

Notes

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

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Oscillations are observed at $50 \pm 0.1^\circ\text{C}$ 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

Computer calculations lead to the conclusion that this would be so. Simulations also predict steady state at lower temperatures in agreement with experimental results.

Belousov-Zhabotinskii (B-Z) reaction system with mixed organic substrates (organic reductant + ketone) has been the subject of detailed study during recent years¹⁻⁴. Since acetone can also act as reductant, it was thought to investigate the title system in detail. Earlier reports about oscillations in BrO_3^- + Mn^{2+} + H_2SO_4 + acetone system are conflicting. Stroot and Janjic⁵ have reported oscillations with 5 molar acetone. These are not convincing. However, such oscillations have not been confirmed by Noszticzius⁶. Nevertheless, oscillations for systems containing fluoroacetone, cyclohexanone and other ketones have been reported^{5,7-8}. At lower temperature, the rate of oxidation of acetone is slow, hence the system does not oscillate and an additional organic or inorganic reductant is necessary. By increasing the temperature, the rate of oxidation 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 earlier².

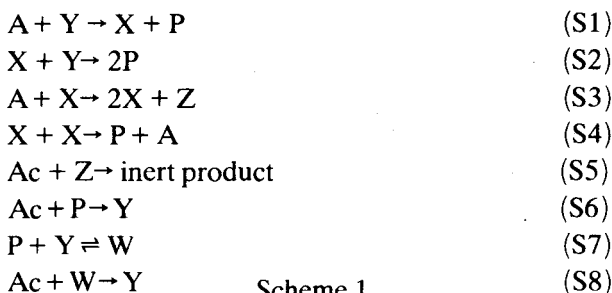
Experiments were performed in a specially designed cell (see Fig. 1). A condenser was attached to the cell as shown in Fig. 1 to prevent evaporation of acetone at higher temperature. Stirring was achieved magnetically and the reaction cell was thermostated ($50 \pm 0.1^\circ\text{C}$).

Kinetics of oxidation of acetone by Ce^{4+} at 25°C was investigated spectrophotometrically. The rate constant was estimated to be $6.0 \times 10^{-4} \text{ s}^{-1}$.

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.



Scheme 1

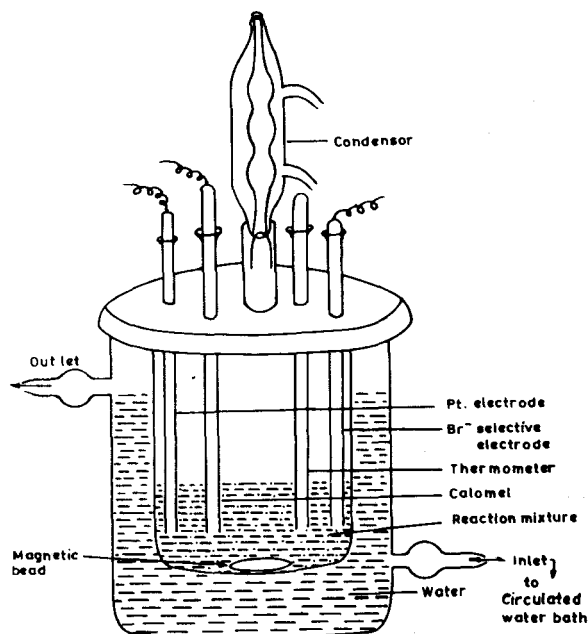


Fig. 1 - Schematic diagram of the reaction cell

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 HBrO_2 , Ce^{4+} , Br^- , HOBr and Br_2 as intermediates, we obtain the kinetic equations (D1-D5) for the respective species.

$$\frac{dX}{dt} = k_1AY - k_2XY + k_3AX(C-Z)/C - 2k_4X^2 \quad (\text{D1})$$

$$\frac{dY}{dt} = -k_1AY - k_2XY + k_6P - k_7PY + k_{-7}W + k_8W/(1 \times 10^{-7} + W) \quad (\text{D2})$$

$$\frac{dZ}{dt} = k_3AX(C-Z)/Z - k_5Z \quad (\text{D3})$$

$$\frac{dP}{dt} = k_1AY + 2k_2XY + k_4X^2 - k_6P - k_7PY + k_{-7}W \quad (\text{D4})$$

$$\frac{dW}{dt} = k_7PY - k_{-7}W - k_8W/(1 \times 10^{-7} + W) \quad (\text{D5})$$

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 Boyd³, 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 ($6.0 \times 10^{-4} \text{ s}^{-1}$) 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-

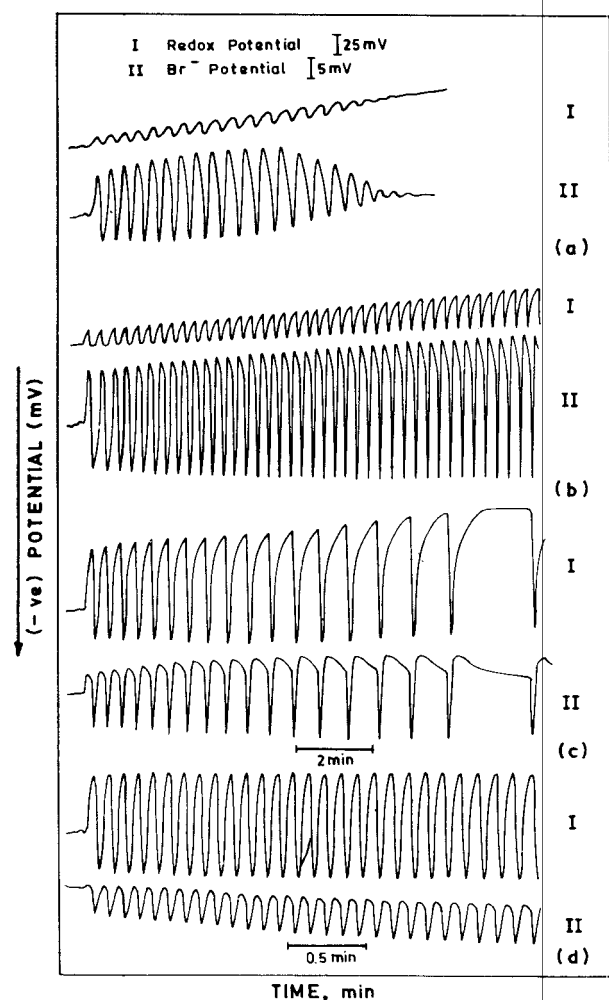


Fig. 2—Oscillations in redox potential (I) and Br^- potential (II) [System: (a) Acetone (3.4 M) + Ce^{4+} ($1.5 \times 10^{-3} \text{ M}$) + KBrO_3 ($7.14 \times 10^{-2} \text{ M}$) + H_2SO_4 (1.5 M); (b) acetone (3.4 M) + Mn^{2+} ($1.57 \times 10^{-3} \text{ M}$) + KBrO_3 ($7.14 \times 10^{-2} \text{ M}$) + H_2SO_4 (1.5 M); (c) cyclohexanone (0.16 M) + Ce^{4+} ($1.5 \times 10^{-3} \text{ M}$) + KBrO_3 ($7.14 \times 10^{-2} \text{ M}$) + H_2SO_4 (1.5 M); and (d) cyclohexanone (0.16 M) + Mn^{2+} ($1.57 \times 10^{-3} \text{ M}$) + KBrO_3 ($7.14 \times 10^{-2} \text{ M}$) + H_2SO_4 (1.5 M); temperature = $50 \pm 0.1^\circ\text{C}$]

Table 1—Numerical values of parameters* used in computation

Parameter	Value
k_1	$4.5 \text{ M}^{-1} \text{ s}^{-1}$
k_2	$4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
k_3	$6.3 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$
k_4	$3.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
k_7	$1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
k_{-7}	110.0 s^{-1}
k_8	$2.84 \times 10^{-5} [\text{acetone}] [\text{H}^+] \text{ M}^{-1} \text{ s}^{-1}$
$[\text{H}^+]$	1.5 M
$[\text{BrO}_3^-]$	$7.14 \times 10^{-2} \text{ M}$
[acetone]	3.4 M
Total cerium (IV)	$1.5 \times 10^{-3} \text{ M}$

*Values of parameters k_1 - k_4 , k_7 and k_{-7} are due to Field and Försterling¹⁰. Value of k_8 is due to Duobois *et al.*¹¹

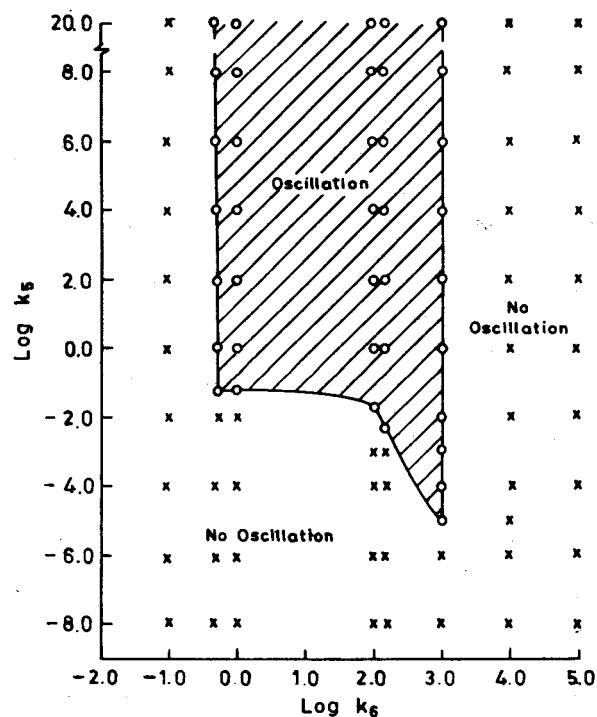


Fig. 3—Plot of $\log k_5$ versus $\log k_6$ showing oscillatory and non-oscillatory regions based on computer simulation. ([Acetone] = 3.4 M, $[\text{BrO}_3^-] = 7.14 \times 10^{-2}$ M)

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

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