

Periodic Investigation of Properties of Oscillating Reactions: A 14-Membered Tetraazamacrocyclic Complex Catalyzed Zhabotinskii System

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The dependence of period of oscillation (T) on the initial concentrations of reactants for a Belousov-Zhabotinskii system is studied. This B-Z system is composed of sodium bromate, sulfuric acid, pyruvic acid and nickel(II) complex $[\text{NiL}](\text{ClO}_4)_2$, where L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-deca-4,11-diene. We place our emphasis on the properties of the period of homogeneous oscillations. It is found that T depends on the initial concentrations of reactants: $T(s) = 0.125[\text{BrO}_3^-]_0^{-1.22} [\text{H}_2\text{SO}_4]_0^{2.97} [\text{CH}_3\text{COCO}(\text{OH})]_0^{0.73} \text{mol dm}^{-3})^{-3.46}$. The period is not perfectly constant. The effects of concentrations of the components on the waveforms are also discussed.

Key Words: Oscillation period, B-Z system, 14-Membered Tetraazamacrocyclic complex.

INTRODUCTION

Oscillating chemical reactions are a complex system involving a large number of chemical species as reactants, products and intermediates that interact *via* unusual mechanism. The first experiment of Belousov-Zhabotinskii system catalyzed by tetraazamacrocyclic complexes¹ was reported in 1982. Since then, various approaches²⁻⁷ have been used to demonstrate the occurrence of oscillations involving various organic substrates. However, only scant work has been done on the mechanisms of these kinds of systems due to their complicated kinetic behaviour. In order to understand the kinetics involved, we placed our emphasis on the properties of the period of homogeneous oscillations, because previous researches⁸ showed that the period of oscillations is related to the chemical mechanism through the rate equation. A study of the period as a function of initial concentrations of reactants is so valuable that it provides a relatively simple test of the validity of a proposed mechanism.

Several B-Z systems catalyzed by tetraazamacrocyclic complexes by using pyruvic acid as an organic substrate have been reported⁹⁻¹¹. In this paper, the properties of the period of homogeneous oscillations in the case of a B-Z oscillation system: the sulfuric acid-sodium bromate-pyruvic acid- $[\text{NiL}](\text{ClO}_4)_2$, where ligand

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L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene have been discussed.

EXPERIMENTAL

The catalyst $[\text{NiL}](\text{ClO})_2$ was prepared according to literature¹². All the chemicals used in this investigation were of AR grade. Bidistilled water was used in all cases. A glass container, thermostated at $25 \pm 0.2^\circ\text{C}$, was filled, in this sequence: aqueous solutions of sodium bromate, sulfuric acid, pyruvic acid and $[\text{NiL}](\text{ClO})_2$ at intervals of 1 min. The volume of the reaction was 40 mL. The mixture was homogenized by magnetic stirring. Changes of the potential of the sample were followed by a platinum electrode and a bromide selective electrode. Potentials of these two electrodes *vs.* time were measured and recorded by using two ion meters (Model PXD-II, Jiangsu, China) connected to a Y-t recorder (model XWT-464 Shanghai, China).

RESULTS AND DISCUSSION

A. Period dependence on initial concentrations

The effect of the concentrations of sodium bromate, sulfuric acids and pyruvic acid have been investigated. The ranges of initial concentrations used are listed in Table I:

TABLE-I
RANGES OF INITIAL CONCENTRATIONS OF SODIUM BROMATE,
SULFURIC ACID, PYRUVIC ACID AND CATALYST

Conditions	NaBrO_3 (mol dm^{-3})	H_2SO_4 (mol dm^{-3})	Pyruvic acid (mol dm^{-3})	$[\text{NiL}](\text{ClO}_4)_2$ (mol dm^{-3})
(1)	0.044–0.228	1.00	0.5	1.3×10^{-3}
(2)	0.175	0.3–1.05	0.50	1.3×10^{-3}
(3)	0.175	1.00	0.175–1.36	1.3×10^{-3}
(4)	0.175	1.00	0.50	8.0×10^{-4} – 4.6×10^{-3}

The period as a function of the initial concentrations of sodium bromate, sulfuric acid and pyruvic acid is given in Figs. 1–3. Each dot represents the mean period T , averaged for five consecutive oscillations in a single sample.

Fig. 1 shows the dependence on bromate ion in Eqn. (1).

$$T(s) = x[\text{BrO}_3^-]_0^y (\text{mol dm}^{-3})^y \text{ s} \quad (1)$$

with $y = -1.22$ and $x = 0.32$ [condition (1) in Table-1]. The dashed line is constrained at $y = -1.22$ and corresponds to $x = 0.32$.

In Fig. 2, the dependence of the period on the initial concentration of the sulfuric acid is given by Eqn. (2),

$$T(s) = x[\text{H}_2\text{SO}_4]_0^y (\text{mol dm}^{-3})^y \text{ s} \quad (2)$$

with $y = -2.97$ and $x = 9$ [condition (2) in Table-1]. The dashed line is constrained at $y = -2.97$ and corresponds to $x = 9$.

The period dependence on the initial concentration of pyruvic acid is shown in Fig. 3. We obtain Eqn. (3).

$$T(s) = x[\text{CH}_3\text{COCOOH}]_0^y (\text{mol dm}^{-3})^y \text{ s} \quad (3)$$

with $y = 0.73$ and $x = 33.4$ [condition (3) in Table 1]. The dashed line is constrained at $y = 0.73$ and corresponds to $x = 33.4$.

The above results can be summarized in the general expression (4).

$$T(s) = 0.125[\text{BrO}_3^-]_0^{-1.22} [\text{H}_2\text{SO}_4]_0^{-2.97} [\text{CH}_3\text{COCOOH}]_0^{0.73} (\text{mol dm}^{-3})^{-3.46} \quad (4)$$
 with $[[\text{NiL}](\text{ClO}_4)_2] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$ at temperature = $25 \pm 0.2^\circ\text{C}$.

The period of these oscillations depends on the initial concentrations of reactants. This result is not surprising if we assume that these oscillations are of the limit cycle type. However, it is strange that the index of $[\text{CH}_3\text{COCOOH}]_0$ is not negative but positive. This phenomenon needs further investigation.

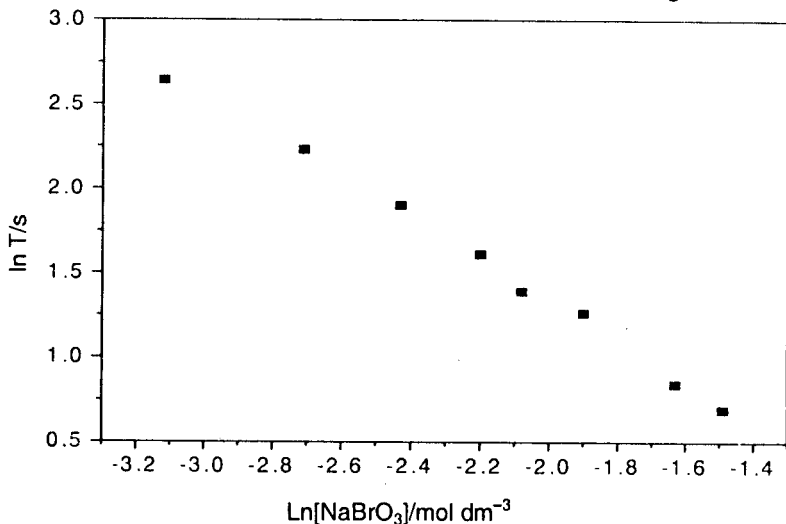


Fig. 1. Period as a function of the initial concentration of sodium bromate. Initial concentrations of other reactants: conditions (1) in Table-1. Solid line: slope = -1.22 , $R = -0.9978$

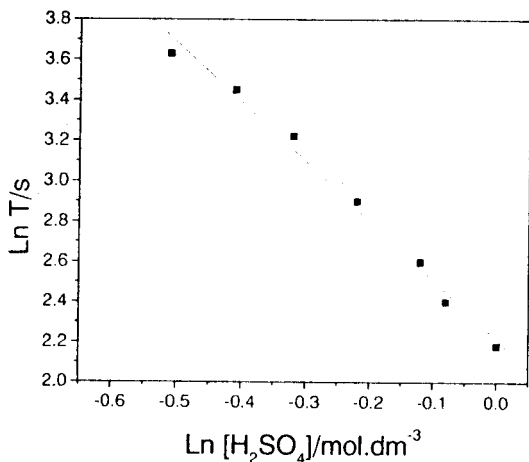


Fig. 2. Period as a function of the initial concentration of sulfuric acid. Initial concentrations of other reactants: conditions (2) in Table-1. Solid line: slope = -2.97 , $R = -0.9948$

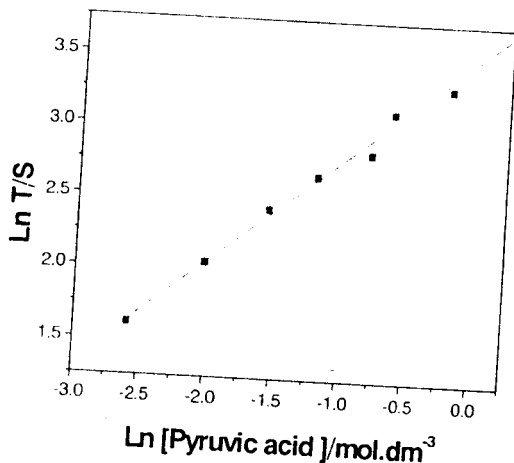


Fig. 3. Period as a function of the initial concentration of pyruvic acid. Initial concentrations of other reactants: conditions (3) in Table-1. Solid line: slope = 0.73, $R = 0.9954$

It is instructive to compare the periods of B-Z oscillations for various catalysts. Smoes⁸ found that for ferriin-catalyzed oscillation system:

$$T(s) = 0.43[\text{BrO}_3^-]_0^{-1.6} [\text{H}_2\text{SO}_4]_0^{-2.7} [\text{CH}_3\text{COCOOH}]_0^{-0.27} (\text{mol dm}^{-3})^{-4.57}$$

In view of these differences, we may expect some differences in the mechanisms for ferriin and tetraazamacrocyclic nickel complex-catalyzed oscillations.

B. Waveforms for different concentrations of the components.

Fig. 4 shows three waveforms for different concentrations of sodium bromate, with the condition (1) in Table-1. From top to bottom, $[\text{BrO}_3^-]_0 = 0.044, 0.175$ and 0.2 mol dm^{-3} . The corresponding average periods are 16, 8 and 4 s.

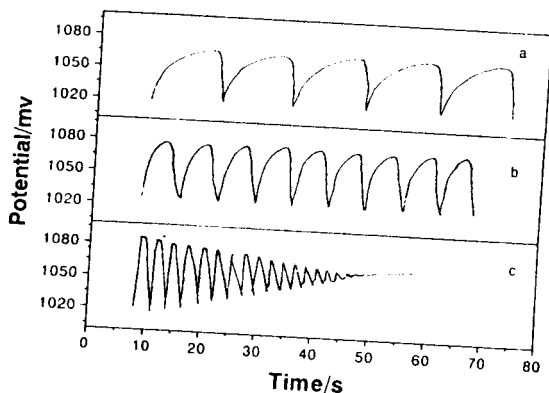


Fig. 4. Influence of the concentration of bromate ion on the oscillation. From top to bottom: $[\text{BrO}_3^-]_0 = 0.044, 0.175$ and 0.2 mol dm^{-3} , with $T = 16, 8$ and 4 s . Other initial concentrations: conditions (2) in Table-1.

Fig. 5 represents the marked change in waveform due to a change in initial concentration of sulfuric acid, with condition (2) in Table-1. We have, from top to bottom, $[\text{H}_2\text{SO}_4]_0 = 0.6, 0.8$ and 1 mol dm^{-3} .

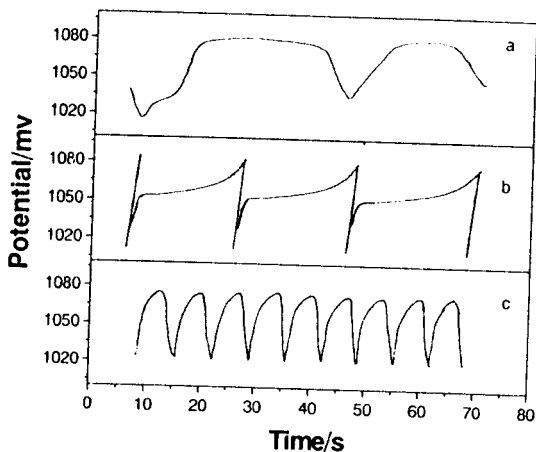


Fig. 5. Influence of the concentration of sulfuric acid on the oscillation. From top to bottom: $[\text{H}_2\text{SO}_4]_0 = 0.6, 0.8$ and 1 mol dm^{-3} , with $T = 40, 25$ and 8 s . Other initial concentrations: conditions (2) in Table-1.

The effect of initial concentrations of pyruvic acid was indicated in Fig. 6. From top to bottom, $[\text{CH}_3\text{COCO}(\text{OH})]_0 = 0.1, 0.5$ and 0.6 mol dm^{-3} .

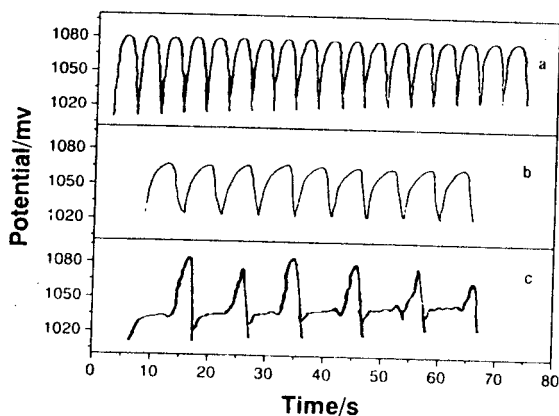


Fig. 6. Influence of the concentration of pyruvic acid on the oscillation. From top to bottom: $[\text{CH}_3\text{COCO}(\text{OH})]_0 = 0.1, 0.5$ and 0.6 mol dm^{-3} , with $T = 4, 8$ and 13 s . Other initial concentrations: conditions (3) in Table-1.

The waveform of the oscillations depends on the initial concentrations on reactants. This phenomenon could also be explained by the fact that these oscillations are of the limit cycle type. Complex mechanisms may be involved in the oscillations due to the existence of the slow decomposition of the catalyst.

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