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Belousov-Zhabotinskii Reaction with 2,3-Diones

Masao Tsukada* and Naoki Inamoto
Department of Chemistry, Juntendo University, Inba-gun, Chiba 270-16
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Synopsis. 2,3-Butanedione and 2,3-pentanedione have been found to generate chemical oscillations in 2,3-dione/BrO_3^-/Ce^{4+}/H_2SO_4 system. The concentration range within which the oscillatory behavior can be observed for each reactant is reported.

The Belousov-Zhabotinskii(BZ) reaction is probably the best studied chemical oscillation reaction.[1] In BZ reaction, malonic acid is oxidized by bromate ions in sulfuric acid medium in the presence of cerium(IV) ions. After an induction period, the concentration of bromide ions and the redox ratio (=log [Ce^{4+}]/[Ce^{3+}]) oscillate with a frequency and an amplitude which depend on the initial composition of system and temperature. It has been known that cerium(IV) ion, malonic acid, and sulfuric acid in this oscillating system may be replaced by the other appropriate compounds. Most of the organic species capable of replacing malonic acid contain an "active" methylene group. The use of acetone alone as the substrate does not yield any oscillations, but generates oscillations in mixed-substrate BZ systems.[2] We have examined the effects of replacing malonic acid with 2,3-butanedione or 2,3-pentanedione which is of interest in a similarity to acetone.

Experimental

All reagents used were the highest grade commercially available except for 2,3-butanedione which was purified by vacuum distillation. The redox potential was monitored with a platinum electrode. A double junction Hg/Hg_2SO_4/K_2SO_4 electrode was used as a reference. In most experiments, the reaction was performed in a glass container with magnetic stirrer under aerobic conditions.

Results and Discussion

Typical responses of platinum and bromide selective electrodes in the dione/BrO_3^-/Ce^{4+}/H_2SO_4 system are shown in Figs. 1 and 2 along with the oscillations of the malonic acid system for a comparison. In the case of diketone system its oscillatory state consists of a dozen oscillations, while in the malonic acid substrate its oscillation continues for about three hours. On comparing the two systems, each level of bromide ion concentrations overlaps with the other, although the oscillation range of redox potential is considerably different. It has been shown that bromide ion concentration plays a vital role in the BZ system.[1] Thus it could be suggested that dione substrate plays a similar role to malonic acid. There was no gas evolution

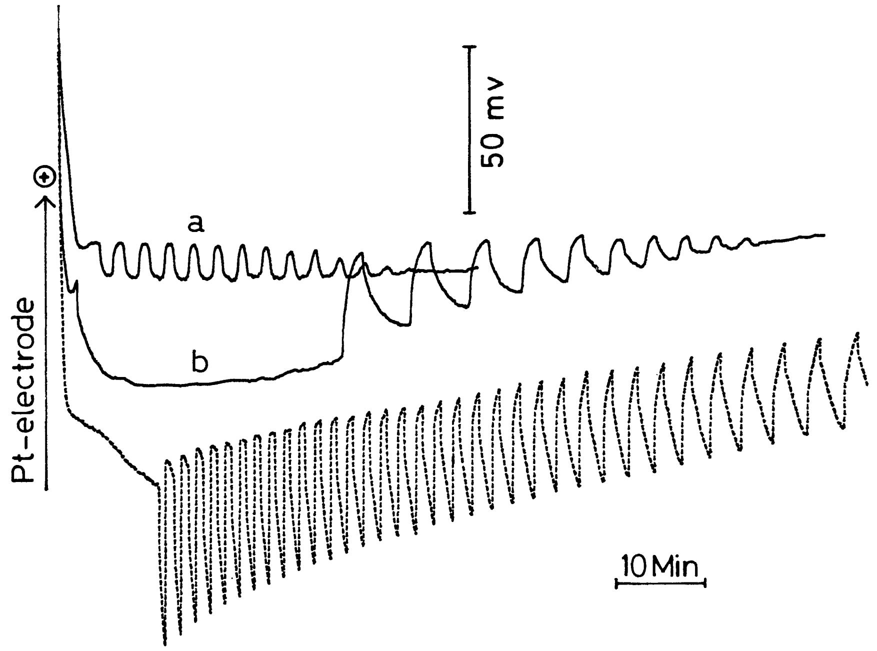

Fig. 1. Uncalibrated potential of platinum electrode in the system of following initial composition: 0.0014 M $Ce(SO_4)_2$, 0.14 M $KBrO_3$, 0.74 M H_2SO_4, and 0.032 M organic substrate. Full curve: (a) 2,3-butanedione, (b) 2,3-pentanedione; dotted curve: malonic acid. At 30 °C. The arrow indicates the direction in which the potential becomes more positive. M= mol dm^{-3}.

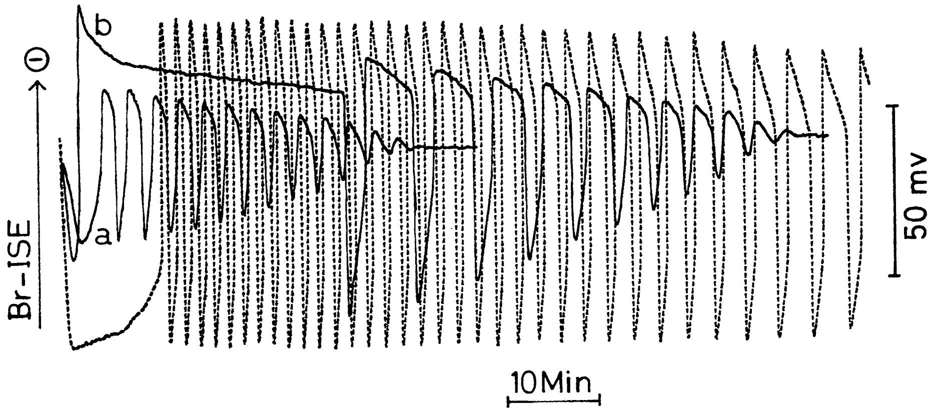

Fig. 2. Uncalibrated potetial of bromide-selective electrode (Br–ISE) in the same system as that in Fig. 1. The arrow indicates the direction in which the potential becomes more negative.

Table 1. Conditions for Oscillating Reaction[a)]

	2,3-Butanedione	2,3-Pentanedione
[Dione]/10^{-2} M	2.3 —3.8	1.3 —5.1
[H_2SO_4]/M	0.69—0.81	0.64—1.1
[$KBrO_3$]/M	0.13—0.15	0.12—0.19
[$Ce(SO_4)_2$]/10^{-3} M	0.84—2.0	0.28—3.4
Temp/°C	29—33	28—40

a) M=mol dm^{-3}.

during the oscillating reaction. In view of this fact, 2,3-dione behaves in a similar fashion to 2,4-pentanedione.[3)]

Chemical oscillations were observed in a definite range of initial concentrations for the four components, $KBrO_3$, $Ce(SO_4)_2$, H_2SO_4, and dione. We adopted the concentrations used for the reaction shown in Fig. 1 as a standard condition. The range of concentrations is shown in Table 1 where the concentration of one of the four components was varied under the fixed concentrations of the other three components at the standard condition. It is remarkable that the concentration range in which oscillations appear is very narrow for both $KBrO_3$ and H_2SO_4 in the case of 2,3-butanedione.

The induction period (t_{ind}) and the period of oscillation(t_{osc}) varied with temperature. The plots of log $(1/t_{\mathrm{ind}})$ and of log $(1/t_{\mathrm{osc}})$ were linear with inverse of absolute temperature in the range shown in Table 1. The values of two activation energies, E_{ind} and E_{osc} which correspond to t_{ind} and t_{osc} respectively, were found to be 68±6 and 69±8 kJ mol^{-1} for 2,3-butanedione, 67±9 and 71±7 kJ mol^{-1} for 2,3-pentanedione. E_{osc} can be attributed to the reduction reaction of BrO_3^- with brominated substrate which requires an activation energy between 60 and 70 kJ mol^{-1}.[4)] The value of E_{osc} obtained by us lies in this range.

The induction period depends on the concentrations of dione and of Ce^{4+}, but it is not affected by the concentrations of BrO_3^- and of H^+. This means that the reaction of dione with Ce^{4+} is closely related to the induction period. It has been found that acetone does not yield oscillations when acetone is used alone in the cerium(IV) ion catalyzed BZ system, because acetone can be brominated but is not oxidized.[5)] In the case of dione, it could form a five-membered chelate ring by the coordination of Ce^{4+} with its two carbonyl groups and the complex thus formed would initiate oxidation of dione.

It has been known that mechanical stirring can, in some cases, sensibly affect the oscillation.[6)] For example, in the case of malonic acid substrate system, the oscillations stop suddenly without a change of amplitude when the stirring rate rises more than a threshould and immediately start again when the stirring rate falls below the threshold. In the dione system, more rapid stirring than a threshold resulted in termination of the oscillations, but a switch to slow stirring did not cause the oscillation again. It was also observed that the addition of dione after damping of the oscillations does not regenerate the oscillations, but that under nitrogen atmosphere the addition of dione cause the oscillations again. It would be sure that some mechanical stirring effects are attributed to an increased oxygen transfer into the system. Thus the results suggest that some reaction products formed by oxygen inhibit the oscillation.

Further detailed studies on the mechanism in this system are in progress.

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