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Short Communication

Kinetic determination of hydroquinone by a Belousov–Zhabotinskii oscillating chemical reaction

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Abstract

A novel and convenient method with good selectivity and high sensitivity for the determination of hydroquinone (HQ) based on the Belousov–Zhabotinskii (B–Z) oscillating chemical reaction has been presented. The optimum condition for the determination has also been investigated. In the B–Z reaction system, when the sample was injected, the change of the amplitude is linearly proportional to the logarithm of the concentration of HQ in the range 1.0×10^{-2}–2.0×10^{-4} M ($r = 0.9965$), whereas, when the concentration of HQ is over the range from 2.5×10^{-4} to 4.0×10^{-7} M, the calibration curve fits a second-order polynomial equation very well ($r = 0.9983$). © 2002 Published by Elsevier Science B.V.

Keywords: Kinetic determination; Hydroquinone (HQ); Belousov–Zhabotinskii (B–Z) oscillating chemical reaction

1. Introduction

Studies in nonlinear dynamics are part of a rapidly developing interdisciplinary research field. One important investigation is that of chemical oscillation [1–4]. Since the paper of Belousov [5] was published and Prigogine proposed the dissipation structure theory [6], research into oscillating chemical reactions has developed more rapidly. There has been a focus on the theoretical and experimental chemical kinetics in recent years [3,7]. In these complicated systems of chemical reactions, the concentrations of some reaction intermediates vary systematically with time.

A typical example of an oscillating chemical reaction is the Belousov–Zhabotinskii (B–Z) reaction [7], which was named after the two Russian scientists who first studied the oscillatory chemical phenomenon. This reaction involves the oxidation of an organic species such as malonic acid by an acidified bromate solution in the presence of a metal ion catalyst. Among the catalysts, the Ce(III)–Ce(IV) and $[Fe(II)(phen)]^{2+}$/$[Fe(III)(phen)]^{3+}$ (ferroin–ferriin) couples are two of the most widely used catalysts. In a closed (batch) system, the B–Z system exhibits a short induction period, followed by an oscillatory phase. The color of the solution alternates between yellow and colorless (for the Ce(III)–Ce(IV) couple) with a period of approximately 1 min. The oscillations may last over 2 h. Ultimately, with the concentrations of the major reactants such as potassium bromate and malonic acid decreasing continuously during the reaction process, the system progresses in the direction of decreasing Gibbs energy. In consequence, the oscillations die out and the system then drifts slowly and monotonically towards its chemical equilibrium state.

The mechanism for the B–Z reaction has been investigated extensively. The famous FKN mechanism proposed by Field et al [8] is generally accepted. It describes two major processes (Process A and Process B), which control the B–Z reaction alternately and result in oscillations in the concentration of the intermediate species. A third process (Process C) is a link between Process A and Process B. The overall reactions are as follows.

Process A:

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

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Process B:

$$BrO_3^- + 4Ce^{3+} + 5H^+ \rightleftharpoons HOBr + 4Ce^{4+} + 2H_2O \quad (2)$$

Process C:

$$HOBr + 4Ce^{4+} + BrCH(COOH)_2 + H_2O \rightleftharpoons 2Br^- + 4Ce^{3+} + 3CO_2\uparrow + 6H^+ \quad (3)$$

The heart of the mechanism is the autocatalytic, single-electron oxidation carried out by BrO_2. in Process B. The autocatalytic species is $HBrO_2$. The process can be inhibited by any species that competes for $HBrO_2$ in the chain-branching sequence. The concentration of Br^- in the B–Z system plays an important role [9] and it determines whether Process A or B is in control at a particular time. Process B is suppressed when $[Br^-]$ is too high as the following reaction then starts.

$$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr \quad (4)$$

This reaction removes $HBrO_2$ before it can enter the chain-branching sequence. The net effect of Process A, however, is to remove Br^- from the system. The autocatalytic oxidation by Process B begins when Process A has driven $[Br^-]$ to a sufficiently low value that reaction 4 can no longer compete successfully for $HBrO_2$. The onset of Process B is accompanied by a rapid production of Ce(IV), which becomes a reactant in Process C to regenerate Br^-. Beyond supplying Br^- to suppress Process B, Process C also resets Process B by reducing Ce(IV) back to Ce(III). The reaction continues until the concentration of one of the reactants falls below the level necessary to sustain the cycle.

The B–Z reaction has also been of interest to a few analytical chemists who have designed kinetic methods of analysis based on the reaction [10]. The first paper concerning the use of regular chemical oscillations for the determination of trace amount of ruthenium(III) ions was published in 1978 [11]. Since then, studies on the possibility of analytical application of the B–Z reaction have been performed [12–19], but most of them referred to the effect of metal ions and inorganic anions [20].

In a survey of the oscillation effect, we found that HQ can decrease the amplitude of the B–Z reaction sharply; the oscillating periods also appear to change. At 30 °C, the decrease in amplitude $\Delta A = A - A_0$ (where A_0 and A are the amplitudes before and after the injection respectively) was linearly proportional to the logarithm of concentration of HQ in the range 1.0×10^{-2}–2.0×10^{-4} M, $\Delta A/V = 0.7183 + 0.1247 \ln[HQ]$, ($r = 0.9965$). However, when the concentration of HQ was in the range 2.5×10^{-4}–4.0×10^{-7} M, $\Delta A/V = 0.9494 (\ln[HQ])^2 + 0.3164 \ln[HQ] + 0.0265$, ($r = 0.9983$), the decrease in amplitude versus the logarithm of the concentration of HQ fitted a second-order polynomial equation very well. Most foreign ions did not interfere with the determination. Cyclic voltammetry (CV) and other techniques were employed to study the mechanism. A qualitative explanation based on the experimental results is proposed.

2. Experimental

2.1. Chemicals

All chemicals were of analytical-reagent grade and were used as received. Solutions of HQ were freshly made just before the experiments. Solutions of 0.2 M potassium bromate, 0.5 M malonic acid and 0.04 M cerium sulfate $[Ce(SO_4)_2 \cdot 4H_2O]$ in 0.8 M H_2SO_4 were prepared separately. Doubly distilled deionized water was used throughout.

2.2. Apparatus

The oscillating assembly comprised a 50 ml glass reaction vessel fitted with a Model CS-501 thermostat and a magnetic stirrer Model ML-902 (both from Shanghai Pujiang Analytical Instrumental Factory) for homogenization. A CHI 832 electrochemical analytical instrument (Shanghai Chenhua Instrumental Company) was used to record the potential change. A Type 213 platinum electrode was used as the working electrode, a Type 213 platinum electrode as the counter electrode and a Type 217 saturated calomel electrode as the reference electrode against which all potentials were reported. A Type 302 bromide selective electrode was used to measure the concentration of bromide.

2.3. Procedure

2.3.1. Potentiometric measurements

Potentiometric measurements were performed in a closed thermostat-regulated glass container equipped with a magnetic stirrer. The stirring rate was kept at 500 rpm. The characteristics of the oscillations (induction period, amplitude and frequency) depend greatly on temperature. To obtain stable background values (A_0), all of the experiments were performed at 30 ± 0.05 °C. The reagents were maintained respectively as the following concentrations: $KBrO_3$, 0.2 M, 7.5 ml; $CH_2(COOH)_2$, 0.5 M, 6.5 ml; Ce(IV), 0.04 M, 1 ml; H_2SO_4, 0.8 M, 5.0 ml.

After the induction period, the oscillating system was run for several cycles, and then variable amounts of HQ were added to the reaction system at the bottom of the potentiometric cycle with a trace injector, to perform the perturbation experiments. The system was allowed to resettle until several oscillation cycle appeared again.

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2.3.2. Cyclic voltammetry

In order to understand the mechanism of the inhibitory effect of HQ on the B–Z reaction, CV was applied to monitor the species in the B–Z system, which reacted with HQ.

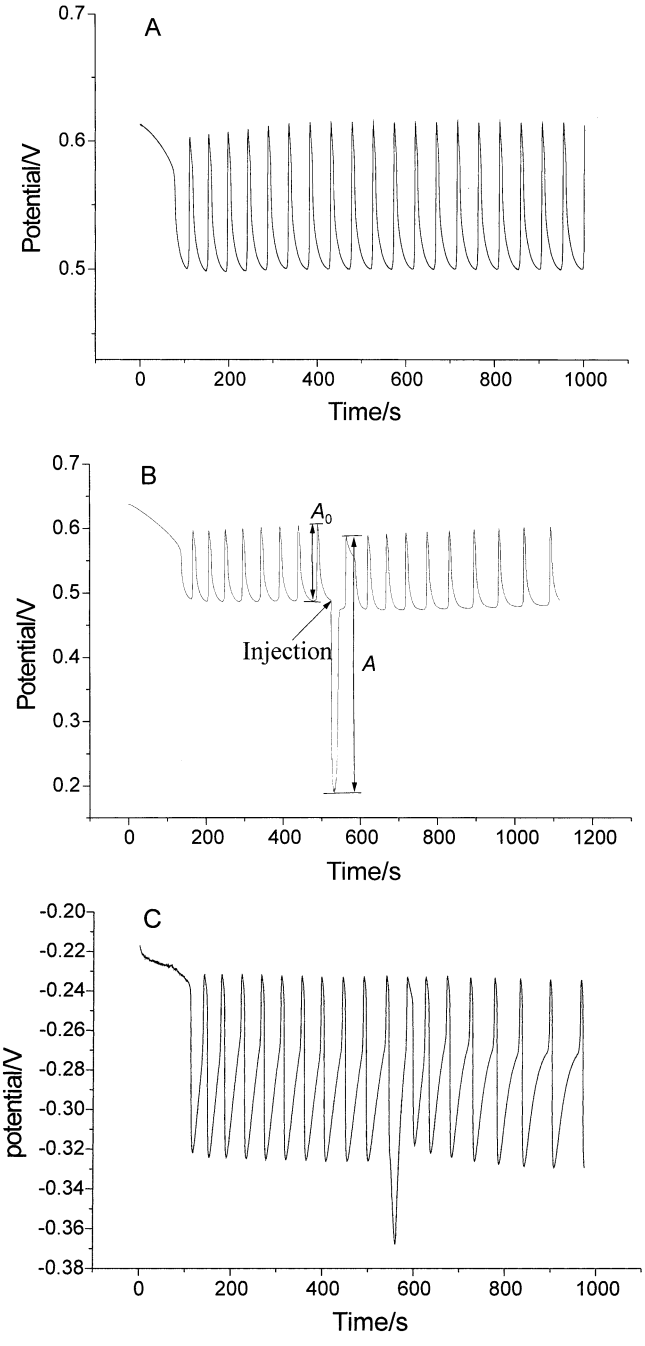

Fig. 1. Typical oscillation profiles for the proposed oscillating system obtained in the absence and in the presence of variable amounts of HQ perturbation using platinum and bromide ion-selective electrodes: (A) [HQ] = 0; (B) [HQ] = 4.0×10^{-5} M, platinum electrode; (C) [HQ] = 4.0×10^{-5} M, bromide ion-selective electrode. Common conditions: $KBrO_3$, 0.2 M, 7.5 ml; $CH_2(COOH)_2$, 0.5 M, 6.5 ml; Ce(IV), 0.04 M, 1 ml; H_2SO_4: 0.8 M, 5.0 ml.

3. Results and discussion

3.1. Results

When HQ is added to the B–Z medium, the first amplitude of oscillation (A) appears to decrease. Fig. 1 shows a typical oscillation profile for the B–Z oscillating chemical system in the absence and in the presence of HQ perturbation (where the potentials were monitored with platinum electrodes (A and B) and a Br^- selective electrode (C) respectively as the WE). When the concentration of HQ is in the range 1.0×10^{-2}–2.0×10^{-4} M, ΔA is linearly proportional to the logarithm of the concentration of HQ. The calibration data obey the following linear regression equation:

$$\Delta A/V = 0.7183 + 0.1247 \ln[\mathrm{HQ}] \quad (r = 0.9965)$$

When the concentration of HQ is in the range 2.5×10^{-4}–4.0×10^{-7} M, the potential decreases as before, but the oscillation behavior is different. The period of the oscillations changes greatly and the calibration data obey the following second-order polynomial equation (Fig. 2).

$$\Delta A/V = 0.9494 (\ln[\mathrm{HQ}])^2 + 0.3164 \ln[\mathrm{HQ}] + 0.0265 \quad (r = 0.9983)$$

These phenomena are different from those brought about by Vitamin B_1 [14], hexacyanoferrate [13], Ru(III) [11] and ascorbic acid [19].

More than 20 foreign ions were studied with respect to their possible influence on the determination of HQ. The results are shown in Table 1. Large amounts of alkali and alkaline earth metal ions have no effect on the determination, and most common anions do not interfere, apart from chloride and iodide.

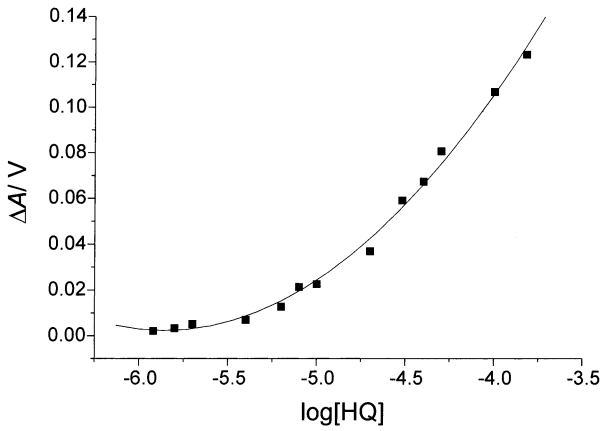

Fig. 2. Calibration curve of the decrease in amplitude versus the logarithm of [HQ] in the range 2.5×10^{-4}–4.0×10^{-7} M (other conditions are the same as those in Fig. 1).

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Table 1
Effect of foreign ions on the determination of 4.0×10^{-5} M HQ

Foreign ions	Maximum tolerated molar ratio
Na^+, K^+, Mg^{2+}, HPO_4^{2-}, NO_3^-, $H_2PO_4^-$, Li^+, SO_4^{2-}	5000
Cu^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, CN^-	3000
Co^{2+}, Ni^{2+}, Mn^{2+}, SCN^-	1000
OAc^-	500
F^-, Fe^{2+}, Fe^{3+}	200
Cl^-, I^-	10

3.2. Effect of reaction components on the determination

To obtain a constant and maximum value of ΔA in the determination of HQ, the effect of the concentrations of sulfuric acid, potassium bromate and cerium(IV) were examined.

The effect of potassium bromate concentration was studied over the range from 0.15 to 0.45 M. When the concentration of potassium bromate was 0.25 M, the maximum response of the HQ perturbation was obtained (Fig. 3A). The concentration of Ce(IV) and sulfuric acid were also studied, and similar results were obtained (Fig. 3B and C). The influence of the malonic acid concentration was investigated over the range 0.35–0.65 M. The results show that a higher concentration of malonic acid caused a larger change of amplitude (Fig. 3D). Hence, we finally adopted the following conditions as optimal: $[KBrO_3] = 0.2$ M, $[Ce(IV)] = 0.04$ M, $[H_2SO_4] = 0.8$ M, $[CH_2(COOH)_2] = 0.5$ M.

3.3. Mechanism

To clarify which species in the B–Z system reacted with HQ, the cyclic voltammograms of HQ were recorded in the following media: (I) $H_2SO_4 + Ce(IV) + HQ$; (II) $H_2SO_4 + KBrO_3 + HQ$; (III) $H_2SO_4 + CH_2(COOH)_2 + HQ$. The results indicate that only Ce(IV) can react with HQ, as is shown in Fig. 4.

A possible mechanism is that when HQ is introduced into the system, it can immediately be oxidized into quinone by Ce(IV) in the system, so that the concentration of Ce(IV) in the system decreases and that of

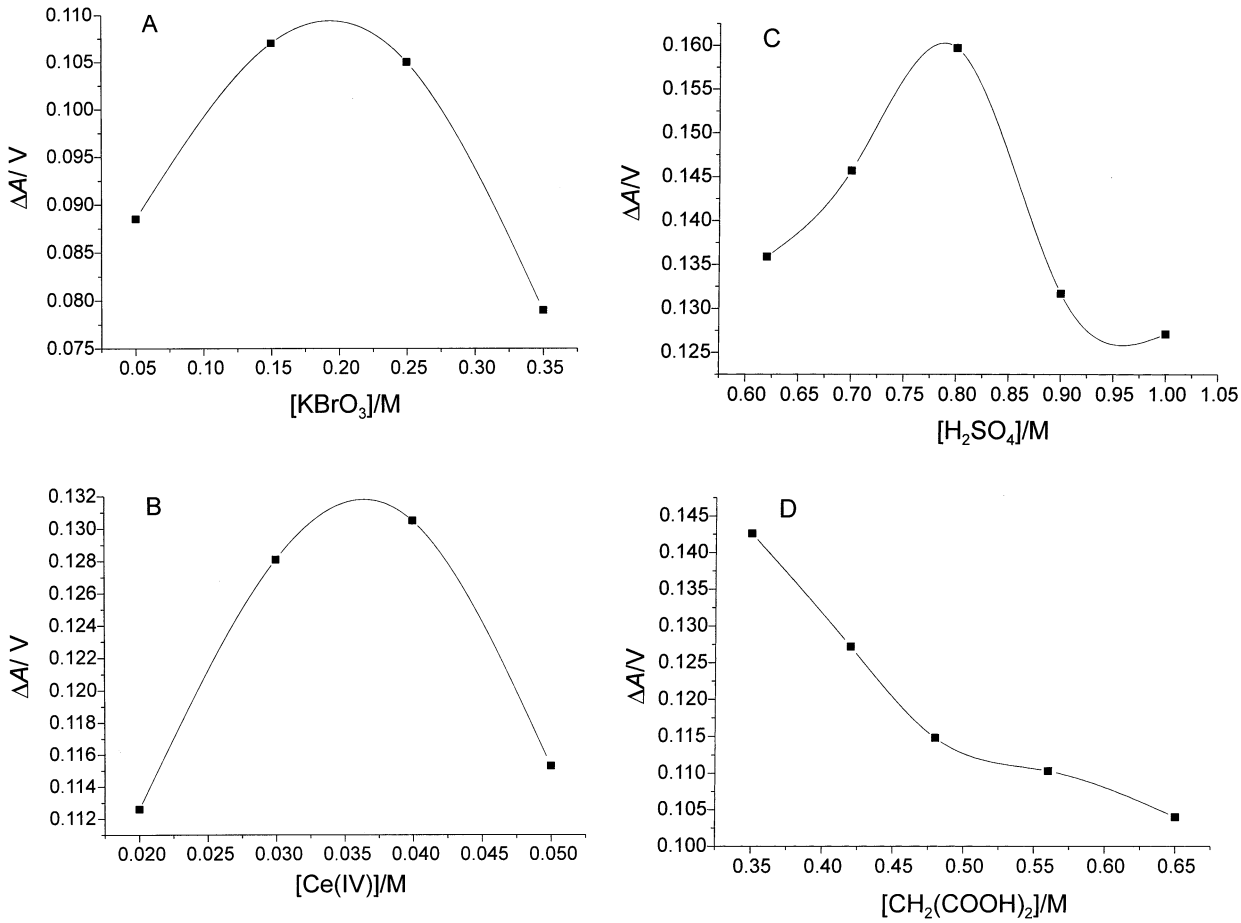

Fig. 3. Influence of the concentration of: (A) potassium bromate; (B) cerium(IV); (C) sulfuric acid; and (D) malonic acid on the HQ perturbed oscillating reaction. (A) 0.04 M Ce(IV) + 0.5 M $CH_2(COOH)_2$ + 0.8 M H_2SO_4; (B) 0.2 M $KBrO_3$ + 0.5 M $CH_2(COOH)_2$ + 0.8 M H_2SO_4; (C) 0.2 M $KBrO_3$ + 0.5 M $CH_2(COOH)_2$ + 0.04 M Ce(IV); (D) 0.2 M $KBrO_3$ + 0.04 M Ce(IV) + 0.8 M H_2SO_4. Common condition: $[HQ] = 4.0 \times 10^{-5}$ M.

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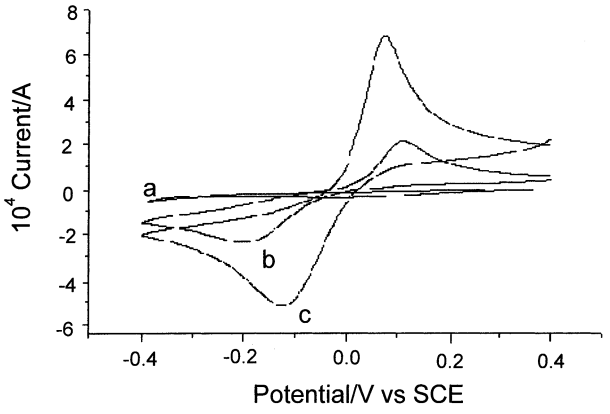
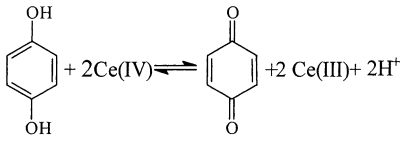


Fig. 4. Cyclic voltammograms of the reactions between HQ and Ce(IV) obtained in the absence and in the presence of variable amounts of HQ: (a) [HQ] = 0; (b) [HQ] = 3.5×10^{-4} M; (c) [HQ] = 3.5×10^{-3} M. Common conditions: [Ce(IV)] = 0.04 M, [H_2SO_4] = 0.8 M.

Ce(III) increases, so the value of ln([Ce(IV)]/[Ce(III)]) decreases sharply and the potentiometric oscillations are seen to decrease. The reaction is as follows:



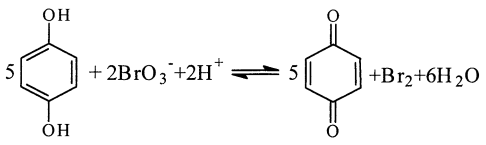
(5)

As the concentration of Ce(III) increases, it can react with free radicals $BrO_2\cdot$,

$$BrO_2\cdot + Ce(III) + H^+ \rightleftharpoons HBrO_2 + Ce(IV) \quad (6)$$

Reaction 6 occurs very quickly, and the Ce(IV) regenerates in a very short time. So the system can reconvert to the same regular oscillation state as initially. This is consistent with the variation of [Br^-] over time (Fig. 1C).

When the concentration of HQ added into the B–Z medium is higher than 2.5×10^{-4} M, the behavior is different. Once a large amount of HQ is added to the B–Z system, some of it reacts with Ce(IV) as was discussed before; the remainder of the HQ can be oxidized by BrO_3^-, so that the solution gradually becomes yellow. When this solution is extracted with carbon tetrachloride, the organic layer appears yellow. After separation, addition of potassium iodide turns the organic layer purple. When sodium thiosulfate is added the purple disappears. These phenomena indicate that bromine is generated in the system. The reaction is as follows:



(7)

Although BrO_3^- can also react with Br^- to generate bromine, the concentration of Br^- is very low in the system, so a large amount of the bromine comes from reaction 7.

In reaction 7 a large amount of BrO_3^- is consumed, so reaction 2 cannot take place as fast as before and the regeneration of Ce(IV) is inhibited. On the other hand, the concentration of malonic acid does not change in the system, so a large amount of Br_2 could not be removed. Therefore, the [Br_2]–[Br^-] ratio does not remain in the same range as before. Thus the oscillating reactions are inhibited temporarily. This is shown in Fig. 1C.

Clarifying the exact mechanism is difficult because of the lack of certain relevant thermodynamic data. However, computer simulation may be useful for solving the oscillation problem and corresponding studies are in progress.

Acknowledgements

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