



## Identification of four isomers of Dihydroxynaphthalene by using a Briggs-Rauscher oscillating system



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### ABSTRACT

A novel method for identification of four isomers of dihydroxynaphthalene (DHN) was reported by their different perturbation effects on a Briggs-Rauscher (BR) oscillating system. In the system, macrocyclic nickel (II) complex  $\text{NiL}(\text{ClO}_4)_2$  is used as the catalyst, where the ligand L in the complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. By putting equal amount of the same concentrations of four isomers (1,4-dihydroxynaphthalene (1,4-DHN), 1,5-dihydroxynaphthalene (1,5-DHN), 2,3-dihydroxynaphthalene (2,3-DHN) and 2,7-dihydroxynaphthalene (2,7-DHN)) into BR system, the system could or couldn't be perturbed, being reflected in quite different oscillating behaviors after addition of isomers. These four isomers were identified in their concentration range of  $5.0 \times 10^{-6}$  to  $2.5 \times 10^{-4}$  mol/L. An explanation of such perturbation mechanism is that, 1,4-DHN couldn't be oxidized by BR matrix, but 1,5-DHN, 2,3-DHN and 2,7-DHN could be oxidized by  $\text{HOO}\cdot$  to yield 5-Hydroxy-1,4-naphthoquinone, phthalic acid and 6,7-dihydroxypereylene-1,12-quinone (DHPQ), respectively.

### 1. Introduction

Chemical oscillating system is a complex mixture which exhibits periodic changes in the concentration of one or more intermediate. Hundreds kind of chemical oscillating systems have been reported among which Briggs-Rauscher [1–5] (BR) reaction and Belousov-Zhabotinsky [6–15] (BZ) reaction were thoroughly investigated. Both of these oscillators were extensively studied using metal ions ( $\text{Ce}^{4+}/\text{Mn}^{2+}$ ) or macrocyclic complexes as catalysts [16–19]. Apart from being used to create waves [20] and patterns [21–23], these two kinds of oscillating systems were utilized in the quantitative technique i.e. exploring energy conversion [24, 25], determination of ions [26,27], organic reagent analysis [28–30], antioxidant analysis [31–33], but they were rarely utilized in qualitative analysis. Thus, enhancing the application of chemical oscillation in qualitative analytical aspect is highly appreciated.

Recently, our group has successfully explored the applications of chemical oscillating systems by utilizing them as qualitative technique for the isomers identification [34–38]. In 2015, a novel method for the identification of two aliphatic position isomers between  $\alpha$ -ketoglutaric acid and  $\beta$ -ketoglutaric acid by their different was presented [34]. Similarly, BR oscillator was used to distinguish cyclohexanedione isomers

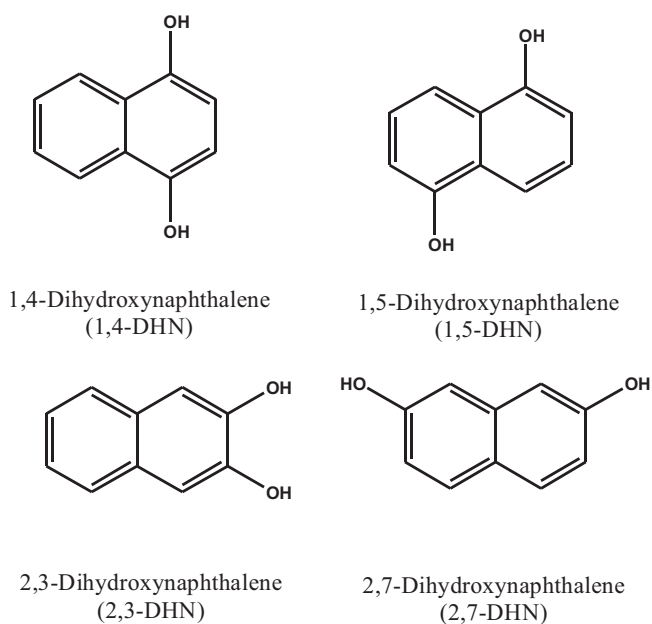
(cyclohexane-1,3-dione from 1,4-cyclohexanedione) [35] and disubstituted or polysubstituted benzoic isomers (2- and 3-hydroxy benzoic acid, ortho and para vanillin) [36, 37]. So far, BZ oscillator was only utilized for disubstituted benzoic isomers (3- and 4-hydroxy benzoic acid) [37]. Because some specific structural isomers have different perturbation effects on oscillating system and they undergo different oxidation process during perturbation, exploring utilization of oscillators to distinguish more different kinds of isomers is expected.

However, previous work has shown that the isomers identified by using oscillators were limited to aliphatic compounds, and substituted benzoic compounds or cyclohexanedione compounds in the structures. The work on identification of polynuclear aromatic isomers has not yet been reported. Moreover, during a process for identification of isomers, the number of analytes was limited in two. Therefore, these four isomers of dihydroxynaphthalene (DHN), a polynuclear aromatic compound, were good candidates for analytes, to which a BR oscillating system was applied as a matrix to identify.

In present work, BR oscillator was successfully applied for identification of four dihydroxynaphthalene isomers (DHN) i.e. 1,4-dihydroxynaphthalene (1,4-DHN), 1,5-dihydroxynaphthalene (1,5-DHN), 2,3-dihydroxynaphthalene (2,3-DHN) and 2,7-dihydroxynaphthalene (2,7-DHN) (Scheme 1). Separately injection of all the four isomers of

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Scheme 1. Structure of four isomers of dihydroxynaphthalene.

DHN into BR mixture could be seen on their different perturbations behavior's. At higher concentration ( $5.0 \times 10^{-5}$  to  $2.5 \times 10^{-4}$  mol/L), the addition of 1,4-DHN could hardly disturb the oscillation; the addition of 1,5-DHN produced a spike toward downside and then suddenly resumed oscillation with a short inhibition time; the addition of 2,3-DHN caused the quenching and regenerating oscillations after long inhibition time ( $t_{in}$ ) while the addition of 2,7-DHN permanently terminated the oscillation without regeneration of it. However, at lower concentration ( $5.0 \times 10^{-6}$  to  $2.5 \times 10^{-5}$  mol/L), the obtained perturbation effect of the three isomers (1,4-DHN, 1,5-DHN and 2,3-DHN) were almost the same as that at higher concentration but 2,7-DHN isomer shown a unique perturbation behavior. The addition of 2,7-DHN decrease potential and regenerate oscillations after long inhibition time at low concentrations. Thus, these four isomers could be distinguished both at their low and high concentrations.

In this article, a new methodology based on a Briggs-Rauscher oscillator was introduced to identify dihydroxynaphthalene isomers. One advantage for this technique is that the isomers could be directly identified by their different perturbation effects. Besides, it has other advantages such as being easy to setup, being quite precise, and having high range of detection.

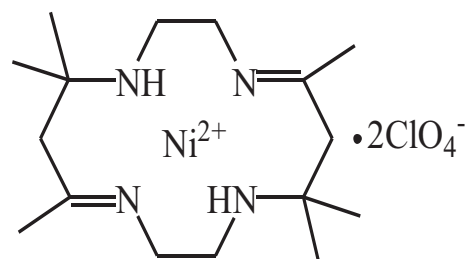
## 2. Experimental section

### 2.1. Apparatus

The oscillation reactions were performed in a 50 mL glass container under constant magnetic stirring (type 793, Jiangsu, China) at 0 °C and the stirring rate was kept at 500 rpm. A type of 213 platinum electrode (Shanghai, China) and reference electrode were placed into the beaker. These two electrodes were linked to an amplifier (Vernier Software Technology, USA) and a Go!Link sensor interface (Vernier Software Technology, USA) that was controlled by a personal computer (PC). Signals were recorded by a Logger Lite data-acquisition programme.

### 2.2. Reagents

Reagents,  $H_2SO_4$  (98%),  $KIO_3$ , Malonic acid, and  $H_2O_2$  (30%) 1,4-DHN (TCI), 1,5-DHN (Aladdin), 2,3-DHN (Aladdin), and 2,7-DHN (Aladdin) were purchased and were used without further purification.



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

The catalyst  $[NiL](ClO_4)_2$  (Scheme 2) was prepared according to the literature [39, 40] and was identified by its elemental analysis and IR.

### 2.3. Procedure

The solution of  $2.5 \times 10^{-2}$  mol/L  $H_2SO_4$  (98%) was prepared and was used as the solvent for preparation of 0.15 mol/L mol/L  $KIO_3$ , 2.00 mol/L malonic acid, 0.017 mol/L  $[NiL](ClO_4)_2$ , and 4.00 mol/L  $H_2O_2$  solutions. The solutions were mixed into beaker by the following order: 15.5 mL of 0.025 mol/L  $H_2SO_4$  solution, 5.5 mL of 0.15 mol/L  $KIO_3$  solution, 3.2 mL of 2 mol/L malonic acid solution, 1.8 mL of 0.017 mol/L  $[NiL](ClO_4)_2$  solution, 14 mL of 4 mol/L  $H_2O_2$  solution. When the final reactant ( $H_2O_2$ ) was put into the reactor, the potential over time was recorded using the computer with the help of the logger lite programme as shown in Fig. 1a. Different concentrations of 1,4-DHN, 1,5-DHN, 2,3-DHN or 2,7-DHN were used to perturb the oscillations.

## 3. Results and discussion

### 3.1. Distinguishing four polynuclear aromatic isomers of dihydroxynaphthalene

Identification experiments were carried out by adding equal amounts of the same concentration of 1,4-DHN, 1,5-DHN, 2,3-DHN or 2,7-DHN into active BR oscillators, respectively. The different perturbation behaviors of four isomers were noticed. In order to understand the methodology for distinguishing these four isomers, we classified our experiments into two categories: at higher and lower analyte concentrations. When the concentration of the these additives is higher ( $5.0 \times 10^{-5}$  to  $2.5 \times 10^{-4}$  mol/L), the addition of 1,4-DHN could hardly disturb the oscillation (in Fig. 1b,c,d); the addition of 1,5-DHN produced a spike toward downside and then suddenly resumed oscillation with a short inhibition time as shown in Fig. 1e,f,g; the addition of 2,3-DHN caused the quenching and regenerating oscillations after long inhibition time ( $t_{in}$ ) as shown in Fig. 1h,i,j; the addition of 2,7-DHN terminated and the oscillation couldn't be revived as shown in Fig. 1k,l,m. Thus, these four isomers could be identified in their concentration range from  $5.0 \times 10^{-5}$  to  $2.5 \times 10^{-4}$  mol/L.

It was also clearly noticed that change in inhibition time ( $t_{in}$ ) is independent of the concentration of 1,5-DHN (Fig. 1o), while change in inhibition time ( $t_{in}$ ) is dependent of the concentration of 2,3-DHN. As shown in Fig. 1p, a quite accurate linear relationship was obtained by plotting  $t_{in}$  vs 2,3-DHN concentrations, giving a correlation coefficient of 0.993.

At lower concentration of these additives ( $5.0 \times 10^{-6}$  to  $2.5 \times 10^{-5}$  mol/L), the addition of 1,4-DHN could hardly disturb the oscillation as shown in Fig. 2(a,b,c). The addition of 1,5-DHN produced a spike toward downside and then suddenly resumed oscillation with a shorter inhibition time (in Fig. 2d,e,f). The addition of 2,3-DHN caused the quenching and regenerating oscillations after longer inhibition time ( $t_{in}$ ) as shown in Fig. 2g,h,i. The addition of 2,7-DHN decrease potential and regenerating oscillations after longest inhibition time (in

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