# Background Emission of Electrogenerated Chemiluminescence during Oxidation of Tri-*n*-propylamine from the Dimeric $^1\Delta_g$ State of O$_2$

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S *Supporting Information*

ABSTRACT: The background electrogenerated chemiluminescence (ECL) emission observed only upon electrochemical oxidation of tri-*n*-propylamine (TPrAH) on a platinum electrode is a limiting factor in ECL analytical techniques and is poorly understood. We studied this reaction in aerated acetonitrile (MeCN) solution with TPrAH oxidized at a constant potential at the Pt surface and observed ECL spectra with an emission band at 630 nm, which is characteristic of the emission of the dimeric $^1\Delta_g$ state of O$_2$. No ECL emission was observed when the same solution was deaerated. This background ECL emission is attributed to the reaction between dissolved oxygen and two different products of TPrAH oxidation: the TPrAH$^\bullet$ radical that reduces O$_2$ to the superoxide ion and the TPrAH$^{\bullet+}$ radical cation that oxidizes this species to singlet O$_2$.
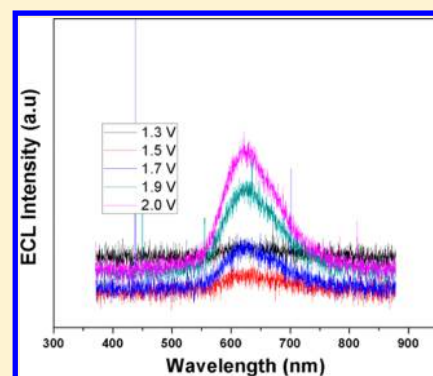
Tri-*n*-propylamine (TPrAH) is a widely used coreactant in electrogenerated chemiluminescence (ECL) sensors, e.g., for immunoassay.[1−3] In this reaction electro-oxidation of TPrAH in an aqueous medium produces a highly reducing intermediate that reacts with the oxidized luminophore, Ru(bpy)$_3^{3+}$, to produce intense ECL emission.[4,5] The TPrAH reaction is complex with both oxidant and reductant intermediates produced.[6] In nonaqueous solvents TPrAH also behaves as a coreactant to produce ECL signals with many luminophores.[7] However, even in the absence of luminophores, like Ru(bpy)$_3^{2+}$, electro-oxidation of TPrAH produces a weak ECL signal that, in fact, limits the sensitivity of ECL analytical methods.[8] The nature of this reaction is not understood, e.g., what species in this system is the ultimate ECL emitter and how it is produced.

ECL processes that involve oxygen have been studied previously. Our laboratory proposed a mechanism for producing the electronically excited state $^1O_2$ by the ECL annihilation reaction between the one-electron reduction product of oxygen, superoxide (O$_2^{\bullet-}$), and ferricenium cation in nonaqueous solution.[9] Moreover, Wang et al.[10] reported that very weak luminescence was produced at a Pt electrode during evolution of oxygen in an aqueous medium, which they attributed to recombination between excited singlet oxygen molecules. Further, Reshetnyak and Kovalchuk[11] observed ECL by the electroreduction of peroxydisulfate on a Pt electrode and proposed a scheme for singlet oxygen formation. In this work we show that the background TPrAH ECL emission involves formation of the dimeric $^1\Delta_g$ state of O$_2$ and propose a mechanism for the reaction.

■ EXPERIMENTAL DETAILS

Chemicals. Tri-*n*-propylamine (TPrAH), the electrochemical grade of acetonitrile (MeCN), and tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$) were used as received from Sigma-Aldrich. TPrAH was distilled under vacuum conditions and kept in an Ar atmosphere glovebox.

Instrumentation and Procedures. A 2 mm diameter Pt disk inlaid in glass was used as the working electrode (WE, surface area = 0.024 cm^2) and was bent at a 90° angle (L-type electrode) so that the electrode surface faced the detector in the ECL experiments. Before each experiment the WE was polished with 0.3 μm alumina and then sonicated in ethanol and water for 5 min. Pt wire served as a counter electrode and a Ag wire as a quasi-reference electrode (QRE). All glassware and electrodes were dried at 120 °C for 2 h prior to transfer to the Ar atmosphere glovebox (Vacuum Atmospheres Corp., Hawthorne, CA). All solutions were prepared in an Ar atmosphere glovebox and placed in an airtight electrochemical cell with a Teflon cap for measurements completed outside of the box. Cyclic voltammetry (CV) and potential step experiments were performed with an Autolab electrochemical workstation (Eco Chemie, The Netherlands). The ECL along with CV signals were measured simultaneously with a photomultiplier tube (PMT, Hamamatsu R4220p). The PMT was held at −750 V with a high-voltage power supply Kepco (New York, NY). The photocurrent generated at the PMT was converted to a voltage
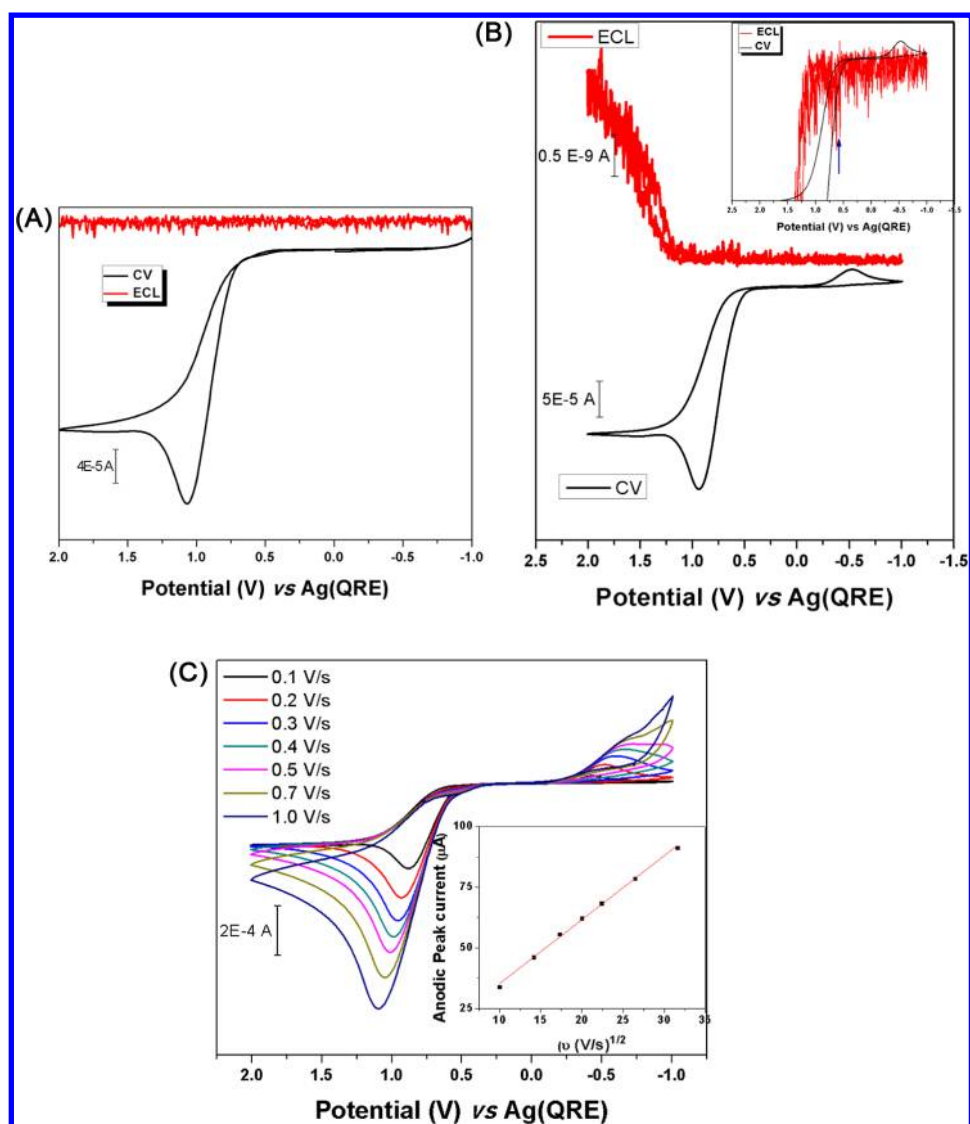
Figure 1. (A) CV (black line) and ECL (red line) curves of 30 mM TPrAH in a 0.1 M TBAPF$_6$ MeCN solution under Ar at a scan rate of 0.1 V/s. Initial potential at 0 V scanning first to positive potentials. (B) CV (black line) and ECL (red line) curves under the same solution conditions with 30 mM TPrAH in 0.1 M TBAPF$_6$ MeCN solution with aerated O$_2$-saturated conditions. Inset: close-up of the "y" scale of panel B. (C) CV at different scan rates with 30 mM TPrAH in an aerated 0.1 M TBAPF$_6$ MeCN solution. Inset: plot of anodic peak current vs square root of scan rate of panel C.

using an electrometer system (model 6517, Keithley, Cleveland, OH) and connected to the Autolab via an analog-to-digital converter (ADC). ECL emission spectra were recorded with a charge-coupled device (CCD) camera (Princeton Instruments, SPEC-10) that was cooled to −100 °C by applying a constant potential to the electrode for 1 min with the potentiostat.

RESULTS AND DISCUSSION

Electrochemistry and ECL in Aerated and Deaerated Solutions. Figure 1A shows a typical CV and ECL response for a 30 mM TPrAH, 0.1 M TBAPF$_6$ in MeCN solution on a Pt electrode under an inert atmospheric, i.e., a solution prepared in Ar glovebox in a gastight Teflon-capped cell. An irreversible anodic wave for oxidation of TPrAH appeared at 1.1 V vs Ag (QRE), and in this inert atmosphere, no corresponding ECL signal above the noise was observed. However, a repeat of this experiment after several hours in the open atmosphere or with O$_2$ gas purging for 20 min produced a clear ECL signal (Figure 1B) (red line). The CV (black line) in oxygen also showed a

reduction peak at −0.5 V vs Ag (QRE) attributable to O$_2$ reduction to form O$_2^{\bullet-}$. The irreversible oxidation wave corresponds to formation of TPrAH$^{\bullet+}$, which then rapidly deprotonates to generate TPrA$^{\bullet}$, a highly reducing intermediate species.[6] The instability of TPrAH$^{\bullet+}$ by deprotonation is rapid on the time scale of the CV, and no reverse oxidation wave was found up to a scan rate of 1 V/s (see Figure 1C). As can be seen in Figure 1, the TPrAH oxidation at 0.1 V/s scan rate, oxidation peak starts at about 0.7 V and the current limits at 1.4 V constant to 2.0 V. This can be attributed to the onset of natural convection at the L-shaped electrode where the electrode surface is oriented perpendicular to the cell bottom.[12,13] However, at higher scan rates, v, TPrAH oxidation peak current linearly increases with $v^{1/2}$ (inset of Figure 1C) indicating a typical diffusion-controlled reaction. The ECL starts at about 0.7 V, where the TPrAH oxidation begins and becomes more intense with the onset of natural convection (inset of Figure 1B). At lower concentrations of TPrAH in the presence of O$_2$, a single ECL peak starting at the onset of

oxidation of TPrAH (see Figure S1 in the Supporting Information) and only with a concentration of 20 mM TPrAH or higher was the ECL peak observed more intense at 1.3 V vs Ag (QRE), probably because of more significant natural convection at the higher concentrations. We also carried out chronoamperometric (i−t curve) measurements with a constant potential step for 5 s to study the ECL under the same experimental solution conditions as Figure 1B; a graph of applied electrode potential versus ECL intensity is shown in Figure 2. These results clearly indicate that ECL signals start at 0.6 V, where TPrAH oxidation also starts. An increase in signal and convective effect is also seen.
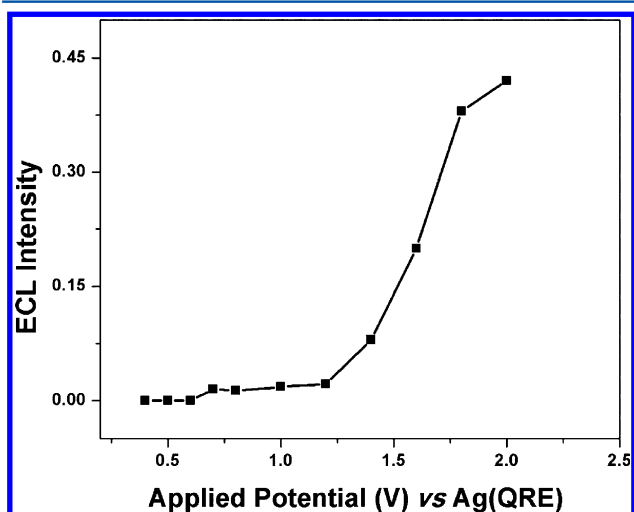
Figure 2. ECL intensity as a function of applied potential for 5 s in 30 mM TPrAH in a 0.1 M TBAPF$_6$ MeCN solution with O$_2$-saturated conditions.

We also performed a control experiment of the CV and ECL behavior at a Pt electrode in both deaerated and O$_2$-saturated conditions without adding TPrAH in MeCN solution (Figure 3). In deaerated solution the CV showed no oxidation or reduction waves, whereas in the aerated solution waves for the formation of Pt oxide (e.g., PtO), anodic peak potential about
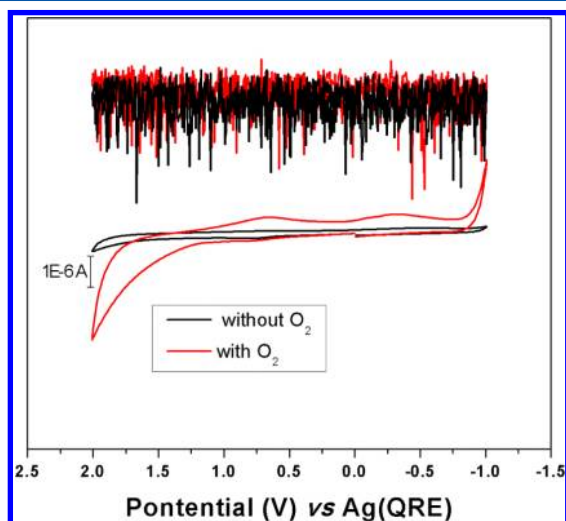
Figure 3. CV and corresponding ECL with a Pt electrode in a 0.1 M TBAPF$_6$ MeCN solution in the absence of TPrAH with (red line) and without (black) O$_2$ saturation.

1.25 V and its reduction at 1.0 V vs Ag (QRE), as well as the well-known peaks for reduction of dissolved oxygen on Pt and the oxidation of O$_2^{•−}$ were observed. No ECL signals were seen in either case. Thus, both TPrAH and oxygen are needed for ECL emission.

ECL Emission Spectrum. A question about the background emission from TPrAH oxidation has been the nature of the emitting species, since the emission is in the visible region near that of Ru(bpy)$_3^{2+}$ and there are few obvious candidates. Because this emission is weak, it has also been difficult to obtain a spectrum. However, under our conditions, we could record the ECL spectrum in MeCN under the conditions of Figure 1B with different constant potential pulses in the TPrAH oxidation region applied for 1 min (Figure 4). The ECL emission occurs
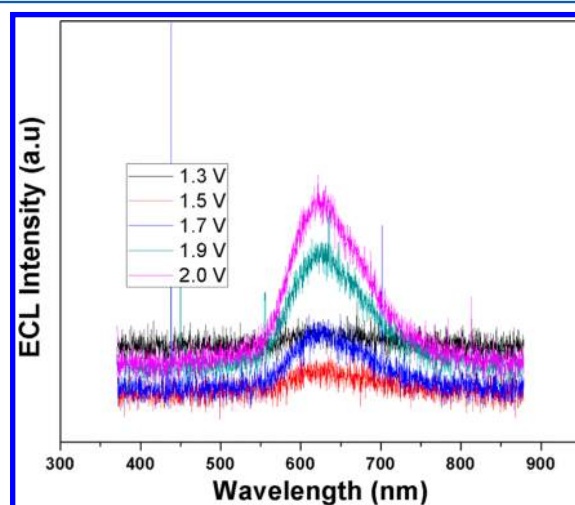
Figure 4. ECL spectrum of 30 mM TPrAH in a 0.1 M TBAPF$_6$ MeCN solution with aerated O$_2$-saturated atmosphere at several applied potentials for 1 min.

with a peak at 630 ± 4 nm for applied potentials >1.3 V vs Ag (QRE), with the intensity increasing up to 2 V vs Ag (QRE). Khan and Kasha reported that the characteristic oxygen emission at 634 nm is due to the singlet oxygen dimol state involving collisions of two ^{1}O$_2$ molecules in the gas phase to form (^{1}O$_2$)$_2$ at an emission wavelength at twice the energy of the direct ^{1}O$_2$ near-infrared emission at 1270 nm.[14] Hence, the background ECL emission at 630 nm band indicates the formation of the dimeric state of singlet oxygen. Although the applied electrode potential versus ECL intensity curves in Figure 2 show the ECL emission is stable with time at 0.7 V and more positive, but the light intensity is not of sufficient intensity to obtain an ECL spectrum with the CCD, so only at potentials of 1.3 V onward was the intensity strong enough to record the ECL spectrum.

Proposed Reaction Mechanism. Formation of excited states in ECL are based on an electron-transfer annihilation reaction with sufficient energy to form the excited state of an emitting species from one of the reactants, i.e.:

$$A^{•−} + D^{•+} \rightarrow A^* + D \tag{1}$$

It is thus necessary to explain how, simply on oxidation of TPrAH, one can form the needed reduced and oxidized species. However, an earlier examination of the oxidation of TPrAH showed that both the oxidized TPrAH$^{•+}$ and the reducing product, TPrA$^•$, both have sufficient lifetimes in a typical ECL reaction to cause electron-transfer reactions.[6]

$$TPrAH \rightarrow TPrAH^{\bullet+} + e^- \tag{2}$$

$$TPrAH^{\bullet+} \rightarrow TPrA^{\bullet} + H^+ \tag{3}$$

The $TPrA^{\bullet}$ radical is a strong reductant ($E° = -1.7$ V vs SCE)[7] and so clearly can reduce O_2 to $O_2^{\bullet-}$ ($E° = -0.9$ V vs SCE):[15]

$$TPrA^{\bullet} + O_2 \rightarrow TPrA^+ + O_2^{\bullet-} \tag{4}$$
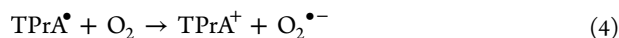
The estimated potential of $TPrAH^{\bullet+}$ is 0.9 V vs SCE, so the annihilation reaction

$$TPrAH^{\bullet+} + O_2^- \rightarrow TPrAH + {}^1O_2 \tag{5}$$
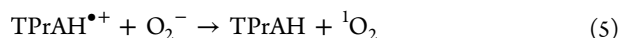
thus has an energy of about 1.7 eV (assuming an entropic loss of about 0.1 eV) that clearly can produce $^1O_2$ with an excitation energy of about 1 eV. This is followed by the dimerization reaction to produce the emitting dimol species

$$2 {}^1O_2 \rightarrow ({}^1O_2)_2^* \tag{6}$$

$$({}^1O_2)_2^* \rightarrow 2 {}^3O_2 + h\nu \quad (630 \text{ nm}) \tag{7}$$
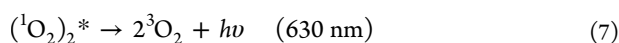
He et al. also reported direct electro-oxidation of TPrAH in alkaline pH solution to produce $TPrAH^{\bullet+}$, which then reacts with dissolved oxygen to yield $O_2^{\bullet-}$ by electron transfer from $TPrAH^{\bullet}$.[16] Earlier, Bader and Kuwana reported very low level ECL emission on a Pt electrode in Me_2SO/0.2 M $LiClO_4$ or MeCN/0.1 M $LiClO_4$ containing dissolved oxygen, when the potential was scanned in a negative direction to the reduction of oxygen and then reversed to the positive direction that was assigned to singlet oxygen emission.[17] A firm mechanism for the formation of the excited state of oxygen was not established, but as the authors point out, chemiluminescence is a general phenomenon in processes involving oxidation with O_2. The work described here provides an interesting, but probably not unique, path where oxidation of a suitable coreactant molecule can provide both the reductant and oxidant to produce the emitting oxygen excited state.

CONCLUSION

We demonstrate here that background ECL emission at 630 nm during the electrochemical oxidation of tri-n-propylamine (TPrAH) in the presence of dissolved O_2 in MeCN solution can be attributed to the dimeric $^1\Delta_g$ state of O_2. The formation of the excited state is based on TPrAH forming both an oxidizing species, the radical cation, and a reducing species, the radical that results from deprotonation of the cation radical. These results suggest that the sensitivity of analytical applications of ECL could be improved by the rigorous exclusion of O_2.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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