

ON THE REPORTED EMISSION FROM THE T_2 STATE DURING ECL OF 9,10-DIPHENYLANTHRACENE

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The long wavelength component of the emission occurring during the electron transfer reaction of the electrogenerated radical ions of 9,10-diphenylanthracene (DPA) in acetonitrile and 1,2-dimethoxyethane solutions, previously attributed to $T_2 \rightarrow T_1$ emission, was investigated. Several sources contributing to detection of emission at wavelengths beyond 620 nm are discussed and the major source is attributed to a stable product formed by a small amount of decomposition of DPA radical cation.

1. Introduction

The emission occurring during the electron transfer between electrogenerated species (frequently radical ions) in electrogenerated chemiluminescence (ECL) frequently shows components at longer wavelengths than those for the fluorescence of the precursor molecules. Such longer wavelength emission is frequently quite intense and has been ascribed to excimers [1–6], exciplexes [7,8], phosphorescence [9], and products from the decomposition of the radical ions [3, 10]. Recently Perisamy and Santhanam [11] reported weak emission (≈ 0.16 to 5.3% of singlet emission) during the ECL of 9,10-diphenylanthracene (DPA) at wavelengths longer than about 620 nm and attributed this emission to the $T_2 \rightarrow T_1$ transition from the T_2 state of DPA produced by the electron transfer reaction. We were intrigued by this suggestion, since T_2 emission is rarely observed in photoexcitation experiments [12; 13, p. 235], and the establishment of T_2 formation in ECL could be of importance in the assignment of pathways in the electron transfer reaction. However the measurement of a small amount of long wavelength emission in the presence of short wavelength emission about one hundred times more intense is fraught with many difficulties. Thus we sought to measure the spectrum of this long wavelength emission (rather than use the filter technique

previously employed [11]) to see if the emission is centered near 875 nm, as expected for the DPA $T_2 \rightarrow T_1$ transition, and to study the effect of triplet quenchers on this emission.

2. Experimental

The DPA, gold label, Aldrich Chemical Co., was vacuum sublimed twice and zone refined twice under helium. The white crystals from the resulting middle fraction were retained (mp 245–246°C) and stored in a Vacuum Atmospheres dry box under helium. Tetra-*n*-butylammonium perchlorate (TBAP), polarographic grade, Southwestern Analytical Chemicals (Austin, Tx.) was twice recrystallized from warm ethanol, dried in vacuo at 100°C for 48 h, and stored in the dry box. Neutral alumina, ROC/RIC Chemical Co., was dried in vacuo at 300°C for 48 h. Biphenyl (BP), Eastman Organic, and *p*-terphenyl (PTP), Nuclear Equipment Chemical Co., were vacuum sublimed and stored in the dry box. 1,2-dimethoxyethane (DME), Matheson Coleman and Bell, was stirred with occasional freeze–pump–thaw cycles over $LiAlH_4$ for 48 h. The DME was removed by vacuum distillation and was transferred to the dry box where it was passed through a column of neutral alumina. The resultant solution was stored under vacuum as a $LiAlH_4$

slurry in the dark after additional freeze-pump-thaw cycles. Acetonitrile (ACN), Matheson Coleman and Bell, spectro grade, was purified as previously described [7].

Dry chemicals were weighed in the dry box and transferred to a vacuum line under helium where DME or ACN was added by vacuum distillation. The resultant solution was returned to the dry box and the ECL fluorescence cells were filled. Approximately 0.2 g neutral alumina was added to the ECL cell per ml solution [14]; similar results were found in solutions not treated with alumina. The ECL cells were subjected to several freeze-pump-thaw cycles on the vacuum line prior to any experiment.

The cell used for electrochemical and ECL studies was a three electrode type of conventional design [15]. Single ECL pulses were generated using double 100 ms potential steps as described in previous papers in this series with a delay time of at least one minute between ECL pulses. The intensity of the ECL pulses generated in this manner varied by less than 5% at 430 nm over the duration of any ECL experiment.

The ECL and fluorescence emission was monitored with a dry ice cooled RCA 7102 photomultiplier tube (S1 response) in conjunction with an Oriel model 7240 monochromator utilizing a grating blazed at 1 micron (1.0 mm slits). The second and higher order radiation was removed, when necessary, with Ditic Optics and Kodak broad bandpass filters. Optical grade quartz lenses were used to focus the emission onto the monochromator. The photomultiplier tube output was monitored with a Nicolet 1090A digital oscilloscope in ECL experiments and with a Houston 2000 recorder with fluorescence experiments. Fluorescence excitation was accomplished using a 150 W Hg source with appropriate filters to pass only 350–410 nm. This was verified by taking a scattered light spectrum of a colloidal silica solution (DuPont). The system response was determined by using a tungsten bulb powered by a constant voltage supply and Jarrell-Ash monochromator employing a broader bandpass than the Oriel monochromator as an emission source. The intensity of this source as a function of wavelength was determined with a calibrated EGG model 550-1 radiometer/photometer. Spectra presented here were corrected for system response and normalized to the emission maximum unless otherwise noted.

3. Results and discussion

Cyclic voltammetry of the solutions in the cells prior to ECL experiments (fig. 1) demonstrated that the anion and cation radicals were quite stable in both ACN and DME. The dianion was also quite stable in DME, suggesting that concentrations of O_2 or proton donors in that solvent were very small. The stability of the dianion decreased after many ECL pulses (≈ 300) indicating a possible build up of impurities in the solution, but no peaks attributable to impurities were found using cyclic voltammetry on the fresh solutions.

When broad bandpass colored glass filters were used to distinguish between long and short wavelength components of the ECL emission, considerable emission beyond 600 nm was monitored. The long wavelength component intensity was enhanced when repetitive pulsing, rather than a single pulse technique, was used. This effect varied considerably from experiment to experiment with enhancements of as much as order of magnitude being found using filters passing emission of wavelength greater than 800 nm. Typical results are given in table 1. The relative intensity of the long wavelength component was found to increase steadily as the successive filters passed shorter wavelength emission. However, no combination of experimental conditions allowed us to obtain relative emission intensities as large as those previously reported [9].

Typical ECL and fluorescence spectra are given in

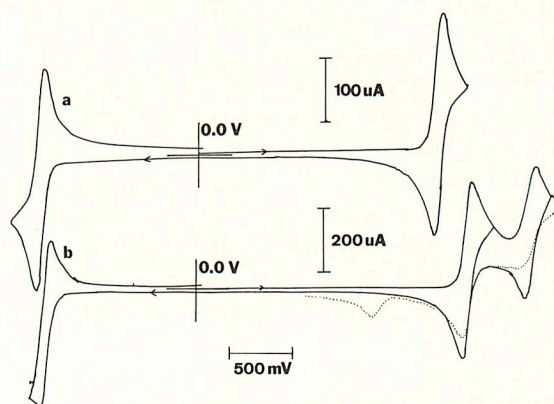


Fig. 1. (a) Cyclic voltammetry of 0.95 mM DPA in 0.10 M TBAP/ACN solution. Scan rate was 200 mV/s. (b) Cyclic voltammetry of 2.5 mM DPA in 0.13 M TBAP/DME solution. Scan rate was 200 mV/s. Before ECL, —; after extensive ECL, ...

Table 1
Relative ECL intensity at longer wavelengths as obtained with different cut-on filters a)

Wavelengths (nm) beyond b)	Normalized ECL intensity c)
530	1.6×10^{-2}
550	6.9×10^{-3}
570	4.2×10^{-3}
590	2.7×10^{-3}
620	1.7×10^{-3}
720	3.2×10^{-4}
780	1.5×10^{-4}
800	7.5×10^{-5}
(no filter)	1.0

- a) Relative ECL intensity taken with colored glass filters. The intensity was monitored with repetitive 100 ms pulsing of the ECL cell containing 1.5 mM DPA and 60 nM TBAP in ACN.
- b) Ditic "cut on" colored glass filters were used. The numbers correspond to the wavelength (in nm) where transmission is 50% that of the maximum transmission of the filter (ca. 80%).
- c) Relative intensities not corrected for filter or RCA 7102 photomultiplier tube response.

fig. 2. The ECL spectrum differed from that obtained by fluorescence (photoexcitation) in that it possessed a long wavelength tail. The intensity of this long wavelength component in ECL varied from experiment to experiment by as much as a factor of 3. The ECL pulse shape was the same for both long and short wavelength components of the spectra. With single pulse ECL experiments, no emission could be detected beyond 730 nm (to 1 micron) within the inherent noise level of the system (ca. 6×10^{-5}). However, rapid repetitive pulsing of the ECL cell caused a considerable increase in the long wavelength component intensity with a slight decrease in the emission at 450 nm (fig. 2). This suggests the presence of at least two distinct emitting species in the ECL scheme, since the intensity variation would be expected to be similar at all wavelengths for only one emitting species or state. A build-up of an absorbing product could explain the loss of ECL intensity at short wavelengths, but not the increase in intensity at long wavelengths. The addition of the triplet quenchers biphenyl ($E_{T_1} = 2.84$ eV) [13, p. 182] or *p*-tphenyl ($E_{T_1} = 2.55$ eV) [13, p. 182] to the ECL solution failed to quench the long wavelength component to any

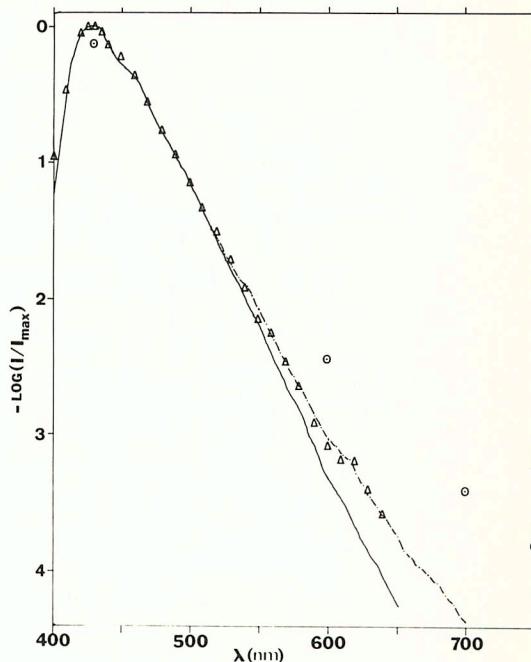


Fig. 2. Fluorescence/ECL spectra of 2.5 mM DPA in 0.13 M TBAP/DME solution. (a) Initial fluorescence spectra, —; (b) fluorescence spectra after ECL experiment, -.-.-; (c) ECL spectra obtained from single pulses, Δ ; (d) ECL intensity upon repetitive pulsing at 5 Hz, \circ . Excitation wavelength, 360–410 nm.

noticeable extent, suggesting that no relatively long lived triplet species were involved.

Fluorescence spectra of the DPA solutions taken after ECL experiments showed the build-up of a long wavelength component (fig. 2). The relative intensity of this fluorescence tail never exceeded that found with the ECL pulses for a given solution, but it was found to increase with the number of double potential step pulses passed in the ECL experiments. The possibility that the products producing the long wavelength emission were formed via some reaction involving the DPA radical cation was examined by generation of DPA^{\ddagger} by controlled potential coulometry. In DME the n_{app} value obtained for coulometric oxidation producing DPA^{\ddagger} was 2.25 after a $2\frac{1}{2}$ h electrolysis at 1.35 V. Reverse coulometry at 0 V, causing reduction back to DPA, yielded an n_{app} value of 1.15. Other coulometric experiments in DME gave larger n_{app} values for longer durations of electrolysis. The final solutions had a dark green color. DPA^{\ddagger} was more stable in ACN, yielding an n_{app} value of 1.16

for coulometric oxidation. This agrees with the DPA⁺ half-life in ACN (50 min) reported by Sioda [16]. After reverse coulometry however, the solution had developed a yellowish-green tint. The fluorescence spectra of these solutions are given in fig. 3. In both solvents fluorescence emission at about 540 nm with a significant long wavelength tail was observed following oxidation and reduction.

In addition to absorption by DPA below 410 nm, an absorption spectrum of the solution showed a broad shoulder extending from 410 nm to beyond 510 nm. Because of the relatively high absorbance of the solution, the fluorescence spectrum was taken from emission at a corner of the fluorescence cell to reduce the effective light path through the solution, thus reducing inner filter effects. DPA singlet emission as well as the long wavelength emission was observed.

The components following the ECL experiments were extracted from the TBAP residue following evaporation of solvent with anhydrous ether. After evaporation the resultant crystals were dissolved in benzene and fractionated on an alumina column. DPA was isolated from the mixture, as well as com-

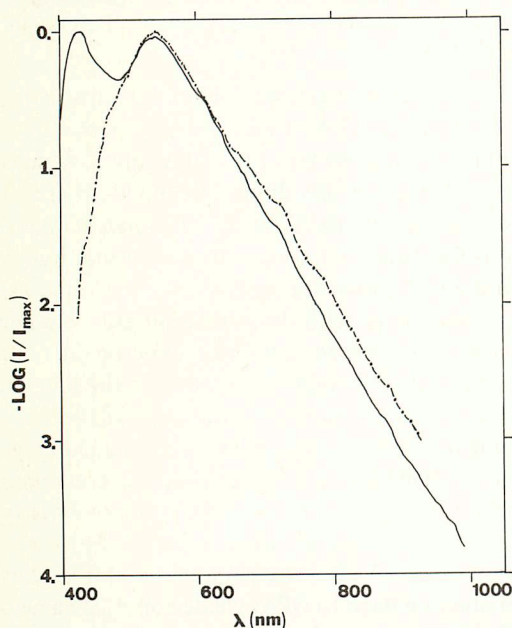


Fig. 3. Fluorescence spectra of DPA solution after coulometric oxidation of DPA and re-reduction. (a) In TBAP/ACN solution, —; (b) in TBAP/DME solution, -.-.-. Excitation wavelength, 360–410 nm.

ponents producing fluorescence with peaks at about 400 nm and 540 nm. Further analysis is being undertaken to identify these.

During the course of these experiments a number of factors were uncovered which could lead to the observation of emission at longer wavelengths in ECL experiments, especially when glass filter techniques are employed. These include the transmittance of the filter itself at short wavelengths (e.g., a Corning type 2-58 filter showed a transmittance of about 3×10^{-4} for radiation of 350–580 nm) as well as the well-known effect of filter fluorescence [17]. The fluorescence tail of DPA singlet emission itself can give only a small ($< 10^{-4}$) response at wavelengths beyond 650 nm (fig. 2). However the evidence presented here suggests that the long wavelength component observed in ECL of DPA originates predominantly from products of a reaction involving the radical cation. These products can be excited either by electron transfer reactions as in ECL, by absorption of DPA fluorescence, or by energy transfer from excited DPA singlet. Thus these results are similar, but with a much smaller extent of side reaction, to those previously found with anthracene [10]. They also explain the variability of long wavelength emission found in this and the previous study [11] from one trial to the next and the apparent effect of solvent. Emission from the T_2 state of DPA would be difficult to detect under these conditions, and we feel that the evidence for it in ECL experiments is ambiguous. This does not mitigate against the production of the T_2 state in electron transfer reactions, as previously suggested [11,18]; the fate of this T_2 state would probably be radiationless deactivation to the ground state.

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