Electrochimica Acta 180 (2015) 196–201

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrogenerated Chemiluminescence (ECL) Quenching of the Ru(bpy)$_3^{2+}$/TPrA System by the Explosive TNT

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ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 30 July 2015
Accepted 19 August 2015
Available online 22 August 2015

Keywords:
Electrogenerated chemiluminescence (ECL)
2,4,6-Trinitrotoluene (TNT)
Explosive
Quenching
Stern-Volmer constant

ABSTRACT

We report the quenching behavior of 2,4,6-trinitrotoluene (TNT) on the electrogenerated chemiluminescence (ECL) of the Ru(bpy)$_3^{2+}$/TPrA [bpy = tris(2,2′-bipyridine), TPrA = tri-*n*-propylamine] system at a Pt electrode in acetonitrile containing tetra-*n*-butylammonium perchlorate supporting electrolyte. Effective ECL quenching of the system upon the addition of TNT was observed, with a Stern-Volmer constant of $2 \times 10^4\,M^{-1}$. The quenching constant calculated from the Stern-Volmer plot was found to be $2.1 \times 10^{10}\,M^{-1}\,s^{-1}$ which suggests the efficient quenching of ECL by TNT. The competitive processes of consuming TPrA$^{\bullet}$ free radicals and Ru(bpy)$_3^{+}$ species (produced as a result of reduction of Ru(bpy)$_3^{2+}$ by TPrA$^{\bullet}$) by TNT largely contributed to this quenching, in which the consumption of Ru(bpy)$_3^{+}$ by TNT was more favorable than that of TPrA$^{\bullet}$ free radicals. TNT was also found to quench the fluorescence of Ru(bpy)$_3^{2+}$, with a Stern-Volmer and a quenching constant of $5.2 \times 10^3\,M^{-1}$ and $5.5 \times 10^9\,M^{-1}\,s^{-1}$, respectively. This collisional (dynamic) based fluorescence quenching process contributed approximately one quarter of the overall ECL quenching efficiency. The present ECL quenching scheme could be used to detect TNT at submicromolar levels.

1. Introduction

2,4,6-Trinitrotoluene (TNT) is a flammable odorless solid that exists as colorless orthorhombic crystals or yellow monoclinic needles but does not occur naturally in the environment [1]. The groundwater or seawater contamination has occurred due to the production, storage, testing, and disposal of explosives at military installations, resulting in the environmental problems because these toxic and persistent compounds can leach from soil [2–4]. At the end of World War II, an estimated 300,000 tons of explosives (mainly TNT) were disposed to the sea [1]. TNT is considered as toxic as it produces toxic and mutagenic effects to life including human being [5].

The methods with ability for rapid on-site detection of TNT are highly desired. Currently, several methods of detection of TNT are used, which include those based on fluorescence [6–17], amperometry [18,19], surface plasmon resonance [5,20–28], mass spectrometry [29–34], chromatography [35–39], Raman spectroscopy [40–44], and ion mobility spectroscopy [45,46]. In addition to amperometry, other electrochemical techniques have also been used to detect TNT [47–51]. Each individual detection method described above has its own advantages, but some drawbacks remain. For example, fluorescence techniques generally suffer from the luminescent impurities, the ion mobility spectroscopic technique suffers from the matrix effects, and chromatographic separation-mass spectrometric detection methods require sample preparation and are not appropriate for field tests. These techniques use expensive instruments that frequently require skilled manpower to operate. The immunoassay-based electrogenerated chemiluminescence (ECL) technique, which possesses very high sensitivity and selectivity but requires extra effort in sample preparation, has been used to detect TNT in soil and water samples [52–54]. Methods based on ECL quenching have been recently employed in the detection and quantification of e.g., phenols, quinones, and catechols [55,56], as well as the explosives triacetone triperoxide and tetryl in acetonitrile (via the Ru(bpy)$_3^{2+}$ ion annihilation ECL scheme) [57,58].

Because each nitro group in TNT could undergo sequential 4e$^-$ to 6e$^-$ reduction to form hydroxylamine and amine within a potential range of 0 to ~-1.0 V vs SCE [59–64], TNT could be used to quench or inhibit the ECL signals generated from a known "oxidative-reduction" type standard such as the Ru(bpy)$_3^{2+}$/TPrA (TPrA = tri-*n*-propylamine) system as detailed below.

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http://dx.doi.org/10.1016/j.electacta.2015.08.107
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When the $Ru(bpy)_3^{2+}$/TPrA system is used, both $Ru(bpy)_3^{2+}$ and TPrA are oxidized upon the anodic potential scanning:

$$\mathrm{TPrA} - \mathrm{e} \rightarrow \mathrm{TPrA}^{\bullet +} \tag{1}$$

$$\mathrm{Ru(bpy)_3}^{2+} - \mathrm{e} \rightarrow \mathrm{Ru(bpy)_3}^{3+} \tag{2}$$

$TPrA^{\bullet}$ free radicals are produced after the deprotonation of the newly produced $TPrA^{\bullet +}$:

$$\mathrm{TPrA}^{\bullet +} \xrightarrow{-\mathrm{H}^+} \mathrm{TPrA}^{\bullet} \tag{3}$$

The $TPrA^{\bullet}$ radical is a strong reducing agent with a redox potential of ~-1.7 V vs SCE [65], and is the key species of ECL generation. In the absence of TNT, the $TPrA^{\bullet}$ radical reduces Ru $(bpy)_3^{2+}$ to $Ru(bpy)_3^{+}$ that annihilates with $Ru(bpy)_3^{3+}$ to form the excited state $Ru(bpy)_3^{2+*}$ that emits light [66]:

$$\mathrm{Ru(bpy)_3}^{2+} + \mathrm{TPrA}^{\bullet} \rightarrow \mathrm{Ru(bpy)_3}^{+} + \mathrm{Product} \tag{4}$$

$$\mathrm{Ru\,(bpy)_3}^{3+} + \mathrm{Ru\,(bpy)_3}^{+} \rightarrow \mathrm{Ru(bpy)_3}^{2+*} + \mathrm{Ru\,(bpy)_3}^{2+} \tag{5}$$

$$\mathrm{Ru\,(bpy)_3}^{2+*} \rightarrow \mathrm{Ru\,(bpy)_3}^{2+} + h\nu \tag{6}$$

Alternatively, the excited state $Ru(bpy)_3^{2+*}$ can be produced via the following process:

$$\mathrm{Ru(bpy)_3}^{3+} + \mathrm{TPrA}^{\bullet} \rightarrow \mathrm{Ru(bpy)_3}^{2+*} + \mathrm{Product} \tag{7}$$

In the presence of TNT, however, part or the entire portion of the $TPrA^{\bullet}$ radicals could be consumed by TNT, resulting in significant decrease or complete quenching of the initial ECL signals of the Ru $(bpy)_3^{2+}$/TPrA system:

$$n\mathrm{TPrA}^{\bullet} + \mathrm{TNT} \rightarrow \mathrm{TNT}^{n-} + \mathrm{Product} \tag{8}$$

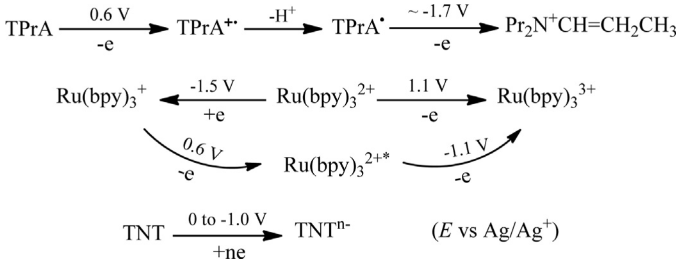
Additionally, $Ru(bpy)_3^{+}$, another key species for ECL generation (Eqs. (4)–(5))could be consumed by TNT:

$$n\mathrm{Ru(bpy)_3}^{+} + \mathrm{TNT} \rightarrow \mathrm{Ru(bpy)_3}^{2+} + \mathrm{TNT}^{n-} \tag{9}$$

which leads to further decrease in ECL intensity.

The aforementioned electron transfer processes could be better understood with the redox potentials associated with TPrA, Ru $(bpy)_3^{2+}$, $Ru(bpy)_3^{2+*}$, TNT, and their derivatives as shown in Scheme 1 [66].

The present work focuses on the studies of the ECL quenching behavior of the $Ru(bpy)_3^{2+}$/TPrA system by TNT. Fluorescence investigations will be conducted so that the respective contributions of the electron-transfer reactions and the collisional (dynamic) process to the overall ECL quenching can be estimated. Data obtained from this study could be used to develop a new strategy that is simple, inexpensive, and sensitive for TNT detection and quantification.



Scheme 1. Redox potentials of TPrA, $Ru(bpy)_3^{2+}$, $Ru(bpy)_3^{2+*}$, TNT, and their derivatives.

2. Experimental

2.1. Chemicals

The chemicals used in this study were: acetonitrile (MeCN, 99.8%, HPLC grade), tris-(2,2'-bypyridine) dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2{\cdot}6H_2O$, 99.95%), and tri-*n*-propylamine (TPrA, 99+ %) (all from Sigma-Aldrich, St. Louis, MO, USA); 2,4,6-trinitrotoluene (TNT, 99.6%, 1000 μg/mL in MeCN, Supelco analytical, PA, USA); sodium phosphate, monobasic monohydrate (J.T. Baker Chemicals Co., Phillipsburg, NJ, USA); and silver nitrate (99.5 %) and tetra-*n*-butylammonium perchlorate (TBAP, 99+%, electrochemical grade) (both from Fluka, Milwaukee, WI, USA). All chemicals were used as received.

2.2. Electrochemical and ECL studies

Cyclic voltammetry (CV) was performed with an electrochemical workstation (Model 660A, CH Instruments, Inc., Austin, TX, USA). The ECL and CV responses were simultaneously recorded with a homemade ECL instrument [67,68], where the CHI electrochemical workstation was combined with a photo-multiplier tube (PMT, Hamamatsu R928, Japan) installed under the electrochemical cell. A voltage of -700 V was supplied to the PMT with a high voltage power supply (Model 472A Brandenburg PMT power supply, England). The light signal (as photocurrent) was detected with a high sensitive Keithley 6514 electrometer (Keithley, Cleveland, OH, USA) and converted to a voltage (in ±2 V) that was fed to the electrochemical workstation and displayed on the computer monitor. A conventional three-electrode electrochemical cell system was used with a Pt disk (2 mm diameter) as the working electrode, a Pt gauge as the counter electrode, and a Ag/Ag^+ (with 10 mM $AgNO_3$ and 0.10 M TABP in MeCN) as the reference electrode (~0.186 V vs NHE). The Pt working electrode was polished before every run with 0.3-0.05 μm alumina slurry, washed with water and dried with the Kim wipes facial tissue. Note that the test solution was used without purging with nitrogen as the electrode potential was scanned in anodic direction and oxygen from air had no effect on ECL production.

2.3. Fluorescence studies

Fluorescence experiments were carried out on a PTI Qunata Master^{TM} 40 intensity based spectrofluorometer (Photon Technology International, Inc., NJ, USA), with a slit width of 1.00 nm, excitation wavelength at 350 nm, and an emission wavelength range from 500 to 690 nm.

All experiments were conducted at the room temperature of 20 ± 1 °C.

3. Results and discussion

3.1. ECL generation from the $Ru(bpy)_3^{2+}$/TPrA system

Fig. 1A shows the CV and ECL responses of 1.0 μM $Ru(bpy)_3^{2+}$-25 mM TPrA in MeCN containing 0.10 M TBAP at a Pt electrode with a scan rate of 50 mV/s. TPrA is oxidized at ~0.6 V vs Ag/Ag^+ and the generation of ECL light starts from 0.9 V vs Ag/Ag^+ at which $Ru(bpy)_3^{2+}$ gets oxidized to $Ru(bpy)_3^{3+}$. The optimum concentration of ECL coreactant was determined by running an ECL experiment with 1.0 μM $Ru(bpy)_3^{2+}$ and different concentrations of TPrA with a Pt electrode. As shown in Fig. 1B, the maximum ECL response occurs with a TPrA concentration of 25 mM, which is in good agreement with the data reported previously [69]. This