Electrogenerated Chemiluminescence 69: The Tris(2,2′-bipyridine)ruthenium(II), (Ru(bpy)$_3$$^{2+}$)/Tri-$n$-propylamine (TPrA) System Revisited—A New Route Involving TPrA$^{•+}$ Cation Radicals

Wujian Miao, Jai-Pil Choi, and Allen J. Bard*

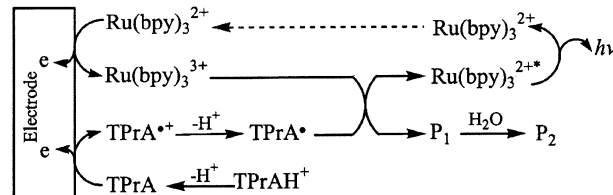*Contribution from the University of Texas at Austin, Department of Chemistry & Biochemistry, Austin, Texas 78712*

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Abstract: The reaction occurring on electrooxidation of Ru(bpy)$_3$$^{2+}$ (bpy = 2,2′-bipyridine) and tri-n-propylamine (TPrA) leads to the production of Ru(bpy)$_3$$^{2+*}$ and light emission. The accepted mechanism of this widely used reaction involves the reaction of Ru(bpy)$_3$$^{3+}$ and a reduced species derived from the free radical of the TPrA. However, this mechanism does not account for many of the observed features of this reaction. A new route involving the intermediacy of TPrA cation radicals (TPrA$^{•+}$) in the generation of Ru(bpy)$_3$$^{2+*}$ was established, based on results of scanning electrochemical microscopy (SECM)-electrogenerated chemiluminescence (ECL) experiments, as well as cyclic voltammetry simulations. A half-life of ~0.2 ms was estimated for TPrA$^{•+}$ in neutral aqueous solution. Direct evidence for TPrA$^{•+}$ in this medium was obtained via flow cell electron spin resonance (ESR) experiments at ~20 °C. The ESR spectra of the TPrA$^{•+}$ species consisted of a relatively intense and sharp septet with a splitting of ~20 G and a g value of 2.0038.
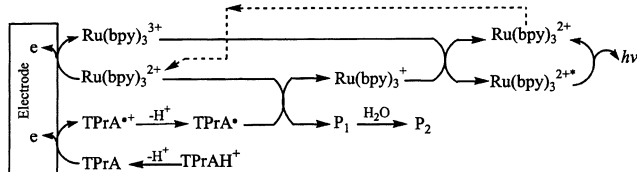
Introduction

Noffsinger and Danielson[1] first reported the chemiluminescence of Ru(bpy)$_3$$^{3+}$ with aliphatic amines. Following this study, Leland and Powell reported the electrogenerated chemiluminescence (ECL) of the Ru(bpy)$_3$$^{2+}$ (bpy = 2,2′-bipyridine) with tri-n-propylamine (TPrA) as a coreactant.[2] Since then, a wide range of ECL analytical applications involving Ru(bpy)$_3$$^{2+}$ or its derivatives as labels have been reported.[3] The Ru(bpy)$_3$$^{2+}$ (or its derivatives) with TPrA exhibit the highest ECL efficiency, and this system forms the basis of commercial systems for immunoassay and DNA analysis.[2,3,4] The ECL intensity for this system is proportional to the concentration of both Ru(bpy)$_3$$^{2+}$ and TPrA species[2,4–6] and also depends on the solution pH and the electrode material.[1,2,5] The ECL mechanism of this reaction has been investigated by many workers[1,2,4,5,7] and follows the now familiar coreactant mechanism[8] where oxidation of TPrA generates a strongly reducing species. This oxidation can be via a "catalytic route" where electrogenerated Ru(bpy)$_3$$^{3+}$ reacts with TPrA as well as by direct reaction of TPrA at the electrode described by both Scheme 1 and Scheme 2: [where TPrA$^{•+}$ =
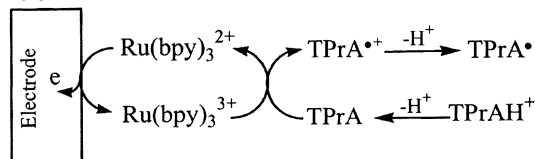
Scheme 1

Scheme 2

Scheme 3

(CH$_3$CH$_2$CH$_2$)$_3$N$^{•+}$, TPrAH$^+$ = Pr$_3$NH$^+$, TPrA$^{•}$ = Pr$_2$NC$^{•}$HCH$_2$-CH$_3$, P$_1$ = Pr$_2$N$^+$C=HCH$_2$CH$_3$, and P$_2$ = Pr$_2$NH + CH$_3$CH$_2$-CHO]. The "catalytic" route involving homogeneous oxidation of TPrA with Ru(bpy)$_3$$^{3+}$ is shown in Scheme 3. The contribution of this process to the overall ECL intensity depends on the Ru(bpy)$_3$$^{2+}$ concentration and is small when relatively low concentrations of Ru(bpy)$_3$$^{2+}$ are used.[5]

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