INFLUENCE OF SUBSTRATE ON MODIFIED OSCILLATION REACTIONS OF THE BELOUSOV-ZHABOTINSKII TYPE

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The kinetic parameters of the reaction steps of the oscillation cycle and the parameters of modified oscillation reactions of the Belousov–Zhabotinskii (BZ) type with oxalic acid, tartaric acid, and hypophosphite ions were compared with predictions of Edelson's analysis based on the mechanism of the classical BZ reaction.

Noszticzius and Bodiss[1] discovered a cerium-catalysed heterogeneous oscillation reaction of the BZ type with oxalic acid as substrate during removing bromine from the reaction solution by bubbling hydrogen. Similarly, we found for the first time oscillations in a completely inorganic system of the BZ type with hypophosphite ions as substrate[2], with tartaric acid[3], and oxalic acid[4]. These substrates, in contrast to those in the classical BZ reaction, do not form brominated derivatives which by reacting with the oxidised form of the catalyst would form Br^- ions. The latter are considered to be an intermediate product of principal importance in the oscillation reaction[5]. Noszticzius attributes a decisive role in the reaction mechanism of heterogeneous oscillation reactions to bromine[6].

Recently Edelson[7], starting from a modified mechanism of the BZ reaction[8], evaluated the relative importance of the individual reaction steps of the oscillation cycle and their influence on the basic reaction parameters. The aim of the present work is to compare the connexion between the kinetic parameters of the reaction steps and those of the oscillation reactions with the predictions of Edelson's analysis. Although the kinetics of some reactions of the studied substrates with bromine, Mn(III) and Ce(IV) ions was already described[9,10], it was necessary for the purpose of our work to investigate it under the conditions characteristic for the oscillations.

EXPERIMENTAL

The chemicals used were of reagent grade and the solutions were prepared from redistilled water. A solution of Mn(III) ions was prepared by reduction of permanganate with an excess of $MnSO_4$ in the medium of 5M-H_2SO_4. The reaction solution was bubbled with pure nitrogen.

The oscillation reactions took place in a tempered glass vessel of 20 ml holding capacity, from which volatile products were transferred by bubbling nitrogen into a polarographic Kalousek cell, filled with 1·5M-H_2SO_4. Here, the concentration of bromine, the only electroactive substance, was determined continually at a potential of −0·6 V against Hg/Hg_2SO_4 electrode (M.S.E.) filled with 1M-H_2SO_4. The rate of flow of nitrogen was maintained constant by using a UPLS type universal flow meter. In this way, the solution was stirred and its oversaturation was prevented. The experimental details were given previously[4].

The kinetics of oxidation of oxalic acid, tartaric acid, and hypophosphite ions was followed polarographically by recording the dependence of the limiting diffusion current of bromine at −0·6 V against M.S.E. The oxidation of these substrates with the oxidized form of the catalyst was followed at −0·2 V (M.S.E.), which corresponds to the limiting diffusion current of Mn(III) and Ce(IV) ions in 1·5M-H_2SO_4. The kinetics and the oscillations were followed on an OH 105 type polarograph (Radelkis, Hungary).

RESULTS

On the basis of the preceding work, we found the conditions under which the systems with oxalic or tartaric acid or $H_2PO_2^-$ ions oscillate, the initial reactant concentration being the same in each case. With Mn(II) as catalyst at a concentration of $3 . 10^{-3}$ mol/l, the initial concentrations were $8 . 10^{-3}$ mol/l BrO_3^-, 0·03 mol/l substrate, and 1·5 mol/l H_2SO_4 at 20°C, rate of flow of nitrogen 600 ml/min, and reaction volume 10 ml (Fig. 1).

When the system was catalysed by cerium, no oscillations in the presence of tartaric acid were observed. The initial concentrations in the presence of oxalic acid or hypophosphite ions were 0·02 mol/l BrO_3^-, 0·1 mol/l substrate, $2 . 10^{-3}$ mol/l Ce(III), and 1·5 mol/l H_2SO_4 at 20°C, rate of flow of nitrogen 600 ml/min, and reaction volume 10 ml.

The following parameters of the oscillation reactions were considered as characteristic: the period of oscillations (PO) – the time interval between two successive maxima of the bromine concentration; the amplitude (A) – the difference between

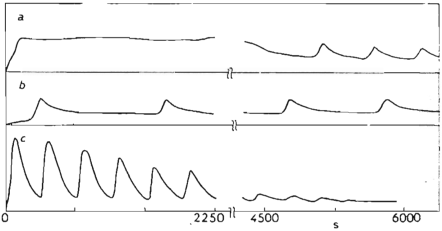

FIG. 1

Oscillations in the presence of Mn(II) (current in arbitrary units). $8 . 10^{-3}$ mol/l BrO_3^-, $3 . 10^{-2}$ mol/l substrate, $3 . 10^{-3}$ mol/l Mn(II), 1·5 mol/l H_2SO_4, 20°C, 600 ml N_2 per min *a* tartaric acid; *b* hypophosphite ions; *c* oxalic acid the maximum and minimum polarographic current during the oscillation; the induction period (IP) – the time after which the system starts to oscillate; and the critical concentration (c_k) of bromine corresponding to the minimum polarographic current (Table I).

We found that the noncatalysed oxidation of the substrate with BrO_3^- ions at concentrations used in the oscillation reactions proceeds very slowly. After 60 min, the concentration of BrO_3^- ions drops by 7% during the reaction with oxalic or tartaric acid and by 5% during the reaction with $H_2PO_2^-$ ions, the reaction solution being bubbled with nitrogen.

Redox reactions of bromine with the substrate were followed in solutions of 0·03 mol/l substrate, $2{\cdot}5 \,.\, 10^{-4}$ mol/l Br_2, and 1·5 mol/l H_2SO_4 at 20°C. The rate constant of the pseudo first-order reaction with $H_2PO_2^-$ ions, k_p, was evaluated from the linear dependence $\ln(I_0/I) = f(t)$, where I denotes the limiting diffusion current of bromine. The second-order rate constant, k, was calculated from the linear dependence of k_p on the concentration of $H_2PO_2^-$ ions. In the case of slower reactions of bromine with oxalic and tartaric acids, the rate constant was calculated as in ref.[11].

In the case of the reactions of the oxidized form of the catalyst with the substrate, the measured first-order rate constants are given (Table II), since the reactions are of fractional order with respect to the substrate concentration. For the reaction with oxalic acid, the lower limit of the rate constant for Ce(IV) and Mn(III) was determined.

DISCUSSION

Oscillations of the concentration of bromine in the studied reaction systems indicate that the rates of the formation and consumption of bromine

$$BrO_3^- + \text{reduced catalyst} \rightarrow Br_2 + \text{ox. catalyst} \qquad (1)$$

$$Br_2 + \text{substrate} \rightarrow Br^- + \text{product} \qquad (2.1)$$

$$Br_2 \text{ removed by streaming nitrogen} \qquad (2.2)$$

are different for most of the reaction time; they are equal only at the minimum or maximum of the bromine concentration. The drop in the bromine concentration due to the nitrogen streaming at 600 ml/min resembled a kinetic first-order equation with a reaction half-time of 32 s and a rate constant $k_{2,2} = 2{\cdot}16 \,.\, 10^{-2}\ s^{-1}$. The rate of nitrogen flow was so high that the bromine concentration decreased relatively rapidly even without contribution of reaction (2.1). Owing to the limited rate of transfer of bromine, the maxima and minima in the second cell are shifted in time by 40 s.

The oscillation cycle is finished by the regeneration of the catalyst:

$$\text{Ox. catalyst} + \text{substrate} \rightarrow \text{red. catalyst} + \text{products} \qquad (3)$$

Since the quantity of bromine produced in one oscillation cycle may be larger than would follow from the kinetics and stoichiometry of reaction (*1*), the role of the substrate is not restricted to the following regeneration of the reduced form of the catalyst. According to the experimental results, both bromine and the catalyst oscillate synchronously and when their concentration is a maximum, the rates of production and consumption of bromine are equal to each other.

According to Edelson's analysis[7], the oscillation period in the case of classical BZ substrates is most strongly influenced by the rate of formation of their enol form and

TABLE I

Parameters of oscillation reactions. Experimental data for Mn(II) as in Fig. 1, for Ce(III) 0·02 mol/l BrO_3^-, 0·1 mol/l substrate, 0·002 mol/l Ce(III), 1·5 mol/l H_2SO_4, 20°C, 600 ml/min N_2

Substrate	PO_1, s		A_1, parts		IP, s		c_k, parts		No of oscil.	
	Mn(II)	Ce(III)	Mn(II)	Ce(III)	Mn(II)	Ce(III)	Mn(II)	Ce(III)	Mn(II)	Ce(III)
$C_2H_2O_4$	360	200	20	86	45	~0	4	45	16	12
$C_4H_6O_6$	555	—	4	—	5 100	—	4	—	17	—
$H_2PO_2^-$	1 350	405	4	54	300	1 600	3	5	10	8

TABLE II

Kinetic parameters for reactions of substrates with Mn(III), Ce(IV), and Br_2. 1·5 mol/l H_2SO_4, about $1 \cdot 10^{-3}$ mol/l Mn(III), $1 \cdot 10^{-3}$ mol/l Ce(IV), $2{\cdot}5 \cdot 10^{-4}$ mol/l Br_2, $3 \cdot 10^{-2}$ mol/l substrate

Substrate	k, s^{-1}		
	Mn(III)	Ce(IV)[a]	Br_2
$C_2H_2O_4$	$\geqq 0{\cdot}1$	$\geqq 0{\cdot}12$	$2{\cdot}3 \cdot 10^{-3}$[b]
$C_4H_6O_6$	$5{\cdot}1 \cdot 10^{-3}$	$6{\cdot}5 \cdot 10^{-4}$	$1{\cdot}8 \cdot 10^{-3}$[b]
$H_2PO_2^-$	$2{\cdot}8 \cdot 10^{-3}$	$7{\cdot}4 \cdot 10^{-4}$	$0{\cdot}5$[c]

[a] 0·1 mol/l substrate; [b,c] second-order rate constants; [b] evaluated according to ref.[11]

of the subsequent bromination. In our case, however, the substrates cannot form bromo derivatives. Instead of removing bromine from the reaction system chemically, it is removed by a physical process. The rate constant of its reaction with 0.03M-$-H_2PO_2^-$ ions suggests that about 59% of the bromine formed in every cycle is removed by nitrogen streaming at a rate of 600 ml/min. In the case of 0·03M oxalic or tartaric acid, the same rate of flow is sufficient to remove nearly all the produced bromine.

The reaction rate of bromine with $H_2PO_2^-$ ions, oxalic and tartaric acid are in the ratio of 284 : 1·3 : 1 and the corresponding oscillations periods in the presence of Mn(II) as catalyst are 1 350, 360, and 555 s. Also with Ce(III) as catalyst, the oscillation period with $H_2PO_2^-$ ions was longer than with oxalic acid. On the other hand, the higher is the reaction rate of the substrate with the oxidized form of the catalyst, the shorter is the oscillation period. No oscillations were observed in the system with 0·1M tartaric acid containing Ce(III) ions, the rate constant of the first-order reaction of Ce(IV) with tartaric acid being as low as $6 \cdot 5 \cdot 10^{-4} \text{ s}^{-1}$.

The oscillation amplitude of bromine at constant rate of flow of nitrogen can be considered as a measure of the concentration changes of bromine in the reaction system. According to Edelson[7], reactions leading to the formation of Ce(IV) through BrO_2. radicals have the greatest influence on the amplitude of Ce(IV) concentration. We used always the same initial concentration for the given catalyst, hence the oxidation rate of its reduced form by the BrO_2. radical should be also the same. According to Edelson[7], the amplitude (A) depends also on the rate of the reaction of the oxidized catalyst with the substrate. According to the theory, this dependence is indirect; according to the experiments, the amplitude decreases in the order oxalic acid > tartaric acid > $H_2PO_2^-$ ions with Mn(II), and oxalic acid > hypophosphite with Ce(III).

The same trend was observed at an increased rate of flow of nitrogen, namely 1 100 ml/min, whereby the concentration of bromine in the reaction solution was decreased with a half-time of 18 s. The increased rate of flow caused a diminution of the induction period in the reaction of tartaric acid with Mn(II) ions from 5 100 to 2 700 s, and an increase of the induction period in the reaction with hypophosphite ions from 300 to 1 575 s. In the former case, a higher concentration of bromine is established than in the latter, so far as the induction period is concerned.

Edelson's analysis was applied to the mechanism of the classical BZ reaction with malonic acid[7]. A constant concentration of certain reactants was assumed, whereby the oscillations became well reproducible with a constant period and amplitude. Under our experimental conditions, we observed a decrease both of the reactant concentrations (BrO_3^- ions and substrate) and of the total concentration of all bromine compounds in the system. The studied group of substrates is distinguished by the fact that removal of the bromine formed is necessary for the oscillations to take place.

This may be the reason why the analysis based on the mechanism of the classical BZ reaction does not give adequate estimates of the parameters of the oscillation reactions under study.

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