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ORIGINAL ARTICLE

Identification of two aromatic isomers between 3- and 4-hydroxy benzoic acid by their perturbation on the potential oscillations of a Belousov-Zhabotinsky system

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Identification

Abstract A novel method for identification of two aromatic isomers of mono hydroxy benzoic acid (HBA) was reported by using their different perturbation effects on the potential oscillations of a Belousov-Zhabotinsky (BZ) system. In such a system, a macrocyclic complex of Cu [CuL] $(ClO_4)_2$ was used as catalyst in which ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. To the BZ system, 3-hydroxy benzoic acid (3-HBA) could temporarily quench and regenerate potential oscillations with damping characters after inhibition time (t_{in}) while 4-hydroxy benzoic acid (4-HBA) could only change the oscillation amplitude (ΔA) to give damping oscillations with no inhibition time. Thus, these two isomers of HBA were identified. Reaction mechanisms of BZ have been proposed by FKN model. An explanation of perturbation mechanism is that, although 3-HBA reacted with $BrO_2^{\cdot}$ while 4-HBA reacted with BrO_3^-, they all produced 1,4-quinone.

1. Introduction

Isomers are molecules of identical atomic compositions, but with different bonding arrangements of atoms or orientations of their atoms in space (Petrucci et al., 2002). Because isomers of a compound may have different functions, that is why humans desire to create different types of drugs using specific isomers that will help us overcome pain (Katzung et al., 2009), allergies, psychological problems, infection, and many other medical problems. For example, methylated xanthines have two isomers (theophylline and theobromine) which are used for a variety of function due to different positioning of the methyl group in the rings: theophylline is used as an antidote in bronchodilation and anti-inflammatory while theobromine remediate the vasodilation effect. Similarly, ethambutol is a cure for tuberculosis while excess L-ethambutol can cause

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blindness (Lim, 2006). Thalidomide is nontoxic while S-thalidomide causes horrible birth defects (Miller and Marylin, 1991). Thus, the identification and correct selection of the specific isomer both in the field of medicine and chemistry, by different methods, is of great importance.

In field of isomers identification, traditionally different instrumental techniques, such as Mass Spectrometry (MS) (Chen et al., 2015; Yuan et al., 1994), Liquid Chromatography-Mass Spectrometry (LC–MS) (Pan et al., 2005; Chen et al., 2014), Gas Chromatography-Mass Spectrometry (GC–MS) (Sheng and Chen, 2009) and Mass Spectrometric-Molecular Statistic (MS–MS) (Buryak, 1990), show their immense advantages. Among these, MS has the advantages of reducing background interference and better sensitivity for the identification of suspected compounds with molecular weight and isotopic evidence. However, MS technique has the following demerits: (1) – it often fails to distinguish between optical and geometrical isomers; (2) – it fails to show the positions of substituent in o-, m- and p-positions in an aromatic ring; (3) – its scope is limited in identifying hydrocarbons that produce similar fragmented ions. Therefore, the direct use of MS technique for identifying sample may cause error and that is why MS technique has to be coupled with other techniques to identify samples. In comparison to MS, LC–MS is a powerful technique with higher sensitivity and selectivity for the probable identification of chemicals of particular masses in the presence of reference chemicals. One of the disadvantages of LC–MS is reflected in its facing difficulties in selection of suitable mobile phase. Meanwhile, GC–MS has been used for many decades for identification of isomers and detection of drugs in chemical analysis. The drawbacks concerning with GC–MS include, higher operating temperature, being easy to overload the phase (less sample capacity). Therefore, new approaches are desirable for identification of organic isomers to avoid these disadvantages that the techniques are involved. Thus, we developed a new chemical method (using oscillating chemical system) which is advantageous over some instrumental techniques with good detection limitations and being easy to set up.

The chemical oscillation, which is prototypical phenomenon of nonlinear chemical dynamics, shows the temporally periodic, or nearly periodic, variation of the concentration of one or more species in a reaction. Oscillating reaction is classified into various kinds such as Bray-Liebhafsky (BL reaction) (Bray, 1921; Bray and Liebhafsky, 1931), Belousov-Zhabotinsky (BZ reaction) (Zhabotinsky and Rovinsky, 1987; Scott, 1989; Lamprecht and Schaarschmidt, 1978), Briggs-Rauscher (BR reaction) (Briggs and Rauscher, 1973; Kim et al., 2002) and uncatalyzed reaction of aromatic componds with bromate (Orban and Koros, 1978). Among all oscillating reactions, both BZ and BR involve metal ions (Ce^{4+}, Mn^{2+}, $Fe(phen)_3^{2+}$, or $Ru(bipy)_3^{2+}$) and macrocyclic complex of Cu and Ni as catalysts, and these oscillators were extensively studied for qualitatively measurements of various compounds including antioxidants (Cervellati et al., 2001, 2002, 2000; Hu et al., 2014), ions (Hu et al., 2006a; Chen et al., 2009) and some organics (Hu et al., 2007, 2009; Chen et al., 2008; Zeng et al., 2014). Jiménezprieto et al. (1998) and Ren et al. (2013) have given some critical reviews on the analytical use of oscillating reactions. Also, sensitivity of the oscillations of the BZ reaction on the addition of different chemicals is useful also for computing purposes (Gentili et al., 2012). However, all the previous works concerning the oscillating chemical reaction are limited to quantitative measurements and needs on its applications are growth in progress. In order to widen the application of oscillating chemical system, we utilized chemical oscillators for the identification of isomers of a compound.

Previously, our group successfully utilized BR chemical oscillator for the identification of two aliphatic isomers (α-ketoglutaric from β ketoglutaric acid) in 2015 (Zhang et al., 2015), and another two cyclohexane isomers (cyclohexane-1,3-dione from 1,4-cyclohexanedione) in 2016 (Chen et al., 2016). In order to find out if some types of chemical oscillator rather than BR type could be utilized for identifying other types of isomers, we consider the BZ oscillator for identification of two aromatic isomers.

Compared with the BZ oscillator catalyzed by Cerium, ferroin and ruthenium, BZ oscillating reactions involving tetraazamacrocyclic complexes as catalysts have their unusual oscillating behavior (Hu et al., 2006b), which is suitable to be selected as the matrix for analytical purpose. Such unusual behavior is reflected in three aspects: (a) these kinds of BZ systems have lower activation energy; (b) higher oscillating frequencies are observed in those systems owing to the presence of the extended π-system in the macrocyclic ligand L which ensures a high rate for reactions involving electron transfer at individual steps of the oscillating process; (c) these kinds of BZ systems are more vulnerable to the external perturbations.

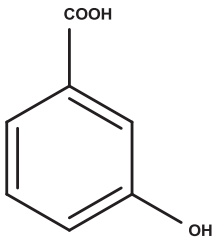
In this paper, we presented a novel technique using a BZ oscillator for the identification of two aromatic isomers of hydroxybenzoic acid (HBA), 3- hydroxy benzoic acid (3-HBA) and 4-hydroxybenzoic acid (4-HBA), as shown in Scheme 1. This methodology was based on the perturbation effects of two aromatic isomers of HBA on the potential oscillations of a BZ system. The macrocyclic complex of copper, $[CuL](ClO_4)_2$, was used as catalyst in BZ oscillator, where the ligand L in complex (Yatsimirskii et al., 1982) is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

In this paper, these two aromatic isomers of HBA were separately injected into the active BZ system with different perturbation effects on the potential oscillations: addition of 3-HBA could quench and regenerate potential oscillations with damping characters after inhibition time (t_{in}) while the addition of 4-HBA could only change the oscillations amplitude (ΔA) to give damping oscillations with no inhibition time. The 3-HBA and 4-HBA were thus distinguished from each other by using such a BZ oscillator. A new method could be expected to exploit this behavior to identify two aromatic isomers of HBA on the basis of perturbation technique on a BZ chemical oscillating system using macrocyclic complexes of Cu as catalyst. Such technique based on oscillating system has good detection limits and is easy in setup. This analytical method could also be extended for the identification of other isomerides as well.

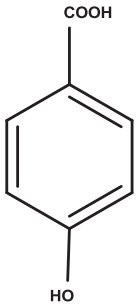
2. Experimental section

2.1. Reagents

All the reagents were of analytical grade without further purification. H_2SO_4 (Aldrich, 98%), sodium bromate (Sinopharm



3-Hydroxy Benzoic Acid (3-HBA)



4-Hydroxy Benzoic Acid (4-HBA)

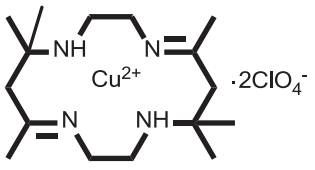
Scheme 1 Structure of isomers of Hydroxy benzoic acid.

chemical reagent, China), malic acid (aladdin, Shanghai, China), 3-HBA (aladdin, Shanghai, China), 4-HBA (aladdin, Shanghai, China), were all commercially obtained except catalyst, $[CuL](ClO_4)_2$. The Cu-Complex catalyst was synthesized according to literature (Curtis and Hay, 1966; Curtis, 1972) and was identified by IR spectrum and elemental analysis. The IR spectrum of $[CuL](ClO_4)_2$ was provide in Fig. S1 in Supplementary Materials. The structures of Cu-Complex catalyst were shown in Scheme 2.

For BZ system, solution of 1 mol L^{-1} H_2SO_4 was prepared while 2 mol L^{-1} malic acid, 0.65 mol L^{-1} $NaBrO_3$, 1.74×10^{-2} mol L^{-1} of $[CuL](ClO_4)_2$ were prepared within 1 mol L^{-1} H_2SO_4. Solutions of different concentration of these two isomers of HBA were freshly prepared before use. Double distilled water was used in all cases.

2.2. Apparatus

The apparatus assembly for BZ consists of a glass reactor and a potentiometric measuring system. The potentiometric system consists of two electrodes: a platinum electrode (model 213 Shanghai, China) works as a working electrode and a saturated calomel electrode (SCE) (Model 217 Shanghai, China) acts as a reference electrode. Both electrodes were dipped into the solution in the glass reactor. The glass reactor consists of a magnetic stirrer (Jiangsu, China), which was used to homogenize the reaction solution by keeping under stirring rate of 500 rpm. The temperature controller (Model (DZCS-IIC, Nanjing Dazhankejiao Institute of Instrument, China) was used to keep the reaction temperature at 23 ± 0.5 °C. Changes in potential *v.s.* time were recorded in a personal computer (PC) through a GO!Link sensor interface (Vernier Software Technology, USA) and an amplifier (Vernier Software Technology, USA), which is connected to two electrodes. A Logger Lite data-acquisition program was utilized for collection of data. The UV–Visible spectrum was obtained by a Ultraviolet spectrometer (model UV-1750, Shimadzu, Japan) and cyclic voltammetry experiments were performed through a cyclic voltammeter (model CH1660, Shanghai Chenhua instruments Ltd, China).



Scheme 2 Structure of $[CuL](ClO_4)_2$.

2.3. Procedure

In a 50 mL-glass-reactor, 40 mL of BZ reagents were mixed by the following order: 1 mL of 0.65 mol L^{-1} $NaBrO_3$ solution, 29 mL of 1 mol L^{-1} H_2SO_4 solution, 4 mL of 2 mol L^{-1} malic acid and 6 mL of 1.74×10^{-2} mol L^{-1} $[CuL](ClO_4)_2$ solution. The total volume of the reaction mixture is 40 mL. A platinum electrode and a reference electrode were dipped into the glass reactor and potentials *v.s.* time were recorded in the PC. Desired concentration of 3-HBA, or 4-HBA was separately used to perturb the active BZ oscillation. The same oscillation experiment and perturbation experiment repeated three times.

3. Results and discussions

3.1. Typical oscillation for BZ reaction

Fig. 1(a) shows the typical potential oscillation profile for BZ system, obtained by the mixing of the reagents in the above-stated order. In Fig. 1a, the oscillations last for more than 2000 s and the oscillation amplitude nearly keeps unchanged. It is known that oscillation reactions show a periodic deviations in the concentrations of few species that are replicated in repeated color, pH or in redox-potential variations, depended on the specific systems (Beck et al., 1991). For sodium bromate-H_2SO_4-malic acid-$[CuL](ClO_4)_2$ reaction, the periodic fluctuations in the concentration of the reduced form $[CuL]^{2+}$ and oxidized form $[CuL]^{3+}$ of catalyst were noticed, accompanying periodic changes in color (red-orange-red) that were observed during oscillation. This phenomenon indicates the following electron- transfer process:

$$[CuL]^{2+}\ (\text{red}) \rightleftharpoons [CuL]^{3+}\ (\text{orange})$$

3.2. Perturbation of BZ potential oscillation

In order to distinguish 3-HBA and 4-HBA from each other, we perturbed typical potential oscillations by an equal amount (40 μL) of the same concentration of 3-HBA or 4-HBA. The original concentration ranges of 3-HBA and 4-HBA were tested from 0.07 to 0.25 mol L^{-1} (final concentrations of 3-HBA and 4-HBA in the system are from 7.0×10^{-5} to 2.5×10^{-4} mol L^{-1}). The different perturbation behaviors of

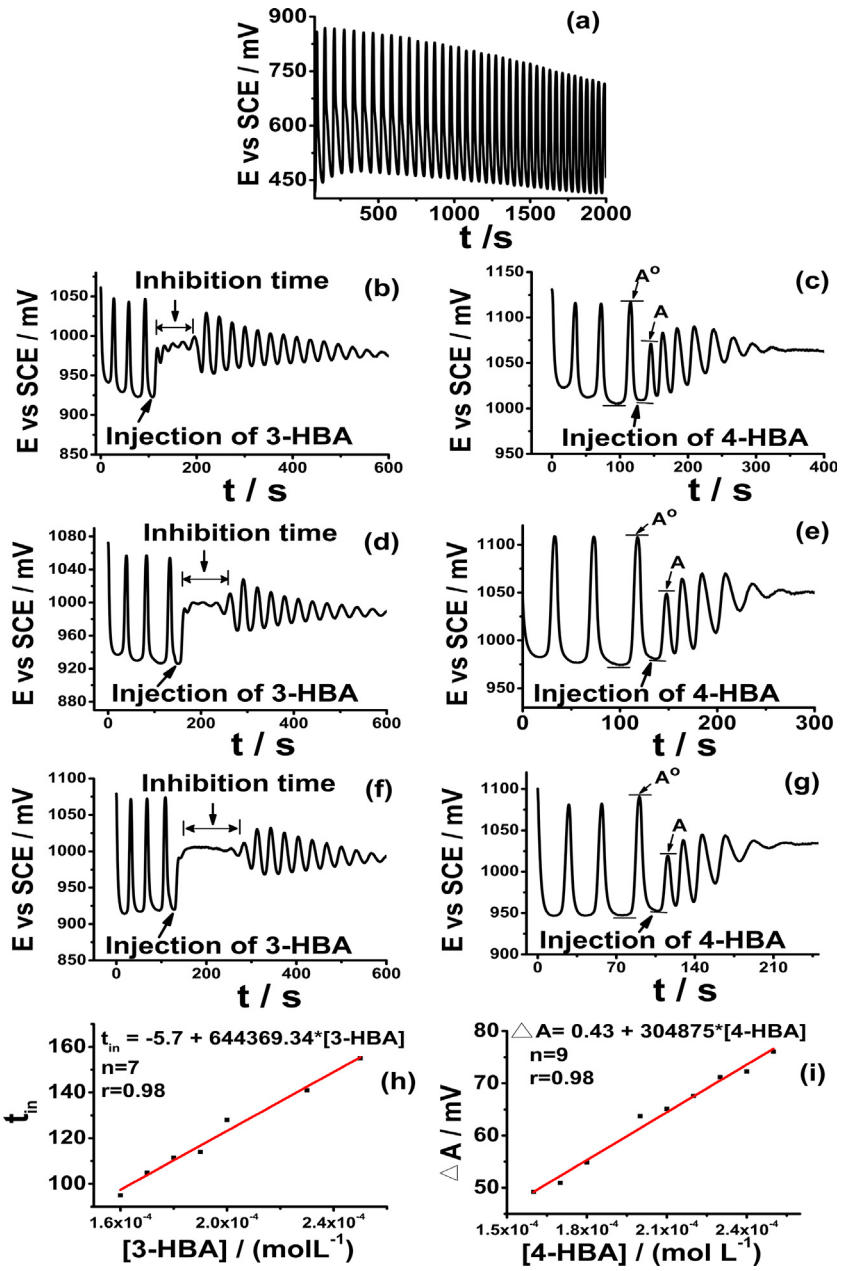


Fig. 1 (a) The typical potential oscillation profile for the proposed BZ oscillation system. (b) Perturb oscillation by injection of 1.6×10^{-4} mol L^{-1} [3-HBA]; (c). Perturb oscillation by injection of 1.6×10^{-4} mol L^{-1} [4-HBA]; (d) Perturb oscillation by injection of 2×10^{-4} mol L^{-1} [3-HBA]; (e) Perturb oscillation by injection of 2×10^{-4} mol L^{-1} [4-HBA]; (f) Perturb oscillation by injection of 2.5×10^{-4} mol L^{-1} [3-HBA]; (g) Perturb oscillation by injection of 2.5×10^{-4} mol L^{-1} [4-HBA]; (h) Linear regression curves obtained for the inhibition time *vs* [3-HBA]; (i) Linear regression curve obtained for the change in oscillation amplitude (ΔA) *vs* [4-HBA]; Common condition; $[H_2SO_4] = 7.25 \times 10^{-1}$ mol L^{-1}; $[NaBrO_3] = 1.625 \times 10^{-2}$ mol L^{-1}; [malic acid] = 0.2 mol L^{-1}; $[CuL]^{2+} = 2.61 \times 10^{-3}$ mol L^{-1}; t = 17.5 °C.

both isomers were noticed. The addition of 40 μL of 0.16 mol L^{-1} 3-HBA (final concentration in the system is 1.6×10^{-4} mol L^{-1}) into the active BZ system could quench and then successfully regenerate the potential oscillations with damping characters after an inhibition time (t_{in}), as shown in Fig. 1(b). Contrastingly, the injection of 1.6×10^{-4} mol L^{-1} 4-HBA into the system only caused the change in the oscillation amplitude (ΔA) to give damping oscillations with no inhibition time, as in Fig. 1(c). It is found that, without perturbation, the oscillations which last for more than 2000 s while the oscillations, after addition of either 3-HBA or 4-HBA, last only a few hundreds of seconds. It seems that the oscillations after addition of 3-HBA last less than when 4-HBA was added. Further examination indicated that, as the concentration of 3-HBA increased in the system, the inhibition time (t_{in}) increased as showed in Fig. 1(d and f). It was observed that t_{in} is linearly proportional to the concentration of 3-HBA over a range between 1.6×10^{-4} to 2.5×10^{-4} mol L^{-1} with a correlation coefficient of 0.98 as in Fig. 1(h). Similarly, ΔA was increased when the concentration of 4-

HBA was increased in the system, as showed in Fig. 1(e and g). It was found that ΔA is linearly proportional to the concentration of 4-HBA over a range between 1.6×10^{-4} to 2.5×10^{-4} mol L^{-1} with a correlation coefficient of 0.98 as in Fig. 1(i).

Here we have successfully shown to identify 3-HBA from 4-HBA by their perturbation effects on BZ system in their concentration range from 7.0×10^{-5} to 2.5×10^{-4}: 3-HBA had inhibitory effect besides its damping effects on the oscillations whereas 4-HBA couldn't cause the inhibition time and it only caused changes in the oscillation amplitude to give damping oscillations.

3.3. Mechanism for BZ oscillating reaction

The chemical oscillation frequently contains numerous kinetic steps concerning some independent variables (Luo et al., 1989). That is why the mechanisms of oscillating system are slightly complex. According to the renowned FKN mechanism (Field et al., 1972) and available literature (Hu et al., 2005, 2006b, 2007) the $[CuL]^{2+}$-Catalyzed oscillation can be described by below mention equations:

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \quad (1)$$

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

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \quad (3)$$

$$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons\rightleftharpoons BrO_2^{\cdot} + H_2O \quad (4)$$

$$Br_2 + HOOCCHOHCH_2COOH \rightarrow Br^- + H^+ + HOOCCHOHBrCHCOOH \quad (5)$$

$$BrO_2^{\cdot} + [CuL]^{2+} + H^+ \rightarrow [CuL]^{3+} + HBrO_2 \quad (6)$$

$$HOOCCHOHBrCHCOOH + 6[CuL]^{3+} + 3H_2O \rightarrow 6[CuL]^{2+} + Br^- + 2HCOOH + 2CO_2 + 7H^+ \quad (7)$$

All reactions from (1) to (4) are reversible. They consist of some bromine species with various oxidation states as reactants or products. Reaction (5) is irreversible and represents the bromination of the malic acid in the present system. Reaction (6) is also irreversible which represents the oxidation of $[CuL]^{2+}$ into $[CuL]^{3+}$ in acidic condition. When $[CuL]^{2+}$ was oxidized into $[CuL]^{3+}$ in reaction (6), the color of the solution turn from red to orange. The orange color of the solution turn back to red color according to reaction (7), which represents the reduction of $[CuL]^{3+}$ into $[CuL]^{2+}$ in the presence of HOOCCHOHBrCHCOOH.

3.4. Cyclic voltammetry experiments for 3-HBA and 4-HBA in BZ

In the presence and absence of 3-HBA, the CV experiments was performed in order to check weather redox reactions exists between 3-HBA and initial reagents in the following media: H_2SO_4 + $NaBrO_3$, H_2SO_4 + malic acid, H_2SO_4 + $[CuL](ClO_4)_2$. Cyclic voltammograms confirmed the redox reaction between 3-HBA and $NaBrO_3$ as shown in Fig. 2(a). Cyclic voltammograms have also confirmed no redox reaction between 3-HBA and $[CuL](ClO_4)_2$, nor redox reaction between 3-HBA and malic acid. Cyclic voltammogram of $[CuL](ClO_4)_2$ with 3-HBA is showed in Fig. S2(a) in Supplementary Materials. However, even though Cyclic voltammograms have showed the redox reaction between 3-HBA and $NaBrO_3$, the possibility of direct reaction of 3-HBA with $NaBrO_3$ should be reconsidered, because perturbation of 3-HBA on the system caused the inhibition time as showed in Fig. 1(b, d and f). Inhibition time is usually caused by the involvement of intermediate radical ($BrO_2^{\cdot}$, for an example), which was produced during oscillation and which reacted with additive (3-HBA). Thus we proposed that, the inhibition time was due to the reaction between 3-HBA with intermediate radical ($BrO_2^{\cdot}$) as mentioned in the below-listed reaction (8).

In contrasting experiments to explore the redox reaction between 4-HBA with initial reagents, similar CV experiments were performed into the following media: H_2SO_4 + $NaBrO_3$, H_2SO_4 + malic acid, H_2SO_4 + $[CuL](ClO_4)_2$ in the presence and absence of 4-HBA. The results of cyclic voltammograms have confirmed the redox reaction between 4-HBA and $NaBrO_3$ as showed in Fig. 2(b). Here, we assume the direct reaction between 4-HBA and BrO_3^- because the perturbation of 4-HBA has only caused the change in oscillation amplitude (ΔA) without inhibition time (t_{in}). Cyclic voltammograms have also confirmed no redox reaction between 4-HBA and $[CuL](ClO_4)_2$, nor redox reaction between 4-HBA and malic acid. Cyclic voltammogram of $[CuL](ClO_4)_2$ with 4-HBA is showed in Fig. S2(b) in Supplementary Materials.

3.5. Product identification in the BZ system

In 2009 (Masood et al., 2009), it was reported that these two isomers of mono hydroxy benzoic acid in BZ system could be converted into quinones. It was reported [40] that the UV

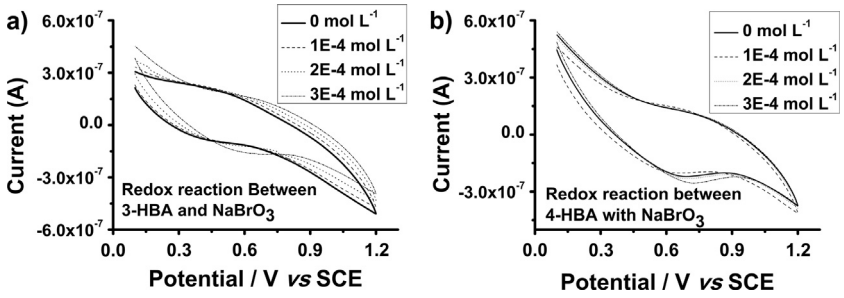


Fig. 2 (a) Cyclic Voltammogram of $NaBrO_3$ with 3-HBA; $[NaBrO_3] = 1.625 \times 10^{-2}$ mol L^{-1}; (b) Cyclic Voltammogram of $NaBrO_3$ with 4-HBA; $[NaBrO_3] = 1.625 \times 10^{-2}$ mol L^{-1}; Common condition: $[H_2SO_4] = 1$ mol L^{-1}. Scan rate = 100 mV/ s.

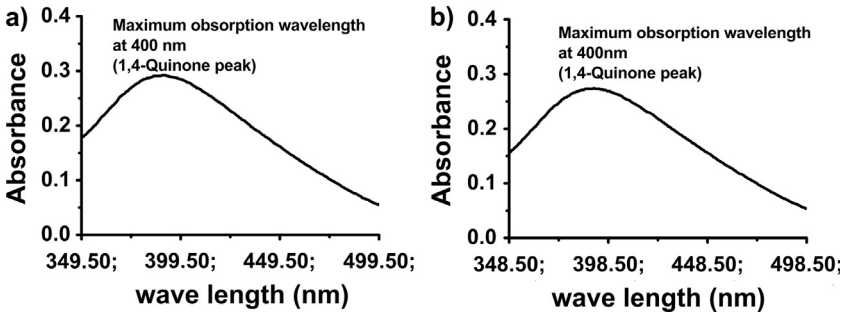


Fig. 3 (a) The UV–Visible absorption spectrum of 3-HBA in presence of H_2SO_4 and $NaBrO_3$, conditions: [3-HBA] = 1×10^{-4} mol L^{-1}, [H_2SO_4] = 1 mol L^{-1}, [$NaBrO_3$] = 1.625×10^{-2} mol L^{-1}, (b) The UV–Visible absorption spectrum 4-HBA in the presence of H_2SO_4 and $NaBrO_3$. system, conditions: [4-HBA] = 1×10^{-4} mol L^{-1}, [H_2SO_4] = 1 mol L^{-1}, [$NaBrO_3$] = 1.625×10^{-2} mol L^{-1}.

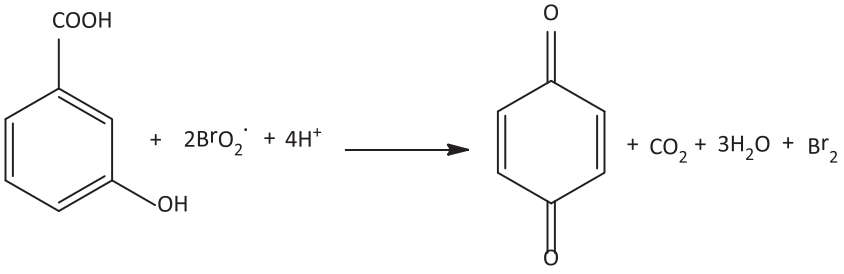
absorbance peak for quinone lies in a range of 350–450 nm. We performed UV experiments in order to confirm the product formation (1,4-quinone) from the additives (3-HBA and 4-HBA) in BZ system. A small amount (40 μL) of 0.1 mol L^{-1} solution of 3-HBA or 4-HBA was respectively put into a mixture consisting of 39 mL of 1 mol L^{-1} sulfuric acid and 1 mL of 0.65 mol L^{-1} of sodium bromate (here we not use malic acid and $CuL(ClO_4)_2$ because both reagents couldn't show redox reaction in cyclic voltammetry experiment with additives). Thus we prepared two samples, sample A and sample B. Sample A was the mixture of 1×10^{-4} mol L^{-1} of 3-HBA with 1 mol L^{-1} sulfuric acid and 1.625×10^{-2} mol L^{-1} of sodium bromate while sample B was the mixture of 1×10^{-4} mol L^{-1} of 4-HBA with 1 mol L^{-1} sulfuric acid and 1.625×10^{-2} mol L^{-1} of sodium bromate. The UV spectra for both the samples were obtained that clearly show their peaks absorbance at the wavelength of approximately 400 nm (as shown in Fig. 3(a) for sample A and Fig. 3(b) for sample B), which is in agreement with the peak absorbance for 1–4 quinone in the literature (Paakkonen et al., 2010).

Thus on the basis of both CV and UV experiments, we had proposed two reactions (reaction (8) and reaction (9)) which were placed in above FKN mechanism in order to explain the influence caused by the 3-HBA and 4-HBA over BZ system.

3.6. Reaction of 3-HBA with $BrO_2^{\bullet}$ radical (interpretation of reaction (8))

Reaction (8) indicates that the $BrO_2^{\bullet}$ radical was consumed by 3-HBA with the products of Br_2 and 1,4-quinone. The consumption of $BrO_2^{\bullet}$ radical temporarily terminated reaction (6) and that is why inhibition time was noticed. When all amount of 3-HBA was completely oxidized to 1,4-quinone, oscillation was regenerated. The probable explanation of oscillation regeneration is as followings. In the reaction (8), Br_2 was produced and thus the Br_2 concentration in the system increased. Such an excess in Br_2 concentration caused two effects. First, increase in Br_2 shifted the reaction (3) in the reverse direction and HOBr concentration in the system increased. This upsurge in the amount of HOBr led to shifting reaction (2) in the reverse direction with increased production of $HBrO_2$. However, higher $HBrO_2$ amount shifted reaction (4) in the forward direction and generated $BrO_2^{\bullet}$ radical which was resumed reaction (6). Secondly, increase in Br_2 amount from reaction (8) accelerated the oxidation of malic acid according to reaction (5), resulting in the accumulated production of Br^-. The Br^- is the main reactant in reactions (1−3) and thus reactions from (1−4) were resumed. In short, the oscillation was regenerated.

We noticed that the regenerated oscillation was characterized with the decreased oscillation amplitude, as showed in Fig. 1(b, d and f). The reason for the change in the oscillation amplitude (ΔA) was due to the consumption of $BrO_2^{\bullet}$ radical in reaction (8), which affected the net concentration of the system. Such decrease in amount of $BrO_2^{\bullet}$ radical led to the decrease in the net production of $[CuL]^{3+}$ according to reaction (6). Such a decrease in the amount of $[CuL]^{3+}$ can cause the decrease in the value of $\log\{[CuL]^{3+}/[CuL]^{2+}\}$, resulting in the maximum potential (correspond to the maximum concentration of $[CuL]^{3+}$) of oscillation dropped. Because the concentration of $[CuL]^{3+}$ decreased, the concentration of $[CuL]^{2+}$ increased (the total concentrations of $[CuL]^{3+}$ and $[CuL]^{2+}$ are fixed). As the $[CuL]^{2+}$ concentration has increased, the minimum potential (correspond to the maximum concentration of $[CuL]^{2+}$) would increase. Therefore, decrease in oscillation amplitude (from minimum potential to maximum potential) was noticed after inhibition time as mention in Fig. 1(b, d and f).

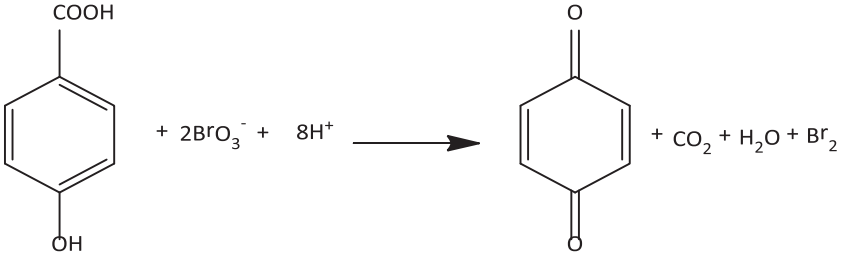


(8)

The appearance of an inhibition time was also observed in a ferroin-catalyzed BZ system by Paul (2005) and Rossi et al. (2008). In those cases where the surfactant's effects on the BZ oscillations were studied, molecular bromine played a fundamental role. The surfactant which creates micellar environment changes the effective concentration of Br_2, and hence the inhibition time was observed. As contrast, there are no surfactants in such a macrocyclic complex-catalyzed BZ system, molecular bromine cannot play a fundamental role as it plays in that with the surfactant. We have shown that 3-HBA and 4-HBA undergo oxidation process during the oscillations. As Bromate or $BrO_2^{\cdot}$ is stronger oxidation species than Br_2, the role bromine cannot act as oxidation species either.

3.7. Interpretation of reaction (9) (reaction of 4-HBA with BrO_3^-)

When 4-HBA was added into the system, it was quickly oxidized into 1,4-quinone by BrO_3^- and bromine was produced. Due to the occurrence of reaction (9), the reaction (1) and (4) were greatly affected because BrO_3^- is the main reactant in reactions (1) and (4). In reaction (9), when a sufficient amount of bromine was accumulated, it shifted reaction (3) in the reverse direction. As a result, the concentration of HOBr and Br^- was increased. The increase in the amount of HOBr led to shifting reaction (2) in the reverse direction with increase in amount of $HBrO_2$, which in turn to increase the concentration of $[CuL]^{2+}$ to some extent and decrease the concentration of $[CuL]^{3+}$ according to reaction (6). As a result, the value of $\log\{[CuL]^{3+}/[CuL]^{2+}\}$decreased abruptly. Accordingly, a decrease was observed in the maximum potential, and this decrease led to the decrease in oscillation amplitude, as showed in Fig. 1(c, e and g). The decrease in $[CuL]^{3+}$ concentration led to decrease in the amount of Br^- according to reaction (7), which caused a shorter period of oscillation.



(9)

The kinetics of the oxidation of the 4-HBA by bromate in acidic environment were studied. We have, by following quinone's UV absorbance, monitored the increasing concentration of the quinone in time. The order rate for 4-HBA with bromate is calculated to be 0.5167.

Although reaction 8 is the reaction between the $BrO_2^{\cdot}$ and 3-HBA, the order rate for 3-HBA with bromate is of valuable for reference. The order rate for 3-HBA with bromate is calculated to be 0.5267.

It must be enhanced that 1,4-quinone, the oxidation product of 4-HBA, is prone to be quickly and continually oxidized by bromate with sulfuric acid medium. The UV absorption experiments showed that it only takes several minutes for 4-HBA to be fully oxidized into 1,4-quinone by bromate, and 1,4-quinone continually be oxidized, because absorbance of 1,4-quinone increase with time (in five minutes) to its maximum absorbance and then decrease with further increasing time. This phenomenon means that quick formation of 1,4-quinone (in five minutes) was accompanied by further consuming (oxidation) of 1,4-quinone with time.

4. Conclusion

We demonstrated that, for the first time, a new method for identification of two aromatic isomers of HBA was successfully accomplished by using their different perturbation effects on a Belousov-Zhabotinsky oscillator. The 3-HBA and 4-HBA was shown identified from each other by putting them into the BZ system because 3-HBA caused a decrease in the oscillation amplitude to give damping oscillations after inhibition time while 4-HBA only changed the oscillation amplitude to give damping oscillations with no inhibition time. Though both 3-HBA and 4-HBA were found to be converted into 1,4-quinone, it is confirmed that 3-HBA was oxidized by $BrO_2^{\cdot}$ radical (intermediate species) while 4-HBA was oxidized by BrO_3^-.

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Conflict of interest

Waqar Uddin, Gang Hu, Xuanxuan Sun, Hui Zhang, Yegui Wang and Lin Hu declare no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.arabjc.2017.09.010.

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