

A Completely Inorganic BZ-Type Oscillator in a Closed Homogeneous System

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(Received December 26, 1996)

In a batch reactor, an absolutely homogeneous inorganic Belousov–Zhabotinskii (BZ)-type oscillator has been designed in the system of BrO_3^-–$H_2PO_2^-$–Mn^{2+}–$Fe(phen)_3^{2+}$–H_2SO_4. The oscillations of both $[Br^-]$ and $[Mn^{3+}]/[Mn^{2+}]$ as well as $[Fe(phen)_3^{3+}]/[Fe(phen)_3^{2+}]$ were observed by monitoring the changes of either the potential on a bromide electrode or the absorbance at the maximum absorbance wavelength for Mn^{3+} and $Fe(phen)_3^{3+}$, respectively. Both of those two metallic ions are essential in the present system to give rise to the oscillations; their roles in the oscillation are discussed. It is found that Mn^{2+} can not be replaced by other substances, while $Fe(phen)_3^{2+}$ can be replaced by either N_2 flow or acetone. However, it can not be replaced by other metallic ions, including Mn^{2+} and Ce^{3+}. Those results suggest that Mn^{2+} is the real oscillating catalyst for an autocatalytic formation of $HBrO_2$ and $Fe(phen)_3^{2+}$ is a catalyst for the catalytic reduction of Br_2 by $H_2PO_2^-$ to remove any excess Br_2 produced during the oscillations.

In a closed system, essentially all known Belousov–Zhabotinskii (BZ)-type oscillators contain organic substrates,[1—5] which serve as both reducing and brominating agents.[6] In some cases, acetone or N_2 flow is used to remove Br_2 when the organic compound, such as oxalic acid and glucose, is difficult to be brominated.[7—9] Inorganic BZ-type oscillations are observed only in CSTR[10] or in a heterogeneous system in which N_2 flow is bubbled through the solution to remove excess Br_2 in the system.[11] Those oscillations could be observed only in an open system in which some of the physical factors (external conditions), such as the liquid flow rate (k_0), controlled by a pump, or the gas-flow rate controlled by the pressure of the gas, play an important role to give rise to the oscillations. In fact, reductants such as $H_2PO_2^-$, SO_3^{2-}, and AsO_3^{3-} are not essential to give rise to oscillations, since it has been reported that BrO_3^-–Ce^{3+}(Mn^{2+})–H^+ could give rise to oscillations in a CSTR system without any other reductants.[12] We report here on a completely inorganic BZ-type oscillator in which the oscillations could be observed, even in a closed homogeneous system. It is found that the reductant ($H_2PO_2^-$) plays the key role during the oscillations. Unlike the classical BZ-type oscillators, both Mn^{2+} and $Fe(phen)_3^{2+}$ are necessary in the present system. The discovery of new chemical oscillators is of great importance, since it supplies a new way to design more chemical oscillators in a closed system as well as further information for understanding the chemical oscillating mechanism.

Experimental

All of the materials are of analytical grade and used without further purification. $Fe(phen)_3^{2+}$ is prepared by mixing 0.70 g $FeSO_4\cdot 7H_2O$ and 0.50 g phenanthroline (phen) in 100 ml aqueous solution. The experiments are performed in a batch reactor with a constant temperature controlled through a thermostat. The reactants are mixed in the order of H_2O, H_2SO_4, $H_2PO_2^-$, Mn^{2+}, $Fe(phen)_3^{2+}$ and BrO_3^-. The reaction mixture is stirred homogeneously during the reaction by a magnetic stirrer. The oscillations are started by adding BrO_3^- to the reaction mixture. The potential oscillations are monitored with a bromide ion selective electrode (Br^- ISE) against mercury(I) sulfate electrode as a reference, and recorded as E–t curves by an XWT autobalanced potential recorder. The changes in $[Mn^{3+}]/[Mn^{2+}]$ and $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ are observed by measuring the absorbance of Mn^{3+} and $Fe(phen)_3^{3+}$ at 480 and 630 nm (maximum absorbance for Mn^{3+} and $Fe(phen)_3^{3+}$, respectively)[13] by using a HP 8451 A spectrophotometer.

Results and Discussion

Existence of Inorganic Oscillations. The oscillations of $[Br^-]$ were observed by monitoring the potential change on a bromide ion selective electrode in a suitable concentration range of the reactants, as shown in Table 1. A typical potential oscillatory trace is shown in Fig. 1.

After adding bromate to the reaction mixture, the oscillations begin immediately without a common induction period. During the oscillations, the amplitude increased while the frequency quickly decreased. Only a few oscillations (less than 5) have been observed. Once the oscillation comes to completion, it can be restarted by introducing a small amount of NaH_2PO_2, indicating that the oscillations disappear because of the exhaustive consumption of NaH_2PO_2 in the system. Those results also demonstrate that unlike the inorganic oscillators observed in the CSTR system,[10,12] the reductant (NaH_2PO_2) plays a key role to give rise to the oscillations in the present system.

Table 1. The Range of the Reactants' Concentrations for the Oscillations (M)[a]

$[BrO_3^-]_0$	$[H_2PO_2^-]_0$	$[Mn^{2+}]_0$	$[Fe(phen)_3^{2+}]_0$	$[H_2SO_4]_0$
0.030—0.15	0.056	0.010	0.0035	3.6
0.050	0.040—0.12	0.010	0.0035	3.6
0.050	0.056	0.0020—0.032	0.0035	3.6
0.050	0.056	0.010	0.00025—0.0070	3.6
0.050	0.056	0.010	0.0035	2.15—4.30

a) $1\ M = 1\ mol\ dm^{-3}$. Other reaction conditions are given in Fig. 1

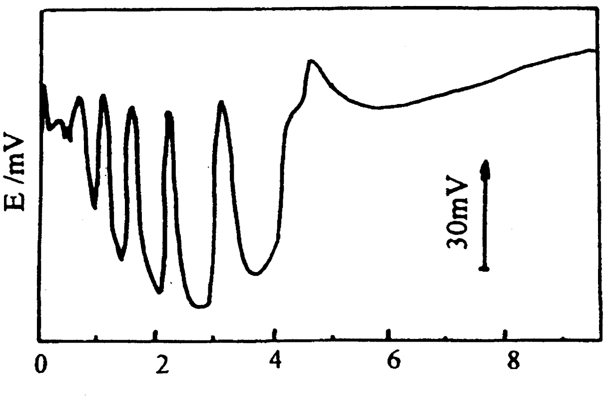

Fig. 1. Typical potential oscillatory trace in inorganic BZ type oscillator. $[BrO_3^-]_0 = 0.050$ M, $[H_2PO_2^-]_0 = 0.056$ M, $[Mn^{2+}]_0 = 0.010$ M, $[Fe(phen)_3^{2+}]_0 = 0.0035$ M, $[H_2SO_4]_0 = 3.60$ M, $V = 50$ ml, $T = 303$ K.

The oscillations in $[Mn^{3+}]/[Mn^{2+}]$ and $[Fe(phen)_3^{3+}]/[Fe(phen)_3^{2+}]$ are also observed by using a UV spectrophotometer, as shown in Fig. 2.

Since phenanthroline (phen) is the only one organic substance which exists in the present system, the role of phen in the oscillations has been investigated in order to prove that the present oscillator is absolutely inorganic. No oscillations have been observed by using phen instead of $Fe(phen)_3^{2+}$ in the above-mentioned system. Also, compared with the standard $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$, no significant structural changes of phen in $Fe(phen)_3^{3+}$ and $Fe(phen)_3^{2+}$ were determined during or after oscillations. Those results indicate that the role of phen in the present system is only a ligand to form $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$, which could adjust the potential of $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ from 0.77 to 1.06 V. The phen does not anticipate any reactions occurring in the oscillations. Those results confirmed that the oscillator reported here is absolutely inorganic.

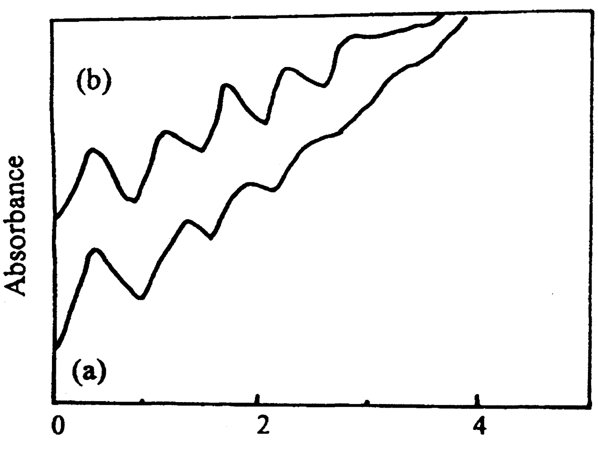

Fig. 2. Oscillations in (a) $[Mn^{3+}]/[Mn^{2+}]$ and (b) $[Fe(phen)_3^{3+}]/[Fe(phen)_3^{2+}]$ by measuring the absorbance at $\lambda_{max,Mn(III)} = 480$ nm and $\lambda_{max,Fe(III)} = 630$ nm, respectively.

Analysis of the Products and the Stoichiometry of the Reaction. The reaction mixture was left for 48 h to allow the reaction to go to completion. The PO_4^{3-} was identified as the only product for $H_2PO_2^-$ during the reaction by a regular chemical analysis. Neither precipitates nor gas bubbles were observed during the oscillations, indicating that the oscillations occurred in an absolutely homogeneous system. The reaction stoichemitric ratio between BrO_3^- and $H_2PO_2^-$ was determined to be 2 : 3 by iodimetry. Therefore, the total reaction could expressed as

$$2BrO_3^- + 3H_2PO_2^- \xrightarrow{Mn^{2+}\text{ and }Fe(phen)_3^{2+}} 3PO_4^{3-} + 6H^+ + 2Br^-, \quad (1)$$

Inhibitors of the Inorganic Oscillations. Similar to those found in the classical BZ-type oscillators,[6] the oscillations in the above-mentioned system could be effectively inhibited by radical scavengers, including acrylonitrile and acrylamide, indicating that the oscillations occur by a free-radical mechanism.[9] Cl^- is also an effective inhibitor to the oscillations, which can be understood by considering the following reaction:[14]

$$Cl^- + HBrO_2 + H^+ \longrightarrow HOCl + HOBr, \quad (2)$$

Effect of the Reactants' Concentrations on the Inorganic Oscillations. Both the oscillating period (t_p) and oscillation lifetime (t_l) change with a variation in the reactants' concentrations. The quantitative relationship between the average t_p, t_l and the reactants' concentrations could be obtained by plotting $\log t_p$ or $\log t_l$ vs. $\log C$. The results are summarized in the following equations:

$$t_p \propto [BrO_3^-]_0^{-1.2}[H_2PO_2^-]_0^{-0.90}[Mn^{2+}]_0^{-0.05} \times [Fe(phen)_3^{2+}]_0^{-0.15}[H_2SO_4]_0^{-2.0}, \quad (3)$$

$$t_l \propto [BrO_3^-]_0^{-0.66}[H_2PO_2^-]_0^{-0.25}[Mn^{2+}]_0^{-1.2} \times [Fe(phen)_3^{2+}]_0^{-0.15}[H_2SO_4]_0^{-4.30}, \quad (4)$$

which could be explained according to the FKN mechanism.[6] As mentioned above, $H_2PO_2^-$ is not sufficient in the above oscillating reaction. Therefore, the oscillation lifetime (t_l) mainly depends on the concentration of $H_2PO_2^-$. Thus, although t_l increases with increasing $[H_2PO_2^-]_0$, t_l decreases along with an increase in the other reactants' concentrations due to a rapid consumption of $H_2PO_2^-$.

Effect of the Reaction Temperature on the Inorganic Oscillations and the Oscillation Activation Energy. The oscillating period (t_p), the amplitude of oscillations (A), the oscillation lifetime (t_l) and the number of oscillations (n) decrease with the reaction temperature increasing, indicating that the rate of the oscillations increases with increasing temperature. A straight line was obtained by plotting $\log t_p$ vs. $(1/T)$, as shown in Fig. 3, where t_p is the average value of the oscillating periods. According to the slope of the straight line and the Arrhenius equation, the average apparent activation energy (E_p) of the oscillations was calculated to be 60.9 kJ mol^{-1}, which is similar to those of the classical BZ-type oscillations.[15]

Controlling Mechanism of the Inorganic Oscillations. The inorganic oscillations are inhibited by adding both Br^- and Ag^+ to the oscillating system. The oscillations are also inhibited by adding both Br_2 and CCl_4 to the above system. Those results are summarized in Fig. 4. Since Ag^+ could remove Br^- in the system through the formation of a AgBr precipitate, and CCl_4 could remove Br_2 through extraction, the above experimental results demonstrate that inorganic oscillations could occur only in a suitable range of both $[Br^-]$ and $[Br_2]$. Therefore, similar to that found in the BZ-type oscillations with oxalic acid and acetone, as coupled organic substrates,[7] the present inorganic oscillations are controlled by both Br^- and Br_2 through the following reactions:

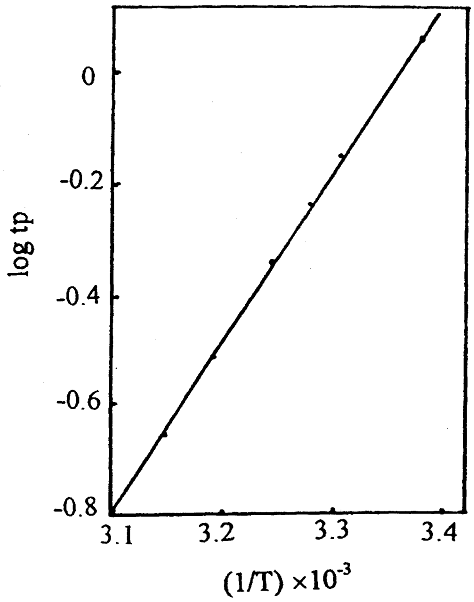

Fig. 3. Dependence of oscillating period (t_p) on the reaction temperature (T). The reaction conditions are the same as given in Fig. 1.

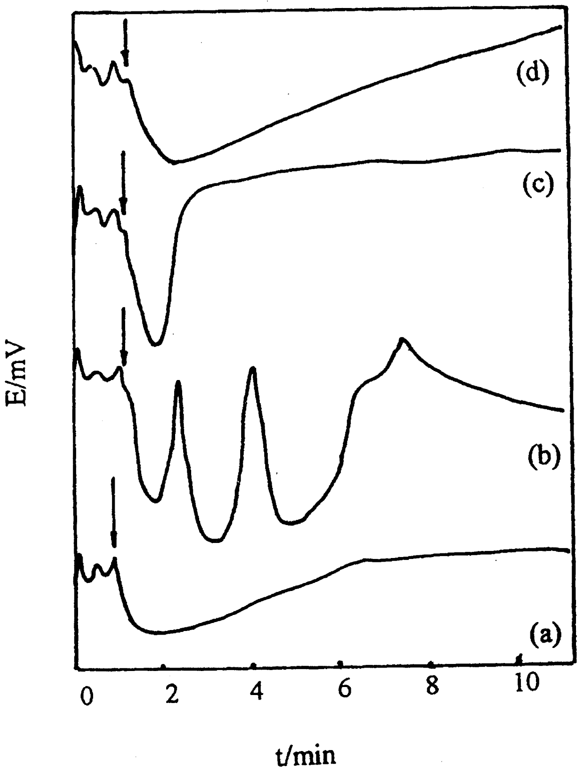

Fig. 4. Inhibitions on the inorganic oscillations by adding (a) 0.50 ml Br_2, (b) 1.0 ml, 0.010 M KBr, (c) 1.0 ml, 0.010 M $AgNO_3$, and (c) 5.0 ml CCl_4 during the oscillating period. The reaction conditions are the same as given in Fig. 1.

$$Br^- + HBrO_2 + H^+ \longrightarrow 2HOBr, \quad (5)$$

$$Br_2 + HBrO_2 + H_2O \longrightarrow 3HOBr. \quad (6)$$

Thus, the Br_2-hydrolysis controlling model[7] based on a revised FKN mechanism is also suitable for inorganic oscillating reactions.

Analysis of the Roles of Two Metallic Ions in Inorganic Oscillations. Both Mn^{2+} and $Fe(phen)_3^{2+}$ are well-known catalysts used in classical BZ-type oscillators.[1] During the oscillations, the metallic ion is oxidized in an autocatalytic formation of $HBrO_2$ and reduced by a brominated organic substrate in which Br^- is generated. The oxidation-reduction cycle is described by the Oregonator Model:[16]

$$BrO_3^- + HBrO_2 + 3H^+ + 2M^{n+} \longrightarrow 2HBrO_2 + 2M^{(n+1)} + H_2O, \quad (7)$$

$$M^{(n+1)+} + BrOrg \longrightarrow M^{n+} + fBr^- + P, \quad (8)$$

where M is the metallic ion, known as an oscillating catalyst, BrOrg is a brominated organic substrate, P is an oxidized organic product, and f is the reaction coefficient, which is between 0.5—1.

In order to understand the roles of Mn^{2+} and $Fe(phen)_3^{2+}$ in the above system, oscillations were tested in the following systems:

(a) BrO_3^-–$H_2PO_2^-$–Mn^{2+}–H_2SO_4; (b) BrO_3^-–$H_2PO_2^-$–$Fe(phen)_3^{2+}$-H_2SO_4; (c) BrO_3^-–$H_2PO_2^-$–acetone–Mn^{2+}–H_2SO_4; (d) BrO_3^-–$H_2PO_2^-$–acetone– $Fe(phen)_3^{2+}$–H_2SO_4; (e) BrO_3^-–$H_2PO_2^-$–N_2–Mn^{2+}–H_2SO_4; (f) BrO_3^-

$-H_2PO_2^-$–Ce^{3+}–$Fe(phen)_3^{2+}$–H_2SO_4; (g) BrO_3^-–$H_2PO_2^-$–Mn^{2+}–Ce^{3+}–H_2SO_4. The results are summarized as follows:

(i) No oscillations were observed in systems (a) and (g). Excess bromine was released during the reaction. The reaction between BrO_3^- and $H_2PO_2^-$ was an autocatalytic reaction in which Br_2 was formed through the following reactions:

$$2BrO_3^- + 3H_2PO_2^- \longrightarrow 2Br^- + 3PO_4^{3-} + 6H^+, \quad (9)$$

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O, \quad (10)$$

The oscillations inhibited because of the rapid autocatalytic accumulation of bromine in the above systems.[7]

(ii) Also, no oscillations were found in systems (b), (f), and (d). However, unlike systems (a) and (g), no significant Br_2 was released during the reactions.

(iii) Oscillations were observed in system (c). A typical oscillatory trace is shown in Fig. 5.

(iv) Oscillations were also observed in system (e).[11]

The above results demonstrate that in the present oscillator (Fig. 1) the roles of the two metallic ions in the oscillations are quite different. Mn^{2+} is necessary for the above oscillations, and can not be replaced by any other materials. (It is not clear why Mn^{2+} can not be replace by Ce^{3+} in the present oscillator because the roles played by them are almost the same in the classical BZ oscillators). Therefore, it is a real oscillating catalyst. The periodic changes in $[Mn^{3+}]/[Mn^{2+}]$ (Fig. 2) could be explained according to the following reactions:

$$BrO_3^- + HBrO_2 + 3H^+ + 2Mn^{2+} \longrightarrow 2HBrO_2 + 2Mn^{3+} + H_2O, \quad (11)$$

$$4Mn^{3+} + H_2PO_2^- + 2H_2O \longrightarrow 4Mn^{2+} + PO_4^{3-} + 6H^+. \quad (12)$$

$Fe(phen)_3^{2+}$ can be replaced by either acetone or N_2 flow. However, it can not be replaced by other metallic ions, including Mn^{2+} and Ce^{3+}. Because acetone could be used as a brominating agent to remove excess bromine in the oscillations when the organic substrate is unable to do so,[7]

$$Br_2 + CH_3COCH_3 \longrightarrow BrCH_2COCH_3 + Br^- + H^+, \quad (13)$$

it can be concluded that the main role played by $Fe(phen)_3^{2+}$ in the inorganic oscillations is to remove any excess bromine

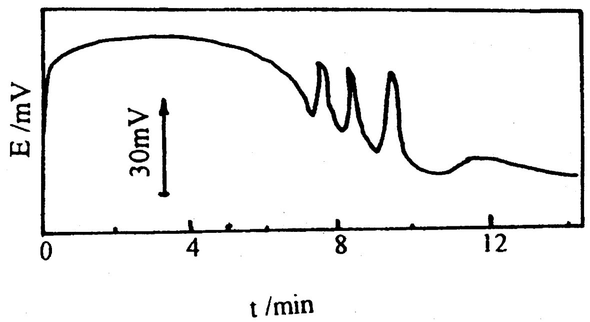

Fig. 5. Oscillatory trace by using acetone instead of $Fe(phen)_3^{2+}$. $[Fe(phen)_3^{2+}]_0 = 0$, $[acetone]_0 = 1.20$ M, Other conditions are given in Fig. 1.

in the system by catalyzing the reaction between Br_2 and $H_2PO_2^-$. A possible mechanism is expressed as follows:

$$Br_2 + 2Fe(phen)_3^{2+} \longrightarrow 2Br^- + 2Fe(phen)_3^{3+}, \quad (14)$$

$$4Fe(phen)_3^{3+} + H_2PO_2^- + 2H_2O \longrightarrow 4Fe(phen)_3^{2+} + PO_4^{3-} + 6H^+, \quad (15)$$

$$2Br_2 + H_2PO_2^- + 2H_2O \longrightarrow 4Br^- + PO_4^{3-} + 6H^+, \quad (16)$$

The catalytic effect of $Fe(phen)_3^{2+}$ in the above reactions has been studied by following the absorbance change of Br_2 at 400 nm with time during a reaction in the Br_2–$H_2PO_2^-$–H_2SO_4 system. The pseudo-first-order rate constant for the uncatalyzed consumption of Br_2 was found to be $5.0\times10^{-4}\ s^{-1}$. In the presence of $Fe(phen)_3^{2+}$, k_{Br_2} greatly increased (about $8.9\times10^{-3}\ s^{-1}$), which is quite similar to that found in the classical BZ-type oscillation ($1.0\times10^{-2}\ s^{-1}$).[6] However, no significant promoting effect on the consumption of Br_2 has been found in the presence of Mn^{2+} or Ce^{3+}. This result can be explained according to their E° values. Since $E^\circ_{Mn^{3+}/Mn^{2+}} > E^\circ_{Br_2/Br^-}$, Mn^{2+} can not be oxidized by Br_2. Thus, Mn^{2+} can be oxidized only in the autocatalytic formation of $HBrO_2$ (Eq. 7). Because $[Br_2]$ changes periodically during inorganic oscillations, the oscillations in $[Fe(phen)_3^{3+}]/[Fe(phen)_3^{2+}]$ could also be observed, as shown in Fig. 2.

Although $Fe(phen)_3^{2+}$ plays a similar role to that of acetone in removing any excess Br_2 produced during oscillations, the following experimental results show the differences between them:

(1) As discussed above, the mechanisms for the consumption of Br_2 with acetone and $Fe(phen)_3^{2+}$ are different.

(2) As shown in Fig. 2, $[Fe(phen)_3^{2+}]$ changes periodically during the oscillations, while no oscillations in [acetone] have been observed and reported so far.

(3) Oscillations in BrO_3^-–Mn^{2+}–acetone–H_2SO_4 have been observed in a closed system,[17] while no oscillations in BrO_3^-–Mn^{2+}–$Fe(phen)_3^{2+}$–H_2SO_4 have been observed, regardless of the reactants' concentrations.

The Role of $H_2PO_2^-$ in the Inorganic Oscillations. As discussed above, the role of $H_2PO_2^-$ in the above-mentioned oscillations is very important. On one hand, it reduces the metallic ions at a high oxidative state through reactions (12) and (15), which results in a regeneration of the metallic catalysts. On the other hand, it reduces Br_2 catalyzed by $Fe(phen)_3^{2+}$ through the reaction (16), which results in the consumption of Br_2 and the regeneration of Br^-. Besides NaH_2PO_2, many inorganic and organic reductants, such as SO_3^{2-}, ascorbic acid, glucose, α-hydroxy acids, α-amino acids, and even peptides, could be used instead of NaH_2PO_2 in the above system to give rise to sustained oscillations in a batch reactor. A typical oscillatory trace with serine as an organic substrate is shown in Fig. 6. A suitable reduction rate seems to be essential for the occurrence of sustained oscillations. Therefore, oscillations in the present system could be observed only within the concentration range of NaH_2PO_2

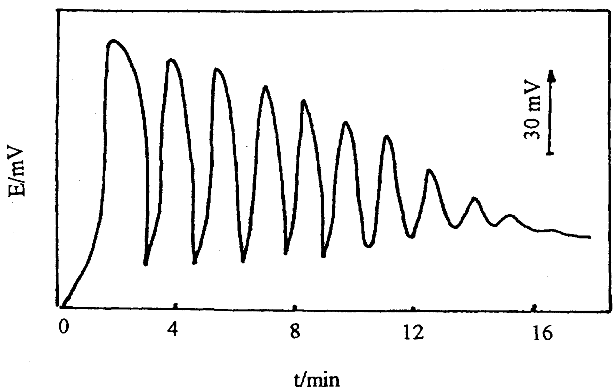

Fig. 6. Oscillatory trace in BZ type oscillator with serine as the substrate. $[BrO_3^-]_0$=0.040 M, $[\text{serine}]_0$=0.011 M, $[Mn^{2+}]_0$=0.0090 M, $[Fe(phen)_3^{2+}]_0$=0.0035 M, $[H_2SO_4]_0$= 2.16 M, V=50 ml, T=294 K.

listed in Table 1. No oscillations could be observed because the reduction rate is extremely slow when $[NaH_2PO_2]$ is less than 0.040 M (1 M=1 mol dm^{-3}) or the reduction rate is too fast when $[NaH_2PO_2]$ is more than 0.12 M. It was also found that $Fe(phen)_3^{2+}$ could not be replaced by some other reductants, such as Fe^{2+}, Sn^{2+}, and BH_4^- because of the unsuitable reduction rate.

Conclusions

A first BZ-type inorganic oscillator was designed in a closed homogeneous system by using NaH_2PO_2 as the single substrate and Mn^{2+} and $Fe(phen)_3^{2+}$ as coupled metallic catalysts. Those substances are essential, and play different roles in the present inorganic oscillations. The oscillating phenomena can be explained on the basis of the Br_2-hydrolysis controlling model proposed by Field etc.[7] The above results give a new way to design more BZ-type oscillators. Further studies on other oscillations are being considered.

We are grateful to the Nature Science Funds of Shanghai Academy of Science of China for providing financial support for this study.

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