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Belousov-Zhabotinskii Oscillating Reaction without Strong Acid Such as Sulfuric Acid

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We have found the existence of oscillatory phenomena in the metal ion catalyzed reaction between malonic acid and potassium bromate without strong acid such as sulfuric acid. In the Ce^{3+}, or Mn^{2+} catalyst system, the pH oscillations have been observed.

The Belousov-Zhabotinskii(BZ) reaction is usually performed under 1 - 2 mol dm^{-3} sulfuric acid medium.[1] In the case of malonic acid substrate system, it would be considered that the oscillating reaction takes place under the acidity of the substrate in the absence of sulfuric acid since pK_a value of malonic acid is 2.8. In the present communication, we are reporting the existence of oscillatory phenomena in the Ce^{3+} or Mn^{2+} catalyzed reaction between malonic acid and potassium bromate without strong acid such as sulfuric acid.

All materials used were of the highest grade commercially available, and were used without farther purification. The potential of a platinum redox electrode, a bromide selective electrode, and a glass electrode against a mercurous sulfate reference electrode were continuously recorded. Experiments were performed in a thermally regulated glass container with magnetic stirrer under the aerobic conditions at 30 °C. Numerical calculations were carried out with use of an Urabe approximation[2] on an NEC PC-9801 microcomputer.

Typical oscillatory responses of platinum, bromide selective, and glass electrodes in the Ce^{3+} catalyst system are shown in Fig. 1. The system under investigation is characterized by the existence of pH oscillation. The pH oscillation has not been reported because the ordinary conditions for acidity exceed the response limit of glass electrode.

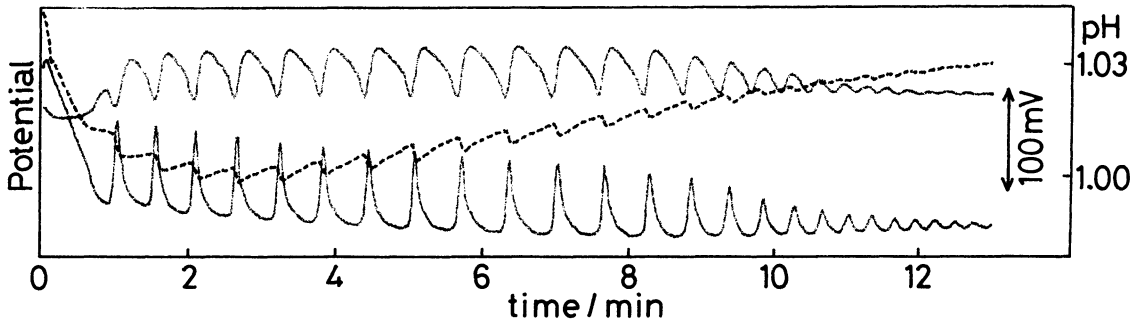

Fig. 1. The shape of the oscillatory traces in the system of following initial composition: 0.0048 mol dm^{-3} $Ce(NO_3)_3$, 0.45 mol dm^{-3} $KBrO_3$, and 2.0 mol dm^{-3} $CH_2(COOH)_2$.

Oscillations were observed for solutions containing a range of initial concentrations for components. We adopted the concentrations used in Fig. 1 as standard conditions. The range of concentrations is shown in Table 1 where the concentration of one of the three components was varied while the concentrations of other two components were fixed at the standard conditions. The effects of higher catalyst concentration have not yet been investigated. The upper limit of the range of potassium bromate concentrations over which oscillations are obtained is restricted by the solubility of potassium bromate. Both ranges of concentrations of malonic acid and of potassium bromate are in more higher regions than the ranges usually used.

Table 1. Conditions for the BZ reaction without H_2SO_4

Reactant	Concentration range / mol dm^{-3}
$KBrO_3$	0.33 - 0.45
$CH_2(COOH)_2$	1.4 - 4.1
$Ce(NO_3)_3$	0.0024 - 0.0044

Figure 2 shows the typical oscillatory traces of potentials in the Mn^{2+} catalyst system. The oscillatory change in pH value is larger than in the Ce^{3+} catalyst system.

Theoretical treatments of the BZ reaction are usually done with reduced versions of the FKN mechanism, and the Oregonator model.[3] Usually the species, H^+, is not included in this model considering its constant concentration. The simplest Oregonator involving hydrogen ion is given by

$$A + Y + 2H \longrightarrow X + P \qquad k_1$$

$$X + Y + H \longrightarrow 2P \qquad k_2$$

$$A + X + 3H \longrightarrow 2X + 2Z \qquad k_3$$

$$2X \longrightarrow A + P + H \qquad k_4$$

$$Z \longrightarrow fY + gH \qquad k_5$$

variable identifications are A = BrO_3^-, X = $HBrO_2$, Y = Br^-, Z = Ce^{4+}, P = HOBr, and H = H^+. f and g are stoichiometric factors. For comparison with the experiment, we adopted the situation [BrO_3^-] = 0.45 mol dm^{-3} and initial [H^+] = 0.1 mol dm^{-3}. The simplest stoichiometric combination of the equations such that there is no net production or destruction of H^+ leads to g = 2.375, and the value is used for calculation. The level of [H^+] increases with passage of time if the value of g is larger than 2.375 and decreases if it is smaller; however, oscillatory behavior did not depend upon the value of g.

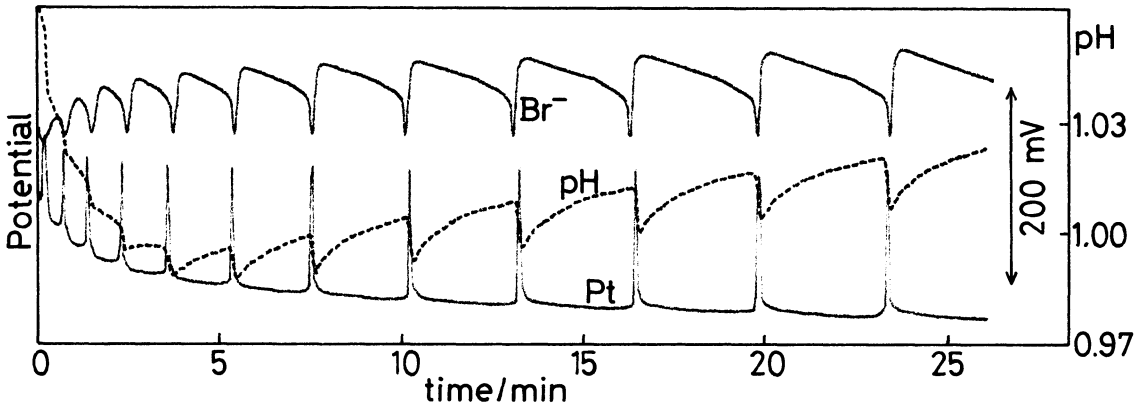

Fig. 2. The shape of the oscillatory traces in the system of following initial composition: 0.0037 mol dm^{-3} $MnSO_4$, 0.45 mol dm^{-3} $KBrO_3$, and 2.0 mol dm^{-3} $CH_2(COOH)_2$.

Figure 3 shows oscillations in pH obtained by numerical integration in which the values of the rate constants and f employed by Tyson[4] was used. Agreement between experimental and simulated waveforms is not good. Moreover, a disparity lies in the value of ΔpH, the difference between maximum and minimum values of pH. The value of ΔpH obtained by the simulation is about one hundredth of the experimental value. From the results described above, it would be considered that the oscillation in pH is owing to another reason.

It has been known that Ce^{4+} and Mn^{3+} are hydrolyzed in low acidic medium as follows,

$$Ce^{4+} + H_2O \rightleftharpoons CeOH^{3+} + H^+$$

$$Mn^{3+} + H_2O \rightleftharpoons MnOH^{2+} + H^+$$

The value of hydrolysis constant for Mn^{3+} ion has been reported as 0.39 at 25 °C.[5] It can be considered that about nine tenth of Mn^{3+} ions are hydrolyzed

under the experimental conditions shown in Fig. 2. The hydrolysis increases the concentration of hydrogen ions as a result, and we obtain ΔpH = 0.014, which is comparable to the experimental value.

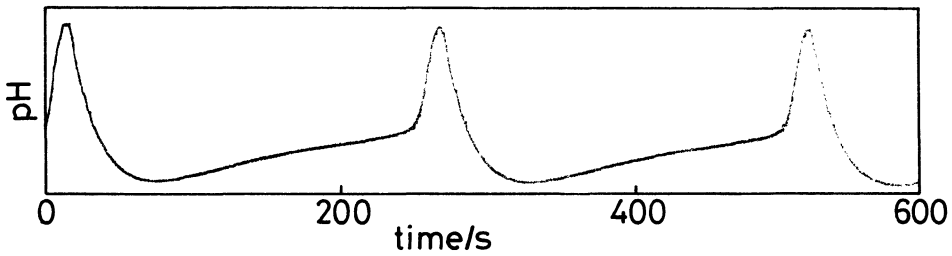

Fig. 3. Numerically calculated solution of Oregonator.

In the case of Ce^{4+} catalyst system, it is difficult to evaluate the value of ΔpH because several values for hydrolysis constant which differ almost one order of magnitude have been reported.[6-8] Assuming that the increase in pH is produced mainly by the hydrolysis, the calculated value for hydrolysis constant of Ce^{4+} lies in the range of reported values.

Further, in the system in which ferroin or tris(2,2´-bypyridine) ruthenium(II) was used as catalyst, there was a little oscillatory change in pH. These results support the above discussion, because these catalysts are scarcely hydrolyzed under the experimental conditions.

References

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