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An Application of Chemical Oscillation: Distinguishing Two Isomers between Cyclohexane-1,3-dione and 1,4-cyclohexanedione

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ABSTRACT

In the analytical field, previous applications of chemical oscillation focused on quantitative analysis. We report in this paper a novel qualitative method electrochemically distinguishing two positional isomers by utilizing their perturbation effects on a catalyzed Briggs–Rauscher (BR) oscillation. The catalyst in the system is a macrocyclic nickel (II) complex $NiL(ClO_4)_2$, where the ligand L in the complex is 5,7,7,12,14, 14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The experimental results indicated that addition of cyclohexane-1,3-dione (1,3-CHD) or 1,4-cyclohexanedione (1,4-CHD) could affect the profiles of potentiometric oscillations, but their changes in the profiles are greatly different. When 1,3-CHD was injected into the oscillating system, there was an initial spiking of the oscillations, accompanying by quenching of oscillations before the regeneration of oscillations. While 1,4-CHD was injected into the dynamic mixture, the oscillatory system responded to the perturbation with only slight decrease followed by a sharp increase in the potential, before it resumed to its normal oscillation state. The perturbation of 1,3-CHD involves inhibition time, whereas the perturbation of 1,4-CHD does not. Hence these two positional isomers could be distinguished by using their different perturbation effects on a BR dynamic system in the range of 9.0×10^{-4} to 8.0×10^{-3} M. Our assumption is that, perturbation of 1,3-CHD on the oscillating system involves a radical oxidization process to produce carboxylic acid, whereas perturbation of 1,4-CHD assumes idiodation and elimination steps to form 1,4-benzoquinone. Such different perturbation mechanisms are responsible for the difference in potentiometric oscillation profiles change. This hypothesis was confirmed by products analysis by FTIR and UV spectra.

1. Introduction

Some chemical systems, being far from equilibrium, show nonlinear kinetic behaviors, such as periodic oscillations [1], chaos [2], wave propagation and pattern formation [3]. Among such nonlinear systems, periodic chemical oscillation not only exhibits the unique kinetic behaviors but it has also been used as unique tools in the analytical field. For example, some quantitive approaches based on oscillatory reaction have been developed for determination of analytes by their perturbation effects on oscillating system since 1978 when the pioneer work was established by Tichonova et al. Some succeeding developments in quantitive analysis include determination of irons (Ru^{3+}, Ru^{4+}, Hg^{2+}), gases (CO, NO, Cl_2) [4] analysis, and organic reagent analysis [5]. Strenuously, analysts utilized both the Belousov-Zhabotinsky (BZ) oscillating reaction and the Briggs-Rauscher (BR) oscillator, exploring the new domain where these two matrixes can be applied.

Like BZ oscillation which occurs in homogeneous solution, the BR system (an acidic solution of hydrogen peroxide, potassium iodate, malonic acid, and catalyst) exhibits typical periodic color changes from colorless to yellow to blue then to colorless with a starch indicator, making it an excellent demonstration in lab at its first emergence in history. Continuous studies on such reaction have revealed its complex mechanism, in which both the non-radical process and the radical process exist during oscillations [6]. Understanding on its unique dynamics has helped analysts utilize BR as a matrix to measure some antioxidants activities [7–11]. Antioxidant activities could be evaluated because antioxidants were found to function as free-radical scavengers to react with the radical intermediate in the BR system.

In our previous studies, we have shown that, some oscillating systems of BR type or BZ type can act as suitable matrixes in measurement of abundant of analytes, such as eugenol [12], Ag^+

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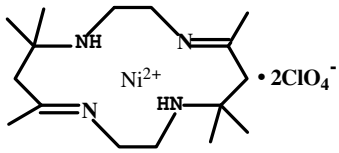


Scheme 1. The structure of $[NiL](ClO_4)_2$, where the ligand L in the complex is 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

[13], pyrogallol [14],catechol [15],calcium pantothenate [16] and alizarin red [17]. Catalysts involved in these BR or BZ systems are macrocyclic complexes, $[CuL](ClO_4)_2$ or $[NiL](ClO_4)_2$ (Scheme 1), where the ligand L in the complex is 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The ligand of the complexes occupies the extended π-system, which ensures a high rate for reactions involving electron transfer at individual steps of the oscillating process [18]. This character makes these chemical oscillatory matrixes vulnerable to the external perturbations. As previous applications of chemical oscillation focus on the quantitative analysis, we report in this paper a novel qualitative method for distinguishing two positional isomers of cyclohexane-1,3-dione (1,3-CHD) and 1,4-cyclohexanedione (1,4-CHD) (Scheme 2) by utilizing their perturbation effects on such a catalyzed BR oscillation.

Some isomers are found tough getting separated and distinguished because they usually possess the same molecular weight, the same physical properties or even the same functional groups. In an attempt to distinguish the isomers, some instrumental methods like MS [19], GC–MS [20] and HPLC-NMR [21] have been employed. The mass spectrometry (MS) is based on the distribution of ions by mass-to-charge ratio and hence it can measure the mass of a molecule. But the method has difficulty in distinguishing isomers because the ion fragments come from two isomers may have the same mass-to-charge ratio and similar distribution. By coupling the high separation efficiency of gas chromatograph (GC) with high sensitivity of mass spectrum (MS), GC-MS method has the advantage of high sensitivity in distinguishing the isomers. But this technique does not work for some compounds with high boiling point because some molecules are prone to be decomposed at high operating temperature. Being insensitive to light and oxygen, the HPLC-NMR method possesses high separation and identification efficiency with high accuracy in structural analysis. However, one of its disadvantages is its low sensitivity. Another disadvantage is that it only works for small molecule but is not suitable for identification of macromolecular isomers. A new electrochemical method for distinguishing isomers is expected.

In this paper, an accomplishment for identification of two position isomers (1,3-CHD and 1,4-CHD) was achieved by using a Briggs–Rauscher oscillating reaction. The concentrations of 1,3-CHD and 1,4-CHD that can be distinguished is over the range from 9.0×10^{-4} to 8.0×10^{-3} M. Compared with our previous application of using BR reaction for quantitative measurement of analytes [12–17], this electrochemical technonogy involving a BR reactor provieds a new rapid qualitative method in identification of two isomers (1,3-CHD and 1,4-CHD) with simpler equipment.

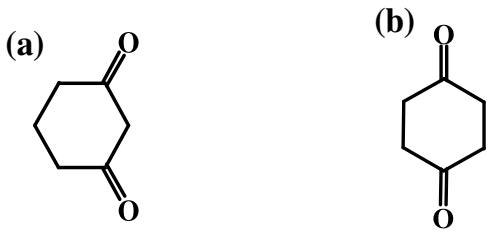
2. Experimental

2.1. Apparatus

All chemicals used were of analytical reagent grade without further purification except for the catalyst $[NiL](ClO_4)_2$, which was synthesized according to a published procedure [22,23] and identified by elemental analysis and IR spectrum. KIO_3, malonic acid, H_2O_2 and sulfuric acid were obtained commercially from Sinopharm Chemical Reagent Co.,Ltd. Cyclohexane-1,3-dione (1,3-CHD) and 1,4-cyclohexanedione (1,4-CHD) were purchased from Shanghai Chemical Industry Development Co.,Ltd. 1,4-benzoquinone is the product of Shanghai Aladdin biochemical Polytron Technologies Inc. The solutions of 0.14 M KIO_3, 2 M malonic acid, 4 M H_2O_2, 0.0173 M $[NiL](ClO_4)_2$ and 0.5 M sulfuric acid were prepared in double-distilled water. The solutions of 1.5 M cyclohexane-1,3-dione, 1.5 M 1,4-cyclohexanedione and 0.1 M of 1,4-benzoquinone were made just before the experiment. All reaction solutions must be homogeneous.

2.2. Apparatus

The experimental assembly consists of an oscillation reactor (40 mL) and a potential measuring system. The reactor was coupled with a thermostat (model DZCS-II C, Nanjing Dazhankejiao Institute of Instrument, China) by which the system was kept at the temperature of 5 °C in order to prolong the duration of the oscillations in the BR system, and a model 79-3 magnetic stirrer (Jiangsu, China) was used to homogenize the solutions. Digital potential measurements as a function of time were made by a personal computer (PC) which connected to an amplifier (Vernier Software Technology, USA), a Go!Link sensor interface (Vernier Software Technology, USA), and two electrodes. One of the electrodes is Pt electrode (Type 213, Shanghai Electricity and Light Instrumental Factory) which acts as working electrode, and the other is a saturated calomel electrode (SCE, Type 217, Shanghai Wei ye Instrumental Plant) via a salt bridge containing 0.5 M Na_2SO_4 which is used as reference electrode. The Logger Lite data-acquisition programme was used. IR measurements were taken by an infrared spectrometer (model Nexus-870 Nicolet 380, Shanghai HOMOO Urban Planning CO., Ltd) and Ultraviolet spectra measurements by a Ultraviolet spectrometer (model UV-1750, Shimadzu, Japan). A micro-pipette was also used in the experiments for injecting different amount of solution samples.



Scheme 2. (a) Structure of cyclohexane-1,3-dione (1,3-CHD); (b) Structure of 1,4-cyclohexanedione (1,4-CHD).