

Belousov—Zhabotinskii reaction with the ethyl ester of 3-oxobutanoic acid in the presence of Mn(II)—Mn(III)

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The kinetics of reduction of the Mn(III) ions by the ethyl ester of 3-oxobutanoic acid as well as the Belousov—Zhabotinskii reaction with this ester in the presence of Mn(II)—Mn(III) has been studied. The dependence of duration time of oscillations on the concentration of substrate is especially remarkable. It exhibits a distinct maximum at the concentration ratio of bromates to substrate $q = 2.0$. The results are discussed from the view-point of a simplified reaction model, the so-called oregonator. At values $q > 2.0$ the oscillations vanish through a stage of chaotic behaviour while the oscillations disappear in the form of regular damped oscillations at $q \leq 2.0$.

Изучалась кинетика восстановления ионов Mn(III) этиловым эфиром 3-оксобутановой кислоты и реакция Белоусова—Жаботинского с этим эфиром в присутствии Mn(II)—Mn(III). Особенного внимания заслуживает зависимость времени продолжительности осцилляций от концентрации субстрата, имеющая ясный максимум при соотношении концентраций броматов и концентрации субстрата $q = 2,0$. Результаты обсуждаются с точки зрения упрощенной реакционной модели, так называемого орегонатора. При значениях $q > 2,0$ осцилляции прекращаются через стадию хаотического поведения, в то время, как при величинах $q \leq 2,0$ осцилляции исчезают посредством регулярных подавленных осцилляций.

The ethyl ester of 3-oxobutanoic acid is a very convenient substrate for the Belousov—Zhabotinskii reaction because no carbon dioxide is liberated in the course of its oxidation and, for this reason, the oscillating system is homogeneous and closed unless an emulsion of the bromine derivative appears. The fundamental characteristics of the BZ reaction with the ethyl ester of 3-oxobutanoic acid was described by *Zhabotinskii* [1, 2], *Heilweil et al.* [3], and *Winfree* [4]. In reference to this reaction, we described the oxidation kinetics of the ethyl ester of 3-oxobutanoic acid by the Ce(IV) ions [5] and the detailed behaviour of the BZ system in the

presence of the Ce(III)—Ce(IV) redox catalyst [6]. Recently, two types of oscillations “high-frequency” and “low-frequency” in the system H_2SO_4 — NaBrO_3 —ethyl ester of 3-oxobutanoic acid—(Ce(III)—Ce(IV)) or (Mn(II)—Mn(III)) have been described [7].

As the BZ oscillating system containing the ethyl ester of 3-oxobutanoic acid in the presence of the Mn(II)—Mn(III) redox catalyst has not yet been investigated in detail, it became the topic of this study. We pay special attention to the duration time of oscillations as a function of substrate concentration which has been given small attention in literature in contrast to the induction period of the inception of oscillations [8, 9].

Experimental

The polarographic method of kinetic measurement of the reduction of the Mn(III) ions by organic substrates by means of a platinum rotating electrode was described in papers [10, 11]. The value of rate constant was measured within the accuracy $\pm 4\%$. The values given in tables are means of four independent measurements. The procedure of polarographic and spectrophotometric investigation of the course of the BZ reaction was described in papers [6, 12] while the way of preparation of the solution with the Mn(III) ions is reported in papers [10—12].

Results

Kinetics of reduction of the Mn(III) ions by the ethyl ester of 3-oxobutanoic acid

The reduction of the Mn(III) ions in solution by the ethyl ester of 3-oxobutanoic acid in 1.5 M- H_2SO_4 is a first-order reaction with respect to the concentration of oxidant and a first-order reaction with respect to the concentration of reductant

$$-\frac{d[\text{Mn(III)}]}{dt} = k[\text{Mn(III)}] [\text{Ester}]$$

The dependence of the logarithm of the numerical value of limiting diffusion current of the Mn(III) ions on time is linear in the interval of the first two half-lives of reaction. The value of rate constant k_{exp} (s^{-1}) is a linear function of substrate concentration in the range 5×10^{-3} — 3×10^{-2} mol dm^{-3} (Table 1). We evaluated the dependence of the second-order rate constant ($\text{s}^{-1} \text{mol}^{-1} \text{dm}^3$) on temperature by using the Eyring equation (Table 2) and thus we obtained for the value of activation enthalpy in electric bulb nitrogen $\Delta H^\ddagger = 54.8 \text{ kJ mol}^{-1}$ while this value in the presence of air oxygen was $\Delta H^\ddagger = 58.1 \text{ kJ mol}^{-1}$. The value of activation entropy in the atmosphere of electric bulb nitrogen was $\Delta S^\ddagger = -45 \text{ J K}^{-1} \text{ mol}^{-1}$ and the corresponding value in the presence of air oxygen was $\Delta S^\ddagger = -35 \text{ J K}^{-1} \text{ mol}^{-1}$.

Table 1

Variation of the experimental rate constant with substrate concentration
 $c(\text{H}_2\text{SO}_4) = 1.5 \text{ mol dm}^{-3}$, $c(\text{Mn(III)}) = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $\theta = 20^\circ \text{C}$

$k_{\text{exp}} \cdot 10^2/\text{s}$	$c(\text{ester}) \cdot 10^2/(\text{mol dm}^{-3})$
2.2	0.5
4.6	1.0
7.0	1.5
9.5	2.0
11.9	2.5
14.2	3.0

Table 2

Temperature dependence of rate constant

$c(\text{H}_2\text{SO}_4) = 1.5 \text{ mol dm}^{-3}$, $c(\text{Mn(III)}) = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) = 10^{-3} \text{ mol dm}^{-3}$

Thermodynamic temperature	Rate constant/ $(\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3)$	
	Air	Nitrogen
K		
278	0.97	1.2
283	1.76	1.99
288	2.6	2.9
293	4.1	4.4
298	6.2	7.3
303	10.1	10.2
308	13.8	14.2
313	19.0	20.4

Oscillation behaviour of the BZ system with the ethyl ester of 3-oxobutanoic acid in the presence of Mn(II)—Mn(III)

The Belousov—Zhabotinskii reaction system ($c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$ in the presence of the ethyl ester of 3-oxobutanoic acid) shows itself by a very short induction period of inception of oscillations (a couple of seconds) and a relatively long duration time of oscillations. The period of the first oscillation decreases with substrate concentration (Fig. 1). The dependence of period of the first oscillation on reciprocal value of substrate concentration is linear. The periods of two successive oscillations have different time course depending on substrate concentration (Fig. 2).

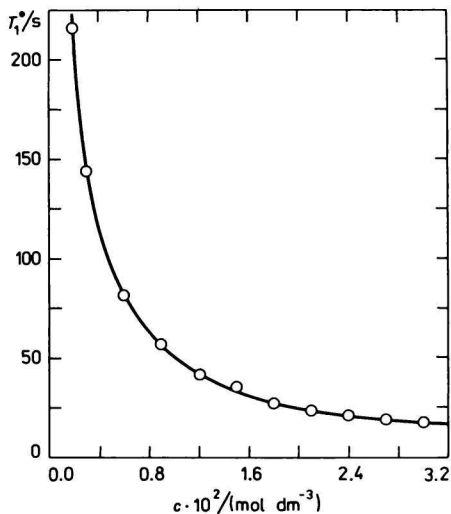


Fig. 1. Variation of the period of the first oscillation with concentration of $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$.
 $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$,
 $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$,
 $\theta = 30^\circ \text{C}$.

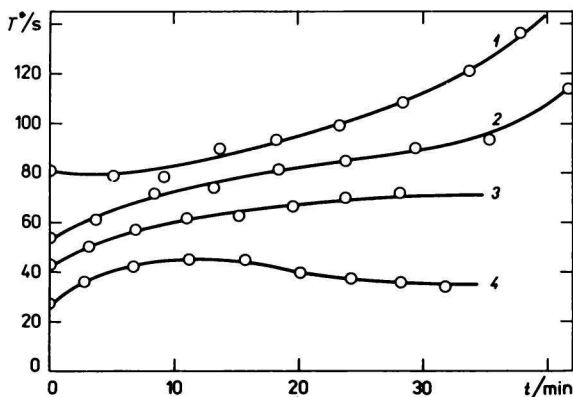


Fig. 2. Time dependence of the period of oscillations at different substrate concentration.
 $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, $\theta = 30^\circ \text{C}$.
 $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) = 0.6 \times 10^{-2} \text{ mol dm}^{-3}$ (1), $0.9 \times 10^{-2} \text{ mol dm}^{-3}$ (2), $1.2 \times 10^{-2} \text{ mol dm}^{-3}$ (3), $1.8 \times 10^{-2} \text{ mol dm}^{-3}$ (4).

The duration of oscillations in the system ($c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) = 8 \times 10^{-3} \text{ mol dm}^{-3}$) varies with bromate concentration (Table 3). The dependence of duration time of oscillations on substrate concentration of the system ($c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$) is more conspicuous (Fig. 3). The duration time of oscillations investigated polarographically with a rotating platinum electrode increases with substrate concentration in the region of low concentrations, reaches the maximum value at $c = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$ and decreases subsequently. If we introduce the ratio of bromate

Table 3

Variation of the duration time of oscillations with KBrO_3 concentration
 $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) =$
 $= 8 \times 10^{-3} \text{ mol dm}^{-3}$, $\theta = 30 \text{ }^\circ\text{C}$

$c(\text{KBrO}_3) \cdot 10^3 / (\text{mol dm}^{-3})$	Duration time of oscillations/min
4.0	29.5
6.0	51.0
8.0	70.4
15.0	49.0
25.0	32.5
35.0	36.0
45.0	47.3

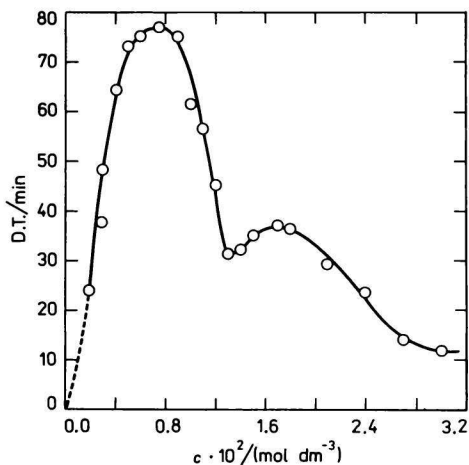


Fig. 3. Variation of the duration time of oscillations with substrate concentration.
 $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, $\theta = 30 \text{ }^\circ\text{C}$.

concentration to substrate concentration q , the position of maximum corresponds to the value $q = 2.0$. The second but rather lower maximum of this relationship corresponds to the value $q \approx 1$. The duration time of oscillations decreases again with further increase in substrate concentration. There is a minimum between two maxima which corresponds to the value $q = 1.15$. The duration time of oscillations in the maximum ($q = 2.0$) and minimum ($q = 1.15$) as a function of temperature has the character conformable to the Arrhenius equation. By using this equation, we evaluated the activation energy corresponding to the maximum ($q = 2.0$) $E = 61 \text{ kJ mol}^{-1}$ and to the minimum ($q = 1.15$) $E = 80 \text{ kJ mol}^{-1}$.

The way of oscillation vanishing is twofold. At low substrate concentrations ($c(\text{ester}) = (2-6) \times 10^{-3} \text{ mol dm}^{-3}$), the oscillations disappear by transition into a chaotic stage, i.e. the oscillations with greater amplitude appear only rarely and irregularly (Fig. 4a). At higher substrate concentrations, the oscillations vanish in the form of damped regular oscillations (Fig. 4b).

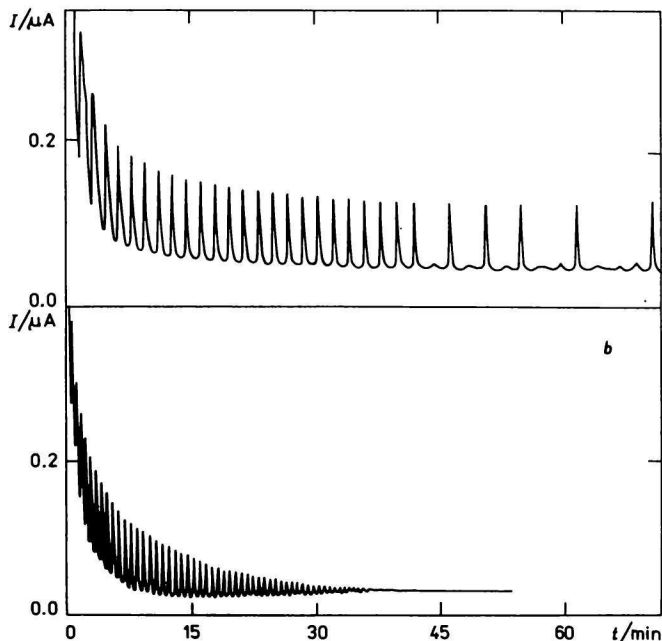


Fig. 4. Two ways of disappearance of oscillations.

$c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, $\theta = 30^\circ \text{C}$.
 a) $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) = 6 \times 10^{-3} \text{ mol dm}^{-3}$; b) $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$.

The duration time of oscillations as well as the pertinent induction period changes with initial concentration of the Br^- ions (Table 4). The duration time of oscillations slightly increases with initial concentration of the Br^- ions, reaches the maximum value at

Table 4

Variation of the induction period and duration time of oscillations with initial concentration of KBr
 $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$, $c(\text{MnSO}_4) = 8 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{KBrO}_3) = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$,
 $c(\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5) = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\theta = 30^\circ \text{C}$

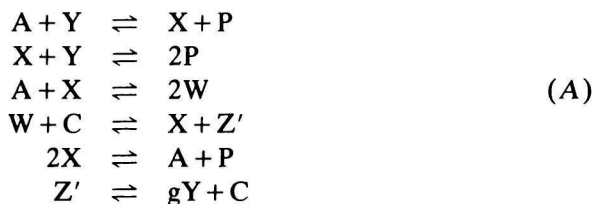
$c(\text{KBr}) \cdot 10^3 / (\text{mol dm}^{-3})$	I.P./min	D.T./min
0.2	2.0	73
0.25	2.3	79
0.5	2.4	86
1.0	3.5	76
2.0	8.1	35
3.0	Pending 2 h no oscillations	

$c(\text{KBr}) = 5 \times 10^{-4} \text{ mol dm}^{-3}$ and decreases afterwards. The system does not oscillate even after 2 h if $c(\text{KBr}) = 3 \times 10^{-3} \text{ mol dm}^{-3}$.

The oscillations in the described system may also be investigated spectrophotometrically at the optimum wavenumber $\bar{\nu} = 36 \times 10^3 \text{ cm}^{-1}$. The character of the relations thus obtained qualitatively corresponds to the above-described relationships. The differences in duration time of oscillations at equal composition of the reaction system are evidently due to the technique of stirring and thus to the degree of access (transport) of oxygen [6].

Discussion

The virtue of the BZ oscillating system with the ethyl ester of 3-oxobutanoic acid in comparison with the BZ system containing malonic acid consists in the fact that the system oscillates even without mechanical stirring [6]. Though the mechanism of the BZ reaction was several times analyzed [13—15], some problems remain open and a complete successive model is missing for the time being. The oscillating behaviour of a BZ system is usually compared with "oregonator" which was originally proposed by *Field* and *Noyes* [16]



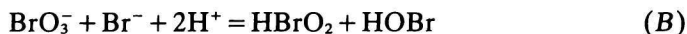
where A, W, X, Y, C, and Z' stand for BrO_3^- ions, BrO_2 radicals, HBrO_2 , Br^- ions, Mn(II) ions, and Mn(III) ions, respectively. Symbol P represents an uneasily definable mixture of HOBr and a bromine derivative of organic substrate.

On the basis of the measured dependence of duration time of oscillation on substrate concentration (Fig. 3), we may state that the distinct maximum at $q = 2$ corresponds to the optimum conditions for the formation of intermediate HOBr . As the substrate in the system is a two-electron reductant, HOBr prevails at the ratio $q = 2$ as reduced form of the BrO_3^- ions. Its quasi-stationary concentration determines the rate of substrate bromination, *i.e.* the level of quasi-stationary concentration of the BrO_2 radicals and thus the quasi-stationary concentration of the Mn(II) ions. The second maximum (Fig. 3, $q \approx 1$) corresponds to the optimum conditions for the formation of intermediate HBrO_2 which, from the view-point of "oregonator", plays the decisive part in origination of oscillations [6, 14]. The corresponding values of the Arrhenius activation energies belong to the overall process at a given substrate concentration and, for this reason, they give information only about the influence of temperature on duration time of oscillations. Since the first maximum in our system is substantially higher, we may conclude that the

intermediate HOBr plays the decisive part concerning the duration time of oscillations in the BZ system containing the ethyl ester of 3-oxobutanoic acid in the presence of Mn(II)—Mn(III). The last step of "oregonator" based on Z' determines the value of stoichiometric factor g which must occur in the interval of the values $<0.25; 1.20>$ [13]. In this way, we may at least qualitatively explain the decrease in duration time of oscillations on either side of the maximum ($q = 2.0$). There are conditions for the disappearance of oscillations through the so-called chaotic stage in the region $q > 2.0$, while the oscillations vanish in the form of gradual damping at $q \lesssim 2.0$.

The linear decrease in period of the first oscillation with reciprocal value of substrate concentration relates to the linear dependence of the experimental rate constant of reduction of the Mn(III) ions by substrate on substrate concentration. The period of the first oscillation (as well as subsequent oscillations) comprises mainly the kinetics of reduction of the Mn(III) ions by substrate and, to a certain extent, by its bromine derivative.

As obvious from Table 4, the induction period and duration time of oscillations in a given system can be affected by an addition of KBr even in the region of low concentrations. If we compare these results with the results concerning the influence of the Br⁻ ions presented in papers [6] and [17], we may state that the BZ system containing the ethyl ester of the 3-oxobutanoic acid is much more sensitive to an addition of bromide than the BZ system containing malonic acid [17]. The value of initial concentration of the Br⁻ ions influences the quasi-stationary concentration of HBrO₂ and HOBr intermediates in the following steps according to the schemes



The dependence of duration time of oscillations on initial concentration of the Br⁻ ions which passes through a maximum (Table 4) in the sense of the above reaction steps gives evidence of the key role of the mentioned intermediates, especially of intermediate HOBr.

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