

Period of Homogeneous Oscillations in the B-Z System Involving a Tetraazamacrocyclic Complex

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This work is primarily an experimental investigation of a tetraazamacrocyclic nickel complex catalyzed system. The complex contains unsaturated macrocyclic ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-1,10,12-triene. We measure the reactions by monitoring the changes of the potentials of platinum and bromide selective electrode. The emphasis is placed on the properties of the period of homogeneous oscillations. It is found that the mean period depends on the initial concentrations of reactants: $T(s) = 0.43[\text{BrO}_3^-]_0^{0.75}$, $[\text{H}_2\text{SO}_4]_0^{-4.45}$, $[\text{CH}_3\text{COCOOH}]_0^{-2.42}$ (mol dm^{-3})^{6,12}. The period is not perfectly constant. The effects of concentrations of the components on the waveforms are also discussed.

Key Words: Homogeneous oscillations, B-Z system, Tetraazamacrocyclic complex.

INTRODUCTION

Oscillations catalyzed by tetraazamacrocyclic complexes were first reported by Yatsimirskii¹ in 1982. Since then, a number of investigations^{2–7} had been made to demonstrate the occurrence of oscillations involving various organic substrates. In contrast, only scant work has been done on the kinetics of the tetraazamacrocyclic complexes catalyzed oscillations. 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 should provide a relatively simple test of the validity of a proposed mechanism.

Earlier reports^{9,10} from us studied several Belousov-Zhabotinskii (B-Z) systems catalyzed by tetraazamacrocyclic complexes using pyruvic acid as an organic substrate. In continuation 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 L is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-1,10,12-triene have been discussed.

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EXPERIMENTAL

All the chemicals used in this investigation were of AR grade. The catalyst $[\text{NiL}](\text{ClO})_2$ was prepared according to literature¹¹. Double distilled water was used in all cases. Reacting mixture was prepared by addition of sulfuric acid, pyruvic acid and $[\text{NiL}](\text{ClO})_2$ to sodium bromate at intervals of 1 min.

Immediately after the last addition, the sample was transferred to a thermostated glass container in which the temperature was at $30 \pm 0.001^\circ\text{C}$. At least 2 min before the beginning of the measurements, the stirring was started. Changes of the potentials 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

Period dependence on initial concentrations

The effect of the concentrations of bromate ion, sulfuric acid and pyruvic acid have been investigated. The ranges of initial concentrations used are given in Table-1.

TABLE-1
RANGES OF INITIAL CONCENTRATIONS OF BROMATE ION, 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	0.13–0.38	0.80	0.50	3.0×10^{-3}
2	0.21	0.5–0.9	0.50	3.0×10^{-3}
3	0.21	0.80	0.35–0.6	3.0×10^{-3}
4	0.21	0.80	0.50	2.4–6.2

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

In Fig. 1, the dependence of the period on the initial concentration of bromate ion is given by Eq. (1),

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

with $y = 0.75$ and $x = 6.1$ [condition (1) in Table-1]. The dashed line is constrained at $y = 0.75$ and corresponds to $x = 6.12$.

Fig. 2 shows the dependence on sulfuric acid in Eq. (2).

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

with $y = -4.45$ and $x = 7.3$ [condition (2) in Table-1]. The dashed line is constrained at $y = -4.45$ and corresponds to $x = 7.3$.

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

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

with $y = -2.42$ and $x = 3.3$ [condition (3) in Table-I]. The dash line is constrained at $y = -2.42$ and corresponds to $x = 3.3$.

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

$$T(s) = 0.43[\text{BrO}_3^-]_0^{0.75} [\text{H}_2\text{SO}_4]_0^{-4.45} [\text{CH}_3\text{COCO}(\text{OH})]_0^{-2.42} (\text{mol dm}^{-3})^{6.12} \quad (4)$$

with $[\text{Ni}(\text{ClO}_4)_2] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ and temperature = $30 \pm 0.001^\circ\text{C}$.

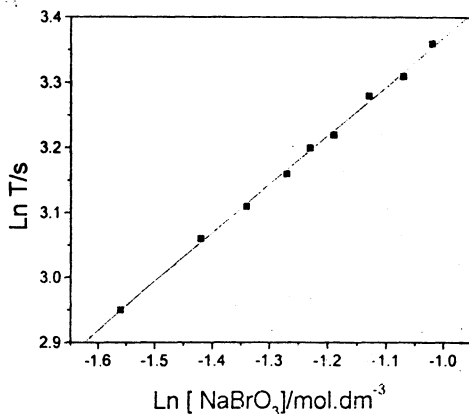


Fig. 1. Period as a function of the initial concentration of sodium bromate. Initial concentrations of other reactants: conditions (1) in Table 1. Solid line: slope = 0.75, $R = 0.9988$

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 $[\text{BrO}_3^-]_0$ is not negative but positive. This phenomenon needs further investigation.

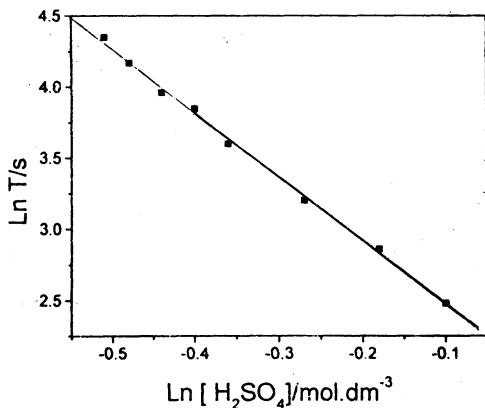


Fig. 2. Period as a function of the initial concentration of sulfuric acid. Initial concentrations of other reactants: conditions (2) in Table 1. Solid line: slope = -4.45, $R = -0.9987$

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

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

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

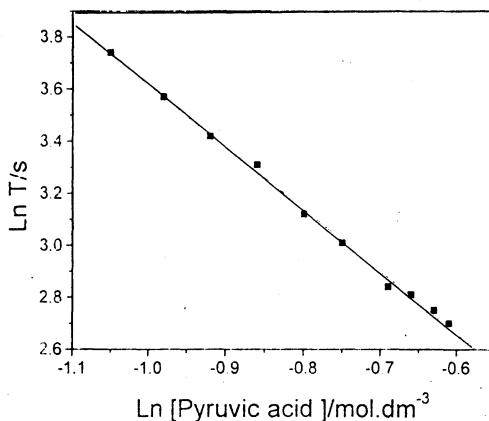


Fig. 3. Period as a function of the initial concentration of pyruvic acid. Initial concentrations of other reactants: conditions (3) in Table 1. Solid line: slope = -2.42 , $R = -0.9987$

Waveforms for different concentrations of the components

Fig. 4 represents three waveforms for different concentration of bromate ion, with the condition (2) in Table-1. From top to bottom, $[\text{BrO}_3^-]_0 = 0.15, 0.2$ and 0.38 mol dm^{-3} . The corresponding average periods are 15, 18 and 36 s.

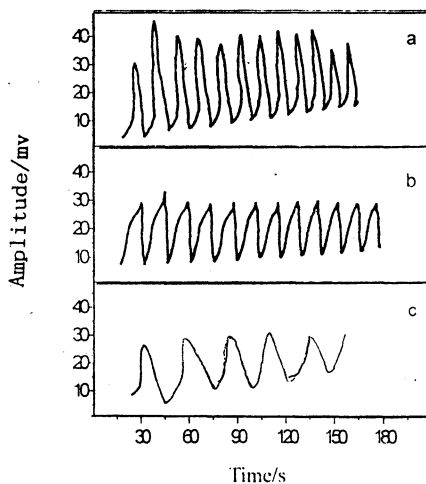


Fig. 4. Influence of the concentration of bromate ion on the oscillation. From top to bottom: $[\text{BrO}_3^-]_0 =$ (a) 0.15, (b) 0.2 and (c) 0.38 mol dm^{-3} , with $T = 15, 18$ and 36 s . Other initial concentrations: conditions (2) in Table-1.

Figure 5 shows the marked change in waveform due to a change in initial concentration of sulfuric acid, with condition (2) in Table. We have, from top to bottom, $[\text{H}_2\text{SO}_4]_0 = 0.6, 0.64$ and 0.72 mol dm^{-3} .

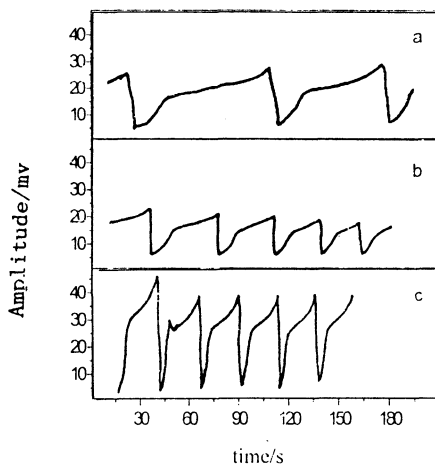


Fig. 5. Influence of the concentration of sulfuric acid on the oscillation. From top to bottom: $[\text{H}_2\text{SO}_4]_0 = 0.6, (b) 0.64$ and $(c) 0.72 \text{ mol dm}^{-3}$, with $T = 72, 51, 33\text{s}$. Other initial concentrations: conditions (2) in Table I

The effect of initial concentrations of pyruvic acid was indicated in Fig. 6. From top to bottom, $[\text{CH}_3\text{COCOOH}]_0 = 0.38, 0.5$ and 0.56 mol dm^{-3} . With increasing period, one observes slight decrease in the relaxational character of the oscillations.

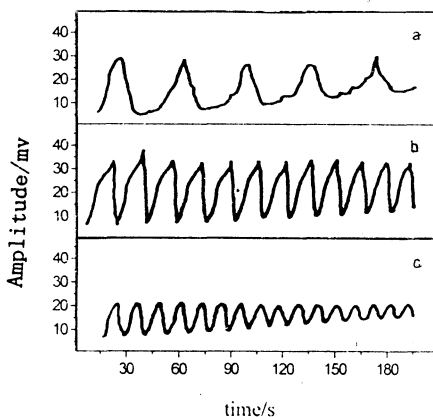


Fig. 6. Influence of the concentration of pyruvic acid on the oscillation. From top to bottom: $[\text{CH}_3\text{CO} \text{O} \text{H}]_0 = 0.38, (b) 0.5$ and $(c) 0.56 \text{ mol dm}^{-3}$, with $T = 33, 18, 12\text{s}$. Other initial concentrations: conditions (3) in Table-1

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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