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ELECTROGENERATED CHEMILUMINESCENCE

FINAL REPORT

ALLEN J. BARD

JANUARY 14, 1985

Investigations of the chemiluminescent reactions of electrogenerated species (ecl) continue. Our work of the past three years is summarized below.

I. Ecl at Polymer Electrodes.

We have become interested in polymer electrodes and in the possibility of studying electron-transfer reactions and ion transport in polymers by utilizing ecl techniques. We have recently reported the ecl of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy=2,2'-bipyridine) incorporated into a Nafion polymer film on an electrode surface.¹ The reaction of electrogenerated $\text{Ru}(\text{bpy})_3^{3+}$ with oxalate dissolved in aqueous solution leads to production of $\text{Ru}(\text{bpy})_3^{2+*}$ and light emission. Digital simulation of the current-potential and current- and light emission- time curves provides information about the mechanism of excited-state production with evidence for penetration of the polymer film by oxalate.

The above is not a regenerative ecl system and involves the irreversible oxidation of oxalate ion in the reaction. A regenerative ecl polymer electrode was prepared by electropolymerization of tris(4-vinyl-4-methyl-2,2'-bipyridyl) ruthenium(II) in an acetonitrile solution onto a platinum electrode.² The surface ecl is rather short-lived. Experiments are underway to design other more rugged polymer layers containing donor and acceptor centers that will produce ecl.

II. Ecl in Solution

The electrochemical behavior and ecl of $\text{Ru}(\text{bpz})_3^{2+}$ (bpz=2,2'-bipyrazine) in acetonitrile solution have been investigated.³ The electrochemical and ecl behavior of the $\text{Ru}(\text{bpz})_3^{2+}$ system parallel those of

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the corresponding bipyridine complex system. We extend these studies to a silicon phthalocyanine and a silicon naphthalocyanine.⁴ Both compounds show well-behaved electrochemical behavior and give near-infrared emission upon electrochemical generation of reduced and oxidized species. Along this line, work continues (in a collaborative project with Professor Harry Gray and his group at Caltech) on studies of ecl of metal cluster compounds, such as diplatinum octaphosphite ($\text{Pt}_2[\text{P}_2\text{O}_5]_4\text{H}_8^{4-}$), $\text{Mo}_6\text{Cl}_{14}^{2-}$, $\text{Mo}_2\text{Br}_4(\text{PMe}_3)_4$ ($\text{Me} = \text{CH}_3$), etc, which give strong photoluminescence and have reasonable chemical stability. Studies on the tetrabutylammonium salt of $\text{Pt}_2[\text{P}_2\text{O}_5]_4\text{H}_8^{4-}$ show that an intense green emission is generated on platinum electrodes in acetonitrile only upon reduction; no oxidation of the platinum compound is required for the generation of ecl. The experimental results suggest that the generation of the excited state of $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$ might involve the reduction of tetrabutylammonium ion, which generates a strong oxidizing radical to oxidize the platinum compound. Both $\text{Mo}_6\text{Cl}_{14}^{2-}$ and $\text{Mo}_2\text{Br}_4(\text{PMe}_3)_4$ show well-behaved electrochemical behavior and give red emission in tetrahydrofuran upon electrochemical generation of reduced and oxidized forms. The oxidized form is less stable (as compared to the reduced form) as suggested from the ecl experiment. The measurement of the ecl quantum yield on $\text{Mo}_2\text{Br}_4(\text{PMe}_3)_4$ is now underway.

The ecl produced by the reaction of electrogenerated $\text{Ru}(\text{bpy})_3^{+5}$ or reduced ^{aromatic} ~~aromatic~~ hydrocarbons⁶ with persulfate, a "reductive oxidation" mechanism (i.e., generation of a strong oxidant on reduction followed by bond cleavage), has been investigated. The ecl efficiency of the $\text{Ru}(\text{bpy})_3^{2+} - \text{S}_2\text{O}_8^{2-}$ system is high (5%) in mixed acetonitrile-water solutions (1:1 by volume) and is insensitive to dissolved oxygen. The relative ecl efficiencies of the aromatic hydrocarbon-persulfate systems

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depend upon the stability of the hydrocarbon radical cations in acetonitrile-benzene solutions. The photooxidation of $\text{Ru}(\text{bpy})_3^{2+}$ by persulfate was investigated by steady-state luminescence quenching and emission lifetime techniques in aqueous and mixed $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solutions.⁷ The results are consistent with the formation of a ground-state ion pair $[\text{Ru}(\text{bpy})_3^{2+} - \text{S}_2\text{O}_8^{2-}]$. The lifetime of the photoexcited ion pair $[\text{Ru}(\text{bpy})_3^{2+} - \text{S}_2\text{O}_8^{2-}]^*$ is unusually long, ranging from 0.11 μs in H_2O to 0.53 μs in 50% CH_3CN .

The ecl produced by the reaction of electrogenerated $\text{Ru}(\text{bpy})_3^{3+}$ with oxalate, an "oxidative reduction" mechanism (i.e., generation of a strong reductant on oxidation followed by bond cleavage), has been investigated.^{8,9} It has been shown that ecl intensity is linearly dependent on the concentration of oxalate over the region 10^{-4} to 10^{-6} M. Initial tests with synthetic urine samples suggest that this method is sufficiently selective for the determination of oxalate in urine. The potential application of the ecl based $\text{Ru}(\text{bpy})_3^{2+}-\text{S}_2\text{O}_8^{2-}$ system as a chemiluminescent label has been evaluated. Because of its specificity, good linearity and high sensitivity (10^{-13} to 10^{-7} M), application of $\text{Ru}(\text{bpy})_3^{2+}$ as a luminescent label in competitive protein binding reactions is suggested.

III. Luminescence at Semiconductor Electrodes and Colloidal Dispersions.

Photoluminescence (pl) and photoinduced oxygen adsorption of colloidal zinc sulfide dispersions have been studied.¹⁰ Three distinct photoluminescence bands (two blue emissions: 428 nm and 418 nm and one orange luminescence (OL): 583 nm) have been observed upon irradiation of doped and undoped ZnS colloidal dispersions with ultraband gap light. The OL is due to Mn^{2+} doping. The intensity of the emission depends upon the dopant concentration, the presence of dissolved oxygen, and the concentration of dissolved sulfide ion in solution. The OL emission is

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PI and electroluminescence (el) on ZnS single crystals and polycrystals doped with different impurities have been studied in various media (air, aqueous or nonaqueous solutions containing various redox couples). In aqueous solutions containing persulfate, hydrogen peroxide, oxygen or cerium(IV), self-activated Al-doped ZnS gives blue emission that peaks at about 460 nm, (Al, Ag)-doped sample generates purplish blue emission with a maximum at about 435 nm. Copper doping shifts the maximum to about 525 nm for a doping density of 100 ppm of Al and Cu each, whereas Mn-activated Al-doped samples give two emission peaks (440 and 580 nm). Temperature, pH, current density and chemical environment have strong effects on the el behavior and efficiency. Photoquenching of el and sub-bandgap photoconductivity have been applied to study the impurity levels. The pl intensity of ZnS crystals strongly depends upon the potential applied to the electrode, the excitation intensity and wavelength and the chemical environment. The detailed mechanisms responsible for these phenomena are under active investigation.

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