

Electrogenerated chemiluminescence. 40. A chemiluminescent polymer based on the tris(4-vinyl-4'-methyl-2,2'-bipyridyl)ruthenium(II) system

Hector D. Abruna, and Allen J. Bard

J. Am. Chem. Soc., **1982**, 104 (9), 2641-2642 • DOI: 10.1021/ja00373a054 • Publication Date (Web): 01 May 2002

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observed in the anodic α methoxylation of *N*-carbomethoxy-piperidine and -pyrrolidine are 1.81 ± 0.05 and 1.84 ± 0.05 , respectively.²¹ The electron-transfer process is also involved in the oxidation of benzyl-*tert*-butylamine by chlorine dioxide, the isotope effect being 1.8.²⁰ In comparison of these isotope effects with those shown in Table II, the good agreement suggests that the electron-transfer process is involved in the selectivity determining step of the microsomal dealkylation of amines and amides. This suggestion may also be supported by the agreement of the selectivity of dealkylation between microsomal and anodic dealkylations shown in Table I.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid for a Special Project Research (1) (No. 56109011).

Registry No. 1, 19009-26-8; 2, 81256-33-9; 3, 81256-34-0; 4, 81256-35-1; 5, 81256-36-2; 6, 81256-37-3; 7, 65100-48-3; 8, 81256-38-4; 10,11-dihydro-*N*-ethyl-5*H*-dibenz[*b,f*]azepine-5-propanamine, 2095-96-7; 10,11-dihydro-*N*-methyl-5*H*-dibenz[*b,f*]azepine-5-propanamine, 50-47-5; 10,11-dihydro-*N*-isopropyl-5*H*-dibenz[*b,f*]azepine-5-propanamine, 2292-76-4; *N*-butyl-10,11-dihydro-5*H*-dibenz[*b,f*]azepine-5-propanamine, 2064-08-6; *N*-ethylbenzenepropanamide, 81256-39-5; *N*-methylbenzenepropanamide, 940-43-2; *N*-isopropylbenzenepropanamide, 56146-87-3; *N*-butylbenzenepropanamide, 10264-11-6; demethylimipramine carbamate, 27097-69-4.

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Electrogenerated Chemiluminescence. 40. A Chemiluminescent Polymer Based on the Tris(4-vinyl-4'-methyl-2,2'-bipyridyl)ruthenium(II) System

Héctor D. Abruña and Allen J. Bard*

Department of Chemistry, University of Texas
Austin, Texas 78712

Received December 14, 1981

We report the electron-transfer chemiluminescence resulting from reaction between oxidized and reduced centers in a polymer produced by electroinitiated polymerization of tris(4-vinyl-4'-methyl-2,2'-bipyridyl)ruthenium(II) ($\text{Ru}(\text{v-bpy})_3^{2+}$) ($\text{bpy} = 2,2'$ -bipyridine) onto a platinum electrode surface. The generation of luminescent excited states via electron-transfer reactions of electrogenerated intermediates (called electrogenerated chemiluminescence, ECL) has been extensively investigated for systems based on organic molecules (e.g., the radical ions of 9,10-diphenylanthracene) as well as for transition-metal complexes (e.g., the +1 and +3 species generated from $\text{Ru}(\text{bpy})_3^{2+}$).¹⁻³ The emission of light arises from the solution in the vicinity of the electrode surface where the reactants are produced. ECL studies are usually carried out in aprotic solvents in which the highly reactive oxidized and reduced forms are stable. We have become interested in polymer electrodes³⁻⁵ and in the possibility of studying

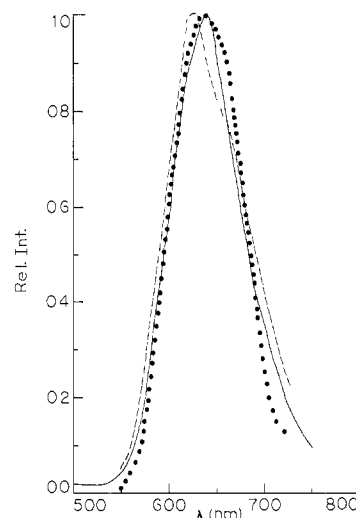


Figure 1. Normalized emission for: (A) luminescence spectrum for $\text{Ru}(\text{v-bpy})_3^{2+}$ in CH_3CN solution (—); (B) electrogenerated chemiluminescence (ECL) for 1.0 mM $\text{Ru}(\text{v-bpy})_3^{2+}$ solution in CH_3CN , 0.1 M TBAP (---); (C) surface ECL for a Pt electrode coated with a film of $\text{Ru}(\text{v-bpy})_3^{2+}$ polymer in CH_3CN , 0.1 M TBAP (···). For B and C, pulses between +1.5 and -1.45 V vs. SSCE with a width of 1 s were used (response (uncorrected) of Hamamatsu Model R928 photomultiplier tube).

electron-transfer reactions and charge transfer in polymers by carrying out ECL experiments with these. Thus we recently reported chemiluminescence of $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a Nafion polymer film on an electrode surface.³ However, this was not a regenerative ECL system and involved the irreversible oxidation of oxalate ion in the reaction.

The polymer employed in the work reported here was prepared by electroreduction of $\text{Ru}(\text{v-bpy})_3^{2+}$ in an acetonitrile solution onto a platinum electrode surface following the procedure of Murray and co-workers.⁵ This method produces a layer of polymer (from ~ 40 Å to ~ 1 μm thick) containing Ru(II) centers distributed along hydrocarbon chains originating from the vinyl groups. The work reported here involves a 3 mm by 3 mm Pt flag electrode covered with a film containing $2-6 \times 10^{-8}$ mol/cm² electroactive species. When such a modified electrode is placed in CH_3CN , 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and the potential of the electrode is pulsed at a frequency of 0.5 Hz between +1.5 and -1.5 V vs. SSCE, an orange emission is observed from the electrode surface (Figure 1C). Since there is no complex in solution, the emission must arise from the immobilized complex, presumably via an electron-transfer (annihilation) reaction between electrogenerated +1 and +3 centers, by analogy to the previous $\text{Ru}(\text{bpy})_3^{2+}$ results.^{2,3} Further evidence that the ECL reaction involves polymer species comes from studies of ECL of the dissolved monomer itself (Figure 1B). The surface ECL (Figure 1C) is blue-shifted by $\sim 15-20$ nm relative both to the luminescence spectrum of $\text{Ru}(\text{v-bpy})_3^{2+}$ obtained in CH_3CN solution (Figure 1A) and to the ECL spectrum observed in solution (Figure 1B).⁶

The surface ECL is rather short-lived (~ 20 min of continuous pulsing at ± 1.5 V vs. SSCE with 1-s pulse durations). As with the $\text{Ru}(\text{bpy})_3^{2+}$ system in solution, this instability is probably associated with the +1 Ru form. Previous studies have shown instability of polymers containing immobilized $\text{Ru}(\text{bpy})_3^{2+}$ centers.⁷ The ECL lifetime is remarkably long, however, considering the thin layer of the film and the very small amount of electroactive

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(7) Abruña, H. D.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1979**, *18*, 3233. Some instability of the reduced forms of $\text{Ru}(\text{bpy})_3^{2+}$ have been previously noticed in solution studies.²

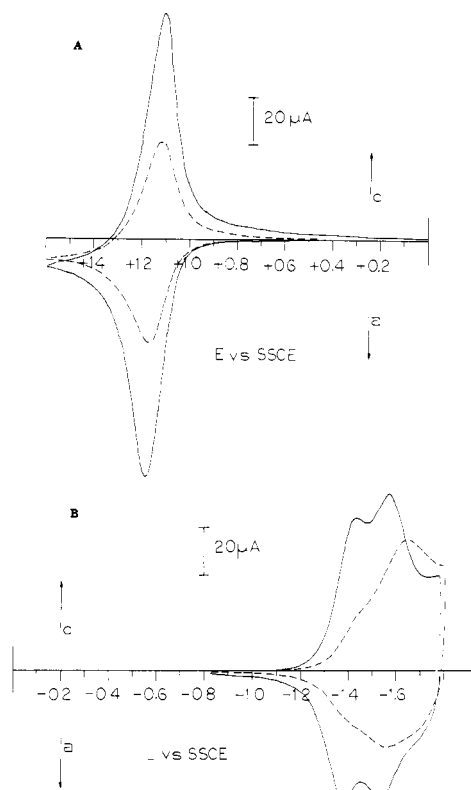


Figure 2. Cyclic voltammograms in CH_3CN , 0.1 M TBAP for a Pt flag electrode ($3 \text{ mm} \times 3 \text{ mm}$) coated with a film of $\text{Ru}(\text{v-bpy})_3^{2+}$ containing $5.2 \times 10^{-8} \text{ mol/cm}^2$ Ru prior to (—) and after (---) ECL: (A) anodic sweeps at 20 mV/s; (B) cathodic sweeps at 10 mV/s.

material. For comparison, ECL cells involving thin solution layers 100–1000 times thicker ($\sim 10\text{--}100 \mu\text{m}$) with the $\text{Ru}(\text{bpy})_3^{2+}/\text{CH}_3\text{CN}$ system usually last only ~ 30 min under continuous pulsing.⁸

The decay mechanism seems to involve at least in part the generation of some electroinactive products. This is evident from the cyclic voltammograms for the oxidation and reduction of the immobilized complex obtained before and after ECL. Cyclic voltammograms in CH_3CN , 0.1 M TBAP (containing no dissolved complex) for an electrode coated with the $\text{Ru}(\text{v-bpy})_3^{2+}$ polymer prior to ECL show well-defined electrochemical surface waves for both the oxidation ($E^0 = 1.13 \text{ V vs. SSCE}$) and reduction ($E^0 = -1.41$ and -1.55 V vs. SSCE) (Figure 2). After extended ECL, cyclic voltammograms for the same electrode showed waves suppressed in height and less well-defined (reduction waves) with somewhat more tailing reminiscent of diffusional processes (Figure 2).

Since no coloration of the solution was observed after ECL, extensive dissolution of the immobilized complex does not take place, and the decrease in the electrochemical response is probably due to some decomposition of the polymer film. If half of the Ru species ($\sim 5 \times 10^{-9} \text{ mol}$) had dissolved in the 5 cm^3 of solution, the micromolar amounts of material would have been readily detectable.

Experiments are currently in progress to determine the nature of the processes in this polymer and to design other polymer layers containing donor and acceptor centers that will produce ECL. These are of interest not only as probes of the behavior of polymer electrodes but also perhaps as a means of obtaining a long-lived display device based on ECL.⁹

Registry No. $(\text{Ru}(\text{v-bpy})_3)^{2+}$, 75675-24-0; $(\text{Ru}(\text{v-bpy})_3)^{2+}\text{X}$, 81206-05-5.

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(9) The support of this research by the Army Research Office and the National Science Foundation (CHE 7903729) is gratefully acknowledged.

Silicon-Directed Nazarov Cyclization

S. E. Denmark* and T. K. Jones

Roger Adams Laboratory, School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801

Received December 30, 1981

Recent interest in the total synthesis of cyclopentanoid and polyquinane natural products has stimulated the development of many new methods for synthesis and annelation of five-membered rings. With regard to cyclopentenone annelation the classical Nazarov¹ cyclization reaction (Scheme I) has received much attention and has been extensively modified in the preparation of the divinyl ketone precursors (or their equivalent) and in the cyclization conditions.² A major limitation common to all of these methods and, indeed, inherent in the cyclization itself is the lack of control over the position of the double bond in the cyclopentenone moiety. Normally, the double bond resides in the thermodynamically more stable position, i.e., that with the highest degree of substitution. We report a new modification of the Nazarov reaction that provides a solution to this problem and constitutes a general method for the preparation of 4,5-annelated 2-cyclopentenones.^{3,4}

The key to this modification lies in the well-documented ability of silicon to control the regio- and stereochemical outcome of certain carbonium ion processes.⁵ This property, also known as the β effect,⁶ has dominated the utilization of organosilicon

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