BELOUSOV-ZHABOTINSKII REACTION WITH ETHYL ESTER OF 3-OXOBUTANOIC ACID

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The modified Belousov-Zhabotinskii oscillation reaction with ethyl ester of 3-oxobutanoic acid is remarkable in that it does not yield carbon dioxide and the reaction system is closed and homogeneous until an emulsion of a bromo derivative of the substrate appears. As long as the system is homogeneous, it oscillates even in the motionless state and its oscillation behavicur in the absence of oxygen is independent of the intensity of stirring. The results obtained by polarography with a rotating platinum electrode are in agreement with those obtained by spectrophotometry.

The Belousov-Zhabotinskii (BZ) reaction is an outstanding example of time-space dissipative structures. Its homogeneity, which is usually disturbed by bubbles of carbon dioxide resulting from decarboxylation of organic acids, can be ensured by effective stirring. If ethyl ester of 3-oxobutanoic acid is used as substrate, no CO_2 is evolved during the oscillations of the BZ reaction, hence the reaction system is closed and homogeneous as long as no precipitate of a bromo derivative of the substrate is formed. The characteristics of the BZ reacticn with ethyl ester of 3-oxobutanoic acid were described by Zhabotinskii[1,2], Heilweil and coworkers[3], and Winfree[4]. Recently, in connexion with this reacticn, we described the kinetics of oxidation of ethyl ester of 3-oxobutanoic acid with Ce(IV) ions[5].

The influence of mechanical stirring on the BZ reaction has caused some controversies in the literature. According to Farage and Janjic[6], the intensity of stirring influences the oscillation behaviour of the BZ reaction with many organic substrates: the oscillations are diminished, since the stirring influences the "dissipative structures" and disturbs the "organization" in time and space. According to Sørensen[15], the oscillations disappear at a certain critical velocity of stirring as a result of turbulence. On the other hand, Patonay and Noszticzius[7] state that the effect of stirring on the BZ reaction is due to atmospheric oxygen and bears no relation to changes of the dissipative structure or to the turbulence. Recently, Habashi-Krayenbuhl and Janjic[8] studied anew the effect of oxygen and stirring and concluded that both these factors influence the number of oscillations and the length of the induction period. The aim of our work was to specify more closely the conditions under which the BZ reaction with the 3-oxobutanoic acid ester leads to oscillations with special regard to the effect of stirring.

EXPERIMENTAL

Polarographic measurements were done with an LP 7 type polarograph (Laboratorní Přístroje, Prague). The electrolytic cell was a Kalousek cell with a separated Hg/Hg_2SO_4 electrode filled with 1M H_2SO_4. The cell was provided with a thermostated mantle piece and was tempered by means of a U 15 type ultrathermostat (Kombinat Medizin und Labortechnik, GDR). The indicator electrode was a rotating platinum electrode of the type M 22 (Radiometer, Copenhagen). The reaction courses were followed by recording the limiting diffusion current of Ce(IV) ions at a potential of 0 V. The reaction solution of a volume of 15 ml was stirred by a polyethylene stirrer fastened to the shaft of the rotating platinum electrode.

Spectrophotometric measurements were done on a SPECORD UV-VIS apparatus (Carl Zeiss, Jena) with 10 mm quartz glass cuvettes; 1M H_2SO_4 was used as a reference solution. The cuvette filled with 3 ml of the reaction solution was tempered by means of the U 15 ultrathermostat. The reaction course was followed by measuring the absorbancy at 31 000 cm^{-1} corresponding to the close proximity of the absorption maximum of Ce(IV) ions (the absorbancies of other components were negligible). The reaction solution was stirred by a laboratory microstirrer[9]. The experimental points in the diagrams are averages from three independent measurements.

The chemicals used were of reagent grade and the solutions were prepared from redistilled water.

RESULTS

The oscillation behaviour of the studied system depends on its composition. At first, we studied the influence of the substrate concentration, which, especially in the low concentration region, is critical for the induction period (Fig. 1). The period of the first oscillation decreases with increasing substrate concentration (Fig. 2); its dependence on the reciprocal concentration is approximately linear. With increasing substrate concentration, whose treshold value is equal to 2 . 10^{-3} mol/l, the duration of oscillations increases up to a maximum of 210 min at 0·015 mol/l, then decreases

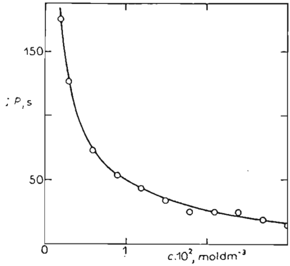

FIG. 1

Dependence of induction period on concentration of $CH_3COCH_2COOC_2H_5$. 1M H_2SO_4; 8 . 10^{-4}M $Ce(SO_4)_2$; 0·015M $KBrO_3$; 30°C

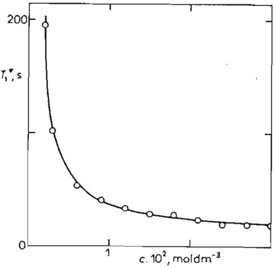

FIG. 2

First oscillation period as function of substrate concentration. 1M H_2SO_4; 8 . 10^{-4}M $Ce(SO_4)_2$; 0·015M $KBrO_3$; 30°C down to 1·5 min at 0·03 mol/l (Fig. 3). It is convenient to define a dimensionless parameter, q, equal to the ratio of the substrate concentration to the bromate concentration. The maximum duration of the oscillations is attained for $q = 1$. In a closed BZ system, the oscillation period increases with the time, the form of this dependence changing with the substrate concentration (Fig. 4) and with the value of q. For $q < 1$, the oscillation period increases monotonously. For $q \geqq 1$, the oscillation period initially increases to a maximum and then decreases. The higher the value of q, the less pronounced is the increase of the oscillation period with the time until it becomes practically constant.

Bromate ions are an indispensable component of the BZ oscillation system; the dependence of the main parameters on their enocentration is given in Table I. At low concentrations of bromate ions, the duration of the oscillations as well as their number are influenced most profoundly. The maximum duration of the oscillations corresponds to $8 \, . \, 10^{-3}$ mol/l BrO_3^- for $q = 1$. With further increasing concentration, the duration of the oscillations decreases nonlinearly. The time dependence of the oscillation period depends on the initial concentration of bromate ions and analogously on the initial concentration of the substrate (Fig. 4).

The main parameters of the BZ reaction depend also on the initial concentration of Ce(IV) sulphate (Table II). The induction period depends on its concentration in

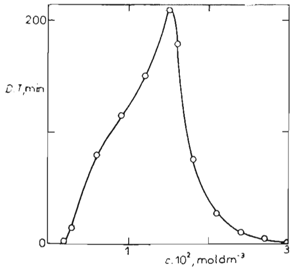

FIG. 3

Duration of oscillations as function of substrate concentration. Experimental conditions as in Fig. 2

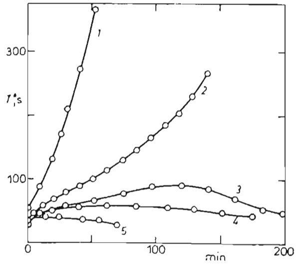

FIG. 4

Dependence of oscillation period on time at various substrate concentrations. 1M H_2SO_4; $8 \, . \, 10^{-4}$M $Ce(SO_4)_2$; 0·015M $KBrO_3$. Conc. of $CH_3COCH_2COOC_2H_5$ (mol/dm^3): *1* $6 \, . \, 10^{-3}$; *2* 0·012; *3* 0·015; *4* 0·016; *5* 0·018; 30°C the interval from $5 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ mol/l; at higher concentrations it is very short (up to 2 min). The influence of Br^- ions was investigated in the presence of $2 \cdot 10^{-4}$ mol/l Ce(IV) (Fig. 5). In the absence of Br^- ions, the induction period was equal to 1 000 s, whereas in the presence of $2{\cdot}5 \cdot 10^{-4}$ mol/l Br^- the system began to oscillate after 40 s, after five oscillations the reaction proceeded monotonously for 650 s and then again it began to oscillate. When, however, $5 \cdot 10^{-4}$ mol/l Br^- was added at the beginning of the reaction, after an induction period of 80 s the system oscillated without interruption.

TABLE I

Dependence of parameters of BZ reaction on bromate concentration. 1M-H_2SO_4; $8 \cdot 10^{-4}$M-$Ce(SO_4)_2$; $8 \cdot 10^{-3}$M-$CH_3COCH_2COOC_2H_5$; 30°C, stirred solution

$KBrO_3$ 10^3c, mol/dm^3	Ind. period s	Per. of 1st osc., s	Duration min	No of osc.
4	75	54	3	3
6	67	54	149	118
8	63	51	207	71
15	54	48	88	33
25	48	52	33	17
35	46	67	12	7
45	49	102	2	1

TABLE II

Dependence of parameters of BZ reaction on Ce(IV) concentration. 1M-H_2SO_4; 0·015M-$KBrO_3$; $8 \cdot 10^{-3}$M-$CH_3COCH_2COOC_2H_5$; 30°C, stirred solution

$Ce(SO_4)_2$ 10^3c, mol/dm^3	Ind. period s	Per. of 1st osc., s	Duration min	No of osc.
0·05	6 100	35	36·5	50
0·1	3 100	45	46·0	50
0·2	1 000	55	62·0	46
0·4	55	40	69·5	39
0·8	70	50	59·5	22
1·4	70	60	51·5	14
2·0	90	70	41·5	9
4·4	145	140	29·0	4
6·0	180	335	23·5	2 to 3

In the presence of the Ce(IV)/Ce(III) redox couple, sulphuric acid is indispensable for the BZ oscillating system. Its increasing concentration causes the duration of the oscillations, their number, and the period of the first oscillation to decrease. The dependence of the duration of the oscillations on the reciprocal concentration of H_2SO_4 is linear in the range from 0·5 to 2 mol/l. With increasing concentration of H_2SO_4, the character of the time dependence of the oscillation period changes: with its increasing value, the slope of the corresponding curves also increases (Fig. 6).

The main parameters of the BZ reaction depend also on the temperature (Table III). The logarithmic dependence of the induction period, period of the first oscillation, and duration of the oscillations on the reciprocal absolute temperature is linear. From the Arrhenius equation, we obtained the corresponding apparent activation parameters. For the induction period, $E = 49{\cdot}9$ kJ/mol, $A = 6{\cdot}9 \,.\, 10^6\ s^{-1}$; for the period of the first oscillation, $E = 46{\cdot}4$ kJ/mol, $A = 1{\cdot}8 \,.\, 10^6\ s^{-1}$; for the duration of the oscillations, $E = 94{\cdot}4$ kJ/mol, $A = 1{\cdot}2 \,.\, 10^{13}\ s^{-1}$.

The influence of the rate of stirring on the BZ reaction parameters was studied polarographically with the rotating Pt electrode. In the presence of air, the rate of stirring influences both the duration and number of the oscillations (Table IV), whereas in the nitrogen atmosphere this is not the case. Spectrophotometric records indicated that the oscillations in the stirred and in the nonstirred system are comparable only

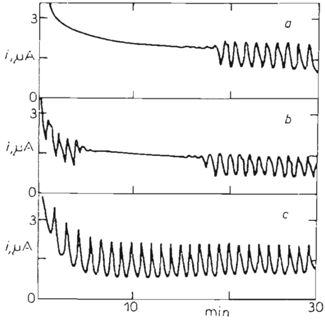

FIG. 5

Influence of Br^- ions on the induction period. 1M-H_2SO_4; 2 . 10^{-4}M-$Ce(SO_4)_2$; 0·015M-$KBrO_3$. *a* Without Br^- ions; *b* 2·5 . 10^{-4}M Br^-; *c* 5·5 . 10^{-4}M-Br^-; 30°C

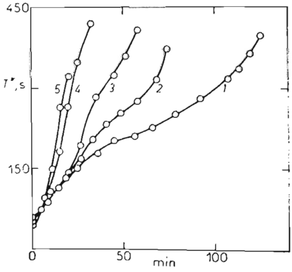

FIG. 6

Oscillation period as function of the time at various concentrations of H_2SO_4. 8·7 . 10^{-4}M $Ce(SO_4)_2$; 0·015M-$KBrO_3$; 8 . 10^{-3}M-CH_3.$COCH_2COOC_2H_5$. Conc. of H_2SO_4 (mol/dm^3): *1* 0·5; *2* 0·75; *3* 1·0; *4* 1·5; *5* 2·0; 30°C at elevated temperatures (35 – 40 °C), or in the initial stages at lower temperatures as long as no precipitate of the bromo derivative of the substrate is formed. If the oscillations stop to proceed in a motionless system, they can be started again by stirring the solution.

DISCUSSION

Based on our results, the ethyl ester of 3-oxobutanoic acid belongs definitely to the group of substrates such as 2,4-pentanedione, 2,4-hexanedione, *etc.*, which are oxidised with Ce(IV) or Mn(III) ions without evolution of CO_2 and in the presence of which the catalyst concentration oscillates even in a nonstirred solution. The BZ oscillation system with the mentioned ester oscillates much longer than the analogous system with 2,4-pentanedione[10]; this is probably related to the rate of oxidation of

TABLE III

Dependence of parameters of BZ reaction on temperature. $1\cdot5\text{M-}H_2SO_4$; $4 \cdot 10^{-4}\text{M}\ Ce(SO_4)_2$; $0\cdot015\text{M-}KBrO_3$; $5 \cdot 10^{-3}\text{M-}CH_3COCH_2COOC_2H_5$; stirred solution

T, K	Ind. per., s	Per. of 1st osc., s	Duration, s	No of osc.
285·6	206	170	14 250	30
291·6	125	110	8 550	27
297·3	80	75	2 950	21
303·1	55	55	1 600	17
308·3	40	40	900	14
313·1	30	30	500	10

TABLE IV

Dependence of duration and number of oscillations on stirring rate. $1\text{M-}H_2SO_4$; $8 \cdot 10^{-4}\text{M-}Ce(SO_4)_2$; $0\cdot015\text{M-}KBrO_3$; $6 \cdot 10^{-3}\text{M-}CH_3COCH_2COOC_2H_5$; 30°C

ω r.p. min	Duration, min		No of oscillations	
	with O_2	without O_2	with O_2	without O_2
900	82	92	24	24
1 200	79	91	22	24
1 700	72	91	19	25

the substrates with Ce(IV) ions. The corresponding rate constants are $k = 140 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for 2,4-pentanedione[10] and $k = 7{\cdot}3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for the ethyl ester of 3-oxobutanoic acid[5].

The induction period is one of the parameters that quantitatively characterize the BZ reaction with the given substrate. In the case of the classical BZ system with malonic acid, the relatively long induction period is interpreted as the time necessary for the formation of a certain quantity of bromomalonic acid, whose oxidation leads to Br^- ions playing a decisive role in the oscillations[11]. In our system in the presence of $CH_3COCH_2COOC_2H_5$ a longer induction period is observed only at low concentrations of Ce(IV) ions, $KBrO_3$, or the ester, which is probably related to a slow accumulation of a minimum quantity of a bromo derivative of the ester necessary for the formation of the oscillations. Its oxidation leads to Br^- ions, which have a key role. This is supported by experiments with the addition of Br^- ions, whereby the induction period is partially or fully eliminated (Fig. 5). Based on these findings, also in our case the process *A* of the Field–Körös–Noyes mechanism[11] can be considered, which leads to an increase of the stoichiometric factor *g* to a supercritical value:

$$\begin{aligned} &BrO_3^- + Br^- + 2\,H^+ \rightarrow HBrO_2 + HOBr \\ &HBrO_2 + Br^- + H^+ \rightarrow 2\,HOBr \\ &HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \\ &Br_2 + \text{ester} \rightarrow \text{Br-ester} + Br^- + H^+ . \end{aligned} \qquad (A)$$

The other characteristic parameter of the BZ reaction is the period of the first oscillation. As already mentioned, it depends on the temperature and decreases nonlinearly with increasing substrate concentration. The period of the first oscillation $T_1 = T_1' + T_1''$, where T_1' corresponds to oxidation of Ce(III) ions and T_1'' to reduction of Ce(IV) ions. In our case $T_1' \ll T_1''$, whence it follows that the period of the first oscillation is determined by the process *C* of the FKN mechanism[11], which essentially corresponds to the reduction of Ce(IV) ions with the substrate or its bromo derivative. The decrease of the value of T_1 with increasing concentration of the esther can be attributed to the fact that the reduction rate of Ce(IV) ions increases at the same time. This interpretation is supported by the finding that the activation energy of the period of the first oscillation, $E = 46{\cdot}4$ kJ/mol, lies close to the activation energy for the reduction of Ce(IV) ions with the given substrate, $E = 49$ kJ/mol (ref.[5]).

The third characteristic of the BZ reaction is the duration of the oscillations. As apparent from Fig. 3, the maximum duration of the oscillations was observed for $q = 1$ (corresponding to equivalent ratio of the reactants). Since the ester of 3-oxobutanoic acid is a two-electron reduction agent[5], the indicated ratio represents the optimum condition for the formation of $HBrO_2$. According to Noyes and coworkers[12], competitive reactions of Br^- and BrO_3^- ions and $HBrO_2$, which destabilize the stationary state, form the basis of the FKN mechanism. Hence follows the key role of $HBrO_2$ with respect to the duration of the oscillations. The corresponding activation energy, $E = 94{\cdot}4$ kJ/mol, involves activation energies of a number of elementary reaction steps. Its rather high value suggests that radical interactions in the FKN mechanism do not limit the duration of the oscillations. The finding that the duration of the oscillations decreases nonlinearly with increasing concentration of sulphuric acid probably bears a relation to the shift in the equilibrium of Ce(IV) complexes[13]:

$$\begin{aligned} &Ce^{4+} + HSO_4^- = CeSO_4^{2+} + H^+ ,\\ &CeSO_4^{2+} + HSO_4^- = Ce(SO_4)_2 + H^+ , \qquad (B)\\ &Ce(SO_4)_2 + HSO_4^- = Ce(SO_4)_3^{2-} + H^+ . \end{aligned}$$

The shift in the equilibrium in favour of the Ce(IV) complexes with more coordinated sulphate ions leads to retardation of the reduction of Ce(IV) ions.

The course of the chemical oscillations can be evaluated as the time dependence of the oscillation period (Figs 4 and 6). During a gradual decrease of the substrate concentration, the mean slope of the curves increases, which can be attributed to the fact that the organic ,,fuel" is gradually exhausted. The relative decrease of the substrate is the more pronounced the lower is its initial concentration.

It follows from our results that the effect of stirring on the BZ reaction with ethyl ester of 3-oxobutanoic acid is conditioned by the presence of oxygen, whose transfer into the liquid phase is accelerated by convection of the solution. As a rule, oxygen influences the course of the BZ reaction[14,15]. In nitrogen atmosphere, the studied reaction is not significantly influenced by stirring; this will probably be true also for other substrates that do not undergo decarboxylation.

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