Talanta 85 (2011) 339–344

Contents lists available at ScienceDirect

Talanta

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

Mechanism study on inorganic oxidants induced inhibition of $Ru(bpy)_3^{2+}$ electrochemiluminescence and its application for sensitive determination of some inorganic oxidants

Bin Qiu, Lingling Xue, Yanping Wu, Zhenyu Lin, Longhua Guo*, Guonan Chen

Ministry of Education Key Laboratory of Analysis and Detection for Food Safety, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, Department of Chemistry, Fuzhou University, Fuzhou, 350002, China

ARTICLE INFO

Article history:
Received 15 December 2010
Received in revised form 21 March 2011
Accepted 25 March 2011
Available online 5 April 2011

Keywords:
Electrochemiluminescence
Inhibitory
Inorganic oxidants
Quenching
$Ru(bpy)_3^{2+}$

ABSTRACT

Inhibited $Ru(bpy)_3^{2+}$ electrochemiluminescence by inorganic oxidants is investigated. Results showed that a number of inorganic oxidants can quench the ECL of $Ru(bpy)_3^{2+}$/tri-*n*-propylamine (TPrA) system, and the logarithm of the decrease in ECL intensity (ΔI) was proportional to the logarithm of analyte concentrations. Based on which, a sensitive approach for detection of these inorganic oxidants was established, e.g. the log–log plots of ΔI versus the concentration of MnO_4^-, $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$ are linear in the range of 1×10^{-7} to 3×10^{-4} M for MnO_4^- and $Cr_2O_7^{2-}$, and 1×10^{-7} to 1×10^{-4} M for $Fe(CN)_6^{3-}$, with the limit of detection (LOD) of 8.0×10^{-8} M, 2×10^{-8} M, and 1×10^{-8} M, respectively. A series of experiments such as a comparison of the inhibitory effect of different compounds on $Ru(bpy)_3^{2+}$/TPrA ECL, ECL emission spectra, UV–Vis absorption spectra etc. were investigated in order to discover how these inorganic analytes quench the ECL of $Ru(bpy)_3^{2+}$/TPrA system. A mechanism based on consumption of TPrA intermediate ($TPrA^{\cdot}$) by inorganic oxidants was proposed.

1. Introduction

Electrogenerated chemiluminescence (ECL) has become an important and valuable detection method in analytical chemistry due to its high sensitivity, good selectivity and wide linear range [1,2]. $Ru(bpy)_3^{2+}$, one of the most well-known ECL luminophores, has been widely studied because of its high chemical stability, redox property and long excited state life [3,4]. Many compounds have been found to be able to inhibit the ECL emission of well-studied $Ru(bpy)_3^{2+}$-coreactant ECL system, such as $Ru(bpy)_3^{2+}$/TprA [5–7], $Ru(bpy)_3^{2+}/C_2O_4^{2-}$ [3,8,9], $Ru(bpy)_3^{2+}$/triethylamine [10] and $Ru(bpy)_3^{2+}$/dibutylamino-ethanol (DBAE) [11]. Up to now, only few quenching mechanisms of $Ru(bpy)_3^{2+}$ ECL systems have been proposed. McCall et al. [12,13] reported the inhibition of $Ru(bpy)_3^{2+}$ ECL by phenolic moiety-containing compounds which was attributed to a mechanism involving the energy or electron transfer between $Ru(bpy)_3^{2+*}$ and the electro-oxidized species of the quencher. Recently, based on the ECL inhibition of some inorganic and organic compounds with electrochemical oxidation activity, Chi et al. [10] proposed an “electrochemical oxidation inhibiting” mechanism to explain the ECL inhibitory phenomenon in a thin-layer flow cell. In our previous studies [11], we found that the addition of dopamine (DA) can quench the ECL of $Ru(bpy)_3^{2+}$/DBAE system effectively, and a mechanism based on the quenching of reductive-form DBAE by DA-oxidation products was proposed. More recently, we also found that significant ECL inhibition was happened when mixing two ECL coreactants, therefore, a mechanism related to the consumption of coreactant intermediates was proposed [14].

MnO_4^-, $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$ are most commonly used strong oxidants in both industrial and laboratorial applications. $KMnO_4$ has been frequently served as disinfectants and bleaching agents in industry; in the laboratory, the acidic $KMnO_4$ solution is an important reagent of oxidimetry. $Fe(CN)_6^{3-}$ is an important additive in paint, ink, leather, drugs, and food. Similarly, $K_2Cr_2O_7$ are used extensively in industrial processes such as corrosion control [15], used in the manufacture of ink pigments, generated largely by metal cleaning processes, surface finishing and metal coating [16]. However, all the above mentioned inorganic oxidants are harmful to human health and environment. For example, $KMnO_4$ may cause the respiratory tract harm and other adverse effect after inhalation; $K_3Fe(CN)_6$ is virulent, reacting with acid and producing virulent hydrocyanic acid, which decompose violently poisonous cyanide under hot conditions; $K_2Cr_2O_7$ is incorporated into the first kind of carcinogen by International Agency for Research on Cancer (IARC). Therefore, accurate determination of these compounds is important for monitoring environmental pollution, for quality control of industrial products as well as for the protec-

---

* Corresponding author. Fax: +86591 22866135.
E-mail address: glonghua@163.com (L. Guo).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.03.063

tion of human health. Several methods have been reported for the detection of MnO_4^-, $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$, e.g. flow injection with fluorescence determination [17,18], spectrophotometry [19–23], electrochemistry [24,25], atomic absorption spectrometry [26–28], ion chromatography [29–32] and so on. However, these methods were either time-consuming or insensitive. In addition, the detection linear range of some methods are relatively narrow [17,18].

In the present study, some inorganic oxidants, such as MnO_4^-, $Cr_2O_7^{2-}$, IO_3^-, $Fe(CN)_6^{3-}$, ClO^-, H_2O_2, were found to be able to significantly inhibit the ECL emission of $Ru(bpy)_3^{2+}$/TprA system. Among them, MnO_4^-, $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$ have the most strongest ability to inhibit this ECL system. Therefore, sensitive approaches for determination of these substances based on inhibited ECL were developed for the first time. The inhibition mechanism of these inorganic analytes to the ECL of $Ru(bpy)_3^{2+}$/TprA system was also investigated and a reasonable reaction route was proposed. We concluded that the competition of TPrA intermediate ($TPrA^{\cdot}$) between $Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$ and these analytes should be the main contribution of the ECL inhibition. It should be noted that, although the mechanism for ECL inhibition proposed herein is attributed to the consumption of radicals of TPrA, which is similar to our previous reports about the ECL inhibition among co-reactants [11,14], the entire process of ECL inhibition is quite different. The ECL inhibitors of co-reactants are produced at the working electrode surface by electrochemical reaction, therefore, only those co-reactants with an electrochemical-oxidation potential close to TPrA have significant ECL inhibition to $Ru(bpy)_3^{2+}$/TPrA system. Case is much different for inorganic oxidants, because under the ECL potential (+1.2 V), the inorganic oxidants investigated herein cannot be oxidized at the electrode surface. Therefore, the ECL inhibitory is only related to the corresponding oxidation ability of inorganic oxidants.

2. Experimental

2.1. Chemicals

Tris(2,2-bipyridyl)dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2{\cdot}6H_2O$) and TPrA were purchased from Sigma Chemical Company (USA) and were used without further purification. Other chemicals were all of analytical purity, and double distilled water was used throughout.

The 0.05 mol L^{-1} stock solution of TPrA was prepared by dissolving the required amount of sample in ethanol. 1×10^{-2} M stock solution of $Ru(bpy)_3^{2+}$ and stock solutions of inhibitors (MnO_4^-, $Cr_2O_7^{2-}$, IO_3^-, $Fe(CN)_6^{3-}$, ClO^-, H_2O_2) with different concentrations were prepared by dissolving the required amount of sample in water. The Britton–Robison (BR) buffer was prepared by titrating stock solution containing 0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid with 0.2 M sodium hydroxide to the desired pH value.

2.2. Apparatus

ECL measurements were performed by using a system fabricated in our laboratory, which had been described in detail previously [33]. A conventional three-electrode system was used for the electrolytic system, including a glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode (sat. KCl) as the reference electrode. A commercial 5 ml cylindrical quartz cell was used as ECL cell, and it was put directly in front of the photomultiplier tube.

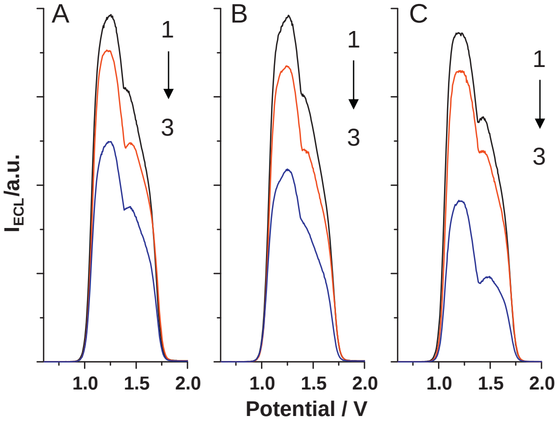

Fig. 1. Inhibition of $Ru(bpy)_3^{2+}$/TPrA ECL by (A) MnO_4^-, concentration from 1 to 3 is 0, 1.0×10^{-6} and 3.1×10^{-5} mol L^{-1}, respectively; (B) $Cr_2O_7^{2-}$, concentration from 1 to 3 is 0, 1.0×10^{-6} and 3.1×10^{-5} mol L^{-1}, respectively; (C) $[Fe(CN)_6]^{3-}$, concentration from 1 to 3 is 0, 1.0×10^{-6} and 3.1×10^{-5} mol L^{-1}, respectively. BR buffer solution (pH 8) was used throughout; scan rate: 50 mV s^{-1}; $[Ru(bpy)_3^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}, $[TPrA] = 1.0 \times 10^{-4}$ mol L^{-1}.

2.3. ECL detection procedures

The working electrode was sequentially polished with aqueous slurries of alumina (α-Al_2O_3) powders with average particle diameters of 1.0, 0.3 and 0.05 μm, respectively, to obtain a mirror-like surface. The electrode was sonicated and thoroughly rinsed with deionized water before each experiment. All experiments were done at room temperature (25 ± 1 °C). A triangular voltage was scanned in the range of 600–1400 mV with the scanning rate of 50 mV s^{-1} in buffer solution and determination was based on the ECL intensity changes (ΔI):

$$\Delta I = I_0 - I_s \quad (1)$$

where I_0 was the ECL intensity without sample, I_s was the ECL intensity with sample. The quenching rate, which was defined as $\Delta I/I_0$, was designated for the investigation of pH effecting on different ECL system.

3. Results and discussion

3.1. Inhibition of $Ru(bpy)_3^{2+}$/TPrA ECL by inorganic oxidants

Our primary results showed that lots of compounds with oxidation capability (such as MnO_4^-, $Cr_2O_7^{2-}$, IO_3^-, $Fe(CN)_6^{3-}$, ClO^-, H_2O_2) had inhibitory effect on $Ru(bpy)_3^{2+}$/TPrA ECL system. Fig. 1 shows the ECL inhibition of $Ru(bpy)_3^{2+}$/TPrA by three typical inorganic oxidants, namely, MnO_4^-, $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$. It can be seen from Fig. 1 that the increase of oxidants concentration leads to significant ECL decrease. Further investigation revealed that the quenched ECL intensity was proportional with the oxidants concentration. Therefore, it is envisioned to develop sensitive ECL approach for determination of these oxidants based on ECL inhibition.

3.2. Optimizing of the analytical parameters

In order to obtain best analytical performance for the detection of MnO_4^-, $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$, different detection conditions, e.g. electrical conditions, detection buffer and $Ru(bpy)_3^{2+}$/TPrA concentration were optimized.

The ECL performances of the three ECL system, namely, $Ru(bpy)_3^{2+}/TPrA/MnO_4^-$, $Ru(bpy)_3^{2+}/TPrA/Cr_2O_7^{2-}$, and $Ru(bpy)_3^{2+}/TPrA/Fe(CN)_6^{3-}$ system at glassy carbon electrode

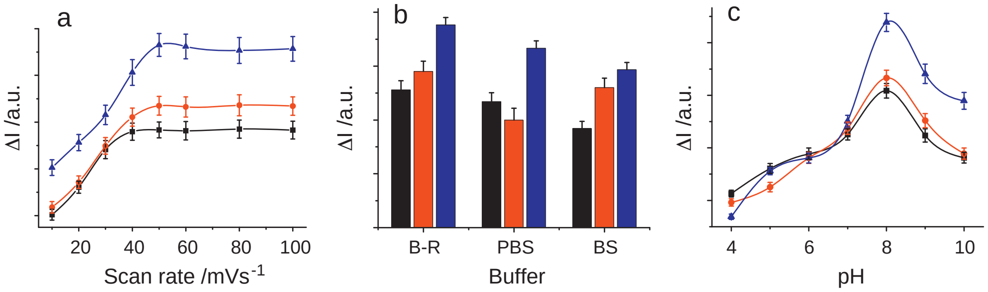

Fig. 2. The optimization of (a) scanning rate. (b) Buffer solution. (c) pH for the detection of $KMnO_4$ (black), $K_2Cr_2O_7$ (red) and $K_3[Fe(CN)_6]$ (blue). The oxidants concentration was 5×10^{-5} mol L^{-1}, the $Ru(bpy)_3{}^{2+}$ concentration was 2.5×10^{-5} M, and the TPrA concentration was 1.0×10^{-4} M. The error bars represent standard deviations of 5 replicates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

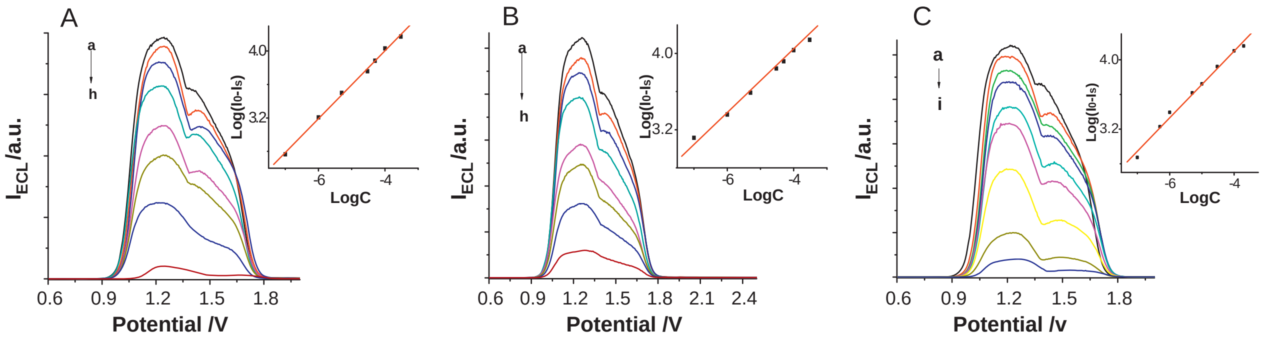

Fig. 3. Dose-response curves for the determination of (A) $KMnO_4$; (B) $K_2Cr_2O_7$ and (C) $K_3[Fe(CN)_6]$ (A) $KMnO_4$ concentration from *a* to *h* was 0, 1.0×10^{-6} M, 5.0×10^{-6} M, 3.0×10^{-5} M, 5.0×10^{-5} M, 1.0×10^{-4} M and 3.0×10^{-4} M, respectively. The insert shows the calibration curve between the logarithm of the inhibitory ECL and the logarithm of concentration of $KMnO_4$. (B) $K_2Cr_2O_7$ concentration from *a* to *h* was 0, 1.0×10^{-7} M, 1.0×10^{-6} M, 5.0×10^{-6} M, 3.0×10^{-5} M, 5.0×10^{-5} M, 1.0×10^{-4} M and 3.0×10^{-4} M. The insert shows the calibration curve between the logarithm of the inhibitory ECL and the logarithm of concentration of $K_2Cr_2O_7$. (C) $K_3[Fe(CN)_6]$ concentration from *a* to *i* was 0, 1.0×10^{-7} M, 5.0×10^{-7} M, 1.0×10^{-6} M, 5.0×10^{-6} M, 1.0×10^{-5} M, 3.0×10^{-5} M, 1.0×10^{-4} M and 3.0×10^{-4} M. The insert shows the calibration curve between the logarithm of the inhibitory ECL and the logarithm of concentration of $K_3[Fe(CN)_6]$.

were investigated under different electrical methods such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and differential pulse voltammetry (DPV). Results showed that maximum ΔI and best signal to noise ratio (S/N) could be obtained by the using of CV. Therefore, CV was chosen for the subsequent experiments.

The scan rate of CV was also optimized (Fig. 2a). In general, ΔI of the three ECL systems increased dramatically with the scan rate in the range of 10 mV s^{-1} to 50 mV s^{-1}. Maximum ΔI could be observed at the scan rate of 50 mV s^{-1}, while further increase the scan rate would not change ΔI notably. Therefore, a scan rate of 50 mV s^{-1} was chosen for the subsequent experiments.

The buffer used in the ECL detection system was the other vital parameter which affects the ECL quenching greatly. Herein, three widely used buffer system, namely, BR buffer, Na_2HPO_4–NaH_2PO_4 buffer (PBS) and H_3BO_3–Na_3BO_3 buffer (BS) were investigated. Fig. 2b shows the effect of these buffer systems to the ECL of the three ECL systems. For all the three ECL system, maximum and stable ECL quenching could be observed when BR buffer was used. Hence BR buffer was chosen for the rest experiments.

The pH of BR buffer was also optimized (Fig. 2c). Results showed that ΔI increased with pH when the pH was equal or less than 8. However, when pH was greater than 8, ΔI was decreasing rapidly with the increasing of pH. Therefore, pH 8 was chosen as the optimal pH for the subsequent experiments.

The concentration of ECL luminophor ($Ru(bpy)_3{}^{2+}$) and coreactant (TPrA) were optimized. First, a fixed TPrA concentration (1×10^{-4} M) and a varying $Ru(bpy)_3{}^{2+}$ concentration was investigated. It was found that ΔI increased with the $Ru(bpy)_3{}^{2+}$ concentration in the range of 1×10^{-6} to 2.5×10^{-5} M. While further increase the $Ru(bpy)_3{}^{2+}$ concentration would not lead to significant increase of ECL quenching but lead to high noise level. Therefore, a $Ru(bpy)_3{}^{2+}$ concentration of 2.5×10^{-5} M was chosen. Similarly, the TPrA concentration was optimized by using a fixed $Ru(bpy)_3{}^{2+}$ concentration. Results showed that a low background ECL was observed when a low TPrA concentration was used. This directly induced a relatively low ΔI. On the other hand, though the ECL background was keeping increasing with TPrA concentration, ΔI was decreasing when the TPrA concentration was higher than 1×10^{-4} M. The TPrA concentration of 1×10^{-4} M was therefore chosen as the optimal concentration.

3.3. *Detection of $MnO_4{}^-$, $Cr_2O_7{}^{2-}$ and $[Fe(CN)_6]^{3-}$*

Standard curves for the detection of $MnO_4{}^-$, $Cr_2O_7{}^{2-}$ and $[Fe(CN)_6]^{3-}$ was obtained under the optimal conditions (Fig. 3). Table 1 shows the linear response range and LOD of these oxidants based on inhibited ECL. The logarithm of the inhibited ECL (ΔI) is well linear with the logarithm of concentration of inhibitors over three orders for all the oxidants, and the LODs were found in 10–80 nM. The precision and accuracy of the proposed ECL method was evaluated by a standard addition approach and the

Table 1
Parameter of regression equations for $Ru(bpy)_3{}^{2+}$/TPrA ECL system.[a]

Sample	Linear range (mol l^{-1})	Detection limit (nM)	Correlation coefficient (*r*)
$MnO_4{}^-$	1×10^{-7} to 3×10^{-4}	80	0.998
$Cr_2O_7{}^{2-}$	1×10^{-7} to 3×10^{-4}	20	0.998
$[Fe(CN)_6]^{3-}$	1×10^{-7} to 1×10^{-4}	10	0.996

[a] Standard stock solution of $KMnO_4$, $K_2Cr_2O_7$ and $K_3[Fe(CN)_6]$ diluted in BR buffer (pH 8) was used throughout; scan rate: 50 mV s^{-1}; $[Ru(bpy)_3{}^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}, $[TPrA] = 1.0 \times 10^{-4}$ mol L^{-1}.

Table 2
Accuracy and precision for the detection of inorganic oxidants by the proposed method ($n = 15$).[a]

Compounds	Concentration added (μM)	Concentration found (μM)	Er (%)	RSD (%)
MnO_4^-	0.500	0.524	4.80	6.08
$Cr_2O_7^{2-}$	0.500	0.528	5.60	8.87
$[Fe(CN)_6]^{3-}$	0.500	0.481	−3.80	7.64
MnO_4^-	5.00	5.25	5.00	5.56
$Cr_2O_7^{2-}$	5.00	4.89	−2.20	4.54
$[Fe(CN)_6]^{3-}$	5.00	5.32	6.40	3.27
MnO_4^-	50.0	47.1	−5.80	5.52
$Cr_2O_7^{2-}$	50.0	48.6	−2.80	3.69
$[Fe(CN)_6]^{3-}$	50.0	50.1	0.200	5.89

[a] Standard stock solution of $KMnO_4$, $K_2Cr_2O_7$ and $K_3[Fe(CN)_6]$ diluted in BR buffer (pH 8) was used throughout; scan rate: 50 mV s^{-1}; $[Ru(bpy)_3^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}, $[TPrA] = 1.0 \times 10^{-4}$ mol L^{-1}.

results were shown in Table 2. The Error and RSD for determination of MnO^{4-}, $Cr_2O_7^{2-}$ and $Fe(CN)_6]^{3-}$ with concentration ranging from 5.0×10^{-7} mol L^{-1} to 5.0×10^{-5} mol L^{-1} was found to be better than 7% and 9%, respectively. Comparing with some methods reported previously [17,18], the proposed inhibited ECL methods for detection of MnO_4^-, $Cr_2O_7^{2-}$ and $[Fe(CN)_6]^{3-}$ were simple, rapid and sensitive. Furthermore, the dynamic range of the proposed method was also much better. Therefore, the combination of this method with some separation approaches, e.g. HPLC or capillary electrophoresis could have great potential for determination of the above mentioned substances in complex matrix.

3.4. Mechanism of inhibition

Apparently the ECL inhibition by these compounds cannot be explained by the electrochemical generation of benzoquiones or any other possible quenchers, and these compounds cannot be electro-oxidized under applied potential, so it also cannot be explained by the "electrochemical oxidation inhibiting" mechanism proposed by Chi et al. [10]. To the best of our knowledge, hitherto there is still no corresponding mechanism to answer for this kind of ECL inhibition. Therefore, a new mechanism is necessary to be addressed for the inhibited $Ru(bpy)_3^{2+}$/TPrA ECL system by the inorganic oxidants.

In our succeeding experiments, we found that hypochlorite could quench $Ru(bpy)_3^{2+}$/TPrA ECL significantly (see Fig. 4A). However, chlorate could not produce an inhibitory effect on $Ru(bpy)_3^{2+}$/TPrA ECL in the exactly same conditions (see Fig. 4B). It has been proved that, under the same conditions, the oxidizing ability of hypochlorite was stronger than chlorate [34]. Therefore, we inferred that the ECL quenching behaviors may be directly related to the oxidation ability of inhibitors. In order to further testify this deduction, the ECL behavior of $Ru(bpy)_3^{2+}$/TPrA/$Cr_2O_7^{2-}$, $Ru(bpy)_3^{2+}$/TPrA/MnO_4^-, and $Ru(bpy)_3^{2+}$/TPrA/$Fe(CN)_6]^{3-}$ system were investigated. The redox reactions of the above systems in solution are as follows:

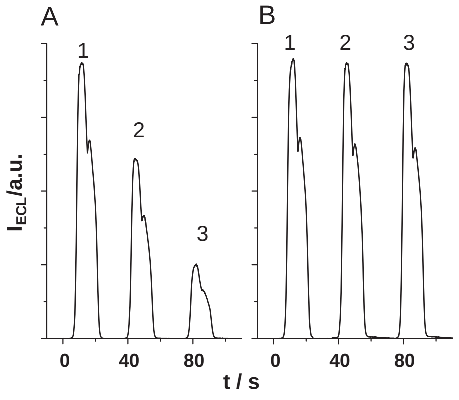

Fig. 4. Inhibition of $Ru(bpy)_3^{2+}$/TPrA ECL by (A) hypochlorite, and (B) chlorate, concentration from 1 to 3 is 0, 1.0×10^{-3} and 1.86×10^{-3} mol L^{-1}, respectively; buffer solution (pH 8) was used throughout; scan rate: 50 mV s^{-1}; $[Ru(bpy)_3^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}, $[TPrA] = 1.0 \times 10^{-4}$ mol L^{-1}.

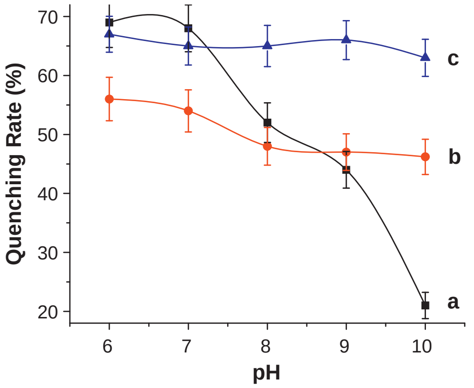

Fig. 5. Effect of pH value on the ECL inhibition of $Ru(bpy)_3^{2+}$/TPrA system by: (a) $Cr_2O_7^{2-}$ (5×10^{-5} mol L^{-1}), (b) MnO_4^- (5×10^{-5} mol L^{-1}) and (c) $Fe(CN)_6^{3-}$ (5×10^{-5} mol L^{-1}). BR buffer solution with varied pH from 6 to 10 was used throughout; scan rate: 50 mV s^{-1}; $[Ru(bpy)_3^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}, $[TPrA] = 1.0 \times 10^{-4}$ mol L^{-1}. The error bars represent standard deviations of 5 replicates.

$$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O \qquad (2)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e + 2Cr^{3+} + 7H_2O \qquad (3)$$

$$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-} \qquad (4)$$

It is known that the oxidation ability of an oxidant is in direct ratio to the corresponding electrode potential, which can be determined by Nernst equation:

$$E = E^0 + \frac{RT}{nf} \log \frac{a_{0x}}{a_{\text{Red}}} \qquad (5)$$

where E is the electrode potential, E^0 is the standard electrode potential at the temperature of interest, R is the universal gas constant, T is the absolute temperature, n is the number of moles of electrons transferred in the reaction, F is the Faraday constant, a is the chemical activity for the relevant species, where a_{Red} is the reductant and a_{Ox} is the oxidant.

According to the Nernst equation (Eq. (5)), the oxidation ability (or E) of MnO^{4-} and $Cr_2O_7^{2-}$ could be greatly affected by the buffer pH, while the electrode potential of $Fe(CN)_6^{3-}$ would not be affected by the buffer pH. Therefore, it is expected to observe ECL quenching variations among the three ECL systems in case of different pH buffer. In order to testify this, ECL behavior of $Ru(bpy)_3^{2+}$/TPrA/$Cr_2O_7^{2-}$, $Ru(bpy)_3^{2+}$/TPrA/MnO_4^-, and $Ru(bpy)_3^{2+}$/TPrA/$Fe(CN)_6]^{3-}$ ECL systems were investigated with the pH of BR buffer varying from 6.0 to 10.0 (Fig. 5). It can be seen from Fig. 5 that the quenching rates of MnO^{4-} and $Cr_2O_7^{2-}$ were closely depending on the pH of buffer solution. In general, the quenching rates decreased with the increasing of pH. In comparison, the pH affected the quenching rate of $Ru(bpy)_3^{2+}$/TPrA/$Cr_2O_7^{2-}$ ECL system more than $Ru(bpy)_3^{2+}$/TPrA/MnO_4^- system, and this is consistent with the theoretical expectation since the ratio of the number of protons to the number of the electrons ([H+]/e) in the two equations is 7/3 versus 4/3. The ECL quenching rates of $Ru(bpy)_3^{2+}$/TPrA/$Fe(CN)_6]^{3-}$ ECL system did not change significantly with the varying of pH, as shown in Fig. 5c. This result was also in good coherent with the theoretical prediction. Based on these results, we proposed that the ECL

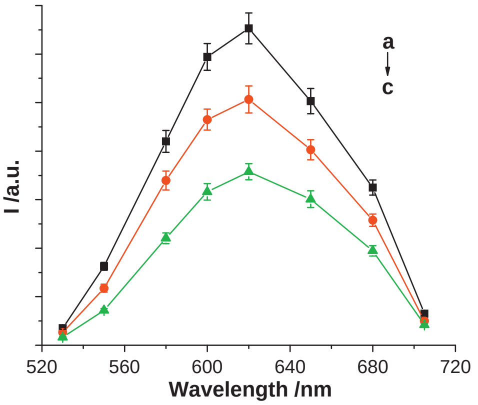

Fig. 6. ECL emission spectra of $Ru(bpy)_3{}^{2+}/TPrA/MnO_4{}^-$ system in BR buffer solution (pH 8), $[Ru(bpy)_3{}^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}, [TPrA] = 1.0×10^{-4} mol L^{-1}, $[MnO_4{}^-]$: (a) 0, (b) 1.0×10^{-5}, (c) 5.0×10^{-5} mol L^{-1}. The error bars represent standard deviations of 5 replicates.

inhibition effect of inorganic oxidants was closely related to their electrode potential (*E*). The higher the *E* was, the bigger the ECL quenching rate could be observed. It should be noted that for the investigation of pH, two different criterions were used for analytical application and mechanism discussion. For analytical application, we choose the maximum ECL intensity changes (ΔI) as the optimal conditions, while for mechanism discussion, we choose the quenching rate ($\Delta I/I_0$) to reveal the possible mechanism. ΔI was chosen for analytical application because it was a more straight forward and simple parameter to be obtained. However, we found it was not appropriate to use ΔI for mechanism explanation because the ECL emission of Ru(bpy)/(TPrA) (I_0) also changes with the pH (maximum ECL intensity appears at pH = 8.0). Taking this into consideration, we conclude that the quenching rate ($\Delta I/I_0$) could be a more accurate parameter for indicating the effect of pH on the three ECL systems.

ECL emission spectrum and UV–Vis absorption spectra were used to investigate the species of ECL reaction. $Ru(bpy)_3{}^{2+}/TPrA/MnO_4{}^-$ system was shown as an example for this purpose. The emission spectra of $Ru(bpy)_3{}^{2+}$/TPrA system and $Ru(bpy)_3{}^{2+}/TPrA/MnO_4{}^-$ system were investigated and the results were shown in Fig. 6. The maximal ECL emission is located at 610 nm no matter with or without the presence of $MnO_4{}^-$. These results suggested that the luminophor of the $Ru(bpy)_3{}^{2+}$/TPrA system and $Ru(bpy)_3{}^{2+}/TPrA/MnO_4{}^-$ system should be the same as that of $Ru(bpy)_3{}^{2+}$ alone, which has been proven to be $Ru(bpy)_3{}^{2+*}$ [35,36]. Fig. 7 shows the UV–Vis absorption spectra of the system without performing electrolysis. $MnO_4{}^-$ had two absorption peaks at 302 and 528 nm, respectively (see Fig. 7a and the insert in Fig. 7). $Ru(bpy)_3{}^{2+}$/TPrA showed absorption peaks at 285, 423 and 453 nm (Fig. 7b), and the absorption spectrum of the mixture of $Ru(bpy)_3{}^{2+}/TPrA/MnO_4{}^-$ (Fig. 7c) was exactly the sum of that of *a* and *b*. It strongly suggested that no new compound was produced when simply mixing the three compounds. Meanwhile, it also indicated that $MnO_4{}^-$ cannot oxidize $Ru(bpy)_3{}^{2+}$ into $Ru(bpy)_3{}^{3+}$ (otherwise the UV–Vis peak from $MnO_4{}^-$ will decrease). Therefore, the ECL inhibition was not come from the interaction between $MnO_4{}^-$ and $Ru(bpy)_3{}^{2+}$.

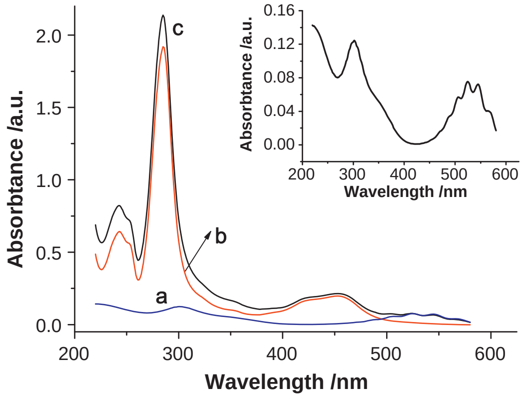

Fig. 7. UV–Vis absorption spectra of inorganic oxidants in BR buffer solution (pH 8). (a) 5×10^{-5} M $MnO_4{}^-$; (b) 2.5×10^5 M $Ru(bpy)_3{}^{2+} + 1 \times 10^{-4}$ M TrPA; (c) mixed solution of a and b. The insert shows the enlarged image of *a*.

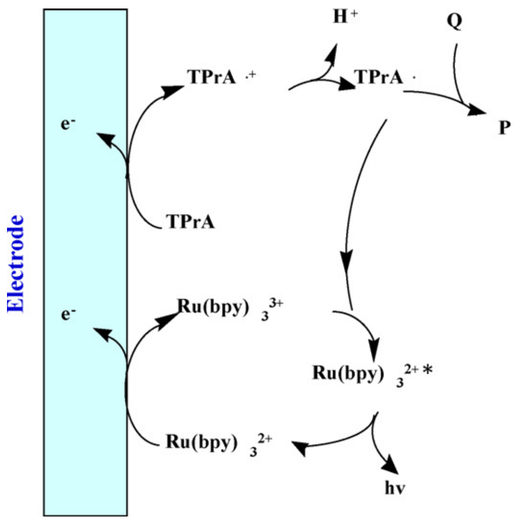

Fig. 8. Mechanism to inhibit $Ru(bpy)_3{}^{2+}$/TPrA ECL system by inorganic oxidants.

The ECL mechanism of $Ru(bpy)_3{}^{2+}$/TPrA had been well summarized by Zu and Bard [37]:

$$Ru(bpy)_3{}^{2+} - e^- \rightarrow Ru(bpy)_3{}^{3+} \tag{6}$$

$$TPrA - e^- \rightarrow [TPrA^\bullet]^+ \tag{7}$$

$$[TPrA^\bullet]^+ \rightarrow TPrA^\bullet + H^+ \tag{8}$$

$$Ru(bpy)_3{}^{3+} + TPrA^\bullet \rightarrow Ru(bpy)_3{}^{2+}{*} + \text{products} \tag{9}$$

$$Ru(bpy)_3{}^{2+*} \rightarrow Ru(bpy)_3{}^{2+} + h\upsilon \tag{10}$$

As shown in Eqs. (8) and (9), TPrA enhances the ECL of $Ru(bpy)_3{}^{2+}$ system through its radical-state ($TPrA^\bullet$), which is a strong reductive intermediate. Therefore, we inferred that it should be the redox reactions between oxidants and $TPrA^\bullet$ which leads to the quenching of ECL intensity. Based on the above discussions, the mechanism for the ECL inhibition of $Ru(bpy)_3{}^{2+}$/TPrA system by inorganic oxidants was proposed in Fig. 8.

First, TPrA and $Ru(bpy)_3{}^{2+}$ are oxidized at the working electrode surface to form their corresponding oxidation products. Then, the short-lived TPrA radical cation ($TPrA^{\cdot+}$) is believed to lose a proton to form the strongly reducing intermediate ($TPrA^{\cdot}$). $TPrA^{\cdot}$ could reduce $Ru(bpy)_3{}^{3+}$ into $Ru(bpy)_3{}^{2+*}$, which would produce ECL emission. However, when inorganic oxidants (*Q*) is present in the solution, it would also react with $TPrA^{\cdot}$, which would consume $TPrA^{\cdot}$ hence leading to ECL quenching.

4. Conclusions

Some inorganic oxidants were employed in the $Ru(bpy)_3{}^{2+}$/TPrA ECL system, and the results showed that they had a strong ability to quench the ECL of this system. The quenched ECL intensity was increasing with the increase of oxidant concentration. Based on which, a sensitive approach for the detection of these inorganic analytes was established. A mechanism for this ECL inhibition behavior was proposed. We considered that the competition of TPrA radical (TPrA$^{\cdot}$) between Ru(bpy)$_3^{2+}$ and these analytes should be the main contribution of the ECL inhibition.

Acknowledgements

This project was supported by the National Nature Sciences Foundation of China (20735002, 40940026), the Key Natural Sciences Foundation of Fujian Province, China (D0520001) and the Key Program of Science and Technology Department of Fujian Province, China (2007Y0026).

References

[1] R. Wilson, C. Clavering, A. Hutchinson, Anal. Chem. 75 (2003) 4244–4249.
[2] P. McCord, A.J. Bard, J. Electroanal. Chem. 318 (1991) 91–99.
[3] I. Rubinstein, A.J. Bard, J. Amer. Chem. Soc. 103 (1981) 512–516.
[4] M. Richter, Chem. Rev. 104 (2004) 3003–3036.
[5] Y.Q. Pang, H. Cui, H.S. Zheng, G.H. Wan, L.J. Liu, X.F. Yu, Luminescence 20 (2005) 8–15.
[6] F. Li, H. Cui, X.Q. Lin, Anal. Chim. Acta 471 (2002) 187–194.
[7] F. Li, Y.Q. Pang, X.Q. Lin, H. Cui, Talanta 59 (2003) 627–636.
[8] H. Cui, F. Li, M.J. Shi, Y.Q. Pang, X.Q. Lin, Electroanalysis 17 (2005) 589–598.
[9] R.D. Gerardi, N.W. Barnett, S.W. Lewis, Anal. Chim. Acta 378 (1999) 1–41.
[10] Y. Chi, Y. Dong, G. Chen, Anal. Chem. 79 (2007) 4521–4528.
[11] L. Xue, L. Guo, B. Qiu, Z. Lin, G. Chen, Electrochem. Commun. 11 (2009) 1579–1582.
[12] J. McCall, C. Alexander, M.M. Richter, Anal. Chem. 71 (1999) 2523–2527.
[13] J. McCall, M.M. Richter, The Analyst 125 (2000) 545–548.
[14] L. Guo, L. Xue, B. Qiu, Z. Lin, D. Kim, G. Chen, Phys. Chem. Chem. Phys. 12 (2010) 12826–12832.
[15] F. Richard, A. Bourg, Water Res. 25 (1991) 807–816.
[16] R. Apak, E. T^{1}tem, M. H^{1}g^{1}l, J. Hizal, Water Res. 32 (1998) 430–440.
[17] T. Razek, S. Spear, S.S.M. Hassan, M.A. Arnold, Talanta 48 (1999) 269–275.
[18] S.S.M. Hassan, A.A. Abdel-Shafi, A.H.K. Mohammed, Talanta 67 (2005) 696–702.
[19] B.D. Paul, A. Jacobs, J. Anal. Toxicol. 29 (2005) 658–663.
[20] Y. Luo, S. Nakano, D.A. Holman, J. Ruzicka, G.D. Christian, Talanta 44 (1997) 1563–1571.
[21] M.C. Pannain, R.E. Santelli, Talanta 42 (1995) 1609–1617.
[22] P.C.C. Oliveira, J.C. Masini, The Analyst 123 (1998) 2085–2090.
[23] J.F. Van Staden, L.V. Mulaudzi, R.I. Stefan, Anal. Chim. Acta 499 (2003) 129–137.
[24] A.M. Bond, G.G. Wallace, Anal. Chem. 54 (1982) 1706–1712.
[25] B.K. Jena, C.R. Raj, Talanta 76 (2008) 161–165.
[26] T. Prasada Rao, S. Karthikeyan, B. Vijayalekshmy, C.S.P. Iyer, Anal. Chim. Acta 369 (1998) 69–77.
[27] M. Sperling, S. Xu, B. Welz, Anal. Chem. 64 (1992) 3101–3108.
[28] A.X.S. Qian, G.H.F. He, X. Han, The Analyst 126 (2001) 239–241.
[29] M. Aguilar, A. Farran, V. Martí, J. Chromatogr. A 767 (1997) 319–324.
[30] Z.L. Chen, M. Megharaj, R. Naidu, Talanta 72 (2007) 394–400.
[31] M. Sikovec, M. Franko, M. Novic, M. Veber, J. Chromatogr. A 920 (2001) 119–125.
[32] W. Buchberger, O.P. Semenova, A.R. Timerbaev, J. High Resolut. Chromatogr. 16 (1993) 153–156.
[33] X. Wu, F. Huang, J. Duan, G. Chen, Talanta 65 (2005) 1279–1285.
[34] T.H. Chen, Anal. Chem. 39 (1967) 804–813.
[35] J. Ferguson, E.R. Krausz, M. Maeder, J. Phys. Chem. 89 (1985) 1852–1854.
[36] G.H. Allen, R.P. White, D.P. Rillema, T.J. Meyer, J. Amer. Chem. Soc. 106 (1984) 2613–2620.
[37] Y. Zu, A.J. Bard, Anal. Chem. 72 (2000) 3223–3232.