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ELECTROGENERATED CHEMILUMINESCENCE. DIRECT HETEROGENEOUS FORMATION OF THE TRIPLET STATE BY REDUCTION OF RUBRENE RADICAL CATION AT AN N-TYPE ZINC OXIDE ELECTRODE

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The electrogenerated chemiluminescence (ECL) of rubrene resulting from direct electron transfer from a zinc oxide semiconductor electrode to rubrene radical cation to form the triplet state of rubrene is reported. ECL characteristic of rubrene fluorescence occurs following triplet-triplet annihilation. Emission is observed at electrode potentials insufficient to form the radical anion of rubrene, although the more intense radical ion annihilation ECL is observed when the ZnO is held at more negative potentials.

1. Introduction

There have been a number of efforts to form an excited state directly at an electrode surface by electron transfer. Zweig and co-workers [1] reported observation of luminescence, assigned to phenanthrene phosphorescence, upon oxidation of phenanthrene radical anion at a platinum electrode in N,N-dimethylformamide (DMF) solution, and suggested direct formation of triplet phenanthrene at the metal electrode. Similarly, in studies with rubrene (5,6,11,12-tetraphenylnaphthacene) in DMF solutions [2], it was suggested that some of the emission was due to the direct formation of an excited triplet at the metal electrode in a heterogeneous electron transfer step followed by triplet-triplet annihilation (TTA). Because metals are good quenchers of excited states [3], such direct production under these conditions should be inefficient.

Chandross and Visco [4] pointed out that a triplet state at the metal electrode would be both more easily oxidized and more easily reduced than the ground state species, leading to electron transfer quenching by the electrode via successive oxidation and reduction steps. They suggested instead that the "pre-annihilation" ECL observed in these systems could be

attributed to reactions with substances produced on electrolysis of impurities or reaction products. Studies on rubrene and other systems [5,6] in various solvents support this latter explanation of pre-annihilation ECL. On the other hand heterogeneous production of an excited state might be possible at a semiconductor electrode with the appropriate band gap (E_g) and flat band potential. In this case some electron transfer reactions will be hindered because of the relative energy level distributions in the semi-conductor and solution [7] and charge transfer quenching by the electrode should be less favorable.

Recently Gleria and Memming [8] reported the direct formation of the excited state of $\text{Ru}(\text{bipy})_3^{2+}$ (bipy = 2,2'-bipyridine) by reduction of the +3 species at an n-type SiC electrode. The luminescence occurs at potentials where reduction of $\text{Ru}(\text{bipy})_3^{3+}$ to the +1 species occurs, so distinction between direct heterogeneous production of ECL and that caused by the +3/+1 annihilation reaction [9] required an analysis of the intensity-time behavior to demonstrate the direct process. Grabner [10] studied the electrochemical behavior of rubrene in benzonitrile solutions at a ZnO electrode and reported that only the usual radical ion annihilation ECL occurred.

In this paper we describe the reduction of rubrene

radical cation (R^+) in a benzonitrile-benzene solution at a ZnO electrode and report the direct formation of triplet rubrene (3R) at potentials where the radical anion (R^-) cannot form. Experiments with a platinum electrode in the same solution demonstrated that impurity-type pre-annihilation ECL does not occur in this system, so that the heterogeneous formation of 3R at ZnO appears unambiguous.

2. Experimental

The electrochemical cell contained a ZnO, a platinum wire and a platinum gauze working electrode, a reference electrode and a platinum wire spiral counter electrode. The reference and counter electrodes were contained in separate compartments, using sintered-glass frits to contact the main working electrode compartment. The single crystal n-type ZnO was 0.1 cm thick with an area of about 0.1 cm² and was purchased from Atomegic Chemetals Co. (Long Island, New York). The single crystal was mounted in a glass tube using silicone rubber adhesive (Dow Corning) which was resistant to acetonitrile, benzonitrile (BZN) and benzene (BZ) and which insulated all electrode parts except the area exposed to solution. Electrodeposited indium provided ohmic contact to this electrode. The ZnO was mechanically polished with 0.3 μ alumina to produce a visually smooth surface before electroplating and mounting. The electrode was washed with acetone and dried in air before use but no etching procedure was employed.

An equal volume mixture of BZN and BZ was used as the solvent. BZN, reagent grade, purchased from Eastman Chemical Co., was purified by a previously reported procedure [11] and then distilled from calcium hydride under vacuum. BZ, spectrograde, obtained from Mallinckrodt, was stored over sodium metal for a day and distilled under vacuum. Rubrene, obtained from Aldrich Chemical Co., was dissolved in hot xylene and recrystallized from methanol. Tetra-*n*-butylammonium perchlorate (TBAP), polarographic grade, obtained from Southwestern Analytical Chemical Co., was vacuum dried and used as the supporting electrolyte. Oxygen was removed from solvents by several freeze-pump-thaw cycles. Solvents were mixed, solutions prepared, and the cell filled in a Vacuum Atmospheres Corporation dry box

(Hawthorne, Cal.) under a helium atmosphere. When it was necessary to work outside the dry box, the cell was sealed with silicone vacuum grease. A Teflon thermometer adapter was used for placement of the semiconductor electrode within the cell. The rubrene solution was converted to its radical cation form by controlled potential electrolysis at the platinum gauze electrode before the ECL studies at ZnO were performed.

A PAR model 170 electrochemistry system, or a combination of a PAR model 173 potentiostat and a PAR model 175 universal programmer (Princeton Applied Research Corp., Princeton, N.J.) were used for electrochemical experiments. The ECL was generated by potential steps and was detected with an Aminco-Bowman spectrophotofluorometer employing an RCA 4832 photomultiplier tube.

3. Results

A cyclic voltammogram of 4 mM rubrene in a 0.1 M TBAP-BZN/BZ solution at a platinum wire electrode (ca. 0.15 cm²) versus a saturated calomel electrode (SCE) is shown in fig. 1a. Rubrene reduces at $E_{pc} = -1.46$ V versus SCE to produce the radical anion and oxidizes at $E_{pa} = +1.03$ V to produce the radical cation; both ions are stable on the cyclic voltammetry time scale. A cyclic voltammogram of the same solution at a ZnO electrode shows a reduction peak at $E_{pc} = -1.85$ V for production of the radical anion (fig. 1b, curve 1); the radical cation cannot be generated in the dark at the n-type semiconductor electrode. When the solution was partially anodically electrolyzed at a platinum gauze electrode at +1.2 V, the original orange color of rubrene solution was gradually changed to the dark orange-brown color of R^+ . The radical cation was stable for several hours during which time the ECL experiments at the ZnO electrode were undertaken. R^+ does not reduce at the ZnO electrode until a potential of -0.1 V is reached (fig. 1b, curve 2). The reduction current of the radical cation rose slowly at -0.1 V and produced a broad peak at -0.5 V; it leveled off as the potential became more negative until a large cathodic peak occurred at -1.85 V where R^- was generated. The ZnO electrode immersed in the R^+ solution was pulsed between 0 V to progressively more negative potentials. Emission was

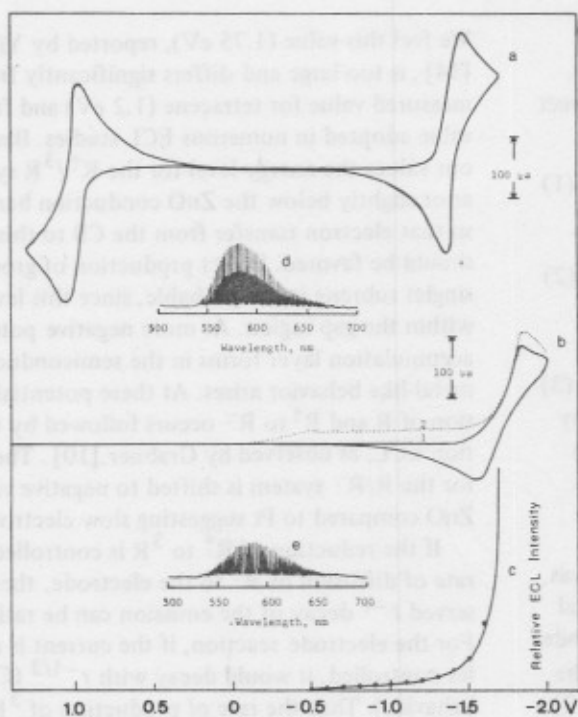


Fig. 1. (a) Cyclic voltammogram of 4 mM rubrene in 0.1 M TBAP-benzonitrile/benzene solution at 200 mV/s at a platinum electrode; (b) as in (a) at ZnO electrode: (1) in parent rubrene solution, (2) in mixture of rubrene/rubrene radical cation solution; (c) relative ECL intensity at ZnO electrode in rubrene radical cation solution with voltage pulsed between 0 V and voltage indicated on X-axis; (d) ECL spectrum at platinum electrode pulsing between +1.2 V and -1.6 V; (e) ECL spectrum at ZnO electrode pulsing between 0 V and -0.7 V in rubrene radical cation solution.

first detected at -0.5 V. The ECL intensity increased slowly with increasing negative potential with a very sharp increase at -1.6 V where $\text{R}^{\cdot-}$ generation commences (fig. 1c). The ECL intensity at -1.7 V was about 100 times that at -0.7 V. The ECL spectrum for pulses between 0 and -0.7 V at ZnO (fig. 1e) is the same as that obtained at a Pt electrode pulsed between +1.2 V and -1.6 V in the same solution (fig. 1d). Both are identical to the fluorescence spectrum of rubrene, as is usual for rubrene radical ion annihilation ECL. No ECL was detected at the Pt electrode in the $\text{R}^{\cdot+}$ solution when the potential was pulsed between 0 V and -0.7 V (or any other voltage up to -1.2 V), so that preannihilation ECL at the Pt electrode does not

occur under conditions where ECL is observed at the ZnO.

The time dependence of the ECL intensity during a potential step from 0 to -0.9 V is shown in fig. 2a. The intensity (I) rises very quickly with the step and then decays during the pulse. Upon stepping back to 0 V the intensity drops to zero within a few milliseconds. The pulse decay seems to follow a t^{-1} dependence (fig. 2b), as can be seen by comparison of the experimental pulse to normalized $I-t$ plots with t^{-1} , $t^{-1/2}$, and exponential decays adjusted to fit the first 0.25 s of the experimental curve.

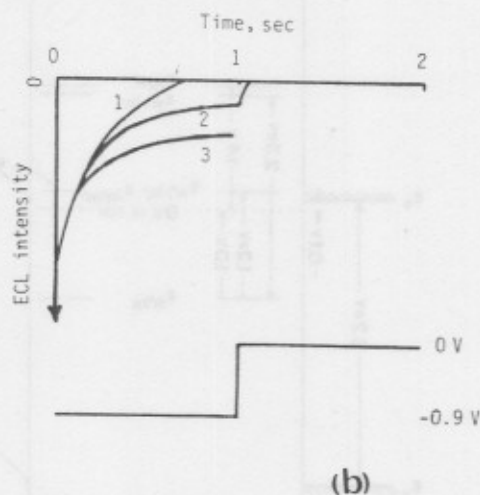
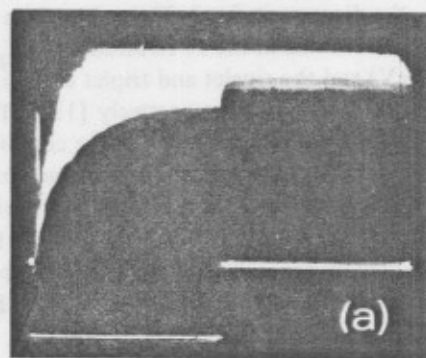


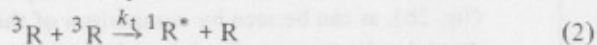
Fig. 2. (a) Time dependence of ECL of rubrene triplet state: intensity (upper curve) increases in downward direction and potential step length (lower curve) is 1 s; (b) calculated ECL intensity curves normalized at 0.25 s and to (a) for (1) $\exp(-t)$, (2) t^{-1} (essentially the same as (a) above), and (3) $t^{-1/2}$ decay.

4. Discussion

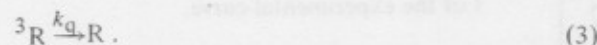
The experimental results strongly suggest the direct production of 3R by reduction of R^+ at the ZnO



followed by TTA



and quenching



The energetics of the generation can be described by the diagram in fig. 3. This is based on the E_p values determined at the Pt electrode, the E_g of ZnO (3.2 eV) and the singlet and triplet energies for rubrene (2.3 and 1.2 eV, respectively [12]). The flat-band potential, used for locating the conduction band, was estimated to be at -0.1 V by observing the potential for the onset of the photocurrent in the solution under irradiation by light from a 450 W Xe lamp [13]. The diagram generally follows that given by Grabner [10], except for the triplet energy used by him for rubrene.

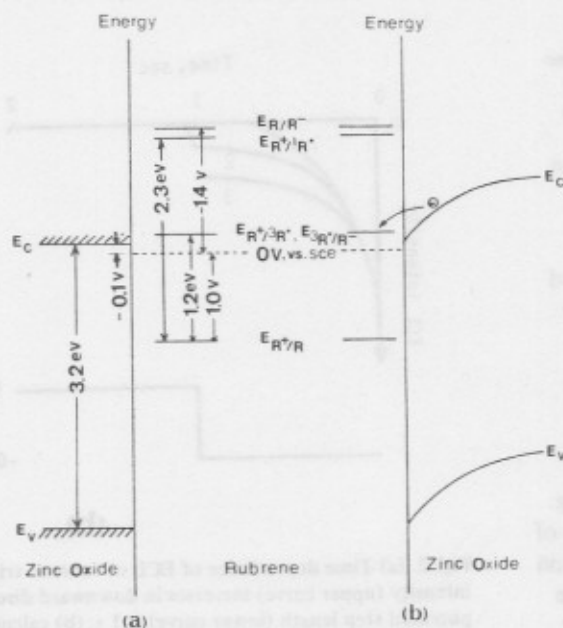


Fig. 3. Energy correlations between a ZnO surface in contact with 0.1 M TBAP-benzonitrile/benzene solution and energy states of rubrene (a) before and (b) during cathodic polarization.

We feel this value (1.75 eV), reported by Yildiz et al. [14], is too large and differs significantly from the measured value for tetracene (1.2 eV) and from the value adopted in numerous ECL studies. Based on our values the energy level for the $R^+/^3R$ system lies at or slightly below the ZnO conduction band, (CB), so that electron transfer from the CB to this level should be favored. Direct production of ground state singlet rubrene is less probable, since this level is well within the gap region. At more negative potentials an accumulation layer forms in the semiconductor and metal-like behavior arises. At these potentials reduction of R and R^+ to R^- occurs followed by the annihilation ECL, as observed by Grabner [10]. The E_p value for the R/R^- system is shifted to negative values on ZnO compared to Pt suggesting slow electron transfer.

If the reduction of R^+ to 3R is controlled by the rate of diffusion of R^+ to the electrode, then the observed t^{-1} decay of the emission can be rationalized. For the electrode reaction, if the current is mass transfer controlled, it would decay with $t^{-1/2}$ (Cottrell behavior). Thus the rate of production of 3R varies as $t^{-1/2}$. The triplet decays by the reactions shown in (2) and (3), so that, if $k_t [^3R]^2 \ll k_q [^3R]$, the instantaneous steady state concentration of 3R also varies as $t^{-1/2}$. Since I is proportional to $[^3R]^2$, it would then vary as t^{-1} , as observed. Similarly direct production of an emitting triplet (e.g. $Ru(bipy)_3^{2+}$) or singlet under diffusion controlled conditions should show I decaying as $t^{-1/2}$. In radical ion annihilation ECL generated by double potential steps I generally decays with an $\exp(-t^{1/2})$ pattern [15,16]. Although this explanation can rationalize the $I-t$ behavior, the plateau observed in the R^+ reduction $I-E$ curve and the increase in I with E in this region (fig. 1c) suggest that other rate limiting steps, aside from diffusion, are also involved in the process and bear further investigation.

Based on the E_{pc} for the R/R^- system and the triplet energy one would predict that 3R would be reduced at the potentials where the reduction of R^+ to 3R occurs [4]. If this happens, R^- will be generated, and, unlike the behavior at a metal where R^- would be rapidly oxidized to R , some R^- will escape the ZnO electrode surface and react with incoming R^+ producing ECL. This route, which also involves 3R as an intermediate, appears to be a possible alternative to TTA for production of ECL.

We also performed similar experiments with an n-type TiO_2 electrode; in this case no emission was observed before R^- generation. For TiO_2 the conduction band probably lies at somewhat more negative potentials (based on measurements in acetonitrile) and the presence of the intermediate level in the band gap region [17] may lead to quenching of the triplet species by electron transfer processes.

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