Oscillations in Belousov-Zhabotinsky system with acetone/cyclohexanone as the organic substrate

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Oscillations are observed at 50 ± 0.1°C in the following systems where acetone/cyclohexanone is the sole organic substrate and no organic acid or saccharide is necessary.

(i) acetone + Mn^{2+} + BrO_3^- + H_2SO_4
(ii) acetone + Ce^{4+} + BrO_3^- + H_2SO_4
(iii) cyclohexanone + Mn^{2+} + BrO_3^- + H_2SO_4
(iv) cyclohexanone + Ce^{4+} + BrO_3^- + H_2SO_4

Results and discussion

Typical results for all the four systems are plotted in Fig. 2. Oscillations are observed in all these systems. The evidence is unequivocal.

We may examine by computer simulation studies as to how oscillations are observed with acetone alone at higher temperatures. For this purpose we consider the reaction sequence shown in Scheme 1.

A + Y = X + P
X + Y = 2P
A + X = 2X + Z
X + X = P + A
Ac + Z = inert product
Ac + P = Y
P + Y = W
Ac + W = Y

Scheme 1

By increasing the temperature, the rate of oxidation of acetone can be enhanced and it is expected that under such conditions the system can oscillate. This idea has now been tested for the following systems: (i) acetone + Mn^{2+} + BrO_3^- + H_2SO_4; (ii) acetone + Ce^{4+} + BrO_3^- + H_2SO_4; (iii) cyclohexanone + Mn^{2+} + BrO_3^- + H_2SO_4; and (iv) cyclohexanone + Ce^{4+} + BrO_3^- + H_2SO_4.

Experimental

Acetone (G R, E Merck) and manganese(II) sulphate monohydrate (E Merck) were used as received. Oscillations were monitored in a manner as described earlier.
where \( X = \text{HBrO}_2 \), \( Y = \text{Br}^- \), \( Z = 2\text{Ce}^{4+} \), 
\( P = \text{HOBr} \), \( W = \text{Br}_2 \), \( A = \text{BrO}_3^- \), and \( \text{Ac} = \text{acetone} \).

Taking \( \text{HBrO}_2 \), \( \text{Ce}^{4+} \), \( \text{Br}^- \), \( \text{HOBr} \) and \( \text{Br}_2 \) as intermediates, we obtain the kinetic equations (D1-D5) for the respective species.

\[
\frac{dX}{dt} = k_1AY - k_2XY + k_3AX(C-Z)/C - 2k_4X^2
\]

(D1)

\[
\frac{dY}{dt} = -k_1AY - k_2XY + k_5P - k_5PY + k_8W/(1 \times 10^{-7} + W)
\]

(D2)

\[
\frac{dZ}{dt} = k_3AX(C-Z)/Z - k_5Z
\]

(D3)

\[
\frac{dP}{dt} = k_1AY + 2k_2XY + k_4X^2 - k_8P - k_5PY + k_8W
\]

(D4)

\[
\frac{dW}{dt} = k_5PY - k_{-7}W - k_{6}W/(1 \times 10^{-7} + W)
\]

(D5)

where \( C \) is total cerium and \( k_1, k_2, k_3, k_4, k_5, k_6, k_7 \) and \( k_8 \) are the rate constants for first and subsequent steps respectively and \( k_{-7} \) is the rate constant of backward reaction of 7th step.

Numerical solutions of kinetic equations (D1-D5) were obtained using the value of parameters as given in Table 1 and the subroutine9 STIFF3. Calculations have been made for different values of \( k_5 \) and \( k_6 \).

If we compare the mechanism in Scheme 1 with bromine-hydrolysis controlled (BHC) model due to Field and Boyd1, we find that the two differ in respect of step (5) and step (6). It may be noted that the experiments reported in the present communication have been performed at 50°C. The rate constants of various steps are likely to change. However, since the energies of activation of bond breaking and bond formation reaction are usually considerably larger than those for the ionic reactions, we may assume that only the energies of activation of step (5) and step (6) would be material. We tried to assess the range of \( k_5 \) and \( k_6 \) values between which oscillations are possible by computer analysis by assigning the rate constants as given in Table 1 for other steps. Results are given in Fig. 3 for \( k_5 \)-\( k_6 \) space. When \( k_5 \) corresponds to the value at 25°C (6.0 \( \times \) 10\(^{-4} \) s\(^{-1} \)) as observed experimentally, no oscillations are observed. However, when there is 8 to 10 times increase in \( k_5 \) which would certainly occur at 50°C, os-

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Numerical values of parameters* used in computation</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 4.5 \text{ M}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 4.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>( 6.3 \times 10^7 \text{ M}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>( 3.0 \times 10^7 \text{ M}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_7 )</td>
<td>( 1.2 \times 10^6 \text{ M}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{-7} )</td>
<td>( 110.0 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( k_5 )</td>
<td>( 2.84 \times 10^{-8} \text{[acetone]} )</td>
</tr>
<tr>
<td>( [\text{H}^+] )</td>
<td>( 1.5 \text{ M} )</td>
</tr>
<tr>
<td>( [\text{BrO}_3^-] )</td>
<td>( 7.14 \times 10^{-2} \text{ M} )</td>
</tr>
<tr>
<td>( [\text{acetone}] )</td>
<td>( 3.4 \text{ M} )</td>
</tr>
<tr>
<td>Total cerium (IV)</td>
<td>( 1.5 \times 10^{-3} \text{ M} )</td>
</tr>
</tbody>
</table>

*Values of parameters \( k_1, k_2, k_3 \), and \( k_{-7} \) are due to Field and Försterling10. Value of \( k_5 \) is due to Duobois et al.11.

Fig. 2—Oscillations in redox potential (I) and Br\(^-\) potential (II) [System: (a) Acetone (3.4 M) + Ce\(^4+\) (1.5 \( \times \) 10\(^{-3} \) M) + \text{KBrO}_3 (7.14 \( \times \) 10\(^{-2} \) M) + H\(_2\)SO\(_4\) (1.5 M); (b) acetone (3.4 M) + Mn\(^{2+}\) (1.57 \( \times \) 10\(^{-3} \) M) + \text{KBrO}_3 (7.14 \( \times \) 10\(^{-2} \) M) + H\(_2\)SO\(_4\) (1.5 M); (c) cyclohexanone (0.16 M) + Ce\(^4+\) (1.5 \( \times \) 10\(^{-3} \) M) + \text{KBrO}_3 (7.14 \( \times \) 10\(^{-2} \) M) + H\(_2\)SO\(_4\) (1.5 M); and (d) cyclohexanone (0.16 M) + Mn\(^{2+}\) (1.57 \( \times \) 10\(^{-3} \) M) + \text{KBrO}_3 (7.14 \( \times \) 10\(^{-2} \) M) + H\(_2\)SO\(_4\) (1.5 M); temperature = 50 \( \pm \) 0.1°C]
NOTES

oscillations appear. We actually observe oscillations at higher temperatures as experiments reported here reveal.

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References

6 Field R J, in reference 1, p. 72.

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Fig. 3—Plot of log $k_s$ versus log $k_6$ showing oscillatory and non-oscillatory regions based on computer simulation. ([Acetone] = 3.4 $M$, [BrO$_2$] = $7.14 \times 10^{-2}$ $M$)