A New Chemical Oscillator with a Macrocyclic Copper(II) Complex as Catalyst and Lactic Acid as the Substrate

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The oscillatory features of a new type Belousov–Zhabotinskii oscillator with a macrocyclic copper(II) complex [CuL]-$(ClO_4)_2$ as catalyst and lactic acid as the substrate have been reported. This complex contains the ligand 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. A tentative mechanism based on FKN has been suggested.

Oscillatory chemical reactions have been of interest for decades.[1] The most extensively studied reaction is the classical Belousov–Zhabotinskii (BZ) oscillator, which involves the oxidation of an organic substrate by acid bromate in the presence of a metal ion catalyst[2–5] (usually Ce^{4+}, Mn^{2+}, $Fe(phen)_3{}^{2+}$, or $Ru(bipy)_3{}^{2+}$). Recently, oscillators involving tetraazamacrocyclic complexes as catalysts have been discussed in literatures.[6–12] In these oscillators, the organic substrates were malonic acid, malic acid, or pyruvic acid. In order to search for the possibilities that other organic substrate species may participate in these kinds of oscillators, we investigated the behavior of lactic acid (lac).

We reported in this letter the discovery of a new oscillator, $NaBrO_3$–H_2SO_4–Lac–$[CuL](ClO_4)_2$, where L is 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The structure of $[CuL]^{2+}$ is shown in Figure 1. Because of the fact that lactic acid is an important intermediate in the energy metabolism of animal and that tetraazamacrocyclic complexes have similar structure to some enzymes, present oscillator is of biochemical importance in that it could be regarded as a good man-made mimic for some observed biochemical oscillators.

The catalyst $[CuL](ClO_4)_2$ was prepared according to literature[13] and was identified by its IR spectra and elemental analyses. All materials were of analytical grade except for lactic acid. Lactic acid is biochemical. All materials were used without further purification except for $NaBrO_3$. $NaBrO_3$ was recrystallized in hot water three times to remove Br^- and other impurities. All oscillation experiments were performed in a closed glass container with a magnetic stirrer at $10 \pm 0.5\,^\circ C$ regulated by a thermostat. The volume of the reaction was 40 mL. The redox potential and instantaneous bromide concentration were monitored by a platinum electrode and bromide-selective electrode, respectively. The reference electrode was a saturated calomel electrode connected via a salt bridge containing 10% KNO_3. Potentials of these two electrode as a function of time were measured and recorded by using two digital voltmeters (DVM) connected to a *x–t* recorder (Model XWT-264); a *x–y* recorder (Model LZ-3) was introduced to investigate the oscillation trajectories of the potentials of platinum electrode vs these of bromide-selective electrode.

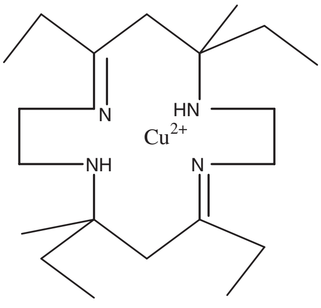

Figure 1. The structure of $[CuL]^{2+}$.

When catalytic quantities of $[CuL](ClO_4)_2$ was added to the homogeneous solution containing $NaBrO_3$, H_2SO_4, and lactic acid (Lac), strongly damped concentration oscillations of platinum electrode and bromide selective electrode were observed (Figures 2a and 2b). During the oscillations, the solution color changed periodically between red and orange, showing the oscillations between $[CuL]^{2+}$ and $[CuL]^{3+}$. Present oscillator could give oscillations only within the concentration range of $[NaBrO_3] = 0.0210$–0.0875 M, $[H_2SO_4] = 0.45$–1.0 M, $[Lac] = 0.2$–0.994 M, $[[CuL]^{2+}] \geqslant 0.00167$ M. When several aliquots of solution of $[CuL](ClO_4)_2$ were successively added to the reaction in which the oscillation had ceased, oscillations took place again and the period remained the same. Addition of solution of lactic acid could also revive the oscillation but addition of solution of $NaBrO_3$ failed to do so. These phenomena show that the damping of the oscillations is not due to the depletion of the $NaBrO_3$ but owing to the depletion of the catalyst and lactic acid.

To $NaBrO_3$–H_2SO_4–Lac–$[CuL](ClO_4)_2$ oscillator, variations in initial concentration of reactants resulted in obvious variation of period of oscillation (tp). The period of oscillation decrease when the concentration of H_2SO_4 increase while the concentration of $NaBrO_3$, Lac, and $[CuL](ClO_4)_2$ fixed.

Smoes[14] reported a ferroin-catalyzed oscillator in which period of oscillation depends on initial concentration. We observed that the dependence of the period of oscillation on the initial concentrations of H_2SO_4 and lactic acid is similar to that of ferroin-catalyzed one. However, different from ferroin-catalyzed oscillator, with the increase in concentrations of $NaBrO_3$, there is a decrease in frequency.

If the concentration of Ag^+ present in the oscillating system exceeds 6.25×10^{-5} M, the potential of bromide selective electrode decreased temporarily due to the formation of AgBr. Apparently Br^- is a control intermediate.[15] The variation of concentration of Br^- can "turn on" and "turn off" certain chemical processes in the oscillatory reactions.

A *x–y* recorder showed that the oscillation trajectories of potentials of platinum electrode vs those of bromide selective electrode are spirals instead of limit cycles.[16]

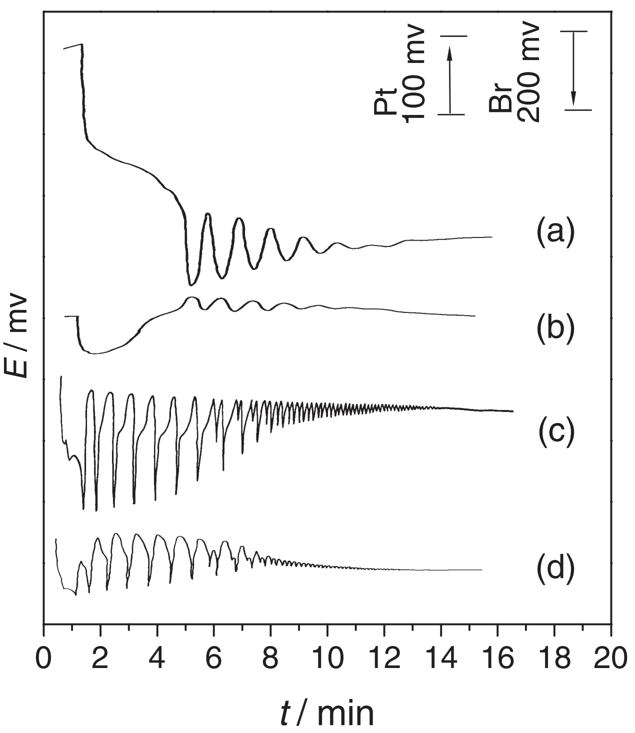

Figure 2. Typical oscillating trace of platinum electrode (a) and bromide selective electrode (b) vs time for the system at 10 °C : $[NaBrO_3] = 0.0315\,M$, $[H_2SO_4] = 0.5\,M$, $[Lac] = 0.5\,M$, $[[CuL]^{2+}] = 0.00334\,M$. Typical oscillating trace of platinum electrode (c) and bromide selective electrode (d) vs time for the system at 26 °C : $[NaBrO_3] = 0.07\,M$, $[H_2SO_4] = 1.0\,M$, [pyruvic acid] $= 0.5\,M$, $[[CuL]^{2+}] = 0.0072\,M$.

Since present organic contains no active methylene for bromination, one may wonder how Br_2 was consumed. Seeing that lactic acid could be oxidized to pyruvic acid and that bromination on pyruvic acid may occur, following reactions may take place during oscillations:

$$\begin{aligned} &HOBr + 2[CuL]^{3+} + 2CH_3CH(OH)COOH \\ &\quad \rightarrow Br^- + 2[CuL]^{2+} + 2CH_3COCOOH + H_2O + 3H^+ \end{aligned} \quad (1)$$

$$Br_2 + CH_3COCOOH \rightarrow Br^- + H^+ + BrCH_2COCOOH \quad (2)$$

If pyruvic acid is used instead of lactic acid in our case, the system oscillates (Figures 2c and 2d). Such experimental result supports the assumption that pyruvic acid was generated as an intermediate during oscillations.

The oxidation product analysis for such system by traditional chemical analysis methods was, however, very arduous because of the difficulty in separating out the products. Instrumentally analytical method like HPLC (high performance liquid chromatography) is more efficient.[17] By using such a method, two products were identified, and the results support the assumption of the generation of pyruvic acid as the reaction intermediate.

According to experimental results and literature,[18] a tentative mechanism based on the widely accepted FKN was proposed as follows:

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \quad (3)$$

$$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr \quad (4)$$

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \quad (5)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2\bullet + H_2O \quad (6)$$

$$Br_2 + CH_3COCOOH \rightarrow Br^- + H^+ + BrCH_2COCOOH \quad (7)$$

$$BrO_2\bullet + [CuL]^{2+} + H^+ \rightarrow [CuL]^{3+} + HBrO_2 \quad (8)$$

$$\begin{aligned} &BrCH_2COCOOH + [CuL]^{3+} + H_2O \\ &\quad \rightarrow [CuL]^{2+} + Br^- + HCOOH + CH_3COOH + H^+ \end{aligned} \quad (9)$$

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