$$SO_4^{\overline{\cdot}} + Ar \rightarrow Ar^{\dot{+}} + SO_4^{2-} \quad (14)$$

$$Ar^{\overline{\cdot}} + Ar^{+} \rightarrow Ar^* + Ar \quad (15)$$

As discussed below, we feel that the direct formation of excited state via the reaction

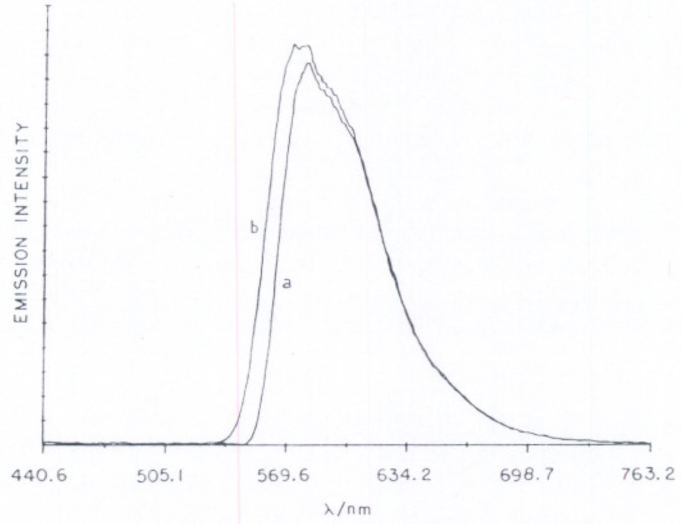

Fig. 4. UV-VIS emission spectrum in 2:1 CH_3CN-benzene of: (a) ECL from the $S_2O_8^{2-}$ catalyzed reduction of RUB, (b) photoexcited fluorescence of solution (a) (λ_{ex} = 400 nm).

(16) makes only a small contribution to the observed emission. Other reactions

$$\mathrm{Ar}^{\cdot -} + \mathrm{SO}_4^{\cdot -} \rightarrow \mathrm{Ar}^* + \mathrm{SO}_4^{2-} \tag{16}$$

which scavenge the energetic intermediate $SO_4^{\cdot -}$ (e.g., by reaction with solvent or supporting electrolyte) must also occur. Unexpectedly, some luminescence was also observed during initial positive scans at filmed electrodes in RUB solutions. This phenomenon was observed from electrodes which had been previously scanned over the RUB reduction wave in the presence of $S_2O_8^{2-}$. Moreover, emission was only observed for the first oxidation scan and might therefore be attributed to the presence of some reduced material generated during the negative scan. This reduced material could then react with radical cations to produce light.

Intensity vs. time

The ECL intensity (I) vs. time curves for cathodic potential steps in the presence of $S_2O_8^{2-}$ were qualitatively different than those obtained from the more conventional double potential step ECL experiments (Fig. 5). In the latter case, for RUB above, I reached a maximum within 0.1 s following the potential step and decayed rapidly to zero. The shape of these I–t curves were typical for double potential step experiments [1,7]. However, for single potential steps in the $RUB/S_2O_8^{2-}$ solution, the light intensity reached a maximum within 0.25 s and decayed more slowly (to 40% of the maximum after 5 s). If at this time the potential was stepped backed to zero, I decayed to zero within 0.2 s. The shape of the I–t curves was similar for all of

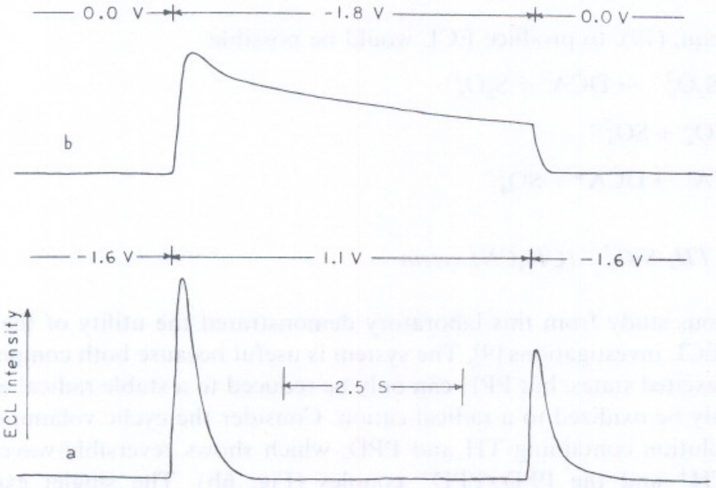

Fig. 5. ECL intensity vs. time for: (a) double potential step ECL from 1.0 m*M* RUB in 2:1 CH_3CN–benzene (0.1 *M* $TBABF_4$). (b) $S_2O_8^{2-}$ catalyzed ECL from solution (a) with 20 m*M* $(TBA)_2S_2O_8$.

the fluorophore–$S_2O_8^{2-}$ systems studied. Relative ECL intensities integrated for cathodic potential steps of 15 s duration are included in Table 1. The *I–t* curves for the $S_2O_8^{2-}$ catalyzed system are analogous to those reported during oxalate oxidation ECL [8], except that in the $S_2O_8^{2-}$ case the luminescence intensity peaked and decayed somewhat more slowly.

In addition to the above mentioned fluorophores, single potential cathodic steps in the presence of $S_2O_8^{2-}$ also generated very low, but detectable, amounts of emission during the electroreduction of PPD and DCA. Note that unlike the previous examples, PPD and DCA do not show oxidation to the radical cation within the solvent limits. An irreversible one-electron oxidation of PPD has been reported to occur at +2.20 V vs. Ag wire in CH_3CN [9]. However, only the foot of this wave could be observed in the solvent system employed in this study. The low $S_2O_8^{2-}$ ECL yield for PDD might therefore be attributed to the instability of $PPD^{\dagger}$ in CH_3CN. For DCA, ECL was not observed during the first reduction wave. Although the potential for reduction of $SO_4^{\bar{\cdot}}$ is not known, it has been estimated as > 3.15 V vs. SCE [10]. Under these conditions, reaction of $SO_4^{\bar{\cdot}}$ with $DCA^{\bar{\cdot}}$ should be sufficiently energetic to produce the excited state of the aromatic compounds. The absence of light under these circumstances suggests a very small contribution from the $A^{\bar{\cdot}}/SO_4^{\bar{\cdot}}$ reaction pathway, eqn. (16), in ECL. This is probably the result of instability and loss of $SO_4^{\bar{\cdot}}$ (e.g., by reaction with solvent) when an alternative reaction path involving the aromatic compound is unavailable. Low intensity ECL was observed, however, when the electrode potential was stepped onto the second DCA reduction wave. The reaction of DCA^{2-} with $S_2O_8^{2-}$ would chemically generate $SO_4^{\bar{\cdot}}$ in the proximity of $DCA^{\bar{\cdot}}$, a contribution from the $DCA^{\bar{\cdot}}/SO_4^{\bar{\cdot}}$ reaction pathway, eqn. (19), to produce ECL would be possible:

$$\mathrm{DCA}^{2-} + \mathrm{S_2O_8^{2-}} \rightarrow \mathrm{DCA}^{\cdot-} + \mathrm{S_2O_8^{3\cdot-}} \tag{17}$$

$$\mathrm{S_2O_8^{3\cdot-}} \rightarrow \mathrm{SO_4^{\cdot-}} + \mathrm{SO_4^{2-}} \tag{18}$$

$$\mathrm{SO_4^{\cdot-}} + \mathrm{DCA}^{\cdot-} \rightarrow \mathrm{DCA}^{*} + \mathrm{SO_4^{2-}} \tag{19}$$

The PPD, TH, $S_2O_8^{2-}$ (CH_3CN) sytem

A previous study from this laboratory demonstrated the utility of the PPD, TH system in ECL investigations [9]. The system is useful because both compounds have accessible excited states, but PPD can only be reduced to a stable radical anion while TH can only be oxidized to a radical cation. Consider the cyclic volammogram of a CH_3CN solution containing TH and PPD, which shows reversible waves for both the TH/TH^{+} and the $PPD/PPD^{\cdot-}$ couples (Fig. 6b). The singlet excited state energies for TH and PPD, estimated from the overlap of the absorption and emission spectra, were found to be 3.31 eV and 4.00 eV, respectively. Since the $E^{\circ\prime}$'s of these couples are separated by 3.42 eV, ECL is "energy sufficient" [1] only for TH, and ECL resulting from charge annihilation of TH^{+} and $PPD^{\cdot-}$ consists

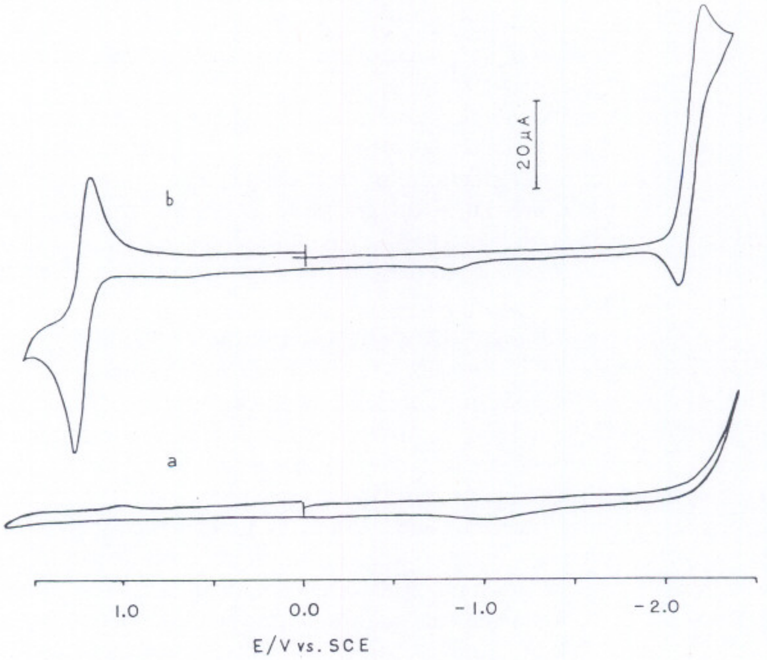

Fig. 6. Cyclic voltammograms (0.1 V s^{-1}) at Pt disk electrode in CH_3CN containing (a) supporting electrolyte (0.1 *M* $TBABF_4$), (b) 3.0 m*M* PPD, 3.0 m*M* TH and 0.1 *M* $TBABF_4$.

predominately of TH fluorescence (Fig. 8b). The cyclic voltammogram of a CH_3CN solution containing 3m*M* PPD, 3 m*M* TH and 30 m*M* $(TBA)_2S_2O_8$ is shown in Fig. 7b. The catalytic wave for PPD reduction was identical to that observed in the absence of TH. Following the negative sweep, two small irreversible oxidation waves occurred at +0.75 V and +1.25 V. The former was due to oxidation of a film deposited during the catalytic reduction. The second was due to the oxidation of TH, following a negative sweep in the presence of $S_2O_8^{2-}$, and is similar to results obtained with the other aromatic compounds. In the presence of TH, ECL was observed when the potential was stepped onto the PPD reduction wave. In this case, the luminescence intensity was over 35 times more intense than in the absence of TH. Furthermore, the emission spectrum was that of TH and not PPD (Fig. 8a). The photoluminescence of this solution was dominated by PPD fluorescence ($\lambda_{ex} = 300$ nm), as would be expected from the larger fluorescence quantum yield of PPD ($\Phi_f = 0.89$ for PPD and $\Phi_f = 0.036$ for TH) [11]. Therefore, the ECL from this system must be due to the chemical involvement of TH^+ and cannot be attributed to TH quenching of PPD luminescence. The ECL from this system was monitored as a

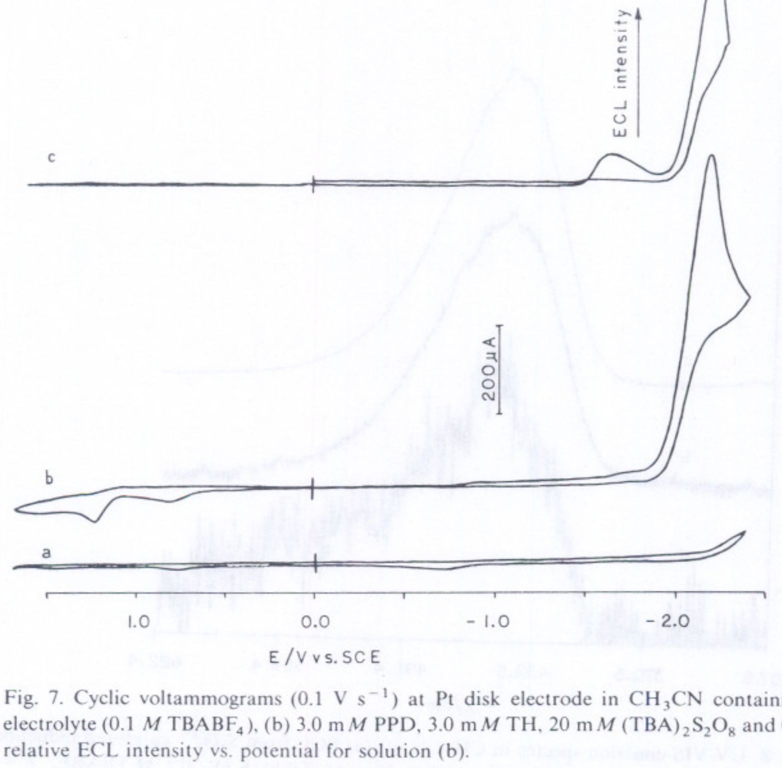

Fig. 7. Cyclic voltammograms (0.1 V s^{-1}) at Pt disk electrode in CH_3CN containing: (a) supporting electrolyte (0.1 *M* $TBABF_4$), (b) 3.0 m*M* PPD, 3.0 m*M* TH, 20 m*M* $(TBA)_2S_2O_8$ and 0.1 *M* $TBABF_4$, (c) relative ECL intensity vs. potential for solution (b).

function of electrode potential (Fig. 7c). The small peak at -1.65 V cannot be accounted for, but may be due to luminescence generated by the electroreduction of an impurity. The position and shape of the large wave at -2.25 V indicates that the TH ECL observed in this system is initiated by the electrochemical reduction of PPD. Thus the mechanism in this system can be written:

$$PPD + e^{-} \rightarrow PPD^{\cdot-} \tag{20}$$

$$PPD^{\cdot-} + S_2O_8^{2-} \rightarrow PPD + SO_4^{2-} + SO_4^{\cdot-} \tag{21}$$

$$TH + SO_4^{\cdot-} \rightarrow TH^{\cdot+} + SO_4^{2-} \tag{22}$$

$$TH^{\cdot+} + PPD^{\cdot-} \rightarrow {}^{1}TH^{*} + PPD \tag{23}$$

DISCUSSION

The results from this study indicate several definite trends which bear heavily upon the mechanism of ECL from $S_2O_8^{2-}$ catalyzed reductions. In every system

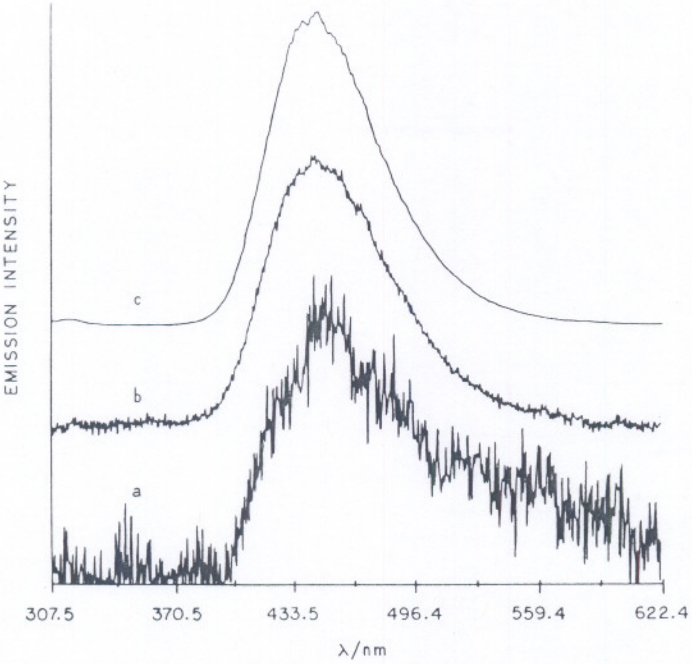

Fig. 8. UV-VIS emission spectra in CH_3CN of: (a) ECL from $S_2O_8^{2-}$ catalyzed reduction of PPD in the presence of TH (3.0 m*M* PPD, 3.0 m*M* TH, 20 m*M* $(TBA)_2S_2O_8$, 0.1 *M* $TBABF_4$. $E = 2.4$ V vs. SCE), (b) double potential step ECL from PPD/TH (3.0 m*M* PPD, 3.0 m*M* TH, 0.1 *M* $TBABF_4$. $E = +1.5$ V → -2.4 vs. SCE), (c) photoexcited fluorescence of TH ($\lambda_{ex} = 300$ nm).

examined, ECL was initiated by the electrochemical reduction of the organic compound and not $S_2O_8^{2-}$. The subsequent reaction (eqn. (13)) was important both for catalytic behavior and the ECL mechanism. This pseudo-first order reaction was fast enough to prevent the appearance of an anodic wave in the cyclic voltammograms of the catalyzed reductions even at scan rates in excess of 10 V s^{-1}. The unusually large catalytic currents obtained in these systems are also partly a result of very fast kinetics in eqn. (13). The dissociation of $S_2O_8^{3-}$ to generate the exceedingly strong oxidant $SO_4^{\cdot -}$ (eqn. (18)) is a well-established reaction. Reports of the ground state redox chemistry of $Fe(bpy)_3^{2+}$ and $S_2O_8^{2-}$ and the photoluminescence quenching of $Ru(bpy)_3^{2+}$ by $S_2O_8^{2-}$ both indicate that $S_2O_8^{2-}$ is a two-electron oxidant [12]. In each case the rapid dissociation of $S_2O_8^{3-}$ was proposed to yield the strong oxidant $SO_4^{\cdot -}$.

The importance of radical cation formation in the ECL mechanism (eqn. (14)) was most evident in the tertiary TH, PPD/$S_2O_8^{2-}$ system. The TH fluorescence observed during the $S_2O_8^{2-}$ catalyzed reduction of PPD can only be explained by formation of TH^+. Furthermore, the only species in solution capable of oxidizing TH was $SO_4^{\cdot -}$.

The stability of the organic radical cation appears to be an important factor in determining the efficiency of fluorophore ECL. RUB, the reagent that gave the highest ECL intensity, was the only fluorophore to show a reversible oxidation in the presence of $(TBA)_2S_2O_8$. DPA and TPP had had reversible oxidation waves in the pure electrolyte solution, but when $(TBA)_2S_2O_8^{2-}$ was added, cathodic currents were not obtainable upon reversal following oxidation. The reasons for instability of $Ar^{\cdot +}$ in the presence of $S_2O_8^{2-}$ are currently unknown. Accordingly, DPA and TPP gave significantly diminished ECL intensities (Table 1). Stable cation radicals of ANT and FLU could not be obtained by cyclic voltammetry in the solvent system employed. The ECL intensities of these fluorophores were also correspondingly small. In the case of PPD and DCA, oxidation occurs on the edge and beyond the solvent oxidation limit. The ECL intensities from these systems were extremely low. Therefore, from the above considerations it appears likely that eqn. (15) represents the principal mode of fluorophore excitation in these ECL systems.

Thermodynamically, eqn. (16) can lead to singlet excited state formation in all the organic fluorophores examined. However, since the ECL intensity depends upon cation stability and not the size of the catalytic current, the reaction of eqn. (16) cannot dominate the ECL mechanism. Furthermore, the detection of only trace intensity ECL from $S_2O_8^{2-}$ catalyzed reductions of PPD and DCA also rules against major involvement of eqn. (16) in the ECL scheme.

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REFERENCES

1 L.R. Faulkner and A.J. Bard in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol. 10, Marcel Dekker, New York, 1977, Ch. 1.

2 N.E. Tokel-Takvoryan and A.J. Bard, Chem. Phys. Lett., 25 (1974) 235; J.C. Luong, L. Nadjo and M.S. Wrighton, J. Am. Chem. Soc., 100 (1978) 5790; J.G. Velasco, I. Rubinstein, R.J. Crutchley, A.B. Lever and A.J. Bard, Inorg. Chem., 22 (1983) 822.

3 (a) H.S. White and A.J. Bard, J. Am. Chem. Soc., 104 (1982) 6891; (b) F. Bolletta, M. Ciano, V. Balzani and N. Serpone, Inorg. Chim. Acta, 62 (1982) 207.

4 O. Hammerich and V.D. Parker, Electrochim. Acta, 18 (1973) 537.

5 (a) R.S. Nicholson and I. Shain, Anal. Chem., 36 (1964) 706; (b) J.M. Savéant and E. Vianello, Electrochim. Acta, 10 (1965) 905; (c) A.J. Bard and L.R. Faulkner, Electrochemical Methods, John Wiley, New York, 1980, pp. 455–460.

6 J. Kim and L.R. Faulkner, Anal. Chem., in press.

7 S.W. Feldberg, J. Am. Chem. Soc., 88 (1966) 390; L.R. Faulkner, J. Electrochem. Soc., 122 (1975) 1190.

8 M.M. Chang, T. Saji and A.J. Bard, J. Am. Chem. Soc., 99 (1977) 5399.

9 C. Keszthelyi, H. Tachikawa and A.J. Bard, J. Am. Chem. Soc., 94 (1972) 1522.

10 R. Memming, J. Electrochem. Soc., 116 (1969) 785.

11 I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 1971.

12 S. Raman and C. Brubaker, J. Inorg. Nucl. Chem., 31 (1969) 1091; F. Bolletta, A. Juris, M. Maestri and D. Sandrini, Inorg. Chim. Acta, 44 (1982) L175.