Perturbation of the tris(2,2′-bipyridine) ruthenium(II)-catalyzed Belousov–Zhabotinsky oscillating chemiluminescence reaction by L-cysteine and its application

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ABSTRACT: Perturbation of the tris(2,2′-bipyridine)ruthenium(II) [Ru(bpy)$_3^{2+}$]-catalyzed Belousov–Zhabotinsky (BZ) oscillating chemiluminescence (CL) reaction induced by L-cysteine was observed in the closed system. It was found that the CL intensity was decreased in the presence of L-cysteine. Meanwhile, oscillation period and oscillating induction period were prolonged. The sufficient reproducible induction period was used as parameter for the analytical application of oscillating CL reaction. Under the optimum conditions, the changes in the oscillating CL induction period were linearly proportional to the concentration of L-cysteine in the range from 8.0×10^{-7} to 5.0×10^{-5} mol L^{-1} ($r = 0.997$) with a detection limit of 4.3×10^{-7} mol L^{-1}. The possible mechanism of L-cysteine perturbation on the oscillating CL reaction was also discussed. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: Tris(2,2′-bipyridine)ruthenium(II); Belousov–Zhabotinsky oscillating reaction; chemiluminesence; perturbation; L-cysteine

Introduction

Since there are some obvious similarities between chemical oscillating systems and life processes that generally exhibit oscillatory behaviors, the investigation of the oscillating systems is of considerable interest. While a substantial number of chemical oscillators are known and have been widely used in analytical detection,[1–14] relatively few oscillating chemiluminescence (CL) reactions in the liquid phase have been described.[15–20] Recently, owing to the particular photochemical and photophysical properties of the tris(2,2′-bipyridine)ruthenium(II) [Ru(bpy)$_3^{2+}$] CL reagent,[21–23] the Ru(bpy)$_3^{2+}$-catalyzed Belousov–Zhabotinsky (BZ) oscillating CL reaction has attracted widespread attention.

The first report about oscillating CL reaction catalyzed by Ru(bpy)$_3^{2+}$ was proposed in 1982 by Bolletta et al.,[24] which was also the first example of oscillating CL reaction in the liquid phase. However, further studies about this oscillating CL reaction have seldom been reported. Until now, most of research has focused on the profile and mechanism of the oscillating CL reaction.[25,26] Herein, we present a new approach to investigate the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL reaction.

Our preliminary work has thoroughly investigated the influences of reactant concentrations on the Ru(bpy)$_3^{2+}$–malonic acid (MA)–KBrO$_3$–H$_2$SO$_4$ BZ oscillating CL reaction.[26] In order to study changes of the oscillating behavior in the presence of an external substance, L-cysteine was added to the system. L-Cysteine is an important amino acid owing to its crucial roles in living systems. Therefore, the investigation of the perturbation of the oscillating CL system induced by L-cysteine helps in the study of life process to some extent. It was noted that, in the presence of L-cysteine, the oscillating CL system was perturbed with the decrease in amplitude. Meanwhile, oscillation period and induction period were changed. Further investigation demonstrated that the induction period of this oscillating CL reaction presented good reproducibility. Because of the inferior stability of the CL intensity in the closed system, it cannot be used as the parameter for detection. Hence, the analytical application of oscillating CL system is limited. Thus, the determination of the oscillating induction period becomes critical for the oscillating CL reaction, which is undoubtedly of great importance for expanding potential analytical applications of the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL reaction.

This paper describes the perturbation of the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL system induced by L-cysteine. Furthermore, it was found that oscillating induction period could be used for L-cysteine detection. The proposed method opened a new avenue for the use of Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL reaction in analytical applications.

Experimental

Reagents and chemicals

L-Cysteine and some other common amino acids were purchased from Shanghai Boao Biotechnology Co. Ltd (Shanghai, China). Ru(bpy)$_3^{2+}$ was synthesized by the procedure reported previously.[26] KBrO$_3$ was obtained from Tianjin No. 3 Chemical Reagent Plant

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College of Science, the State Key Laboratory of Agricultural Microbiology, Huazhong Agricultural University, Wuhan, 430 070, People's Republic of China.
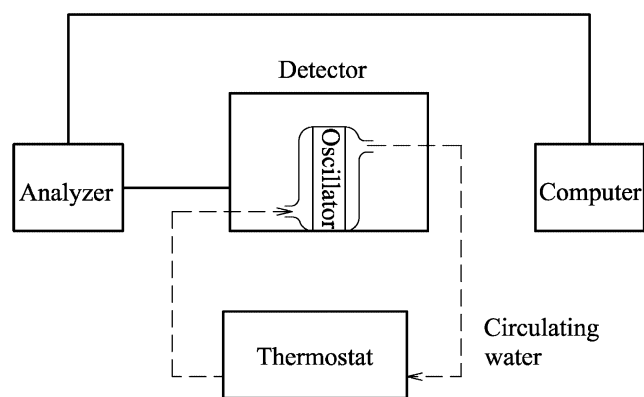
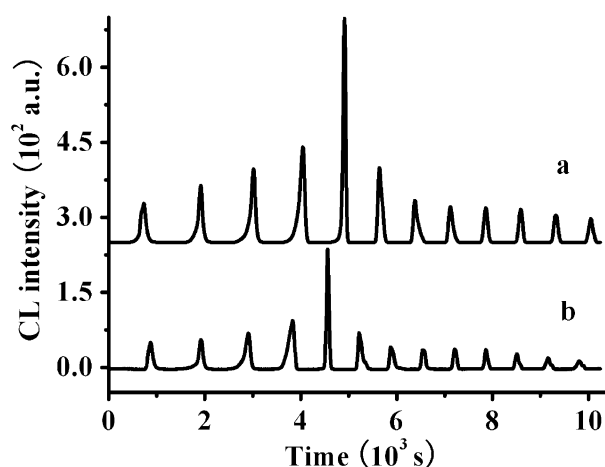**Figure 1.** Experimental set-up for the implementation of the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL reaction.

Figure 2. Typical Ru(bpy)$_3^{2+}$-catalyzed BZ oscillation CL profiles obtained (a) in the absence and (b) in the presence of L-cysteine. Conditions: 2.0 mol L^{-1} H$_2$SO$_4$, 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.06 mol L^{-1} KBrO$_3$, 0.08 mol L^{-1} MA, 3.0×10^{-5} mol L^{-1} L-cysteine, $T = 28°C$.

(Tianjin, China). MA was obtained from Sinopharm Chemical Reagent Co. Ltd (Shenyang, China). All other substances were of analytical-reagent grade and were used without further purification.

Solutions of 2.0 mol L^{-1} H$_2$SO$_4$, 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.06 mol L^{-1} KBrO$_3$ and 0.08 mol L^{-1} MA were prepared. Fresh L-cysteine solutions were prepared every day. The stock solutions of 0.1 mol L^{-1} of other common amino acids were prepared and stored in a refrigerator at 4°C. All solutions were prepared using Milli-Q water (Millipore).

Apparatus

The instrumental set-up (Fig. 1) used to implement the oscillating CL reaction consisted of a homemade thermostatic oscillator, cylindrical reaction glass vessel (4.0×6.0 cm) of 5 mL capacity wrapped in a water recirculation jacket. A CS-501 thermostat (Shanghai Yangguang Experimental Instrumental Factory, Shanghai, China) with an accuracy of ±0.1°C was used to maintain the temperature of the reaction solution. The volume of the reaction mixture was 1.5 mL. The CL intensity was measured with an IFFM-E Flow-injection CL analyzer (Xi'An Remex Analytical Instrumental Co. Ltd, Xi'An, China) and recorded using a model MPI-A/B multifunctional CL detector (Xi'An Remex Electronic Science & Technology Co. Ltd, Xi'An, China). The voltage of the photomultiplier tube (PMT) was set at −600 V in the process of detection.

Procedure

The temperature for the manifold was thermostated at $28 \pm 0.1°C$. In the closed system, the fixed volumes of 0.3 mL of 0.08 mol L^{-1} MA, 0.06 mol L^{-1} KBrO$_3$, 2.0 mol L^{-1} H$_2$SO$_4$ and 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$ and variable concentration of L-cysteine were added to the oscillator. The oscillating CL intensity curves were recorded. As the system was perturbed by a sample containing variable amounts of L-cysteine, the induction period of the oscillating CL reaction was prolonged. The change in the induction period was used to evaluate the response of the oscillating CL system to the perturbation of the L-cysteine.

Results and discussion

The perturbation of the oscillating CL system by L-cysteine

In the process of Ru(bpy)$_3^{2+}$-catalyzed oxidation of MA by KBrO$_3$ in a strong acid medium, the color of the solution switched periodically between yellow and pale green. Fig. 2(a) shows a typical profile of the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL reaction in the closed system. The time of the overall oscillating CL reaction was about 3 h, and the oscillating induction period was less than 600 s. Different from previous results,[26] the CL intensity increased in the early stages of the oscillating reaction and then decreased. In addition, the oscillating CL process consisted of an induction period, oscillating enhancement period and attenuation period.

As a rule, the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL system was highly vulnerable to external perturbations. On interaction with the oscillating CL system, L-cysteine caused changes in the oscillating induction period, amplitude and oscillation period. As shown in Fig. 2(b), the induction period of the oscillating CL system was prolonged in the presence of L-cysteine. Meanwhile, the CL intensity was decreased and oscillation period was changed.

Further studies showed that the induction period of the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL system was stable. By six repeated detections, the induction period of the blank, T_0, was shown in Fig. 3. Results showed that the oscillating induction period presented a good reproducibility. It was promising that Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL system could be used as a tool for analytical application.

Since the induction period could be used as analytical parameter, the response to L-cysteine perturbation was evaluated using ΔT_i ($\Delta T_i = T_i - T_0$), where T_i represented the induction period of the system in the presence of L-cysteine. As described above, change was linearly proportional to the L-cysteine concentration; therefore, we explored the possibility of applying this behavior to the determination of the L-cysteine.

Influence of experimental variables

The influence of the variables on the behavior of the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL system was thoroughly studied in the absence and presence of L-cysteine perturbations using changes of the induction period as the measured parameter. In order to ensure the maximum possible sensitivity and precision in the determination, working conditions were optimized according to
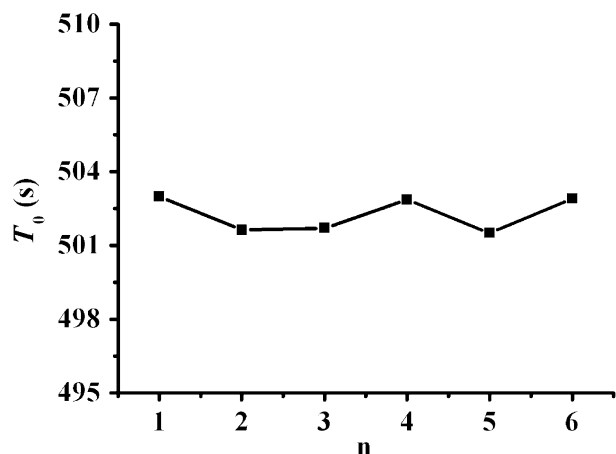
Figure 3. Induction periods of the blanks for duplicate measurements. Conditions: 2.0 mol L^{-1} H_2SO_4, 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.06 mol L^{-1} KBrO$_3$, 0.08 mol L^{-1} MA, $T = 28°C$.

three factors, namely: (a) accomplishing the maximum changes in oscillating induction period to ensure higher sensitivity for the determination of L-cysteine; (b) obtaining the induction period to allow the effect of the L-cysteine perturbation on the system to be accurately determined;[27] and (c) ensuring the maximum stability of the oscillating CL system.

Influence of the concentrations of reactants. The influence of the Ru(bpy)$_3^{2+}$ concentration was investigated in the range 1.0×10^{-4} to 5.0×10^{-4} mol L^{-1}. In the presence of L-cysteine, ΔT_i followed the trend illustrated in Fig. 4(a). When the Ru(bpy)$_3^{2+}$ concentration was more than 4.0×10^{-4} mol L^{-1}, almost no oscillating profile was obtained. Thus we chose to employ 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$.

The effect of H_2SO_4 concentration was studied in the range from 1.0 to 5.0 mol L^{-1}. The perturbation with L-cysteine elicited a response, shown in Fig. 4(b), which depicted the curve of ΔT_i. Actually, if the concentration was too low, it would take a long time for each determination. In addition, higher concentration of H_2SO_4 made a trailing of oscillating CL curves. Therefore, we ultimately selected 2.0 mol L^{-1} H_2SO_4.

The concentration of MA was changed from 0.04 to 0.14 mol L^{-1}. The increment of the MA concentration caused a gradual shortage of the oscillating induction period; the response of L-cysteine perturbation is shown in Fig. 4(c). As a result, 0.08 mol L^{-1} MA was employed as optimal concentration.

The KBrO$_3$ concentration was changed between 0.04 and 0.12 mol L^{-1}. According to the results obtained from Fig. 4(d), the response of perturbation reached the maximum when the KBrO$_3$ concentration was 0.06 mol L^{-1}. Therefore a concentration of 0.06 mol L^{-1} was adopted.

Influence of the temperature. The temperature was a crucial variable for the proposed system. Any changes in temperature, especially those in response to external perturbations, would
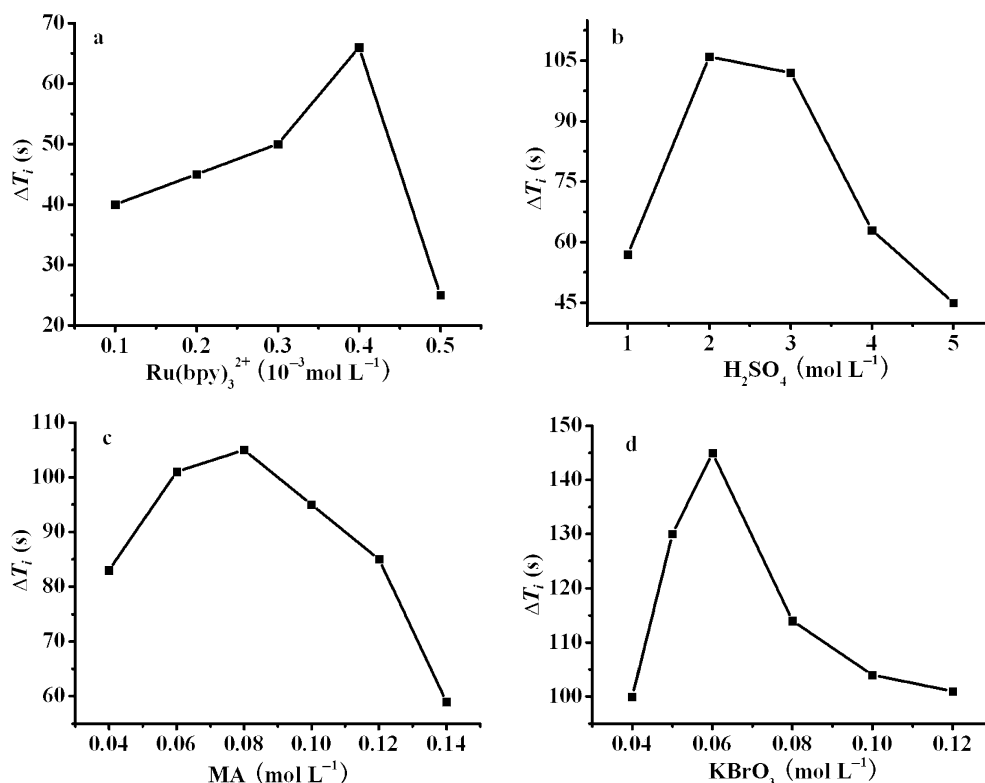

Figure 4. Influence of the concentrations of (a) Ru(bpy)$_3^{2+}$, (b) H_2SO_4, (c) MA and (d) KBrO$_3$ on the L-cysteine-perturbed oscillating CL system. Conditions: (a) 0.1 mol L^{-1} KBrO$_3$, 0.1 mol L^{-1} MA, 2.0 mol L^{-1} H_2SO_4, 1.5×10^{-5} mol L^{-1} L-cysteine, $T = 26°C$; (b) 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.1 mol L^{-1} KBrO$_3$, 0.1 mol L^{-1} MA, 1.5×10^{-5} mol L^{-1} L-cysteine, $T = 26°C$; (c) 2.0 mol L^{-1} H_2SO_4, 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.1 mol L^{-1} KBrO$_3$, 1.5×10^{-5} mol L^{-1} L-cysteine, $T = 26°C$; (d) 0.08 mol L^{-1} MA, 2.0 mol L^{-1} H_2SO_4, 4.0×10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 1.5×10^{-5} mol L^{-1} L-cysteine, $T = 26°C$.
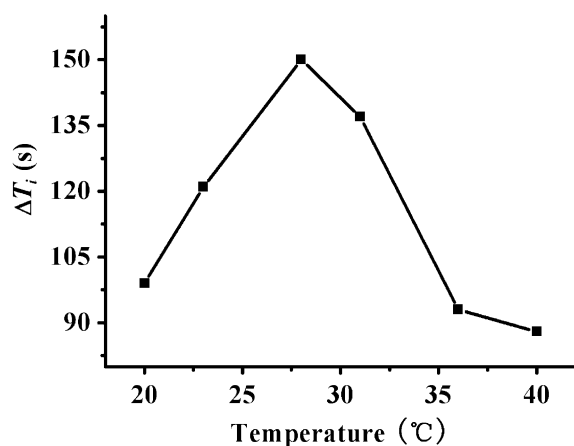
Figure 5. Influence of the temperature on the L-cysteine-perturbed oscillating CL system. Conditions: 2.0 mol L^{-1} H$_2$SO$_4$, 4.0 × 10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.06 mol L^{-1} KBrO$_3$, 0.08 mol L^{-1} MA, 1.5 × 10^{-5} mol L^{-1} L-cysteine.

have some influence on the oscillating parameters, including the induction period, the amplitude and the oscillation period. In the absence of L-cysteine, and with the enhancement of the temperature, the induction period was shortened dramatically. Moreover, in the presence of L-cysteine, the effect of temperature was investigated over the range from 20 to 40°C. As clearly shown in Fig. 5, 28°C was the optimum temperature in terms of sensitivity for the determination of L-cysteine.

Calibration and sensitivity

The oscillating CL system was perturbed with 0.3 mL of various concentrations of L-cysteine under the optimum working conditions described above. Repeated experiments illustrated that there was a good linear relationship between the changes in the induction period and the concentration of L-cysteine over the range from 8.0 × 10^{-7} to 5.0 × 10^{-5} mol L^{-1}, as shown in Fig. 6. The calibration data obeyed the linear regression equation: $\Delta T_i = 79.9153 + 5.0605 \times 10^3$ [L-cysteine] ($n = 8$, $r = 0.997$). The relative standard deviation for six measurements at the concentration of the 1.5 × 10^{-5} mol L^{-1} L-cysteine was 2.20%. The detection limit of the method—calculated as the L-cysteine concentration yielding an analytical signal equal to three times the standard deviation of the induction period in the absence of perturbation, which was taken as the blank—was found to be 4.3 × 10^{-7} mol L^{-1}.

Analytical application

In order to present the analytical application merits of the oscillating induction period, the proposed method was applied to the detection of L-cysteine added to water samples. Table 1 lists the analytical recoveries obtained for different water solutions that contain 1.0 × 10^{-5} to 1.0 × 10^{-6} mol L^{-1} L-cysteine. The relative errors of the L-cysteine determination ranged from −3.04 to 2.13%, which may be considered acceptable.

Oscillating CL system was highly vulnerable to external species. Consequently, we investigated the influence of various amino acids and foreign ions with respect to their possible influence on the determination of L-cysteine with the proposed method in amino acid detection. The tolerance level was defined as the maximum amount of foreign species that produced an

Table 1. Determination of L-cysteine using the calibration presented in Fig. 6

Concentration of L-cysteine (mol L^{-1})		
Added	Found	Relative error (%)
3.00 × 10^{-5}	2.91 × 10^{-5}	−3.04
7.00 × 10^{-6}	7.15 × 10^{-6}	+2.13
2.00 × 10^{-6}	1.95 × 10^{-6}	−2.33

Table 2. Tolerance of foreign ions in the determination of 1.0 × 10^{-6} mol L^{-1} L-cysteine

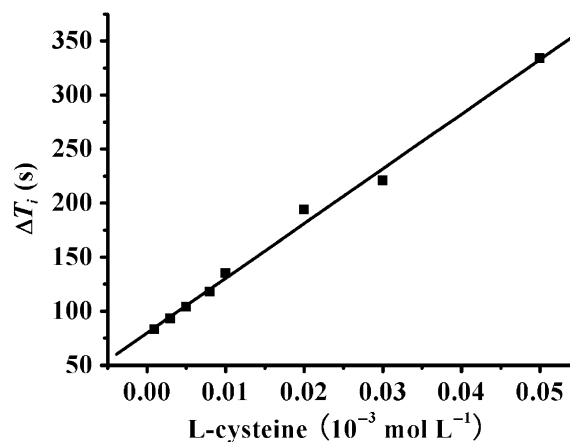| Foreign ions	Tolerated ratio (foreign/L-cysteine)
Na$^+$, SO$_4^{2-}$, K$^+$, Mg^{2+}, NH$_4^+$	100 000
Valine, isoleucine, aspartic acid, proline, glutamic acid, glutamine, serine, glycine, alanine, arginine, lysine, threonine, leucine	>1000
Cl$^-$, C$_2$O$_4^{2-}$	500
Histidine, asparagine, phenylanine	100
Tryptophan	10

Figure 6. Calibration curve of the prolongation in induction period vs concentrations of L-cysteine. Conditions: 2.0 mol L^{-1} H$_2$SO$_4$, 4.0 × 10^{-4} mol L^{-1} Ru(bpy)$_3^{2+}$, 0.06 mol L^{-1} KBrO$_3$, 0.08 mol L^{-1} MA, $T = 28$°C.

error of no more than ±5% for the determination of 1.0 × 10^{-6} mol L^{-1} L-cysteine. The results obtained are shown in Table 2. Some alkali and alkaline earth metal ions and NH$_4^+$ interfered when presented in large amounts (>10^5-fold excess). Chloride and C$_2$O$_4^{2-}$ interfered with the determination of L-cysteine if their concentrations exceeded 500-fold L-cysteine. Histidine, asparagine and phenylanine interfered in 100-fold excess and trypto-phan interfered in 10-fold excess. Other amino acids had little influence on the determination of L-cysteine (<10^3-fold). As could be seen, the proposed method was acceptably selective.

Meanwhile, we have also applied the method for L-cysteine determination in water solutions containing various compounds. The results are presented in Table 3. The relative errors were less

Table 3. Analysis of various mixtures containing L-cysteine			
Mixture taken (mol L^{-1})	Concentration of L-cysteine (mol L^{-1}) in the mixture	Found concentration of L-cysteine (mol L^{-1}) in the mixture	Relative error (%)
10^{-4} Valine 10^{-4} Proline 10^{-4} Glutamine 10^{-4} Alanine 10^{-4} Arginine	1.00×10^{-5}	9.90×10^{-6}	−1.01
10^{-4} Valine 10^{-4} Proline 10^{-4} Glutamine 10^{-4} Alanine 10^{-4} Arginine	1.00×10^{-6}	1.05×10^{-6}	2.69
10^{-4} Valine 10^{-5} Asparagine 10^{-1} K$_2$SO$_4$ 10^{-5} Na$_2$C$_2$O$_4$	1.00×10^{-5}	9.76×10^{-6}	−2.36
10^{-4} Valine 10^{-5} Asparagine 10^{-1} K$_2$SO$_4$ 10^{-5} Na$_2$C$_2$O$_4$	1.00×10^{-6}	1.05×10^{-6}	4.9

than 5%. Moreover, the relative standard deviation for six measurements at the L-cysteine concentration of 1.0×10^{-5} mol L^{-1} was 2.59%, indicating acceptable accuracy.

Possible mechanism of the perturbation induced by L-cysteine on the oscillating CL system

Since the FKN model for the BZ oscillating reaction was first reported by Field *et al.* in 1972,[28] literature has gradually accumulated on the investigation of the mechanism. The model of the oscillating CL reaction that we studied in this research has been reported by our group. It was considered as a sort of a simplified FKN model catalyzed by Ru(bpy)$_3^{2+}$.[26] The basic idea of the mechanism could be summarized in four important processes listed below:
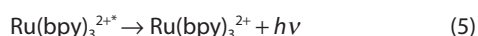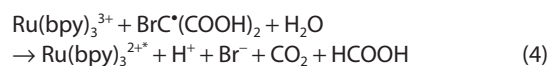
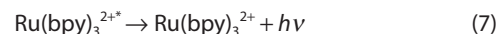*Process A: the accumulated stage of the oscillating CL reaction*

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \rightarrow 3BrCH(COOH)_2 + 3H_2O \quad (1)$$

Process B: the accumulated stage of the CL reaction

$$BrO_3^- + 4Ru(bpy)_3^{2+} + 5H^+ \rightarrow HOBr + 4Ru(bpy)_3^{3+} + 2H_2O \quad (2)$$

Process C: the stage of light emission

$$2Ru(bpy)_3^{3+} + BrCH(COOH)_2 \rightarrow BrC^\bullet(COOH)_2 + Ru(bpy)_3^{2+} + H^+ \quad (3)$$

$$Ru(bpy)_3^{3+} + BrC^\bullet(COOH)_2 + H_2O \rightarrow Ru(bpy)_3^{2+*} + H^+ + Br^- + CO_2 + HCOOH \quad (4)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (5)$$

Otherwise, Ru(bpy)$_3^{3+}$ also can oxidate MA directly.

$$2Ru(bpy)_3^{3+} + CH_2(COOH)_2 + H_2O \rightarrow$$

$$Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+*} + HCOOH + 2CO_2 + H^+ \quad (6)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (7)$$

Process D: the stage of oscillating CL reaction, which can also be named as the stage of Br$^-$ feedback. The concentration of the Br$^-$ as the switch of the oscillation dominated the oscillation and autocatalytic rate. When the concentration of Br$^-$ was high enough, all of the oscillating reactions were dominated by the process A. As the reaction was prolonged, the concentration of Br$^-$ was gradually decreased. When the Br$^-$ concentration has decreased below a critical amount, the control of reaction shifted to the process B where Ru(bpy)$_3^{2+}$ was oxidized by BrO$_3^-$ and HBrO$_2$. In process C, light emission was started. The CL of Ru(bpy)$_3^{2+}$ was caused by the generation of its excited form, Ru(bpy)$_3^{2+*}$, with the reproduction of Ru(bpy)$_3^{2+}$ and accumulation of Br$^-$. When a sufficient amount of Br$^-$ was formed from process C, the control of reaction was returned to the process A and the cycle started again.

The perturbation of L-cysteine on the oscillating CL reaction was rather complex. However, based on the above explanation, an approximation can be put forward. In general, the response of the oscillating system to the L-cysteine perturbation was most strongly affected by the Br$^-$ and Ru(bpy)$_3^{2+*}$ concentration. The proposed reaction mechanism could be represented as follows:

$$2Ru(bpy)_3^{3+} + 2CySH \rightarrow CySSCy + 2H^+ + 2Ru(bpy)_3^{2+} \quad (8)$$

When L-cysteine was added to the oscillating CL system, it could react with Ru(bpy)$_3^{3+}$, which was reduced to Ru(bpy)$_3^{2+}$ directly without light emission. Such a course inhibited the reaction of BrC$^\bullet$(COOH)$_2$ and Ru(bpy)$_3^{3+}$ from Process C. Consequently, the concentration of the Ru(bpy)$_3^{2+*}$ was decreased and the generating rate of Br$^-$ was depressed, which resulted in a decrease in

the CL intensity and the prolonging of the induction period. Moreover, such a reaction restrained the accumulation of intermediates, which prolonged the induction period of the oscillating CL reaction. In addition, no matter what reactions with L-cysteine occurred, the boundary conditions were changed, that is to say the originally stationary thermodynamic state was destroyed and a new oscillating pattern appeared.

Conclusions

In summary, potential exploitation of the perturbation induced by L-cysteine on the Ru(bpy)$_3^{2+}$-catalyzed BZ oscillating CL reaction provided a new platform for the further study of oscillating CL system. Furthermore, it was indicated that the application of the oscillating induction period as a parameter provided a new direction for the investigation of oscillating CL reaction to a certain extent. Although we speculated on the possible mechanism of perturbation, it was difficult to elucidate the exact mechanism due to the lack of certain relevant thermodynamic data. Further research into this issue is in progress.

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