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Dual-frequency oscillations induced by acidity in Belousov–Zhabotinskii reactions with aldosugars as substrates

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Abstract

Depending on the initial concentration of H_2SO_4, two types of dual-frequency oscillations have been observed in Belousov–Zhabotinskii type reactions catalyzed by Mn^{2+} with acetone and aldosugars (arabinose, glucose, galactose, lactose or maltose) as coupled substrates in a batch reactor. No such dual-frequency oscillations have been found when a ketosugar like fructose was used instead of an aldosugar as the substrate; or acetone was replaced by N_2 flow. No oscillations were observed when Ce^{3+} was used instead of Mn^{2+}. The reaction products of aldosugars in different oscillating regimes have been analyzed. The dual-frequency oscillatory patterns have been discussed according to the roles of the substrates and their derivatives formed at different acidity. © 1997 Elsevier Science B.V.

1. Introduction

The Belousov–Zhabotinskii (BZ) reaction 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 his coworkers [2]. Recently, the dual-frequency oscillatory reactions have been caused much interest since they supply a simple way to understand the complex oscillatory behaviors and even the chaotic states in BZ type reactions. However, only a few examples have been reported so far [3–6], such as the dual-frequency oscillations in classical BZ reactions with mixed organic substrates or in the uncatalyzed BZ reactions induced by introducing a metallic catalyst used in classical BZ oscillators. The dual-frequency oscillations in BZ reactions with 3,4-dihydroxybenzoic acid as the organic substrate induced by bromide ion has been reported previously [7]. In the present paper, we report dual-frequency oscillations in BZ reactions catalyzed by Mn^{2+} with acetone and aldosugars (arabinose, glucose, galactose, lactose and maltose) as coupled substrates. Two types of dual-frequency oscillatory patterns have been obtained depending on the initial concentration of H_2SO_4. The characters of each oscillating regime have been described and discussed by considering the roles of the aldosugar and acetone as well as their derivatives formed at different acidity. As we know, no such dual-frequency oscillations induced by acidity have been reported so far.

2. Experimental

All materials were of analytical grade and used without further purification except for $KBrO_3$. $KBrO_3$ was recrystallized in hot water three times to remove Br^- and other impurities. All solutions were prepared with twice distilled water. During the oscilla-

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tions, the reaction temperature was kept at 30 ± 0.2°C by a thermostated water jacket. The reaction mixture was continuously stirred at constant speed (150 rpm) by a magnetic stirrer. The oscillations were observed by monitoring the potential change of a bromide ion selective electrode against a mercurous sulfate electrode as a reference. No further calibration was attempted for the Br^- electrode. Analysis of the reaction products was carried out in the following procedures: After the reaction, the reaction mixture was extracted with ether. The ether solution was treated with anhydrous sodium sulfate and filtered. Subsequently, it was distilled at normal pressure. Ether was obtained at 34°C. Two liquid fractions (A and B) were obtained at 55–57°C and 136–138°C, respectively. By comparing the IR, NMR spectra of pure acetone and bromoacetone with the isolated compounds, A and B were determined as acetone and bromoacetone, respectively, which were further confirmed by IR and elemental analysis. In the aqueous solution, the remaining aldosugar was determined by adding $CuSO_4$ and NaOH, which resulted in the red precipitate(Cu_2O). The mixed organic acids in the aqueous solution were separated on the basis of TLC (thin layer chromatography) and studied by using benzene/acetic acid/methanol (45:8:8). They were identified by comparing the R_f values of the isolated products with those of the pure substances. For example, R_f values were found to be 0.67 and 0.80 for pure arabonic acid and gluconic acid, respectively. The results were further confirmed by IR and NMR.

3. Results and discussion

3.1. Dual-frequency oscillations at low acidity

A typical result of dual-frequency oscillation for glucose at low acidity is shown in Fig. 1. On addition of BrO_3^-, the first oscillations with low-frequency ($\overline{t_p}(l) \approx 4.8$ min) occurred without induction period. Subsequently, the system came to a nonoscillatory period, known as transition period (τ). After a short stable period, the system made a transition to another oscillatory regime, exhibiting high-frequency ($\overline{t_p}(l) \approx 3.3$ min) oscillations. The oscillations finally terminated without the decrease of the amplitude.

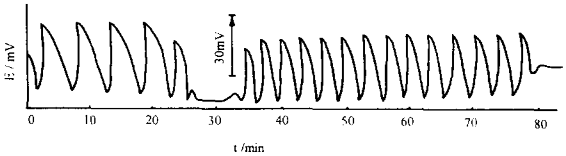

Fig. 1. Dual-frequency oscillation for glucose at low acidity $[BrO_3^-]_0 = 0.050$ M, $[\text{glucose}]_0 = 0.050$ M, $[\text{acetone}]_0 = 0.27$ M, $[Mn^{2+}]_0 = 0.0030$ M, $[H_2SO_4]_0 = 0.12$ M, $V = 50$ ml, $T = 30 \pm 0.2$°C. The potential (E) increase is indicated by the arrow. Bromide ion concentration increases with increasing E.

Similar phenomena have also been found for arabinose, galactose, maltose and lactose as substrates, as shown in Fig. 2. Although the frequency changes between two kinds of oscillations in Fig. 2 are not so striking as that in Fig. 1, they could be distinguished by the transition period (τ) or by comparing the shape of the oscillatory patterns. No such dual-frequency oscillations occurred with ketosugars, e.g. fructose, as organic substrate regardless of the concentration of H_2SO_4.

The dual-frequency oscillations could be observed only in a certain concentration range of H_2SO_4, as shown in Table 1. For example, the dual-frequency oscillations similar to those in Fig. 1 could be observed only in the concentration range of H_2SO_4 from 0.084 to 0.36 M when glucose was used as organic substrate. When $[H_2SO_4]_0 \geq 0.36$ M, an-

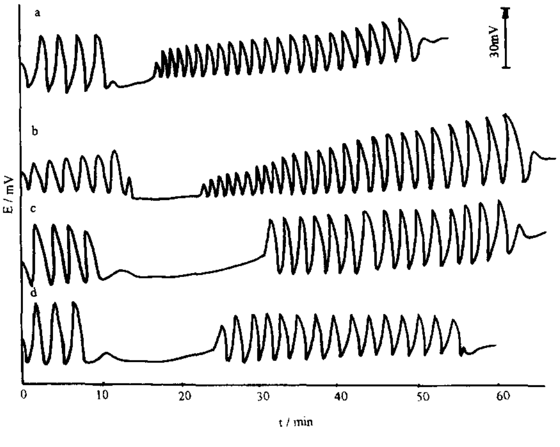

Fig. 2. Dual-frequency oscillations for aldosugars at low acidity: (a) $[\text{galactose}]_0 = 0.040$ M, $[H_2SO_4]_0 = 0.12$ M; (b) $[\text{arabinose}]_0 = 0.050$ M, $[H_2SO_4]_0 = 0.10$; (c) $[\text{maltose}]_0 = 0.050$ M, $[H_2SO_4]_0 = 0.15$ M; (d) $[\text{lactose}]_0 = 0.050$ M, $[H_2SO_4]_0 = 0.18$ M. Other conditions are given in Fig. 1.

Table 1
Range of initial H_2SO_4 concentration (M) for dual-frequency oscillations

No.	Saccharide	At low acidity	At high acidity
1	galactose	0.072–0.18	0.18–2.52
2	glucose	0.084–0.36	0.36–2.38
3	arabinose	0.054–0.12	0.12–3.60
4	maltose	0.090–0.24	0.24–2.88
5	lactose	0.090–0.30	0.30–2.88

other type of dual-frequency oscillations were observed (as discussed in the next section). When $[H_2SO_4] \leq 0.084$ M, the high-frequency oscillations were completely inhibited and only the low-frequency oscillations were found. When $[H_2SO_4] \leq 0.10$ M, the transition period between the low- and high-frequency oscillations disappeared, the high-frequency oscillations occurred immediately following the low-frequency oscillations. No induction period for the low-frequency oscillations has been found regardless of the concentration of H_2SO_4.

Similar results were obtained when H_2SO_4 was replaced by H_3PO_4, indicating that the role of H_2SO_4 in the system was only to adjust the acidity to a suitable range for above dual-frequency oscillations.

Acetone is necessary for the dual-frequency oscillations. Only one kind of oscillations, which were similar to the low-frequency oscillations in Fig. 1, were found in the absence of acetone, indicating the high-frequency oscillations in Fig. 1 occurred only with the help of acetone. Almost the same oscillatory patterns were obtained when N_2 flow was used instead of acetone in above system, indicating that the role of acetone is mainly to remove the excess Br_2 by its bromination [8,9], i.e.

$$CH_3COCH_3 + Br_2 \rightarrow BrCH_2COCH_3 + Br^- + H^+. \qquad (1)$$

In order to understand the mechanism for dual-frequency oscillations at low acidity, the products for glucose after each of oscillating regime have been analyzed. It was noticed that no bubbles were released during the low-frequency oscillations, while a lot of bubbles were given off during the high-frequency oscillations, indicating a decarboxylation occurred during the high-frequency oscillations. The main product for glucose after the low-frequency oscillations was determined as gluconic acid. Two main products after the high-frequency oscillations were identified. One was gluconic acid and the other was arabonic acid. When gluconic acid was used instead of glucose in above system, the oscillations similar to the high-frequency oscillations in Fig. 1 could be observed, in which acetone could be replaced by N_2 flow or some other inert gas. It was also found that no oscillation was observed with either acetone or aldosugar as the single substrate. The above results demonstrated that the high-frequency oscillations in Figs. 1 and 2 were produced by gluconic acid coupled with acetone, while the low-frequency oscillations were produced by glucose itself in BZ system. The result of no induction period for the low-frequency oscillation is the common characteristic for the substrates with aldogroup in BZ reactions, as found by Epstein when glyoxylic acid (OCH–COOH) was used as organic substrate in the BZ system [10].

At high acidity, glucose is easily oxidized by BrO_3^- to produce gluconic acid. No low-frequency oscillations appeared at high acidity because most of glucose has been oxidized and there was no enough glucose left for oscillations in the system. Similarly, only low-frequency oscillations occurred at very low acidity because the reaction between glucose and BrO_3^- was very difficult and not enough gluconic acid for high-frequency oscillations accumulated under this condition. As fructose is difficult oxidize like aldosugars, no such dual-frequency oscillations could be observed at low acidity.

3.2. *Dual-frequency oscillations at high acidity*

A typical oscillatory trace for galactose at high acidity is shown in Fig. 3. On addition of the BrO_3^-, the Br^- electrode potential first decreased and then

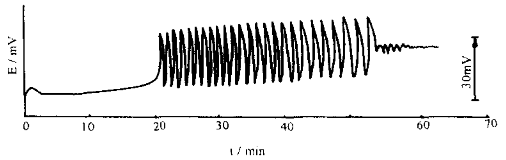

Fig. 3. Dual-frequency oscillation for galactose at high acididy $[\text{galactose}]_0 = 0.040$ M, $[H_2SO_4]_0 = 0.72$ M. Other conditions are given in Fig. 1.

increased almost instantaneously. After a stable period (about 20 min, known as induction period), the system bifurcated into an oscillatory regime where low-frequency and large-amplitude (> 25 mV) oscillations occurred. After about 50 min, the first oscillatory regime disappeared suddenly and was immediately followed by high-frequency and small-amplitude (< 5 mV) oscillations. No transition period was found between those two kinds of oscillations. The second oscillatory region had a short lifetime and only a few oscillating cycles have been observed. The system finally bifurcated to a stable branch again. The induction period (t_{in}) is somewhat similar to the transition period (τ) in Fig. 1. However, they are not exactly the same because of the opposite effects of $[H_2SO_4]_0$ on each of them: τ increased while t_{in} decreased with $[H_2SO_4]_0$ increasing.

Dual-frequency oscillations at high acidity could also be found for glucose, arabinose, lactose and maltose. Typical results are shown in Fig. 4.

The dual-frequency oscillations could be observed only in a narrow range of high acidity, as shown in Table 1. For galactose, such dual-frequency oscillations occurred only in the concentration range (0.18–2.52 M) of H_2SO_4. When $[H_2SO_4] > 2.52$ M, no oscillations appeared; when $[H_2SO_4] < 0.18$ M, another type of dual-frequency oscillations appeared (as discussed above).

In order to understand the mechanism for the dual-frequency oscillations at high acidity, attempts were made to identify the oscillations in the following systems: (a) galactose–BrO_3^-–Mn^{2+}–H_2SO_4; (b) galactose–BrO_3^-–Mn^{2+}–H_2SO_4–N_2 flow; (c) acetone–BrO_3^-–Mn^{2+}–H_2SO_4; (d) BrO_3^-–Mn^{2+}–H_2SO_4–N_2 flow. The results were summarized as follows:

(1) No oscillations occurred in system (a). Excess Br_2 was found in the above system. As there is no active methylene group in saccharides like that in malonic acid, and therefore Br_2 cannot be consumed and removed effectively. Therefore, the oscillations are completely inhibited by excess Br_2 [8].

(2) Within the range of N_2 flow from 85 to 1000 ml/min, no dual-frequency oscillations have been observed in system (b). Only one kind of oscillations, which is similar to the first oscillatory regime in Fig. 3, appeared. Although the decrease of amplitude at the end of the oscillations at lower BrO_3^-

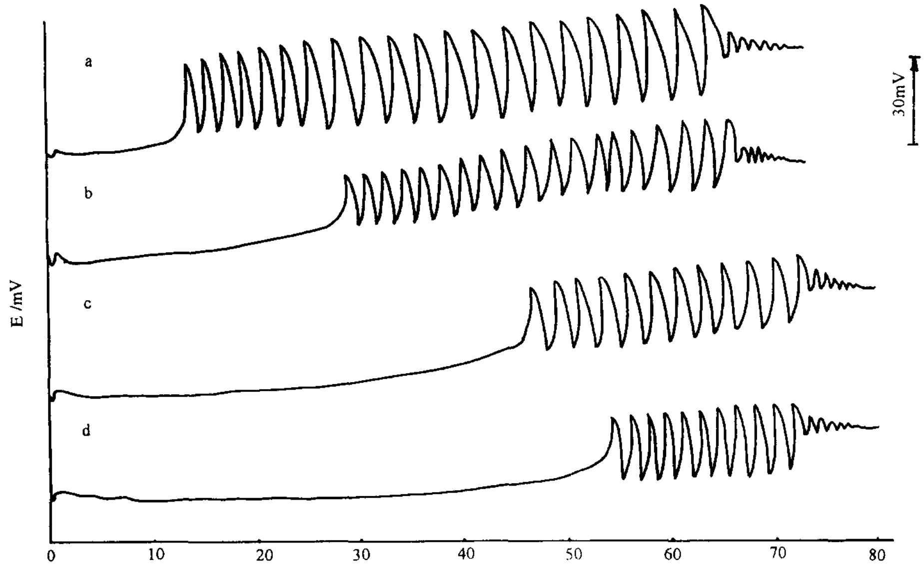

Fig. 4. Dual-frequency oscillations for aldosugars at high acidity: (a) $[\text{glucose}]_0 = 0.050$ M, $[Mn^{2+}]_0 = 0.015$ M, $[H_2SO_4]_0 = 0.40$ M; (b) $[\text{arabinose}]_0 = 0.020$ M, $[Mn^{2+}]_0 = 0.0060$ M, $[H_2SO_4]_0 = 1.08$ M; (c) $[\text{maltose}]_0 = 0.050$ M, $[Mn^{2+}]_0 = 0.10$ M, $[H_2SO_4]_0 = 0.72$ M; (d) $[\text{lactose}]_0 = 0.060$ M, $[Mn^{2+}]_0 = 0.10$ M, $[H_2SO_4]_0 = 0.72$ M. Other conditions are given in Fig. 1.

concentration has been observed [11], it is different from those observed in Figs. 3 and 4. The most striking difference between them is that the amplitude decreased gradually in the system with N_2 flow [11] while the decrease of amplitude decreased suddenly in the systems with acetone. As shown in Figs. 3 and 4, the system jumped from large-amplitude oscillations to small-amplitude ones without a decrease in the amplitude (from about 20 to 5 mV). Therefore it could be concluded that only one kind of oscillatory pattern existed in the system with N_2 flow. The smooth decrease of the amplitude may be caused by the gradual consumption of the reactants. Since the role of N_2 flow is only to remove excess Br_2 [8], the above results indicate that acetone plays the same role as N_2 flow to remove Br_2 during the first oscillatory regime in Fig. 3 [9]. The failure to produce dual-frequency oscillations with N_2 flow instead of acetone in the present system demonstrated that acetone played the key role in the second oscillatory regime in Fig. 3.

(3) System (c) was studied in order to understand the role of acetone in the dual-frequency oscillations in Figs. 3 and 4. Oscillations with small amplitude and long induction period were observed at high concentration of acetone ($[\text{acetone}]_0 > 1.2$ M). A typical oscillatory trace is shown in Fig. 5. The oscillating wave was quite similar to the second one in Fig. 3. High acidity was necessary for system (c) to produce oscillations. Initial concentration of H_2SO_4 should be in the range between 0.20–2.50 M. When $[H_2SO_4]_0 > 2.50$ M or $[H_2SO_4]_0 < 0.20$ M, no oscillations were observed. Although no oscillations were observed when $[\text{acetone}]_0 = 0.27$ M (as used in Figs. 3 and 4), the oscillations similar to Fig. 5 could be observed at high acidity by initially adding small amount (0.050 M) of $BrCH_2COCH_3$ to the system. It was also found that the induction period decreased with increasing $[BrCH_2COCH_3]_0$. Those results demonstrated that the oscillations in the second regime in Fig. 3 resulted from the BrO_3^-–Mn^{2+}–CH_3COCH_3–$BrCH_2COCH_3$–H_2SO_4 system. The second oscillations occurred after a long period because enough $BrCH_2COCH_3$ was essential for this kind of oscillations. This was confirmed because the period could be decreased by adding small amount of $BrCH_2COCH_3$ during the first oscillatory regime in Fig. 3. It is also found that the first kind of oscillations disappeared suddenly upon the onset of the second oscillations, indicating the first oscillations could be inhibited completely by the second ones in Fig. 3. As discussed above, $BrCH_2COCH_3$ could be accumulated during the first oscillatory regime via reaction (1). When enough $BrCH_2COCH_3$ accumulated in the system, the second oscillations similar to those in Fig. 5 occurred, resulting in the sudden disappearance of the first oscillations. Therefore, unlike those observed in the system with N_2 flow, no decrease of amplitude could be observed before the occurrence of the second oscillations in Fig. 3 even at lower BrO_3^- concentration. At low acidity or low $[\text{acetone}]_0$, no oscillations occurred in system (c) due to the failure to produce enough $BrCH_2COCH_3$. High acidity is also necessary in BrO_3^-–Mn^{2+}–CH_3COCH_3–$BrCH_2COCH_3$–H_2SO_4 system to give rise to sustained oscillations because the oxidation–reduction reactions between BrO_3^- and CH_3COCH_3 (or $BrCH_2COCH_3$) are very difficult at low acidity.

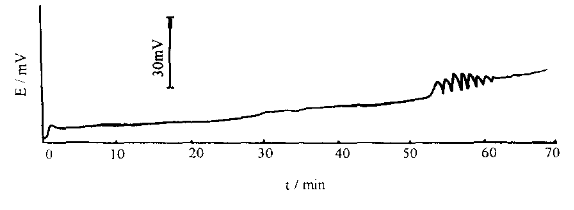

Fig. 5. Oscillation with acetone as the single organic substrate $[\text{acetone}]_0 = 2.2$ M, $[Mn^{2+}]_0 = 0.010$ M, $[H_2SO_4]_0 = 2.40$ M. Other conditions are given in Fig. 1.

(4) As expected, no oscillations in system (d) were observed within the range of N_2 flow rate between 85 and 1000 ml/min, indicating the different functions between N_2 flow and CH_3COCH_3 although they are similar in removing the excess Br_2 during the oscillations in the first regime in Fig. 3.

According to above results, acetone plays an important role for the dual-frequency oscillation at high acidity. On one hand, it couples with galactose, more exactly galactonic acid because most of galactose has been oxidized at such high acidity, to produce the first oscillatory regime (Fig. 3) by removing excess Br_2 just like N_2 flow. On the other hand, acetone acts as a single organic substrate in BZ reaction to give rise to the second oscillatory regime (Fig. 3). Since the high acidity is essential for the oscillation in system (c), no oscillation will occur with acetone as the only organic substrate at low acidity, as shown in the former section.

Ce^{3+} is another widely used metallic catalyst in the classical BZ type oscillators. Although it plays almost the same role as that of Mn^{2+} in those oscillators [2], however no oscillations have been observed in the present system with Ce^{3+} as metallic catalyst. Perhaps, the most important reason is the relatively lower rate in all batch Ce(IV)-saccharides reactions, as observed by Sevcik, etc. [11].

Further studies are being considered to elucidate the reaction mechanism responsible for the dual-frequency oscillations.

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