© 2001 The Chemical Society of Japan Bull. Chem. Soc. Jpn., **74**, 1817–1821 (2001)

Experimental Studies on Complex Oscillations in a Mn^{2+}-Catalyzed Acidic Bromate–Glucose Reaction

Hexing Li* **and Qin Wang**

Department of Chemistry, Shanghai Normal University, Shanghai 200234, P. R. China

(Received January 12, 2001)

Under batch-reactor conditions, the BrO_3^-–glucose–Mn^{2+}–H_2SO_4 system exhibits several types of oscillations, depending on the concentrations of the reactants. In certain cases, dual-frequency oscillations are observed owing to a sequential appearance of different types of oscillations. Since glucose is not subject to bromination, these oscillations may be considered as being typically radical-controlled, and can be distinguished from bromide-controlled oscillations by adding acetone, which also results in dual-frequency oscillations due to the presence of both radical-controlled and bromide-controlled oscillations. Further experimental results demonstrate that the different types of oscillations observed in the absence of acetone can be possibly attributed to the Mn^{2+}-catalyzed reactions between bromate and glucose, or various intermediates produced from the oxidative degradation of glucose. The effects of the $[BrO_3^-]/[\text{glucose}]$ ratio and $[H_2SO_4]$ on the oscillatory behaviors are discussed on the basis of their effects on either the depth of oxidative degradation of glucose or the oxidizing ability of bromate.

The classical Belousov–Zhabotinsky (BZ) reaction, the metal ion catalyzed oxidation of organic substrate by an acidic bromate solution, is the most thoroughly characterized of the known chemical oscillations.[1] A detailed mechanism, known as the FKN mechanism, has been proposed by Field and coworkers,[2] in which they claimed that the oscillations are controlled by bromide, which is produced mainly by the reaction between bromomalonic acid and Ce^{4+}. However, the concept of bromide control is not always true, since the oscillations could also be observed even in the presence of excess silver ions.[3] Noszticzius et al. reported that, under certain cases, the BZ oscillations could also be controlled by the malonyl radical,[4–7] known as the "Rácz" system. They also claimed that the bromide-controlled oscillations usually had an induction period before the oscillations began, while the radical-controlled oscillations occurred immediately without an induction period. However, most of the substrates known so far to give to BZ-type oscillations are easily brominated.[8] In the case where the substrate is not subject to bromination, an effective brominating agent, e.g. acetone, is necessary to remove the product bromine.[9–15] Therefore, doubt arises whether the Rácz system could still be bromide-controlled, because bromide might be produced by the reaction of brominated organic substrates and Ce^{4+} or Mn^{3+}. Pojman and co-workers[16] reported a promising way to suppress the bromide-controlled oscillations by adding acetylacetone, which could effectively consume HOBr and Br_2. They also reported dual-frequency oscillations owing to the coexistence of both the radical-controlled and bromide-controlled oscillations. In our previous paper, dual-frequency oscillations were also reported in the BZ systems by using aldosugars and suitable acidity.[12] However, two types of oscillations involved were both bromide-controlled and could be explained on the bases of the FKN mechanism, since acetone was found to be essential in each type of oscillation. In this paper, we report on the oscillations in the BrO_3^-–glucose (Glu)–Mn^{2+}–H_2SO_4 system, even without acetone as a coupled substrate, which could be considered as typiclly radical-controlled, since Glu is not subject to bromination. The first part of this paper distinguishes the radical-controlled oscillations from the bromide-controlled oscillations by using acetone, as reported in our previous system. The second part analyzes three types of radical-controlled oscillations in the present system by considering the roles of the $[BrO_3^-]/[\text{Glu}]$ ratio and $[H_2SO_4]$. On one hand, the present work might lead to a reconsideration of the FKN mechanism, since there is no active methylene like that in malonic acid, which could be easily brominated. On the other hand, as we know, complex radical-controlled oscillations have never been reported so far. Therefore, it could supply valuable information to further elucidate the mechanism of the radical-controlled oscillations.

Experimental

All of the materials were of analytical grade and were used without further purification. All of the solutions were prepared in twice-distilled water.

The oscillating reactions were performed in a stirred thermostated glass beaker at 30 ± 0.2 °C. The reactants were added in the order of H_2O, H_2SO_4, glucose, Mn^{2+}, and BrO_3^-. The reaction mixture was open to the ambient air. No special precautions were attempted to exclude oxygen from the reaction mixture. The change in $[Br^-]$ was followed by a bromide ion-selective electrode (Br^- ISE) against a $Hg/Hg_2SO_4/K_2SO_4$ electrode as a reference. The potential was recorded as a function of time (E–t) on a XWT x-t recorder. No absolute calibration of the bromide ion electrode was attempted. The reaction products were analyzed by liquid chromatograph with UV @ 210 nm detection under the following conditions: column, Rezex ROA-organic acid; dimensions, 300 × 7.8 mm; mobile phase, 0.0025 M (1 M = 1 mol dm^{-3}) sulfuric acid; flow rate, 0.5 mL/min; temperature, 55 °C.

Results and Discussion

The Radical-Controlled and Bromide-Controlled Oscillations. Typical experimental results on the BrO_3^-–Glu–Mn^{2+}–H_2SO_4 reaction with different acetone concentrations are plotted in Fig. 1. In the absence of acetone or when [acetone] < 0.080 M (1 M = 1 mol dm^{-3}), only one type of oscillation (Fig. 1a) was observed which could be considered to be radical-controlled, since no brominated substance could be formed in the present system, on one hand, and the oscillations started immediately without any induction period on the other hand. Another important reason was that the oscillations could also be observed when a small amount of silver ions was added into the solution. As is well known, no sufficient $[Br^-]$ could be accumulated due to the formation of AgBr precipitate in the presence of silver ions. Therefore, bromide could not be produced by the reaction between the brominated substance and Mn^{3+}. Unlike acetylacetone, the addition of acetone could suppress radical-controlled oscillations, since the number of oscillations decreased rapidly with an increase of [acetone]. The possible reason was that acetylacetone could be easily oxidized by HOBr, $BrO_2\bullet$, and even Br_2.[16] However, the oxidation of acetone was relatively difficult. Therefore, the main role of acetone in the oscillations was to consume Br_2 via the following bromination:

$$CH_3COCH_3 + Br_2 \rightarrow BrCH_2COCH_3 + Br^- + H^+,$$

$$BrCH_2COCH_3 + Br_2 \rightarrow Br_2CHCOCH_3 + Br^- + H^+.$$

The resulting Br^- during the consumption of Br_2 could further react with HOBr:

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O.$$

Because the reaction between bromide and HOBr was very fast, the accumulation of HOBr was delayed in the presence of acetone. Thus, the radical-controlled oscillations were suppressed since such oscillations were due to the oscillations in [HOBr].[5] An increase in [acetone] resulted in the production of more bromide, which could account for the decrease in the number of radical-controlled oscillations. At [acetone] $>$ 0.080 M, a new type of oscillation was induced. This type of oscillation was possibly bromide-controlled, since an induction period appeared before the oscillations began. Acetone was essential for bromide-controlled oscillations in the present system, since bromide was produced via the above-mentioned bromination and, possibly, also the following reaction between $BrCH_2COCH_3$ and Mn^{3+}:

$$BrCH_2COCH_3 + Mn^{3+} \rightarrow Br^- + \text{products}.$$

Dual-frequency oscillations[17,18] were observed in the [acetone] range from 0.080 M to 0.147 M owing to the presence of both the radical-controlled and the bromide-controlled oscillations, as shown in Fig. 1b. With an increase of [acetone], the number of radical-controlled oscillations continued to decrease while the number of the bromide-controlled oscillations increased. At [acetone] $>$ 0.15 M, the radical-controlled oscillations were totally suppressed and only the bromide-controlled oscillations were observed, as shown in Fig. 1c. It was noted that the color of the solution also changed periodically between pink(Mn^{3+}) and colorless(Mn^{2+}), showing the presence of the oscillations in $[Mn^{3+}]/[Mn^{2+}]$ ratio, which could be observed by measuring the absorbance at 480 nm corresponding to the maximum absorbance wavelength of Mn^{3+} on an HP 8451 A spectrophotometer.[19] Those results demonstrated that both the bromide- and radical-controlled oscillations were catalyzed by Mn^{2+}.

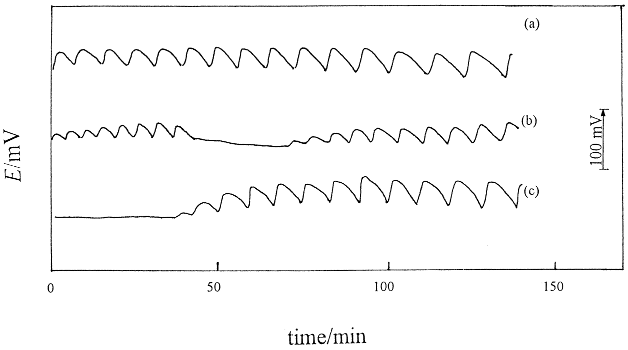

Fig. 1. Oscillatory traces in the Mn^{2+}-catalyzed acidic bromate–glucose reaction in the presence of acetone. (a) $[\text{acetone}]_0 = 0.067$ M, (b) $[\text{acetone}]_0 = 0.11$ M, (c) $[\text{acetone}]_0 = 0.16$ M. Other reaction conditions: $[BrO_3^-]_0 = 0.025$ M, $[\text{Glu}]_0 = 0.020$ M, $[Mn^{2+}]_0 = 0.015$ M, $[H_2SO_4] = 0.18$ M, $V = 50$ mL, $T = 30 \pm 0.2$ °C.

Complex Radical-Controlled Oscillations. In the absence of acetone, the BrO_3^-–glucose–Mn^{2+}–H_2SO_4 system, i.e., a pure Rácz system, also exhibited several types of oscillations, depending on the reactants' concentrations. Fig. 2 shows the effect of [Glu] on the oscillatory pattern when the concentrations of other reactants were fixed at $[BrO_3^-] = 0.010$ M, $[H_2SO_4] = 1.0$ M, $[Mn^{2+}] = 0.040$ M. At very high [Glu] (> 0.1 M), only one overshoot without an induction period was observed, as shown in Fig. 2a. The addition of a small amount of BrO_3^- resulted in another overshoot. This implied that the absence of the sustained oscillations in the present system was mainly due to the limitation of $[BrO_3^-]$. During the reaction, no bubbles were observed. Besides Glu, only gluconic acid was determined in the solution after the reaction. When [Glu] decreased from 0.1 M to 0.0525 M, sustained oscillations appeared immediately following the overshoot, which was denoted as type I. The oscillations in the $[Mn^{3+}]/[Mn^{2+}]$ ratio were also observed by measuring the absorbance at 480 nm. During the oscillations, many bubbles were released from the solution due to the decarboxylation of gluconic acid. According to a product analysis, gluconic acid, arabinose, arabinonic acid, and formic acid were determined in the reaction mixture after the oscillations. However, no significant amount of Glu was detected. In the [Glu] range of 0.0525–0.0475 M, a nonoscillatory period between the overshoot and the type-I oscillations was observed, as shown in Fig. 2c. When the [Glu] further decreased, the overshoot disappeared. From 0.0475 M to 0.035 M, only type-I oscillations appeared, as shown in Fig. 2d. With a further decrease in [Glu], the system exhibited a typical dual-frequency oscilla-

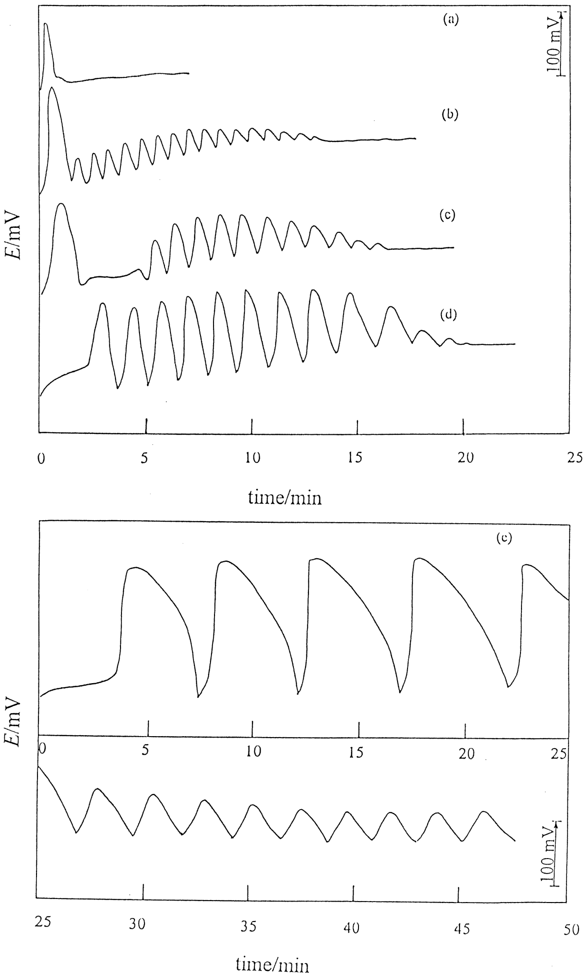

Fig. 2. Dependence of the oscillatory patterns on $[Glu]_0$. (a) $[Glu]_0 = 0.12$ M, (b) $[Glu]_0 = 0.060$ M, (c) $[Glu]_0 = 0.050$ M, (d) $[Glu]_0 = 0.040$ M, (e) $[Glu]_0 = 0.025$ M. Other reaction conditions: $[BrO_3^-]_0 = 0.010$ M, $[Mn^{2+}]_0 = 0.040$ M, $[H_2SO_4] = 1.0$ M, $V = 50$ mL, $T = 30 \pm 0.2$ °C.

tions comprised of two types of sustained oscillations.[17,18] As shown in Fig. 2e, after a short induction period, the system bifurcated into a first oscilatory regime, where low-frequency and large-amplitude oscillations (Type-I) occurred. Both the frequency and the amplitude remained nearly constant with the elapse of the reaction time. Then, type-I oscillations suddenly diminished and another type of oscillation, denoted as type-II, occurred immediately. Type-II oscillations were characterized by a relative high frequency and small amplitude and a nearly symmetric wave form. The number of type-I oscillations decreased while the number of the type-II oscillations gradually increased with the decrease of [Glu]. However, a nonoscillatory period between these two types of oscillations never appeared. During each type of oscillation, bubbles were released from the solution, indicating the occurrence of decarboxylation. After the oscillations totally finished, arabinonic acid, erythrose, and formic acid were found in the reaction mixture.

Similar results were also observed by changing $[BrO_3^-]$ when the other reactant concentrations were fixed at $[Glu] = 0.050$ M, $[H_2SO_4] = 1.0$ M, $[Mn^{2+}] = 0.040$ M. However, the tendency was opposite, i.e., the increase of $[BrO_3^-]$ was corresponded to the decrease of [Glu]. Typical results are summarized in Fig. 3.

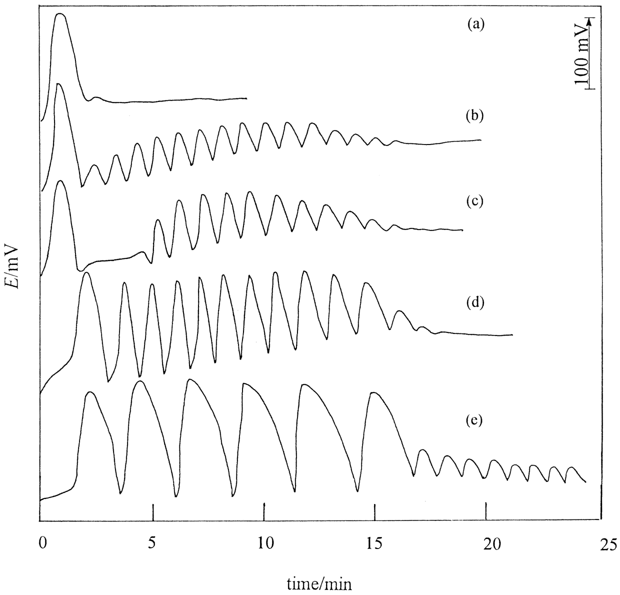

Fig. 3. Dependence of the oscillatory patterns on $[BrO_3^-]_0$. (a) $[BrO_3^-]_0 = 0.0050$ M, (b) $[BrO_3^-]_0 = 0.0090$ M, (c) $[BrO_3^-]_0 = 0.010$ M, (d) $[BrO_3^-]_0 = 0.0125$ M, (e) $[BrO_3-]_0 = 0.015$ M. Other reaction conditions: $[Glu]_0 = 0.050$ M, $[Mn^{2+}]_0 = 0.040$ M, $[H_2SO_4] = 1.0$ M, $V = 50$ mL, $T = 30 \pm 0.2$ °C.

The above results demonstrated that the BrO_3^-–glucose–Mn^{2+}–H_2SO_4 system could exhibit several types of oscillations depending on the $[BrO_3^-]$/[Glu] ratio. All of these kinds of oscillations were radical-controlled because of the absence of a brominating agent. Under certain cases, dual-frequency oscillations were observed due to the coexistence of two types of oscillations. Based on a product analysis and the fact that much CO_2 gas was released during the oscillations, the following oxidative degradation of glucose by acidic bromate may occur in the present system (Scheme 1).

Therefore, it is reasonable to suggest that the influence of the $[BrO_3^-]$/[Glu] ratio on the oscillatory patterns was possibly attributed to its effect on the depth of the oxidative degradation of glucose corresponding to different intermediates, including gluconic acid, arabinose, arabinonic acid, erythrose and formic acid. These intermediates could construct different BZ-type reactions, resulting in different types of oscillations. Obviously, the depth of the oxidative degradation increased with the increase of the $[BrO_3^-]$/[Glu] ratio. At very low $[BrO_3^-]$/[Glu] ratio, since Glu was greatly excess, a large portion of Glu was left and only the gluconic acid was detected as the product after the reactions. Thus, the overshoot could be attributed to the Mn^{2+}-catalyzed bromate–glucose reaction. Only one overshoot was observed, since excess Glu consumed BrO_3^- very rapidly. When [Glu] decreased or $[BrO_3^-]$ increased (i.e. the $[BrO_3^-]$/[Glu] ratio increased), type-I oscillations were observed after the overshoot. According to a product analysis, it could be concluded that the Mn^{2+}-catalyzed bromate–gluconic acid reaction was responsible for the type-I oscillations. This

$$HOCH_2(CHOH)_4CHO \xrightarrow[Mn^{2+}]{BrO_3^-} HOCH_2(CHOH)_4COOH$$

Glucose **Gluconic Acid**

$$HOCH_2(CHOH)_4COOH \xrightarrow[Mn^{2+}]{BrO_3^-} HOCH_2(CHOH)_3CHO + HCOOH$$

Gluconic Acid **Arabinose** **Formic Acid**

$$HOCH_2(CHOH)_3CHO \xrightarrow[Mn^{2+}]{BrO_3^-} HOCH_2(CHOH)_3COOH$$

Arabinose **Arabinonic Acid**

$$HOCH_2(CHOH)_3COOH \xrightarrow[Mn^{2+}]{BrO_3^-} HOCH_2(CHOH)_2CHO + HCOOH$$

Arabinonic Acid **Erythrose** **Formic Acid**

$$HCOOH \xrightarrow[Mn^{2+}]{BrO_3^-} CO_2 + H_2O$$

Scheme 1. Reaction scheme of glucose oxidation by bromate.

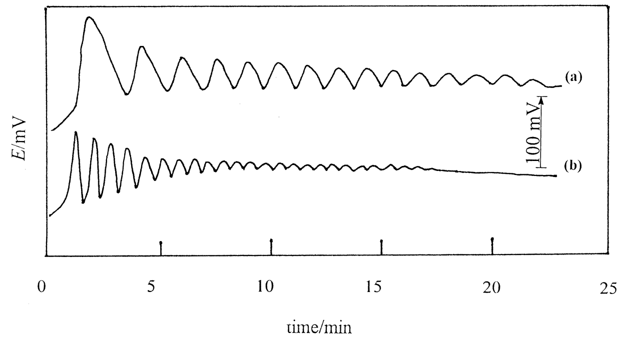

Fig. 4. Oscillatory traces in (a) the Mn^{2+}-catalyzed acidic bromate–gluconic acid reaction and (b) the Mn^{2+}-catalyzed acidic bromate–arabinonic acid reaction. Reaction conditions: $[\text{gluconic acid}]_0 = [\text{arabinonic acid}]_0 = 0.050$ M, $[BrO_3^-] = 0.010$ M, $[Mn^{2+}]_0 = 0.040$ M, $[H_2SO_4]_0 = 1.0$ M, $V = 50$ mL, $T = 30 \pm 0.2$ °C.

was strongly supported by the fact that similar oscillations to type-I were also observed when gluconic acid was used instead of glucose in the title system, as shown in Fig. 4a. Many cycles of type-I oscillations were observed owing to the slow consumption of BrO_3^-, since the reaction between gluconic acid and bromate was more difficult than that of glucose. When the $[BrO_3^-]/[Glu]$ ratio increased further, glucose was immediately oxidized by BrO_3^-, which could account for the disappearance of the overshoot. At a very high $[BrO_3^-]/[Glu]$ ratio, type-II oscillations appeared following type-I oscillations, which can be possibly attributed to the Mn^{2+}-catalyzed bromate–arabinonic acid reaction, since a deeper oxidative degradation product, erythrose, was detected after the reactions. This was confirmed by the fact that similar oscillations were observed by using arabinonic acid instead of glucose in the title system, as shown in Fig. 4b. A further increase in the $[BrO_3^-]/[Glu]$ ratio could accelerate the consumption of gluconic acid on one hand, and increase the accumulation of arabinose and arabinonic acid on the other hand. Therefore, the number of type-I oscillations decreased while the number of type-II oscillations gradually increased. It should be noted that the shapes of the oscillations in Fig. 4 are not exactly the same as those of type-I and type-II oscillations in Fig. 3. On one hand, this can be understood by considering the different initial conditions, since the type-I and type-II oscillations occurred after the oxidation of glucose and gluconic acid, respectively. Therefore, the concentrations of the reactants in type-I and type-II must be different from those shown in Fig. 4. In fact, the shapes of the oscillations in Fig. 4 depend strongly on the initial concentrations of the reactants. On the other hand, some intermediates in the reaction system in Fig. 3 may also disturb the shapes of oscillations.

Figure 5 shows the dependence of the oscillatory patterns on $[H_2SO_4]$ when other reactant concentrations were fixed at $[BrO_3^-] = 0.010$ M, $[Glu] = 0.050$ M, and $[Mn^{2+}] = 0.040$ M, respectively. At medium $[H_2SO_4]$ (1.12–0.083 M), the system exhibited that an overshoot and type-I oscillations were separated by a nonoscillatory period, as shown in Fig. 5b. At higher $[H_2SO_4]$ (> 1.12 M), the overshoot diminished and only type-I oscillations with an induction period were observed, as shown in Fig. 5a. A further increase in $[H_2SO_4]$ caused a decrease in both the induction period and the number of type-I oscillations. At lower $[H_2SO_4]$ (< 0.083 M), the nonoscillatory period between the overshoot and the type-I oscillations suddenly disappeared, as shown in Fig. 5c. When the $[H_2SO_4]$ further decreased, the number of overshoots increased, as shown in Fig. 5d. Finally, the overshoots and the sustained oscillations mixed completely at $[H_2SO_4] < 0.65$ M, as shown in

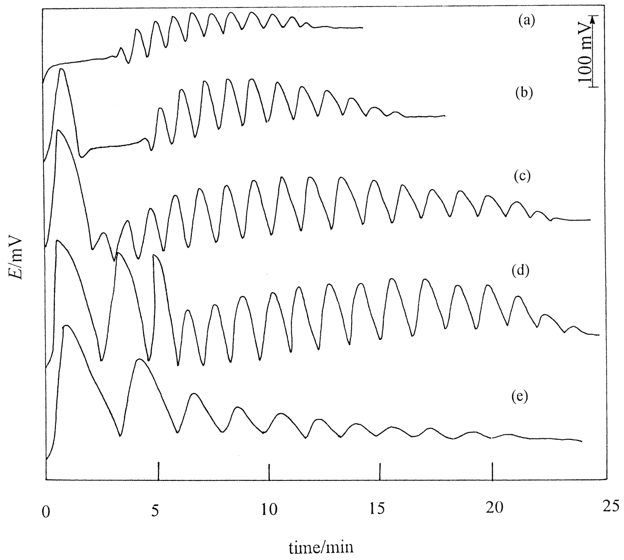

Fig. 5. Dependence of the oscillatory patterns on $[H_2SO_4]_0$. (a) $[H_2SO_4]_0$ = 1.18 M, (b) $[H_2SO_4]_0$ = 1.0 M, (c) $[H_2SO_4]_0$ = 0.792 M, (d) $[H_2SO_4]_0$ = 0.72 M, (e) $[H_2SO_4]_0$ = 0.54 M. Other reaction conditions: $[BrO_3^-]_0$ = 0.010 M, $[Glu]_0$ = 0.050 M, $[Mn^{2+}]$ = 0.040 M, V = 50 mL, T = 30 ± 0.2 °C.

Fig. 5e.

From the above experimental results, one can see that only the overshoots and the type-I oscillations appeared possibly owing to the fixed $[BrO_3^-]$/[Glu] ratio. As discussed above, the absence of type-II oscillations under the present conditions could be attributed to the low $[BrO_3^-]$/[Glu] ratio. The effect of $[H_2SO_4]$ on the oscillatory behaviors could be understood by considering its effect on the oxidizing ability of bromate. At very high $[H_2SO_4]$, the oxidizing ability of bromate was very strong. Therefore, no overshoot was observed, since the reaction between the acidic bromate and glucose was too rapid. According to the above discussion, the type I oscillations corresponded to the Mn^{2+}-catalyzed reaction between acidic bromate and gluconic acid. The increase in $[H_2SO_4]$ also resulted in an increase in the reaction rate between bromate and gluconic acid, which could account for the decrease in the number of type-I oscillations at higher $[H_2SO_4]$. Similarly, the numbers of both the overshoots and the type-I oscillations increased at lower $[H_2SO_4]$ owing to the decrease in the oxidizing ability of bromate.

Conclusions

The Mn^{2+}-catalyzed acidic bromate-glucose reaction exhibited radical-controlled oscillations which could be distinguished from the bromide-controlled oscillations in the presence of acetone, an effective brominating agent. Even in the absence of acetone, the above-mentioned system exhibited the following three types of oscillations owing to the formation of different intermediates of glucose during its oxidative degradation by acidic bromate: (1) the overshoots resulted from the Mn^{2+}-catalyzed acidic bromate–glucose reaction; (2) the type-I oscillations resulted from the Mn^{2+}-catalyzed acidic bromate–gluconic acid reaction; (3) the type-II oscillations resulted from the Mn^{2+}-catalyzed acidic bromate-arabinonic acid reaction. The effect of the $[BrO_3^-]$/[Glu] ratio on the oscillatory patterns could be interpreted in terms of its effect on the depth of oxidative degradation of glucose, which resulted in different intermediates. However, the effect of $[H_2SO_4]$ on the oscillatory patterns could be interpreted in terms of its effect on the oxidizing ability of bromate, which resulted in the different rates of the reactions between bromate and glucose and its corresponding oxidative products.

This work was supported by the National Natural Science Foundation of China (29973025) and Shanghai Natural Science Foundation (98QMAI1402).

References

1 R. J. Field and M. Burger, "Oscillations and Traveling Waves in Chemical Systems," J. Wiley, Interscience, New York (1985).

2 R. J. Field, E. Körös, and R. M. Noyes, *J. Am. Chem. Soc.*, **94**, 8649 (1972).

3 B. Schwitters and P. Ruoff, *J. Phys. Chem.*, **90**, 2497 (1986).

4 H.-D. Försterling and Z. Nosztizius, *J. Phys. Chem.*, **93**, 2740 (1989).

5 H.-D. Försterling, S. Murányi, and Z. Nosztizius, *React. Kinet. Catal. Lett.*, **42**, 217 (1990).

6 H.-D. Försterling, S. Murányi, and Z. Nosztizius, *J. Phys. Chem.*, **94**, 2915 (1990).

7 Z. Nosztizius, Z. Bodnár, L. Garamszegi, and M. Wittmann, *J. Phys. Chem.*, **95**, 6575 (1991).

8 O. Gurel and D. Gurel, "Topics in Current Chemistry," **118**, Springer-Verlag, West Berlin (1983).

9 Z. Nosztizius and J. Bódiss, *J. Am. Chem. Soc.*, **101**, 3175 (1979).

10 H. X. Li and J. F. Deng, *Chem. Lett.*, **1996**, 835.

11 H. X. Li and C. Shun, *Bull. Chem. Soc. Jpn.*, **70**, 1359 (1997).

12 H. X. Li, R. Jin, W. Dai, and J. F. Deng, *Chem. Phys. Lett.*, **274**, 41 (1997).

13 H. X. Li and R. Jin, *Int. J. Chem. Kinet.*, **30**, 243 (1998).

14 R. J. Field and R. M. Boyd, *J. Phys. Chem.*, **89**, 3707 (1985).

15 R. P. Rastogi and M. K. Verma, *Indian J. Chem.*, **22A**, 830 (1983).

16 G. P. Misra, R. P. Washington, and J. A. Pojman, *J. Phys. Chem.*, **102**, 612 (1998).

17 P. Ruoff, M. Varga, and E. Körös, *J. Phys. Chem.*, **91**, 5332 (1987).

18 P. K. Srivastava, Y. Mori, and I. Hanazaki, *J. Phys. Chem.*, **95**, 1636 (1991).

19 C. C. Ou and J. J. Jwo, *Int. J. Chem. Kinet.*, **23**, 137 (1991).