

ELECTROGENERATED CHEMILUMINESCENCE.
XII. MAGNETIC FIELD EFFECTS ON ECL IN THE TETRACENE-TMPD SYSTEM;
EVIDENCE FOR TRIPLET-TRIPLET ANNIHILATION OF TETRACENE†

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The electrogenerated chemiluminescence (ECL) of the energy deficient system tetracene-*N,N'*-tetramethyl-*p*-phenylenediamine (TMPD) in 0.1 M TBAP-DMF solution shows an increase in intensity of up to 19% for magnetic fields of 7.5 kG. The results are interpreted as production of tetracene in the triplet state upon reaction of tetracene anion radical and TMPD cation radical followed by triplet-triplet annihilation.

1. Introduction

Previous studies of the effect of magnetic field in electrogenerated chemiluminescence (ECL) [1] have been useful in demonstrating the involvement of triplet intermediates in the ECL process and have been interpreted in terms of the magnetic field decreasing the rate of both triplet-triplet annihilation (TTA) and the quenching of triplets by radical ions. Delayed fluorescence studies in the presence and absence of radical cation have supported the ECL results [2]. Although several previous reports of radical ion chemiluminescence in systems containing tetracene alone [3, 4] or mixed tetracene-oxidant systems [5, 6] have appeared, no studies of magnetic field effects or a detailed consideration of the energetics of the process have been given.

Many reports giving the values for the energy levels of the triplet and singlet excited states of tetracene have appeared [7-12]. The energy level of the triplet state (E_T) was given as 10250 cm^{-1} (1.27 eV) from measurements of the absorption spectrum of tetracene in chloroform [10]. These authors also give energy

levels of the first excited singlet state (E_S) of 20990 cm^{-1} (2.60 eV) in ethyl iodide and 21225 cm^{-1} in alcohol. Although a number of reports have shown that $2E_T > E_S$ and that TTA (or triplet fusion) occurs in tetracene crystals [7, 13, 14], it has usually been assumed that TTA does not occur in solution [4, 15]. We report here that a magnetic field causes a significant increase in the ECL intensity during the reaction of tetracene anion radical with *N,N'*-tetramethyl-*p*-phenylenediamine (TMPD) cation radical in *N,N*-dimethylformamide (DMF) solutions under conditions where formation of tetracene in the triplet state followed by TTA provides the most reasonable explanation of the results.

2. Experimental

The tetracene used in this work was (99.9% pure grade) supplied by Princeton Organics, Inc. and was used without further purification. TMPD was prepared by the method described previously [1]. TBAP (tetra-*n*-butylammonium perchlorate), used as the supporting electrolyte, was obtained from Southwestern Analytical Chemicals and was dried in vacuo at 100° for 48 hours. DMF, used as solvent, was supplied by Matheson, Coleman and Bell (bp. $152-154^\circ\text{C}$). It was purified by a published procedure [1] and stored

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under a helium (99.995%) atmosphere. The electrolysis cell used for these experiments and the procedures for preparation of solutions have been described [1].

Electrode potentials were controlled by a Wenking Model 61RH fast rise potentiostat. The desired potential program was generated by a Wavetek Model 114 function generator operating in the square wave mode at 10 Hz, with an auxiliary programmer used to trigger the function generator and the oscilloscope. Cyclic voltammetric data were taken by a Princeton Applied Research Model 170 Electrochemistry System using a three electrode cell described previously.

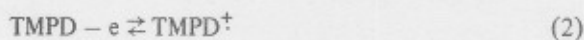
Magnetic field effects were studied using the phosphorimeter described by Faulkner and Bard [16]. A circular graded spectrum filter, produced by Barr and Stroud, Ltd., was added to the phosphorimeter to allow monitoring of emission at selected wavelengths. An electromagnet was used to apply field strengths of up to 7500 gauss to the sample. The detector was a Dumont Model 6467 end-window photomultiplier. Its photocurrent was measured across a 100 Ω resistor using a Tektronix Type 504 oscilloscope.

3. Results

For a solution containing 0.5 mM tetracene (T), 0.5 mM TMPD and 0.1 M TBAP in DMF, the cyclic voltammetric cathodic peak potential (E_{pc}) for reduction of tetracene to the anion radical



is -1.62 V versus SCE, while oxidation of TMPD to the cation radical

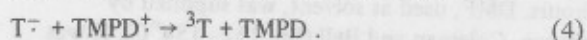


occurs at $E_{pa} = +0.22$ V. The enthalpy of the radical ion electron transfer reaction, calculated from the equation [1]

$$-\Delta H^0 = E_{pa} - E_{pc} - 0.16 \text{ eV} \quad (3)$$

is 1.68 eV, large enough to produce tetracene in the triplet state, but insufficient to produce excited singlets of either species, or the triplet of TMPD.

Therefore, the electron transfer reaction is



The spectra of the ECL emission for the above solu-

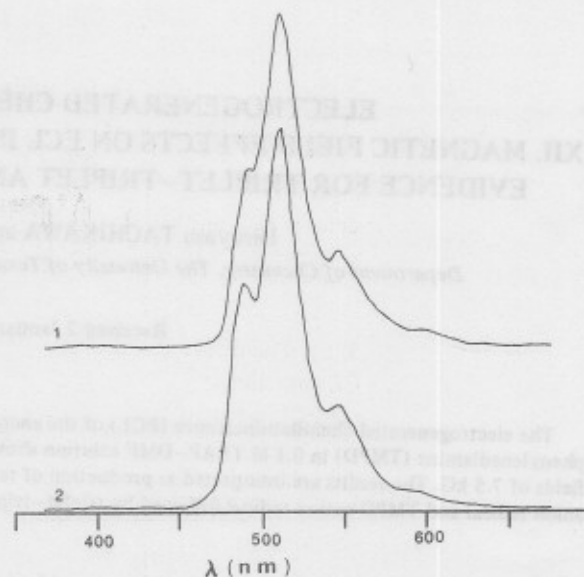


Fig. 1. (1) ECL spectrum of 0.5 mM tetracene, 0.5 mM TMPD and 0.1 M TBAP in DMF. (2) Fluorescence spectrum of 0.5 mM tetracene and 0.1 M TBAP in DMF.

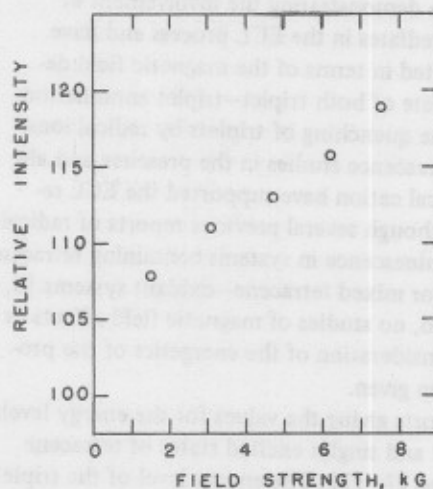
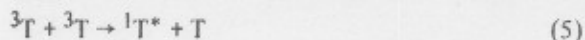


Fig. 2. Magnetic field effects on ECL from tetracene-TMPD system. The solution contained 0.5 mM tetracene, 0.5 mM TMPD and 0.1 M TBAP.

tion (as well as one containing tetracene alone) show peaks at 490, 510 and 545 nm, with that at 510 nm being strongest. The ECL spectrum is essentially the

same as the fluorescence spectrum of tetracene (fig. 1), showing that the emitting species is $^1T^*$, and suggesting the occurrence of TTA, in agreement with the



chemiluminescence results [5, 6]. The effect of magnetic field strength on the ECL emission at 510 nm is shown in fig. 2. The increase in ECL intensity for a field of 7.5 kG is about 19%.

Since these results show the occurrence of TTA of tetracene, we attempted to detect delayed fluorescence of tetracene in DMF solutions. In agreement with the findings of Parker [15], no delayed fluorescence could be observed. Parker was able to observe sensitized delayed tetracene fluorescence in mixtures of anthracene and tetracene, but he ascribed this to a mixed triplet reaction. The observation of TTA in ECL and not in delayed fluorescence experiments might be caused by a much more efficient production of triplets in ECL.

An increase in intensity of prompt fluorescence with an applied magnetic field has been observed in tetracene crystals, which has been ascribed to the effect of field on the fission of singlet excitons into triplet exciton pairs [7, 8, 13, 14, 17]. To look for this effect in solution we studied the prompt fluorescence of 0.1 mM tetracene solutions in cyclohexane in magnetic fields up to 4.5 kG. No significant effect on the intensity of the prompt fluorescence was observed. This lack of observable singlet fission in solution can be ascribed both to the unfavorable energetics for the reaction and the improbability of collision of an excited singlet with a ground state singlet before

emission or deactivation of the excited state, as compared with the conditions in a single crystal environment.

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