POLAROGRAPHIC STUDY OF THE KINETICS AND MECHANISM OF BELOUSOV–ZHABOTINSKY REACTION

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It is shown that the polarographic method with a rotating platinum electrode is suitable for the study of the Belousov–Zhabotinsky reaction. New kinetic data were obtained which are discussed qualitatively with regard to the Field–Körös–Noyes mechanism. The activation parameters for the studied reaction in the presence of Mn^{2+} ions as catalyst were determined as follows: Activation enthalpy $\Delta H^{\neq} = 14{\cdot}8$ kcal mol^{-1} ($=62{\cdot}2$ kJ mol^{-1}) and activation entropy $\Delta S^{\neq} = -14{\cdot}4$ cal K^{-1} mol^{-1} ($= -60{\cdot}5$ J K^{-1} mol^{-1}).

An increased attention has been focussed during the last decade on the study of oscillation reactions, which are remarkable from the point of view of biochemistry and biophysics. Many authors[1–8] have studied mainly the Belousov–Zhabotinsky reaction, in which an organic compound with an active methylene group (typically malonic acid) is oxidised by bromates with the participation of Ce^{3+}, Mn^{2+}, $Fe(phen)_3^{2+}$, or $Ru(dipy)_3^{2+}$ ions as catalysts. This reaction has been studied spectrophotometrically (the time dependence of the absorbancy of Ce^{4+} or Mn^{3+} ions was recorded)[3,9], potentiometrically (the time dependence of the redox potential of the Ce^{4+}/Ce^{3+} or Br/Br^- couple was recorded)[8,10–13], calorimetrically[10,11], and by NMR spectrometry[11]. Prigogine and Lefever[14] pointed out the parallelity between the time periodicity and the dissipative structure of the given reaction system. The reaction components which lead to oscillating concentrations in a mixed solution yield so-called chemical waves in a quiet solution layer[15]. A detailed reaction mechanism was proposed by Field and coworkers[8]; their model consists of five reaction steps with three independent intermediate products ($HBrO_2$, Br^-, and Ce^{4+} ions). This model is described mathematically by three kinetic differential equations whose solution shows an oscillating behaviour[16]. Weisbuch and coworkers[17] proposed a similar mathematical model consisting of three nonlinear differential equations which on integration give oscillating time courses of the concentrations of Br^- and Ce^{4+} ions.

Investigations of oscillating chemical reactions continue while a special attention is directed toward the Belousov–Zhabotinsky reaction. The present work describes another experimental method for its study and brings some new kinetic data which are discussed in terms of the Field–Körös–Noyes mechanism.

EXPERIMENTAL

The time dependence of the limiting diffusion current of Mn^{3+} ions was recorded at a potential of 0 V against saturated mercurous sulphate electrode. Measurements were carried out with

a polarograph of the type Radelkis OH-102 (Hungary). A Kalousek-type electrolytic cell was tempered during the measurements by an ultrathermostat of the type U 10 (G.D.R.). The indicator electrode was usually a rotating platinum electrode with a diameter of 0·1 mm, length 7 mm, and frequency of rotation 600 r.p.m. driven by an electric motor (Radiometer, type 22). The current–concentration relationship was $I = \varkappa c$, where $\varkappa = 0{\cdot}6$ A M^{-1}. For comparison, also a vibrating platinum indicator electrode was used whose dimensions were the same as those of the rotating platinum electrode; it was driven by a vibrator at a frequency of 50 Hz in the horizontal direction. Further a dropping mercury electrode with a rate of flow of 1·3 mg/s and drop time 4 s in distilled water at a height of mercury column 50 cm. During measurements with this electrode the solution was stirred by bubbling nitrogen. Spectrophotometric measurements were done on a Specord UV-VIS apparatus (Carl Zeiss, Jena); the absorbancy at 480 nm corresponding to Mn^{3+} ions was measured as a function of time. All chemicals were of reagent grade.

RESULTS

The most reproducible data about the oscillating course of the Belousov–Zhabotinsky reaction (in a solution of 1·5M-H_2SO_4, 0·3M malonic acid, 0·06M-$NaBrO_3$, and $2 . 10^{-3}$M-$MnSO_4$) were obtained with the aid of the rotating platinum electrode (Fig. 1). On the basis of the time dependence of the limiting diffusion current of Mn^{3+} ions at a potential of 0 V against saturated Hg_2SO_4 electrode it was possible to determine the dependence of the induction period, t_0, frequency of the oscillations and their duration on the concentrations of the individual reaction components.

The induction period of the oscillation reactions, t_0, is generally considered as a poorly reproducible quantity. According to our results, it is practically inde-

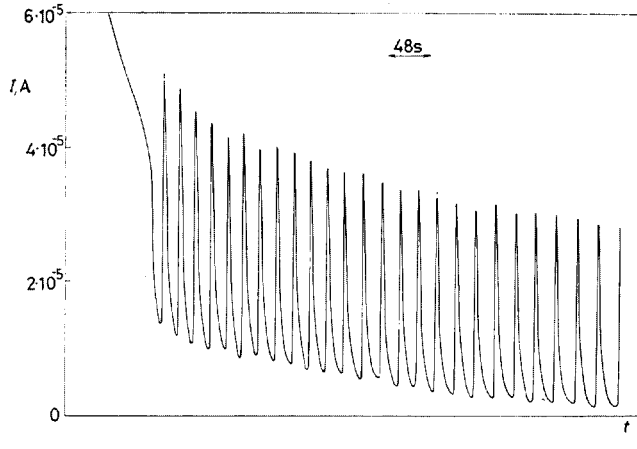

FIG. 1

Oscillating Course of Belousov–Zhabotinsky Reaction: Dependence of Limiting Diffusion Current of Mn^{3+} Ions on Time

$6 . 10^{-2}$M-$NaBrO_3$, 0·3M malonic acid, $2 . 10^{-3}$M-$MnSO_4$, 1·5M-H_2SO_4.

pendent of the concentration of BrO_3^- ions and sulphuric acid; it decreases exponentially with increasing concentration of malonic acid (Fig. 2). A logarithmic analysis gives $t_0 = ac^{-2}$, where the constant a denotes the induction period at a unit concentration of malonic acid. It decreases exponentially also with increasing concentration of Mn^{2+} ions, c_{Mn} (Fig. 3); a logarithmic analysis gives $t_0 = ac_{Mn}^{-0.7}$, where the

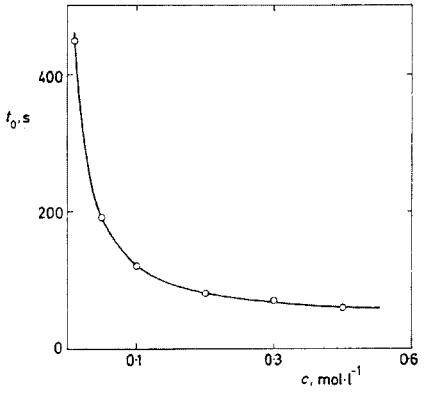

FIG. 2

Dependence of Induction Period on Concentration of Malonic Acid

$2 . 10^{-3}$M-$MnSO_4$, $6 . 10^{-2}$M-$NaBrO_3$, 1·5M-H_2SO_4; 25°C.

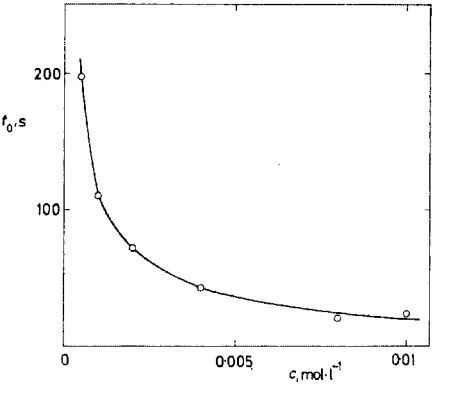

FIG. 3

Dependence of Induction Period on Concentration of Mn^{2+} Ions

0·3M malonic acid, $6 . 10^{-2}$M-$NaBrO_3$, 1·5M-H_2SO_4; 25°C.

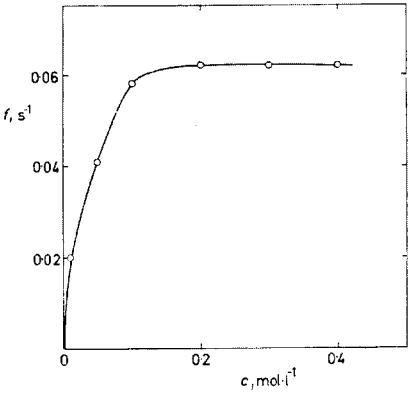

FIG. 4

Dependence of Oscillation Frequency on Malonic Acid Concentration

$2 . 10^{-3}$M-$MnSO_4$, $6 . 10^{-2}$M-$NaBrO_3$, 1·5-H_2SO_4; 25°C.

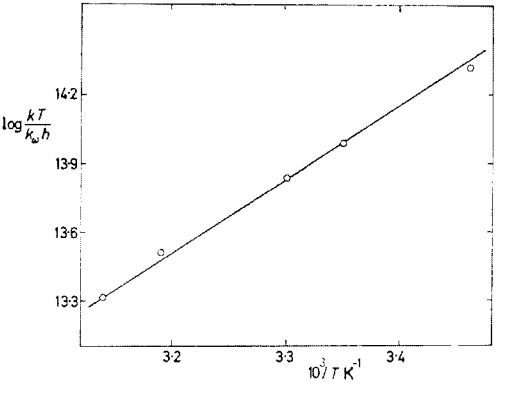

FIG. 5

Temperature Dependence of Rate Constant of Oscillating Reaction

$2 . 10^{-3}$M-$MnSO_4$, 0·3M malonic acid, $6 . 10^{-2}$M-$NaBrO_3$, 1·5M-H_2SO_4.

constant, a, corresponds to the induction period at a unit concentration. With increasing temperature the value of t_0 diminishes; for a solution of 0·3M-$CH_2(COOH)_2$, 0·06M-$NaBrO_3$, 0·002M-$MnSO_4$, and 1·5M-H_2SO_4 we found

T, K	289	298	303	313	318
t_0, s	144	72	50	0	0

The frequency of the oscillations, f, was determined from their number during 240 s after the induction period has elapsed. The value of f increases with the concentration of malonic acid until it reaches a limit (Fig. 4); on the other hand it increases linearly with the concentration of sulphuric acid and bromate ions (Table I). The least necessary concentration of the catalyst is $5 \cdot 10^{-4}$M-Mn^{2+}, above which the frequency of the oscillations does not change any more with the concentration of Mn^{2+} ions.

If we define the rate constant of the oscillating reaction, k_w, as the reciprocal value of the first period of the oscillations, the dependence of $\log(\boldsymbol{k}T/k_w\boldsymbol{h})$ on $1/T$ is linear ($\boldsymbol{k}$ denotes Boltzmann's constant and $\boldsymbol{h}$ Planck's constant; Fig. 5). The activation enthalpy of the studied oscillating reaction is $\Delta H^{\neq} = 14{\cdot}8$ kcal/mol $= 62{\cdot}2$ kJ/mol and the activation entropy $\Delta S^{\neq} = -14{\cdot}4$ cal/K mol $= -60{\cdot}5$ J/K mol. The total duration of the oscillations diminishes with rising temperature similarly as at constant temperature with rising concentration of the Mn^{2+} ions (Table II).

From the methodical point of view, it is interesting to compare the results obtained with the aid of the rotating platinum, vibrating platinum, and dropping mercury electrodes on one hand, and the polarographic with spectrophotometric measurements on the other hand. The results of polarographic measurements with the mentioned electrodes agree well with one another if the solution in the case of the dropping electrode is well stirred (*e.g.*, by bubbling nitrogen). The most reproducible results

TABLE I

Dependence of Oscillation Frequency on Concentration of H_2SO_4 and $NaBrO_3$ 0·3M-$CH_2(COOH)_2$, $2 \cdot 10^{-3}$M-$MnSO_4$; 25°C.

H_2SO_4, M	$NaBrO_3$, M	f, s^{-1}	H_2SO_4, M	$NaBrO_3$, M	f, s^{-1}
0·5	0·06	0·012	3·0	0·06	0·129
1·0	0·06	0·037	1·5	0·03	0·037
1·5	0·06	0·058	1·5	0·06	0·058
2·0	0·06	0·091	1·5	0·09	0·079
2·5	0·06	0·104	1·5	0·11	0·091

were obtained with the rotating platinum electrode at 600 r.p.m. Although the concentration oscillations can be observed also spectrophotometrically, these results are not comparable with the polarographic ones if the solution is not stirred during the measurement. The duration of the oscillations is much shorter in a quiet solution and the reaction system can be set into oscillations by stirring the solution in the cuvette.

DISCUSSION

The polarographic method with a rotating platinum electrode enables to follow reproducibly the course of the Belousov–Zhabotinsky reaction if the oxidized form of the catalyst (Ce^{4+}, Mn^{3+}, $Fe(phen)_3^{3+}$, *etc.*) has a more positive half-wave potential than the bromate wave. The rotating platinum electrode acts not only as an indicator electrode but also as a stirrer. The described method is simpler, more reproducible and often more sensitive than other methods used to study the oscillating reactions.

The results of the kinetic measurements can be discussed from the point of view of the Field–Körös–Noyes mechanism[8], which consisted originally of ten reaction steps and was later simplified to five steps with three independent intermediate products[16] (model *A*):

$$\mathrm{A} + \mathrm{Y} \xrightarrow{k_1} \mathrm{X}, \quad \mathrm{X} + \mathrm{Y} \xrightarrow{k_2} \mathrm{P}, \qquad (a), (b)$$

$$\mathrm{B} + \mathrm{X} \xrightarrow{k_3} 2\,\mathrm{X} + \mathrm{Z}, \quad 2\,\mathrm{X} \xrightarrow{k_4} \mathrm{Q}, \quad \mathrm{Z} \xrightarrow{k_5} \gamma\,\mathrm{Y}, \quad (c), (d), (e)$$

where $X = HBrO_2$, $Y = Br^-$, $Z = Ce^{4+}$ (or Mn^{3+}). When the reaction is considered irreversible and the influence of the acidity is included in the rate constants

TABLE II

Duration of Oscillations (t_1) at Various Temperatures and Concentrations of $MnSO_4$ 0·3M-$CH_2(COOH)_2$, 0·06M-$NaBrO_3$, 1·5M-H_2SO_4.

$MnSO_4$, M	T, K	t_1, min	$MnSO_4$, M	T, K	t_1, min
0·0005	298	56	0·002	289	64
0·001	298	48	0·002	298	36
0·002	298	36	0·002	303	24
0·004	298	26	0·002	313	11
0·008	298	24	0·002	318	6·4
0·01	298	23	0·002	323	2·4

of the individual steps, then A = B = BrO_3^-. The rate constants involve also the concentrations of the reactants that are in excess. In such a case the kinetic behaviour of the simplified model (model *B*) can be described by the equations

$$d[X]/dt = k_1[A][Y] - k_2[X][Y] + k_3[B][X] - 2k_4[X]^2 , \quad (1)$$

$$d[Y]/dt = -k_1[A][Y] - k_2[X][Y] + k_5[Z] , \quad (2)$$

$$d(Z)/dt = k_3[B][X] - k_5[Z] . \quad (3)$$

The oscillating behaviour of the system depends on the values of k_5 and γ. Regardless of the latter, if $k_5 = 0$ then Y is irreversibly consumed and no oscillations occur. Otherwise, if $\gamma = 1$ and k_5 is sufficiently large, the steps (*c*) and (*e*) are replaced by a single one: B + X → 2 X + Y. The model so simplified (with four steps and two intermediate products) does not oscillate and attains quickly a stable steady state. Field and Noyes[16] discussed in detail the range of γ and k_5 values for which the model *A* oscillates.

The model *B*, however, does not account for other observations, *e.g.* the dependence of the induction period on the concentration of malonic acid or on the concentration of Mn^{2+} ions. The shortening of the induction period with increasing concentration of malonic acid can be attributed to the fact that the concentration of the intermediate product, bromomalonic acid, increases in the reaction system more rapidly. If bromomalonic acid is added immediately at the beginning of the reaction, the induction period is completely suppressed[6]. Similarly, the shorterning of the induction period with increasing concentration of Mn^{2+} ions can be qualitatively explained. The rate of increase of the bromomalonic acid concentration will be higher at a higher concentration of Mn^{2+} ions in accord with the overall reaction

$$BrO_3^- + 4\,Mn^{2+} + CH_2(COOH)_2 + 5\,H^+ \rightarrow$$
$$BrCH(COOH)_2 + 3\,H_2O + 4\,Mn^{3+} .$$

The observed increase of the oscillation frequency with increasing concentrations of malonic acid and bromates is related probably also to the mentioned reaction. The linear dependence of the oscillation frequency on the concentration of sulphuric acid can be explained in terms of a catalytic action of H_3O^+ or HSO_4^- ions on one of the reaction steps.

The values of the activation parameters correspond to those for the Belousov-Zhabotinsky reaction in the presence of $Ru(dipy)_3^{2+}$, Ce(III), or Mn(II) as catalysts[10,18]. Neither the activation enthalpy, nor the activation entropy depends on the quality of the catalyst, however the activation entropy depends on the initial concentrations of the compounds which form the oscillating system.

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