A Novel Way to Design Belousov-Zhabotinskii Oscillators

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A new method has been developed to design BZ type oscillators. A lot of new BZ oscillators including inorganic oscillators and oscillators with amino acids and some peptides as substrates have been obtained by this way.

The Belousov-Zhabotinskii (BZ) reaction is the most studied chemical oscillator.[1] Essentially all known oscillators in the batch reactor contain one or several organic substrates which serve as both the reducing and brominating agents.[2] Either acetone or N_2 flow is necessary when the substrate is difficult to be brominated. We report here a new way to design BZ type oscillators in the closed homogeneous system, in which both Mn^{2+} and $Fe(phen)_3^{2+}$ are necessary to give rise to oscillations. By this method, more BZ type oscillators including the inorganic oscillators and the oscillators with amino acids and even some peptides as the single substrate in the closed homogeneous system have been designed. In the conventional BZ reactions so far reported, these substrates can not give rise to sustained oscillations without the help of acetone or N_2 flow.

The fundamental composition of the new type oscillators is BrO_3^-, Mn^{2+}, $Fe(phen)_3^{2+}$, H_2SO_4 and the substrate. The reactions are performed in a batch reactor and stirred homogeneously by a magnetic stirrer. Those substrates are summarized in the following:

1. Almost all the organic substances used in the conventional BZ reactions could be used in our system to produce oscillations.
2. The first inorganic BZ oscillator in the closed homogeneous system has been designed in our system with NaH_2PO_2 as substrate. A typical oscillatory trace measured by bromide ion selective electrode against mercurous sulfate electrode as the reference is shown in Figure 1.

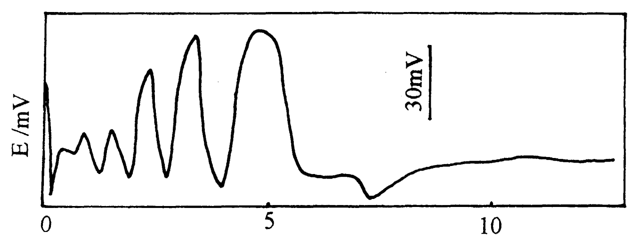

Figure 1. Inorganic BZ oscillation.Conditions: $[BrO_3^-]$=0.050 M, $[H_2PO_2^-]$=0.040 M, $[Mn^{2+}]$=0.0030 M, $[Fe(phen)_3^{2+}]$=0.0050 M, $[H_2SO_4]$=2.0 M, T=303 ± 0.1 K.

3. Some organic compounds, such as ascorbic acid, saccharides, which could not be used as substrates in the conventional BZ oscillators, can give rise to sustained oscillations in our system. By this method almost all the amino acids including glycine(Gly), aspartic acid(Asp), glumatic acid(Glu), alanine(Ala), threonine(Thr), cystine(Cys), tryptophan(Try), tyrosine(Tyr), serine(Ser), methionine(Met) and peptides including glycine-glycine(GGP), glumatic acid-cystine(GCP), glycine-alanine(GAP) could be used as organic substrates in our system to produce oscillations.This is very important to establish the relationship between chemical oscillations and the periodical phenomena in biological system because those substances are essential in the living materials. Typical oscillating traces for alanine and glycine-glycine peptide are shown in Figure 2 and 3. The characters of the oscillations for the above substrates were summarized in Table 1.

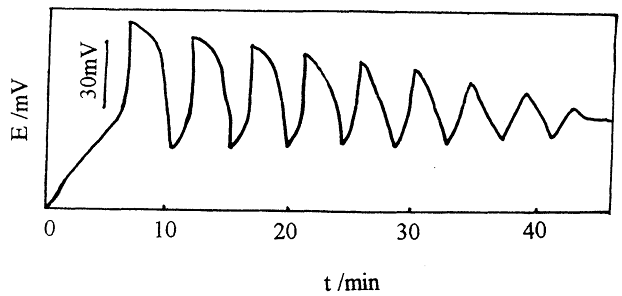

Figure 2. Oscillatory trace for alanine. Conditions: $[BrO_3^-]$ = 0.050 M, [alanine]=0.040 M, $[Mn^{2+}]$=0.0090 M, $[Fe(phen)_3^{2+}]$= 0.0010 M, $[H_2SO_4]$=2.0 M, T=298 ± 0.1 K.

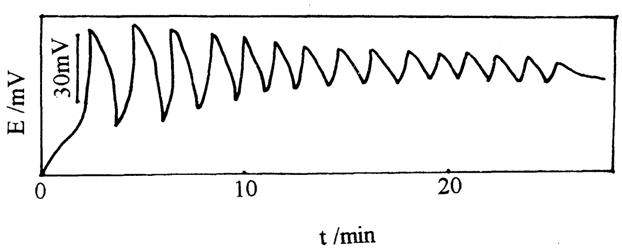

Figure 3. Oscillatory trace for glycine-glycine peptide(GGP). Condition: $[BrO_3^-]$=0.025 M, [GGP]=0.040 M, $[Mn^{2+}]$= 0.0090 M, $[Fe(phen)_3^{2+}]$=0.0010 M, $[H_2SO_4]$=0.98 M, T=308 ± 0.1 K.

The features of the present new type of BZ oscillations are similar to those found in the conventional BZ oscillators. For example, the oscillations are inhibited effectively either by Cl^- or by acrylonitrile; the oscillations are controlled by both Br_2 and Br^-; the oscillations can be observed on both bromide ion selective

Table 1. Characters of oscillations for different substrates[a]

Substrate	Oscillation lifetime/min	Number of oscillation
Gly	19	5
Asp	55	15
Glu	14	4
Ala	45	9
Thr	46	10
Cys	25	7
Try	19	7
Tyr	56	23
Ser	32	11
Met	28	12
GGP	27	15
GCP	35	19
GAP	43	14

[a]Reaction conditions: For amino a cids, $[BrO_3^-]$ = 0.050 M, $[H_2SO_4]$ = 2.0 M, T = 298 ± 0.1 K; For peptides, $[BrO_3^-]$ = 0.025 M, $[H_2SO_4]$= 0.98 M, T=3 08 ± 0.1 K. [substrates] = 0.040 M. Other conditions are given in Figure 2.

electrode and Pt electrode, indicating that the concentration of the catalyst changes periodically during the reaction; the oscillating patterns are changed with the variation of stirring rate, the initial concentrations of reactants or the total volume of the reaction mixture; the activation energies have been calculated according to the effect of reaction temperature on the above oscillations which fall within the range characteric for the conventional BZ oscillations—between 65 and 75 kJ/mol.[3] Those results strongly demonstrate that the fundamental mechanism for the present type of BZ oscillations can be explained according to FKN mechanism,[2] a mechanism generally accepted for the conventional BZ oscillations.

Perhaps the most difficult problems are how to explain the consumption of Br_2 and regeneration of Br^- as well as the roles of the two metallic ions in our system. Unlike the conventional BZ oscillators, no bromination occurs in our systems because usually no brominating agents like malonic acid exist in the systems, as shown in Figure 1, 2, and 3. Therefore, the consumption of Br_2 in above systems is carried out mainly through the chemical reduction of Br_2 by the substrates which also results in the regeneration of Br^-. The reaction could be expressed in the following:

$$Br_2 + H_2PO_2^- + H_2O \longrightarrow 2Br^- + HPO_3^{2-} + 3H^+ \quad (1)$$

According to the analysis using a UV spectrophotometer, the concentrations of both two metallic ions (Mn^{2+} and $Fe(phen)_3^{2+}$) change periodically during the reaction. Mn^{2+} is essential in above oscillations while $Fe(phen)_3^{2+}$ can be replaced by either acetone or N_2 flow. We guess that Mn^{2+} is the necessary catalyst in above oscillation and $Fe(phen)_3^{2+}$ acts to remove excess Br_2 in the system and regenerate Br^- by catalyzing the reduction of Br_2. A pausible mechanism with $H_2PO_2^-$ as substrate is described as follows:

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

$$2Fe(phen)_3^{3+} + H_2PO^- + H_2O \longrightarrow 2Fe(phen)_3^{2+} + HPO_3^{2-} + 3H^+ \quad (3)$$

The catalytic effect of the metallic ions on the reduction of Br_2 has been studied by following the absorbance change of Br_2 at 400nm with the time. The pseudo-first-order rate constant (k_{obs}) for above reaction is 5.0×10^{-4} s^{-1}. In the presence of $Fe(phen)_3^{2+}$, k_{obs} increases to about 8.9×10^{-3} s^{-1} which is quite similar to that found in the conventional BZ oscillators (1.0×10^{-2} s^{-1}).[2] However, no significant promoting effect of Mn^{2+} on reaction(1) has been found suggesting that there is no catalytic effect of Mn^{2+} on above reaction. Those results can be understood by considering their E° values. As $E°_{Mn^{3+}/Mn^{2+}} > E°_{Br_2/Br^-} > E°_{Fe(phen)_3^{3+}/Fe(phen)_3^{2+}}$, $Fe(phen)_3^{2+}$ is easy to be oxidized by Br_2. However because Mn^{2+} can not be oxidized by Br_2, the catalytic reaction like reaction(2) is thermodynamically impossible.

The BZ reactions with two kinds of metal catalysts, such as Ce^{3+} and ferroin, is popular. The different metals in BZ oscillations play the same roles as the catalysts in the autoformation of $HBrO_2$. Therefore anyone of them can be omitted or replaced by other metallic ion, for example, either Ce^{3+} or ferroin can be replaced by Mn^{2+}. However the situation in our system is different because the roles of Mn^{2+} and ferroin are different as discussed above. Neither Mn^{2+} and ferroin can be omitted or replaced by other metallic ions.

Further studies are undertaken in our laboratory to supply more examples of the new type BZ oscillators and elucidate their mechanism.

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References and Notes

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