New Types of Oscillations in the BrO_3^--Serine-Mn^{2+}-H_2SO_4 System

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A novel kind of oscillations was observed in the Ser-BrO_3^--Mn^{2+}-H_2SO_4 system. Unlike other BZ oscillations, this kind of oscillations might be considered as radical-controlled rather than bromide-controlled because no substance subjected to bromination was present. The addition of acetone induced the dual-frequency oscillations, in which the radical-controlled oscillations appeared first following the bromide-controlled oscillations.

Since 1970s, the chemical oscillations have been widely studied owing to their fundamental importance in elucidating both the nonlinear kinetics in chemical reactions and the chemical instinct of various periodic phenomena observed in biological processes.[1] The oscillations driven by BrO_3^-, known as Belousov-Zhabotinskii (BZ) oscillations,[2] are most thoroughly studied, which demonstrated that they are bromide-controlled and the brominating reaction is essential to give rise to sustained oscillations.[3] Thus, the organic substrates in BZ oscillations should contain at least one active methylene group for bromination. A typical example is malonic acid. When the organic substrates are not subject to bromination, such as sugars, amino acids, and peptides etc., a brominating agent like acetone should be employed, as reported previously.[4,5] We report here, however, a novel BZ oscillations observed in the Ser-BrO_3^--Mn^{2+}-H_2SO_4 system, in which no bromination occurs since Ser is unable to be brominated and no additional brominating agent is supplied. Such oscillations may be considered as radical-controlled.[6] The addition of a certain amount of acetone results in the dual-frequency oscillations due to the coexistence of both the radical- and bromide-controlled oscillations.

The oscillating reactions were carried out in a homemade thermostated glass beaker at 30 ± 0.2 °C under vigorous stirring. All the reactants were of analytical grade and used without further purification. The reactants were added in the order of H_2O, H_2SO_4, Ser, Mn^{2+}, and finally BrO_3^-. The total volume of the reaction solution was adjusted to 50 ml by changing the amount of H_2O. The reaction mixture was open to the ambient air. No special precautions were taken to exclude oxygen from the reaction mixture. The change in $[Br^-]$ was measured by following the potential change (E) on a bromide ion-selective electrode (Br^- ISE) against a $Hg/Hg_2SO_4/K_2SO_4$ electrode as a reference and was recorded as a function of time (E vs. t) on a XWT recorder. No absolute calibration was attempted.

One of the most important results was the finding of oscillations in the Ser-BrO_3^--Mn^{2+}-H_2SO_4 system within the concentration ranges of $[Ser] = 0.004$–$0.014\,M$, $[BrO_3^-] = 0.0175$–$0.070\,M$, $[Mn^{2+}] = 0.007$–$0.310\,M$, $[H_2SO_4] = 1.26$–$2.52\,M$. Typical oscillatory pattern is shown in Figure 1. After addition of BrO_3^-, oscillations started immediately with almost no induction period. During the oscillations, the color of the solution changed periodically between pink and colorless, showing the oscillations between Mn^{3+} and Mn^{2+}. Bubbles were observed on the electrode surface, showing the occurrence of the decarboxylation reaction. Besides CO_2, the other main product was determined as $HOCH_2CHO$. The oscillations were strongly damped and only a few of oscillating cycles were achieved. After the oscillations died, the addition of a small amount of Ser may restart the oscillations while addition of other reactants could not regenerate the oscillations, indicating the stop of oscillations was mainly attributed to the exhaustive consumption of Ser in the reaction mixture. Similar to those found in the classical BZ oscillations, the present oscillations could be effectively inhibited by either chloride ions or radical scavengers like acrylonitrile and acrylamide, showing that the oscillations may also occur by a free-radical mechanism. The chloride ions inhibited the oscillations via reaction with $HBrO_2$, a key intermediate (an autocatalyst) in BZ oscillations.

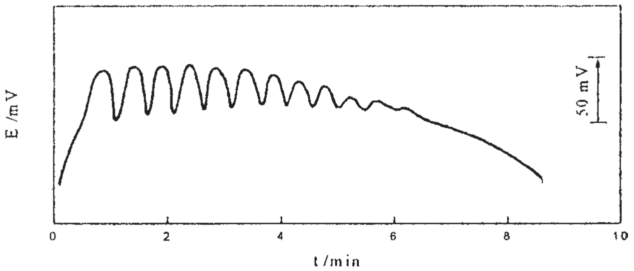


Figure 1. Typical oscillatory trace in the Ser-BrO_3^--Mn^{2+}-H_2SO_4 system. Reaction conditions: $[Ser] = 0.0050\,M$, $[BrO_3^-] = 0.042\,M$, $[Mn^{2+}] = 0.014\,M$, $[H_2SO_4] = 1.98\,M$, $T = 303\,K$, $V = 50\,ml$.

According to the widely accepted FKN mechanism,[3] in the bromide-controlled BZ oscillations, the excess bromine produced during the oscillations may be removed via bromination while the bromide ion and the catalyst may be regenerated via the oxidation of the brominated organic substrate by the metallic ion at high valence. For example, with the malonic acid as an organic substrate and the Mn^{2+} as an oscillating catalyst, the following reactions would occur during the BZ oscillations:

$$Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+ \quad (1)$$

$$Mn^{3+} + BrCH(COOH)_2 \rightarrow Br^- + Mn^{3+} + \text{oxidation products} \quad (2)$$

Unlike the classical BZ oscillations, the present BZ oscillations could be considered as radical-controlled rather than as bromide-controlled based on the following considerations: (i) Almost no induction period was observed before appearance of the oscillations; (ii) No bromination could take place throughout the oscillations since Ser had no active methylene group for bromination and no additional brominating agent was supplied. This was confirmed by the product analysis which revealed that no brominated organic substances were detected. Thus, the bromide ions could not be regenerated via reaction (2) as described by FKN mechanism; (iii) In the presence of excess Ag^+ (0.10 M), although the potential oscillations on the Br^--electrode were totally inhibited, the potential oscillations could still be observed at Pt-electrode. This furnished an important evidence that the BZ oscillations may be not controlled by the bromide ion since its concentration in the reaction mixture was always less than 10^{-10} M because of the formation of the AgBr precipitate ($K_{sp,\,AgBr} = 5 \times 10^{-13}$). Such radical-controlled oscillations were also observed in the BZ oscillations with malonic acid as the organic substrate when its concentration was extremely high.[6] Taking into account the facts that $HBrO_2$ was still an autocatalyst and the oscillations were not controlled by bromide ions owing to the absence of bromination, we proposed the following reaction mechanism:

$$BrO_3^- + HBrO_2 + 2Mn^{2+} + H^+ \rightarrow 2HBrO_2 + 2Mn^{3+} + H_2O \quad (3)$$

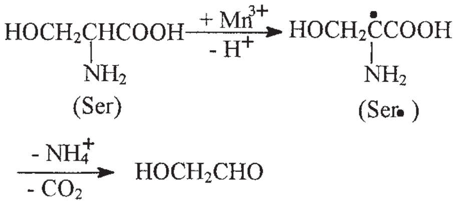
$$HBrO_2 + Ser\bullet + H^+ \rightarrow HOBr + HOCH_2CHO + CO_2 \quad (4)$$

$$Br_2 + Ser\bullet \rightarrow 2Br^- + HOCH_2CHO + CO_2 \quad (5)$$

$$Mn^{3+} + Ser\bullet \rightarrow Mn^{2+} + HOCH_2CHO + CO_2 \quad (6)$$

$$Mn^{3+} + Ser \rightarrow Mn^{2+} + Ser\bullet + H^+ \quad (7)$$

Where Ser• is a radical of Ser. The main difference between the above mechanism and the FKN mechanism was the controlling step (4), in which the $[HBrO_2]$ was mainly controlled by Ser• rather than by Br^-, though the reaction between $HBrO_2$ and Br^- may also occur to form HOBr. In addition, Ser• was also used to remove excess Br_2 (5) and to regenerate the oscillating catalyst (6). These results demonstrated that Ser• played a key role in the present oscillations. Ser• was speculated to be produced in reaction (7) based on the following consideration. On one hand, the Mn^{3+}–Ser reaction in sulfuric acid solution may be effectively inhibited by radical scavengers, such as acrylonitrile and acrylamide, showing that the above reaction contains radical steps. On the other hand, various studies on the oxidation of amino acids by metallic ions demonstrated the presence of the radicals of these amino acids.[7] Thus, the radical of Ser (Ser•) may be produced and consumed via the following scheme:



$$\underset{\text{(Ser)}}{\underset{NH_2}{HOCH_2CHCOOH}} \xrightarrow[-H^+]{+Mn^{3+}} \underset{\text{(Ser}\bullet\text{)}}{\underset{NH_2}{HOCH_2\dot{C}COOH}} \xrightarrow[-CO_2]{-NH_4^+} HOCH_2CHO$$

Another important finding was that the Ser-BrO_3^--Mn^{2+}-H_2SO_4 system might display dual-frequency oscillations in the presence of acetone. The oscillatory patterns were strongly dependent on the concentration of acetone. At very low acetone concentration ([acetone] < 0.027 M), the system displayed only one kind of oscillations similar to that in Figure 1, indicating that the oscillations were still radical-controlled. The dual-frequency oscillations occurred in the range of acetone concentration between 0.027 M and 0.11 M. As shown in Figure 2a, two oscillatory patterns appeared subsequently with a transitional period between them. The transitional period decreased rapidly with the increase of acetone concentration and totally disappeared at [acetone] $\cong 0.10$ M, as shown in Figure 2b and c. With the further increase in acetone concentration ([acetone] > 0.13 M), the first kind of oscillations disappeared and only the second kind of oscillations left, as shown in Figure 2d. Unlike the oscillations in Figure 1, this kind of oscillations had a significant induction period. In addition, the oscillations on either the Br^--electrode or Pt-electrode could be completely inhibited by adding excess Ag^+. Further, the addition of excess Br^- into the system could also suppress the oscillations. These characteristics demonstrated that the oscillations could occur only in a suitable range of bromide concentration, suggesting that the oscillations were bromide-controlled. Here, the acetone acted as a brominating agent to remove excess Br_2 and to form brominated species (e.g., bromoacetone) used for the regeneration of bromide ions as described by FKN mechanism. At very low acetone concentration, the bromide-controlled oscillations could not compete with the radical-controlled oscillations and thus, only the radical oscillations were observed. At very high acetone concentration, the radical-controlled oscillations were totally inhibited since acetone could inhibit the formation of organic radicals,[8] and in turn, only the bromide-controlled oscillations were observed. Within a suitable range of [acetone], dual-frequency oscillations appeared due to the coexistence of both these two kinds of oscillations. Detailed studies are being underway to elucidating the reaction mechanism of different oscillations observed in the present system.

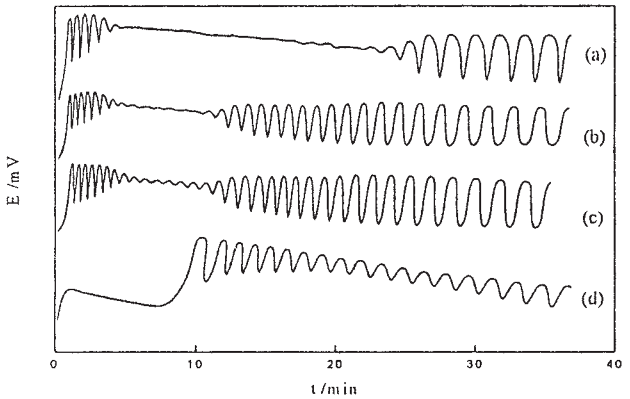


Figure 2. Effects of the acetone concentration on the oscillatory pattern. Reaction conditions: [Ser] = 0.011 M, $[BrO_3^-] = 0.040$ M, $[Mn^{2+}] = 0.0090$ M, $[H_2SO_4] = 2.16$ M, $T = 303$ K, $V = 50$ ml. [acetone] = (a) 0.068 M, (b) 0.098 M, (c) 0.10 M (d) = 0.12 M.

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References and Notes

1 R. J. Field and M. Burger, "Oscillations and Travelling Waves in Chemical Systems," Willey-Interscience, New York (1985).
2 B. P. Belousov, *Sb. Ref. Radiats. Med. Moscow*, **145**, 1959 (1958).
3 R. J. Field, R. M. Noyes, and E. Körös, *J. Am. Chem. Soc.*, **94**, 8649 (1972).
4 H. X. Li and R. H. Jin, *Int. J. Chem. Kinet.*, **30**, 244 (1998).
5 H. Li, *Chin. J. Chem.*, **7**, 434 (1991).
6 Z. Nosztizius, Z. Bodnár, L. Garamszegi, and M. Wittmann, *J. Phys. Chem.*, **95**, 6575 (1991).
7 B. S. Sherigara, K. I. Bhat, and I. Pinto, *Int. J. Chem. Kinet.*, **27**, 675 (1995).
8 G. P. Misra, R. P. Washington, and J. A. Pojman, *J. Phys. Chem. A*, **102**, 612 (1998).