

Chemical Waves in Ferriin-Bromate System

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Velocities of propagation of one-dimensional and two-dimensional phase waves have been measured in ferriin-bromate system as a function of $[\text{BrO}_3^-]$ and $[\text{H}^+]$. The wave velocity (v) in both the cases is given by the relation $v = Ae^{-E_a/RT}$ where A for one-dimensional and two-dimensional cases is different, and E_a is the apparent energy of activation, which is the same for both the cases. Experiments in continuously stirred tank reactor show that the reaction medium is oscillatory. Temporal oscillations are obtained in the system within a definite range of flow rates. Results have been discussed in terms of Field-Körös-Noyes mechanism.

Chemical waves have been investigated in the systems: (I) bromate + ferriin + organic substrate + H_2SO_4 (ref. 1) and (II) bromate + Ce^{4+} (or Mn^{2+}) + ferriin + organic substrate + H_2SO_4 (refs 2, 3). Such waves in chlorate⁴ and iodate⁵ driven oscillators have also been reported. The two-component system, has acquired considerable interest from the view-point of simplicity. Showalter studied chemical waves in the ferriin + bromate + cyclohexane dicarboxylic acid system⁶ which essentially belongs to type-I system mentioned above. We thought it of interest to study the instability in this system⁶ without the organic substrate.

Materials and Methods

1,10-Phenanthroline hydrate (BDH), KBrO_3 (Thomas Baker), FeSO_4 (BDH) and H_2SO_4 (BDH) of analytical grade were used as such. The solutions of ferriin and KBrO_3 of fixed molarities were prepared in 1.5 mol dm^{-3} sulphuric acid.

Oscillations were studied in a continuously stirred tank reactor (CSTR) using the method described earlier⁷. Bistability and chemical waves were also investigated in a manner described earlier⁸. A single blue propagating front was formed and the velocities of propagation for one-dimensional as well as two-dimensional phase wave were measured as a function of $[\text{BrO}_3^-]$ and $[\text{H}^+]$ at different temperatures.

Results and Discussion

In the concentration range $[\text{BrO}_3^-] = 9.58 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{ferriin}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, and $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$ phase waves are formed, although Showalter⁶ has reported the formation of trigger waves in ferriin + bromate + cyclohexane dicarboxylic acid + H_2SO_4 system at $[\text{BrO}_3^-] = 9.51 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{ferriin}] = 1.21 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{KBr}] = 4.79 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{COOH})_2] = 8.97 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{H}_2\text{SO}_4] = 0.189 \text{ mol}$

dm^{-3} . The magnitude of velocity of two-dimensional wave is a little higher than that of one-dimensional wave. The wave velocity (v) depends on $[\text{H}^+]$ and $[\text{BrO}_3^-]$ as shown in Eq. (1).

$$v = k [\text{H}_2\text{SO}_4]^{1/2} [\text{BrO}_3^-]^{1/2} \quad \dots (1)$$

where k is a constant which depends on temperature.

The plot of v against $[\text{H}_2\text{SO}_4]^{1/2} [\text{BrO}_3^-]^{1/2}$ is linear (Fig. 1) for the propagation of both one-dimensional and two-dimensional waves. This is in agreement with the general behaviour of BZ-systems^{1,6,9} without cerium or manganese. The constant, k is related to temperature by an Arrhenius type relation (2)

$$k = Ae^{-E_a/RT} \quad \dots (2)$$

where A is a constant and E_a may be called as apparent energy of activation. The plot of k against reciprocal of temperature (in Kelvin) is linear (Fig. 2) and E_a values are estimated to be 44.8 and 42.3 kJ mol^{-1} for

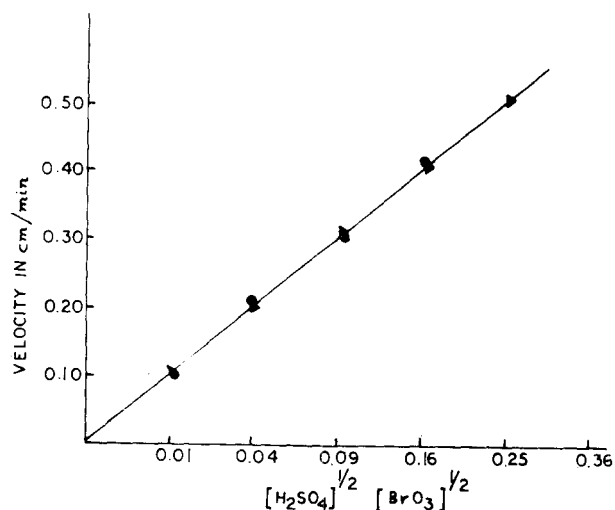
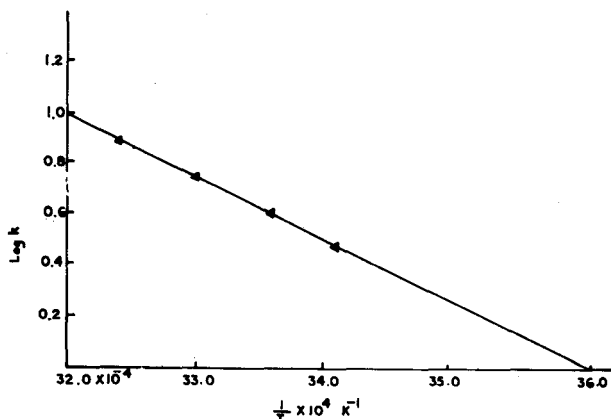
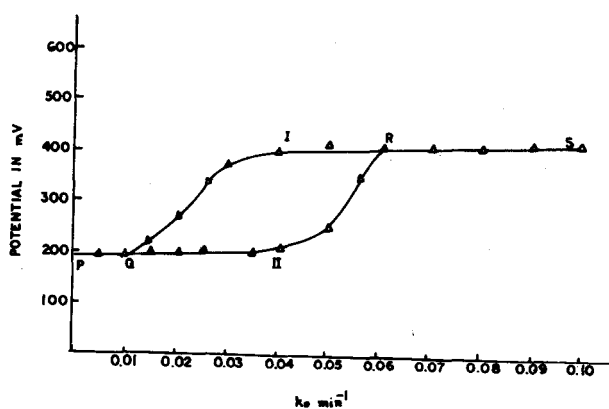
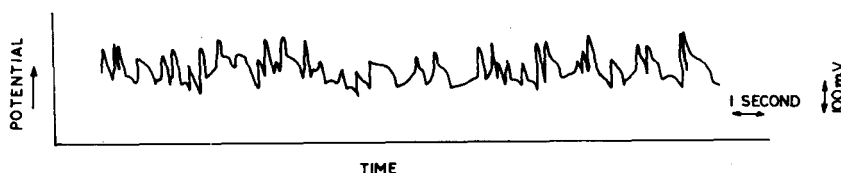


Fig. 1—Dependence of the two dimensional velocity of chemical waves on $[\text{X}]^{1/2}$ where $\text{X} = \text{BrO}_3^-$ (▲—▲) and H_2SO_4 (●—●)

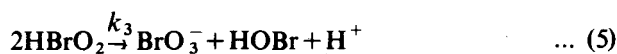

 Fig. 2—Plot of log k against inverse of temperature

 Fig. 3—Plot of steady state potential against k_0

 Fig. 4—Oscillations in CSTR ($k_0 = 0.035 \text{ min}^{-1}$ [Ferriin] = $2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{KBrO}_3] = 6.61 \times 10^{-3} \text{ mol dm}^{-3}$, and $[\text{H}_2\text{SO}_4] = 1.51 \text{ mol dm}^{-3}$)

propagation of one-dimensional and two-dimensional waves, respectively. Similar values have been reported for a number of BZ-systems by Rastogi and coworkers¹⁰. It is remarkable to note that the value of apparent energy of activation is the same for BZ-systems of different types indicating a common mechanism governing wave propagation. Velocity of two-dimensional wave is slightly higher than that of one-dimensional wave. The ratios are 1.08, 1.06 and 1.05 at 20°, 25° and 30°, respectively.

Since the phase waves are produced in the system, it is logical to expect that the medium would be oscillatory. In order to check this point, oscillations in CSTR were studied. The reaction mixture contained BrO_3^- ($6.01 \times 10^{-3} \text{ mol dm}^{-3}$), ferriin ($2.0 \times 10^{-4} \text{ mol dm}^{-3}$) and H_2SO_4 (1.5 mol dm^{-3}). Chaotic oscillations are observed when k_0 , the reciprocal of the residence time is in the range of 0.015 to 0.06 min^{-1} at which wave propagation is observed. (k_0 is the ratio of volume of the reactor and flow rate). When k_0 is gradually increased, the potential follows the path PQ (Fig. 3). Beyond Q chaotic oscillations are observed around mean potential as shown in Fig. 4. Such oscillations are observed all along the path-II. Beyond R the system becomes stable and follows the path RS. However, when k_0 is successively decreased, again at R instability sets in and the system follows the path-I. Again beyond Q, stability is restored. Figure 3 is rather

an uncommon stability diagram but such diagrams have been reported in connection with the stability of a reactor obeying first order kinetics in an exothermic reaction¹¹.

In the blue band, HBrO_2 is autocatalytically produced according to the sequence of reactions as suggested by Field and Noyes (see Eqs 3-5). It may be noted that autocatalytic oxidation of ferriin has been reported to occur¹² in the range of concentration of ferriin and bromate in which wave formation has been studied.



In this band $[\text{Br}^-]$ falls to a very low value and the autocatalytic formation of bromous acid is triggered. Considering the one-dimensional case and assuming $C_A = [\text{HBrO}_2]$ and $C_B = [\text{Br}^-]$, we get

$$\begin{aligned} \left(\frac{\partial C_A}{\partial t} \right)_x &= D_A \left(\frac{\partial^2 C_A}{\partial x^2} \right) + k_1 [\text{H}^+][\text{BrO}_3^-] C_A \\ &\quad - 2k_3 C_A^2 + k_4 [\text{H}^+][\text{BrO}_3^-] C_B \\ &\quad - k_5 [\text{H}^+] C_A C_B \quad \dots (6) \end{aligned}$$

$$\left(\frac{\partial C_B}{\partial t} \right) = D_B \left(\frac{\partial^2 C_B}{\partial X^2} \right) - k_4 [H^+] [BrO_3^-] C_B - k_5 [H^+] C_A C_B \quad \dots (7)$$

where D_A and D_B are the diffusion coefficients of $HBrO_2$ and Br^- respectively. These are supposed to be independent of $[HBrO_2]$ and $[Br^-]$; k_4 and k_5 are the rate constants of the reactions (8) and (9)



If the band moves downward with a velocity (v) we can rewrite Eqs (6) and (7) in the form of Eqs (10) and (11) respectively.

$$D_A \left(\frac{\partial^2 C_A}{\partial X^2} \right) - v \left(\frac{\partial C_A}{\partial X} \right) + k_1 [H^+] [BrO_3^-] C_A - 2k_3 C_A^2 + k_4 [H^+] [BrO_3^-] C_B - k_5 [H^+] C_A C_B = 0 \quad \dots (10)$$

$$D_B \left(\frac{\partial^2 C_B}{\partial X^2} \right) - v \left(\frac{\partial C_B}{\partial X} \right) - k_4 [H^+] [BrO_3^-] C_B - k_5 [H^+] C_A C_B = 0 \quad \dots (11)$$

It is not easy to solve Eqs (10) and (11) together. We can make some simplification if we only retain the dominant chemical reaction term in these equations. Thus, to a first approximation, we can rewrite Eqs (10) and (11) as Eqs (12) and (13) respectively

$$D_A \left(\frac{\partial^2 C_A}{\partial X^2} \right) - v \left(\frac{\partial C_A}{\partial X} \right) + k_1 [H^+] [BrO_3^-] C_A = 0 \quad \dots (12)$$

$$D_B \left(\frac{\partial^2 C_B}{\partial X^2} \right) - v \left(\frac{\partial C_B}{\partial X} \right) - k_4 [H^+] [BrO_3^-] C_B = 0 \quad \dots (13)$$

However, worthwhile result can be obtained from Eq. (12) as shown by Field and Noyes. Thus, from Eq. (12) we obtain

$$v \gg \{k_1 D_A [H^+] [BrO_3^-]\}^{1/2} \quad \dots (14)$$

Experimental results agree with Eq. (14) so far as the concentration dependence of H^+ and BrO_3^- is concerned as Figs. 1 and 2 show. Further it follows that E_A is the square root of sum of the energy of activation of step-3 and the energy of activation of diffusion.

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References

- 1 Field R J & Noyes R M, *J Am chem Soc*, **96** (1974) 2001.
- 2 Rastogi R P, Yadav K D S & Prasad K, *Indian J Chem*, **13** (1975) 352.
- 3 Rastogi R P, Rastogi P & Rai R B, *Indian J Chem*, **16A** (1978) 379.
- 4 De Keeper P, Epstein I R, Kustin K & Orbon M, *J phys Chem*, **86** (1982) 171.
- 5 Rastogi R P, Verma M K, Yadav R D & Singh (K.m.) Sadhana, *J chem Soc, Faraday Transactions* (in press) 1984.
- 6 Showalter K J, *J phys Chem*, **85** (1981) 440.
- 7 Rastogi R P, Das I & Singh A R, *J phys Chem* (in press) 1984.
- 8 Rastogi R P, Das I, Verma M K & Singh A R, *J non-equilib Thermodynamics*, **8** (1983) 255.
- 9 Showalter K, *J phys Chem*, **73** (1980) 3735.
- 10 Rastogi R P, Verma M K & Yadav R D, (under publication) 1984.
- 11 Uppal A, Ray W H & Poore P B, *J Chem Engg*, **29** (1970) 967.
- 12 Rovinskii A B & Zhabotinski A M, *React Kinet Catal Lett*, **11** (1979) 205.