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Distinct Activation Energies for Temporal and Spatial Oscillations in the Belousov-Zhabotinskii Reaction

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Temperature dependence of the frequencies in temporal oscillations and of the moving-wave velocities of concentric waves in spatial oscillation in the Belousov-Zhabotinskii reaction was studied in detail using the same starting concentrations of the reactants. When cerium ions were used as catalyst, the activation energies were found to be 60—65 kJ/mol for the temporal oscillation and 46±4 kJ/mol for the spatial oscillation. The difference in the activation energies was well explained by the theoretical prediction based on kinetic-diffusion coupling. When $[Fe(phen)_3{}^{2+}]$ or $[Fe(bpy)_3{}^{2+}]$ was used as catalyst, the apparent activation energy in the temporal oscillation depends markedly on the concentration of the catalyst used.

During the last decade, sustained oscillations and traveling chemical waves in the Belousov-Zhabotinskii reaction[1,2] have received much attention as a typical cooperative phenomenon in thermal nonequilibrium. When this reaction is allowed to proceed in a well-stirred vessel, sustained oscillation of the concentrations of several chemical species occurs (referred to as the temporal oscillation). On the other hand, when the reaction is run in an unstirred shallow layer (*e.g.* in a petri dish), spatio-temporal structures of the concentrations of chemical species appear.[3] The dynamic structure that has been most commonly studied is the concentration waves with concentric symmetry (referred to as the spatial oscillation).

For the temporal oscillation, the period of the oscillation has been studied as a function of temperature by some workers,[4—8] who demonstrated an Arrhenius dependence of the frequency (inverse period) on temperature. It has also been reported[9] that the period of the oscillation varied with the catalyst used, but the reason for this has not been clarified yet. For the spatial oscillation, on the other hand, only a few experimental studies have been reported on the temperature dependence of the moving-wave velocities of the concentric chemical waves.[10—12]

The present work deals with studies of the temperature dependences of the oscillation periods in the temporal oscillation and of the velocities of the moving-waves in the spatial oscillation, using the same starting concentrations of the reagents. We demonstrated a marked difference in activation energies between the temporal and spatial oscillations. This difference is explained on the basis of the proposed chemical mechanisms.

Experimental

Materials. Reagent grade chemicals were used throughout. Iron phenanthroline (ferroin), $[Fe(phen)_3{}^{2+}]$, was prepared from 1,10-phenanthroline and iron(II) sulfate, and iron bipyridyl, $[Fe(bpy)_3{}^{2+}]$, was prepared from 2,2′-bipyridyl and iron(II) sulfate.

Measurement of Temporal Oscillations. The redox potential was measured by monitoring the e.m.f. generated by a platinum electrode and a calomel reference electrode with a Hitachi-Horiba F-7 pH/mV meter. A double junction reference electrode (Hitachi-Horiba 253A-05T) was used with the bridging solution of saturated potassium nitrate. The reacting mixture was prepared by successive additions of stock solutions of sodium bromate, malonic acid and metal-catalyst ($[Fe(phen)_3{}^{2+}]$ or $[Fe(bpy)_3{}^{2+}]$ or Ce^{3+} or Ce^{4+} or Mn^{2+}) to sulfuric acid in a 50-dm^3 beaker thermostated to a desired temperature between 10 and 45 °C. Throughout the measurement of redox potential, the reacting mixture was constantly stirred under appropriate conditions. The first oxidation peak observed was taken as the onset of the first period of oscillation. As the frequency changes slightly with time in accordance with the changes in the concentrations of the reactants, the average value for the ten periods between the 2nd and the 11th oscillations is taken as the frequency.

Measurement of Spatial Oscillations. The reaction was initiated by adding a metal-catalyst, cerium ion, to a thermostated beaker containing sulfuric acid, sodium bromate, and malonic acid. After being stirred for 5 min, the reaction mixture was poured into a thermostated petri dish with a diameter of 87 mm. The concentrations of the reactants were adjusted to the same concentrations as used for the temporal oscillation. Trigger (concentric) waves were generated by adding a small piece of poly(vinyl alcohol) (Nakarai Chemical, Av. Mol. Wt. 2200) as a pacemaker.[13] Other deformed moving-waves were considered as interferences and are therefore not discussed in this article. The oscillating reaction taking place in the petri dish was photographed at appropriate intervals, and the velocities were determined by measuring the distance from the center (the position of the pacemaker) of the concentric traveling band to the outer propagating bands. Photographs were taken using a Polaroid 600 SE camera with type 667 film under UV light.

Results

Activation Energies in Temporal Oscillations. Figure 1 exemplified the temporal oscillation of redox potential obtained when Ce^{3+} was used as catalyst. It is apparent that the period of oscillation was kept nearly constant. Therefore, the average value of the periods between the 2nd and the 11th oscillation was regarded as the "period" of a given oscillating system. The periods were measured at temperatures ranging from 10 to 45 °C. An Arrhenius plot for the oscillating frequency, F_{osc} (reciprocal of the period), is shown in Fig. 2. From the slope of the figure, 64.9± 2 kJ/mol is obtained as the activation energy, E_a, for the temporal oscillation catalyzed by cerium ion

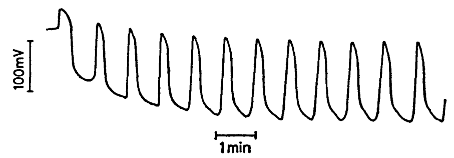

Fig. 1. Temporal oscillation of redox potenital. $[H_2SO_4]_0=0.4$ M, $[NaBrO_3]_0=0.35$ M, $[KBr]_0=0.06$ M, $[\text{Malonic Acid}]_0=0.12$ M, $[Ce(NH_4)_2(NO_3)_5]_0=0.002$ M. Temperature=25.1 °C. Volume, 20 dm^3.

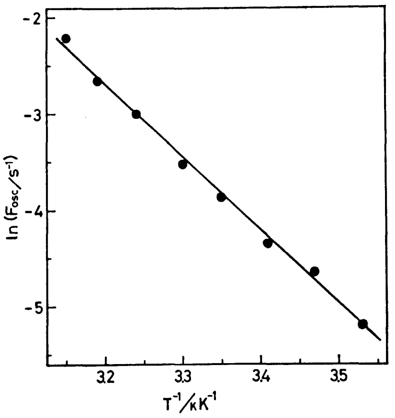

Fig. 2. Arrhenius dependence on temperature of oscillating frequency, F_{osc}, with Ce^{3+} as catalyst. The concentrations are the same as described in the legend to Fig. 1.

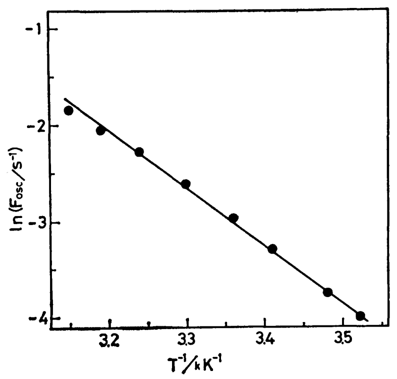

Fig. 3. Arrhenius dependence on temperature of oscillating frequency, F_{osc} with $[Fe(phen)_3{}^{2+}]$ as catalyst (0.002 M). Other concentrations of the reagents are the same as described in the legend to Fig. 1.

($[Ce(NH_4)_2(NO_3)_5]=0.002$ M†).

Table 1. Apparent activation energies in temporal oscillations

Catalyst	Concentration mM	Frequency$^{a)}$ at 25 °C Hz	$E_a{}^{b)}$ kJ mol^{-1}
$[Fe(phen)_3{}^{2+}]$	2	0.051	46.6
	1	0.055	44.9
	0.3	0.056	56.6$^{c)}$
	0.2	0.060	57.4$^{c)}$
	0.1	0.068	72.4$^{c)}$
$[Fe(bpy)_3{}^{2+}]$	0.3	0.071	71.6$^{c)}$
Ce^{3+}	2	0.021	62.4
Ce^{4+}	5	0.021	64.9
	2	0.021	64.9
	1	0.022	59.9
	0.3	0.023	59.9
	0.2	0.025	60.7
	0.1	0.025	60.7
Mn^{2+}	2	0.025	64.1

a) Estimated experimental errors are ±5%. b) Estimated experimental errors are ±2—3 kJ/mol, except for the E_a values marked c). c) Estimated experimental erros are ±5—7 kJ/mol.

We then carried out similar experiments with several different catalysts, such as $[Fe(phen)_3{}^{2+}]$, Ce^{4+}, and Mn^{2+} at the concentration of 2 mM. An Arrhenius plot for the oscillation catalyzed by $[Fe(phen)_3{}^{2+}]$ is shown in Fig. 3. Apparent activation energies for the temporal oscillation obtained with the different catalysts are listed in Table 1. The E_a values with Ce^{3+}, Ce^{4+}, and Mn^{2+} are essentially the same at the same concentration, 2 mM, of the catalyst, but greatly differ from the E_a value with $[Fe(phen)_3{}^{2+}]$. In order to study further the effects of the catalysts on the oscillation, E_a values were determined with different concentrations of the catalysts, $[Fe(phen)_3{}^{2+}]$ and Ce^{4+} (Table 1). The E_a values with Ce^{4+} remain nearly constant at different concentrations, while those with $[Fe(phen)_3{}^{2+}]$ change remarkably, from 46.6 to 72.4 kJ/mol, with decreasing concentration of the $[Fe(phen)_3{}^{2+}]$. A possible explanation for the dependence of the E_a value on the catalyst concentration is that $[Fe(phen)_3{}^{2+}]$ does decompose gradually in the reaction medium and that this, in turn, affects the kinetics of the oscillating reaction. Thus, the rate of the decomposition of $[Fe(phen)_3{}^{2+}]$ in 0.4 M sulfuric acid was measured by monitoring spectrometrically the decrease of the absorption maximum at 522 nm (data not shown). For comparison, the rate of the decomposition of $[Fe(bpy)_3{}^{2+}]$ was also measured under similar conditions. The decreasing rate of the absorption showed that the kinetic constant, k, was 0.007 min^{-1} for $[Fe(phen)_3{}^{2+}]$ and 0.097 min^{-1} for $[Fe(bpy)_3{}^{2+}]$ at 26 °C and that the half-life periods of these iron-complexes at 26 °C are 90 and 7.1 min, respectively. The rate of the decomposition was enhanced at elevated temperatures. It seems that the decomposition of these iron-complexes cannot be ignored during the chemical oscillations, suggesting that these iron-complexes are not suitable as a catalyst for the kinetic study of the Belousov-Zhabotinskii reaction.

Activation Energies in Spatial Oscillations. Concentric trigger waves (spatial oscillation) were generated using cerium ion as catalyst. To compare the activation energy for temporal oscillation with that for spatial oscillation, the oscillating reactions were run with the same starting concentrations of the reagents. Figure 4 shows the time dependence of the distance of each wave from the center of the cylindrical bands. The slopes in Fig. 4 represent the moving-wave velocities, v. Similar experiments were carried out at several temperatures. The results obtained

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† 1 M=1 mol dm^{-3}.

are shown as an Arrhenius plot in Fig. 5. From this figure, the apparent activation energy of 46±4 kJ/mol is obtained for the propagation of the cylindrical waves with Ce^{4+} as catalyst.

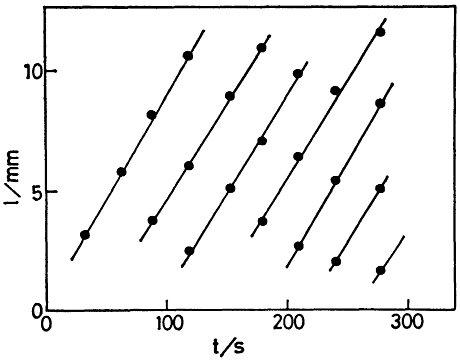

Fig. 4. Time dependence of the band position (distance from the center) in a spatial oscillating reaction with the cylindrical pattern.
The concentrations are the same as described in the legend to Fig. 1. Ce^{4+}-catalyst at 25 °C. Volume, 7 dm^3.

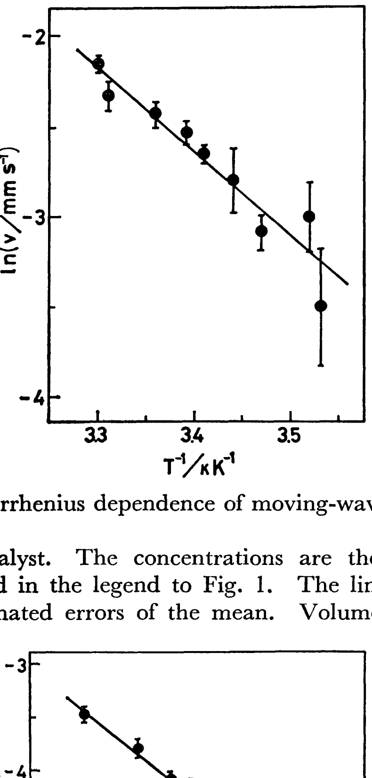

Fig. 5. Arrhenius dependence of moving-wave velocity, v.
Ce^{4+}-catalyst. The concentrations are the same as described in the legend to Fig. 1. The limits shown are estimated errors of the mean. Volume, 7 dm^3.

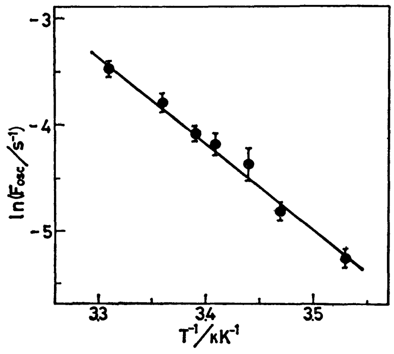

Fig. 6. Arrhenius dependence of oscillating frequency, F_{osc}, at a place 1 cm away from the center in spatial oscillation.
The data were taken from the same experiments as shown in Fig. 5. The limits shown are estimated errors of the mean.

From the photographs of the moving-wave, one can also obtain the frequencies of the chemical oscillation at a fixed position. The frequencies at the position 1 cm distant from the center were obtained and are depicted as an Arrhenius plot in Fig. 6. The activation energy was thus determined to be 69±4 kJ/mol, which is close to that for the temporal oscillation (64.9±2 kJ/mol) obtained at the same concentration of cerium ions (2 mM). The small difference in the activation energies of the frequencies between the temporal and spatial oscillations may have resulted from the different experimental conditions used, *i.e.*, continuous mixing for the former reaction and standing still for the latter.

Discussion

No attempt has been made to compare the kinetics of the temporal and spatial oscillations with the same starting concentrations of the reagents. We demonstrated that the activation energies for the two types of oscillating reactions are apparently different. We now wish to discuss these results in relation to the mechanism of the chemical oscillations.

Field and Noyes proposed[14,15] a mechanism of the spatial oscillation of the concentric wave, coupled with diffusion of the chemical species. Based on the assumption that the velocity of the band propagation is controlled by the concentration of bromide ion and bromous acid in the band front and that the traveling band of bromide ion does not affect the velocity of the band propagation, the following differential equations are obtained:[15,16]

$$\left(\frac{\partial C_A}{\partial t}\right)_x = D_A\left(\frac{\partial^2 C_A}{\partial x^2}\right)_t + k_3[H^+][BrO_3^-]C_B - k_2[H^+]C_AC_B + k_5[H^+][BrO_3^-]C_A - 2k_4C_A^2, \tag{1}$$

$$\left(\frac{\partial C_B}{\partial t}\right)_x = D_B\left(\frac{\partial^2 C_B}{\partial x^2}\right)_t - k_3[H^+][BrO_3^-]C_B - k_2[H^+]C_AC_B. \tag{2}$$

Here $C_A=[HBrO_2]$ and $C_B=[Br^-]$. The definitions of the other symbols in these equations are identical to those in Refs. 15 and 16. Experimentally, the propagating bands move with a constant velocity, as is shown in Fig. 4; then

$$v = \left(\frac{\partial x}{\partial t}\right)_{C_A, C_B}, \tag{3}$$

$$\left(\frac{\partial C_A}{\partial t}\right)_x = v\left(\frac{\partial C_A}{\partial x}\right)_t. \tag{4}$$

The autocatalytic reaction (5) with the rate constant, k_5, is rate-determining in the Belousov-Zhabotinskii reaction.[15,16]

$$BrO_3^- + HBrO_2 + H^+ \xrightarrow{k_5} 2BrO_2\cdot + H_2O. \tag{5}$$

Under the approximation that this autocatalytic term is much more important than others in the face of an advancing band, Eq. 1 can be simplified as follows:

$$D_A\frac{d^2C_A}{dx^2} - v\frac{dC_A}{dx} + k_5[H^+][HBrO_3^-]C_A = 0. \tag{6}$$

Under the condition of maximum sharpness,[15,16] an approximate solution of Eq. 6 is given as follows:

$$v = (4D_A k_5[\mathrm{H^+}][\mathrm{BrO_3^-}])^{1/2}. \tag{7}$$

As for the temporal oscillation, the diffusion term in Eqs. 1 and 2 can be neglected, and the autocatalytic reaction (5) is also most important for the rate of the oscillation.[17] Tyson *et al.*[18] have suggested that the period of the oscillation is determined by Reaction 5 and that the activation energy of the oscillation is nearly equal to that of Reaction 5. Quite recently, from the result of a mathematical analysis for the Belousov-Zhabotinskii reaction using "Oregonator" model, Edelson *et al.*[19] have concluded that the principal factor determining the period of the temporal oscillation is k_5 and that this reaction is almost an order of magnitude more significant than the others. Therefore, the frequency, F_{osc}, is approximately given by (8), using the rate equation of Reaction 5. In

$$F_{\mathrm{osc}} \propto k_5[\mathrm{H^+}][\mathrm{BrO_3^-}]. \tag{8}$$

Eqs. 7 and 8, D_A and k_5 are temperature dependent and may be expressed as follows:

$$D_A = D_0 \exp(-E_D/RT), \tag{9}$$

$$k_5 = k_0 \exp(-E_k/RT). \tag{10}$$

E_D and E_K are the activation energies for the diffusion of A ($=\mathrm{HBrO_3}$) and Reaction 5, respectively. The activation energy of self-diffusion of water has been experimentally reported to be 4.8 kcal/mol (20 kJ/mol).[20] Thus, it is probable that E_D is about 20 kJ/mol. In our experiment, E_K (the activation energy of F_{osc}) is about 69 kJ/mol in the spatial oscillation (Fig. 6) and about 65 kJ/mol in the temporal oscillation (Table 1) when $[\mathrm{Ce^{4+}}]_0 = 2$ mM. The small difference between the activation energies may be due to the stirring effect[9] and/or to the oxygen effect.[21] From Eqs. 7, 9, and 10, the relationship between the activation energies becomes

$$E_v = \frac{1}{2}(E_D + E_k). \tag{11}$$

Here E_v is the activation energy of v in the spatial oscillation. E_v is thus calculated to be $(20+69)\div 2 = 44.5$ (kJ/mol) or $(20+65)\div 2 = 42.5$ (kJ/mol). These values agree well with the value of E_v, 46 kJ/mol, experimentally obtained in this study (Fig. 5).

It may be worthwhile to compare the activation energies obtained in this study with the previously reported values. From the measurement of the frequency of the temporal oscillation at three different temperatures (288, 298, 308 K), Körös[4] has derived an activation energy of 67.5 kJ/mol, which was the same for different catalysts: $\mathrm{Ce^{3+}}$, $\mathrm{Mn^{2+}}$, and $[\mathrm{Ru(bpy)_3}^{2+}]$. Blandamer *et al.*[6] reported an activation energy of 70 kJ/mol for the frequency in the temporal oscillation, using the system of malonic acid–$\mathrm{BrO_3^-}$–$\mathrm{H_2SO_4}$–$\mathrm{Ce^{3+}}$. Rastogi *et al.*[5] have also reported the dependence of the frequency on temperature. Though they did not report the activation energy, we can obtain an activation energy of 54 kJ/mol from the figure of the Arrhenius relation of the oscillation period given in their paper.[5] The large difference of the activation energies may be mainly due to the difference of the concentrations of the reactants and the catalyst. This may be not surprising, as the Belousov-Zhabotinskii reaction is a quite complicated system consisting of many elemental reactions. It is also to be noted that the difference of the experimental conditions causes a large difference of the frequencies of the oscillation, for example, the frequency at 25 °C is 0.05 $\mathrm{s^{-1}}$ in the experiment of Blandamer *et al.*[6] and 0.021—0.025 $\mathrm{s^{-1}}$ in our experiment. It is thus apparent that starting concentrations of the reagents should be the same if one wishes to compare the kinetics between the temporal and spatial oscillating reactions, as has been done in this study.

Thoenes[10] has reported an activation energy of 100 kJ/mol for the oscillation frequency in the spatial oscillation for the system of malonic acid–$\mathrm{BrO_3^-}$–$\mathrm{H_2SO_4}$–$[\mathrm{Fe(phen)_3}^{2+}]$. As he has not shown the actual values of the frequencies at different temperatures in his paper, we can not discuss about the error or accuracy of his experiment. However, it should be pointed out again that ferroin ($[\mathrm{Fe(phen)_3}^{2+}]$) is not suitable as the catalyst for the study of the reaction kinetics in the Belousov-Zhabotinskii reaction.

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