BROMINE AND PERIOD OF BELOUSOV–ZHABOTINSKII TYPE OSCILLATION REACTION

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Belousov–Zhabotinskii type oscillation reaction with oxalic acid proceeds in a closed system, in a flow-through open system, as well as under intermediate conditions. Oscillations are started in either of the following three ways: *1)* Increasing the removal of bromine from solution by bubbling inert gases, *2)* chemically, and *3)* in a flow-through reactor. The oscillation period is largely dependent on the removal rate of bromine, other reactant concentrations being constant.

According to the FKN mechanism[1] of the Belousov–Zhabotinskii oscillation reaction, Br^- ions play the role of a controlling intermediate product, in analogy to the general mechanism of bromate oscillators[2]. The formation of Br^- ions by a reaction of the oxidized form of the catalyst with a brominated substrate is considered to be the main function of "classical" (*i.e.* brominateable) organic substrates. Recently, however, oscillations were described in systems with non-brominateable organic substrates[3−7] or with hypophosphite ions as substrate[8], the reaction solution being bubbled with a gas. Oscillations in the system BrO_3^-–Br^-–catalyst were observed in a stirred flow-through reactor[9], where also many inorganic substrates, including $HClO_2$, SO_3^{2-}, AsO_3^{3-}, N_2H_4, I^-, and Sn^{2+}, show an oscillating behaviour[10,11]. New experimental findings led to the proposal of a mechanism[12,13] based on the known Lotka–Volterra scheme. D'Alba[14] proposed another mechanism based on phase exchange and pulse supersaturation.

Although the FKN mechanism has been successful in describing the classical Belousov–Zhabotinskii reaction, there are some problems related mainly to malonic acid, and lack of experimental facts about organic intermediate products. Therefore, attention has been paid in recent years to simpler organic or inorganic substrates. We chose oxalic acid (OA), which has several advantages. Its oxidation leads only to CO_2, an inert product. It reacts suficiently rapidly with the oxidized form of the catalyst and sufficiently slowly (autocatalytically in a closed system) with BrO_3^- ions. The latter reaction in the presence of a catalyst leads to Br_2, the concentration of which must be decreased by some means in order to bring about oscillations of Br_2 or catalyst[3,4]. This was achieved by bubbling hydrogen[3] or nitrogen[4]. The aim of the present work was to study the influence of the rate of removal of Br_2 from the system BrO_3^-–OA–Ce(III) in 1·5M-H_2SO_4 on the oscillation period.

EXPERIMENTAL

Chemicals

Freshly prepared solutions of reagent grade $KBrO_3$, $(COOH)_2.2 H_2O$, $Ce_2(SO_4)_3.8 H_2O$, and H_2SO_4 in redistilled water were used.

Apparatus and Method

The physical method of removal of Br_2 from the raction system consisted simply in bubbling the solution with hydrogen, nitrogen, or argon. The rate of flow of the gas was measured by a flow meter of the type TG 400 (GDR) and the values were in the range $0.6—2.27$ l/min for hydrogen, $0.433—0.7$ l/min for nitrogen, and $0.425—0.63$ l/min for argon. The volume of the reaction solution was 10 ml and it contained $0.01\text{M-}KBrO_3$, $0.025\text{M-}OA$, and $0.001\text{M-}Ce(III)$ in $1.5\text{M-}H_2SO_4$ at 25°C.

Bromine was from the reaction system removed also chemically, namely by adding a solution of acetone or malonic acid (MA) into the reaction solution. The oscillation reaction proceeded in 10 ml of the same solution as given above in a Kalousek cell thermostated at 25°C. The indicator electrode was a bromide ion-selective electrode Crytur type $35—17$ (Czechoslovakia), and 1M mercurous sulphate electrode served as reference. Oscillations of the potential were recorded on an OH-105 type polarograph (Hungary). The kinetics of the reaction of Br_2 with acetone and MA was followed by means of a spectrophotometer Specord UV-VIS (GDR). The time change of the absorbancy of a Br_2 solution in $1.5\text{M-}H_2SO_4$ containing acetone or MA at 400 nm in 5 cm cuvettes was recorded at 22°C. The concentration of Br_2 was calculated from the absorption coefficient $\varepsilon_{400} = 166 \text{ M}^{-1} \text{ cm}^{-1}$ (ref.[15]). Since BrO_3^- ions are also present in the oscillation system, the kinetics of the reaction of Br_2 with acetone and MA was followed besides in the presence of BrO_3^- ions in the same medium.

As a third possibility, the concentration of Br_2 can be decreased by using a flow-through reactor. The solution volume was $V = 74$ ml, temperature 22°C, and the volume of the glass reactor 100 ml. The starting concentrations were $[BrO_3^-]_0 = 0.01$ mol/l, $[OA]_0 = 0.025$ mol/l, $[Ce(III)]_0 = 0.001$ mol/l, and $[H_2SO_4]_0 = 1.5$ mol/l. Bromate ions were added at last and at the same time a peristaltic pump Zalimp 315 (Poland) was switched on, by means of which three separate reactants in $1.5\text{M-}H_2SO_4$ were supplied into the reactor. The concentrations of their stock solutions were by the factor of 3 higher than the starting concentrations given above. The rate of flow of each of the reactant solution was $u = 36$ ml/min, hence the cumulative rate of flow $U = 108$ ml/min and the flow rate referred to the given volume $k_R = U/V = 2.43$. $. 10^{-2} \text{ s}^{-1}$. The supply of reactants was exactly compensated by the flowing off of partly reacted compounds. The potential oscillations were indicated by the bromide selective electrode immersed in the reactor. A saturated calomel electrode served as reference, connected with the reaction solution by an agar-agar bridge filled with a solution of Na_2SO_4. The potential changes were recorded on the OH-105 polarograph. Prior to switching on the reactor, the reaction and stock solutions were deaerated by bubbling nitrogen. At the given rate of flow, the reaction solution was sufficiently well stirred, the results were reproducible and no stirrer was used. Decreasing the volume rate of flow, U, and the solution volume in the reactor, V, to one half (the value of k_R being the same as before) did not cause changes in the oscillation behaviour of the system.

The oscillations were easily observable visually owing to the intense yellow colour of Ce(IV) ions. The oscillation characteristics did not change on replacing the polarographic Kalousek cell by another one and keeping the rate of removal of bromine constant (*i.e.* constant bubbling rate or constant concentration of the compound reacting with bromine).

RESULTS

Decreasing the Bromine Concentration by Bubbling Gas

Oscillations of the catalyst and bromine concentrations can be started by bubbling gases through the reaction system. The influence of the bubbling rate on the first period of the oscillations (PO_1) is given in Table I. This quantity is defined as the time difference between the first and second maximum of the bromine concentration, and it is identical to the time lag between two successive maxima of the $Ce(IV)$ concentration (observed visually). At the given conditions, the oscillations start practically without any induction period. Calibration experiments showed that the following equation holds good

$$-\mathrm{d}[Br_2]/\mathrm{d}t = k_F[Br_2] , \qquad (1)$$

where k_F depends on the bubbling rate, other conditions being kept constant. However, it is interesting to note that k_F depends on the quality of the gas. Thus, the value of $k_F = 0.023 \text{ s}^{-1}$ (half-time 30 s) corresponds to the rate of flow of hydrogen 1·127

TABLE I

Influence of the rate of gas flow on the oscillation period. Solution of 0.01M-BrO_3^-, 0.025M-OA, 0.001M-Ce(III), and $1.5\text{M-H}_2\text{SO}_4$; volume 10 ml, 25°C

Gas	H$_2$				N$_2$				Ar			
Flow rate, l min^{-1}	0·60	1·137	1·516	2·274	0·433	0·50	0·60	0·70	0·525	0·51	0·60	0·63
PO$_1$, s	360	150	126	102	390	210	150	132	600	222	160	150

TABLE II

Influence of acetone and malonic acid on the oscillation period. Same conditions as in Table I

	B	Acetone			Malonic acid	
c, mol l^{-1}		0·05	0·1	0·2	0·004	0·006
PO$_1$, s		295	150	88	150	114

l/min, nitrogen 0·60 l/min, and argon 0·63 l/min. These rates of flow lead also to the same value of $PO_1 = 150$ s, a time during which the bromine concentration drops to 3·1% of its initial value. Preliminary results indicate that about $5 . 10^{-4}$M-Br_2 is formed during the first oscillation cycle. The form of the oscillations of Br_2 suggests that its concentration in the meantime between the first and second maximum is decreased practically only by bubbling, hence after 150 s it decreases to about 1·5 . $. 10^{-5}$ mol/l. This value may be considered critical (for given concentrations of BrO_3^- and H^+ ions), since after its attainment the oxidation of Ce(III) with BrO_3^- ions can proceed again (*i.e.* another cycle).

Decreasing the Bromine Concentration Chemically

The concentration of bromine in the reaction system can be decreased by adding acetone or malonic acid which are susceptible to bromination. The system BrO_3^-, OA, Ce(III) in 1·5M-H_2SO_4 is caused to oscillate after adding one of these compounds. In the absence of OA, no oscillations can be provoked. To ensure regular oscillations, the solution was stirred electromagnetically or by bubbling slightly with nitrogen (*e.g.* 1 bubble per 2 s). The slow bubbling caused removal of bromine from the solution at a half-time longer than 480 s, an effect which can be neglected against the chemical removal and is by itself insufficient to bring about oscillations. The different modes of stirring did not affect the oscillation characteristics. The results in Table II indicate that the value of PO_1 depends on the concentration of acetone or malonic acid.

We measured the rate of the reaction of bromine with acetone or MA in the given reaction medium. The rate is given as

$$-d[Br_2]/dt = k'_{Ch} , \qquad (2)$$

where the rate constant k'_{Ch} is directly proportional to the concentration of the reactant, *i.e.*

$$-d[Br_2]/dt = k_{Ch}[B] , \qquad (3)$$

where B stands for acetone or MA. For acetone, we found $k_{Ch} = 7·9 . 10^{-5}$ s^{-1} and for MA $k_{Ch} = 1·95 . 10^{-3}$ s^{-1} in the medium of 1·5M-H_2SO_4 at 22°C. In the presence of BrO_3^- ions, bromine is removed more slowly (Fig. 1) and $k_{Ch} = 3·2 .$ $. 10^{-5}$ s^{-1} for acetone and $8·1 . 10^{-4}$ s^{-1} for MA regardless of the concentration of bromate in the range $0·005 - 0·02$M-BrO_3^-. It follows that the reaction of bromine with MA is by the factor of 25 more rapid than that with acetone.

On the assumption that $5 . 10^{-4}$M-Br_2 is generated during the first oscillation cycle, it follows from Eq. (3) that in the presence of 0·1M acetone or $4 . 10^{-3}$M-MA the critical concentration of bromine, $1·5 . 10^{-5}$ mol/l, is attained after about 150 s

(Fig. 2). Indeed, it is seen from Table II that $PO_1 = 150$ s just at the mentioned concentrations of acetone or malonic acid.

Decreasing the Bromine Concentration in Flow-through Reactor

The time course of the potential of a bromide selective electrode in the flow-through reactor containing 0.01M-BrO_3^-, 0.025M-OA and 0.001M-Ce(III) in $1.5\text{M-H}_2\text{SO}_4$ is shown in Fig. 3. The potential oscillations were synchronous with the colour changes due to oscillations of the catalyst. The rate of removal of bromine can be expressed as

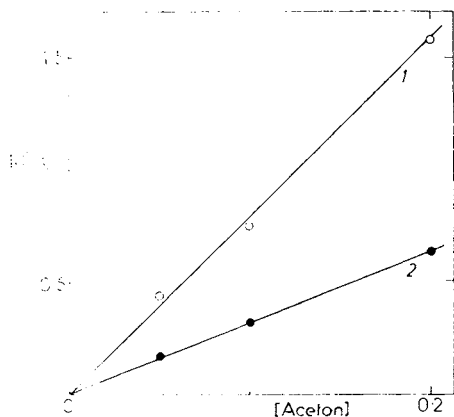$$-\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = k_\mathrm{R}[\mathrm{Br}_2] , \qquad (4)$$

FIG. 1

Influence of acetone on rate constant k'_Ch. *1* 0.001M-Br_2 in $1.5\text{M-H}_2\text{SO}_4$, 22°C; *2* same solution + 0.01M-BrO_3^-
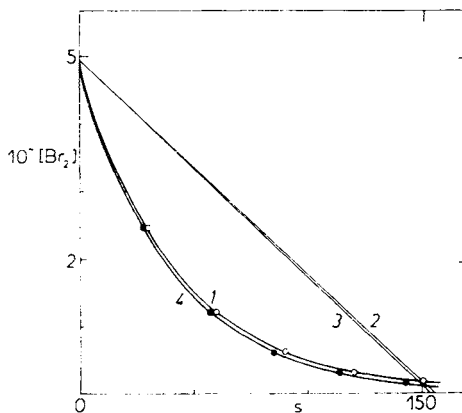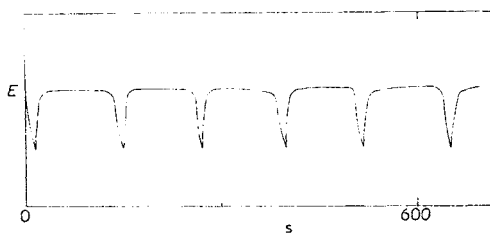

FIG. 2

Time dependence of the concentration of bromine. *1* Physical removal, $k_F = 0.023\ \text{s}^{-1}$; *2* chemical removal with 0.1M acetone; *3* chemical removal with 0.004M-MA; *4* in flow-through reactor, $k_R = 0.0243\ \text{s}^{-1}$

FIG. 3

Potential oscillations of bromide ion-selective electrode in flow-through reactor. Solution of 0.01M-BrO_3^-, 0.025M-OA, 0.001-M-Ce(III), and $1.5\text{M-H}_2\text{SO}_4$ (initial composition); $k_R = 0.0243\ \text{s}^{-1}$, 22°C

where $k_R = 2.43 \cdot 10^{-2} \, s^{-1}$ under our conditions. The corresponding half-time is equal to 28 s. It is seen from Fig. 2 that the critical concentration of bromine, $1.5 \cdot 10^{-5}$ mol/l, is attained after 140 s in good agreement with the first oscillation period in the flow-through reactor, 135 s.

DISCUSSION

Belousov–Zhabotinskii oscillations in a system with oxalic acid can take place in a closed system, in a flow-through open system, as well as under intermediate conditions provided that the bromine formed is continually removed by some means as shown in our work. Since its formation rate depends on the concentrations of the reactants, which were kept constant, it may be assumed that the same concentration of bromine is established at the end of the first cycle in each case. The presence of bromine involves the presence of bromide ions and HOBr, formed by hydrolysis of bromine with a rate constant $k_h = 110 \, s^{-1}$. For the back reaction, $k_{-h} = 8 \cdot 10^9 \, l^2 \, mol^{-2} \, s^{-1}$. If the hydrolysis is rapid enough, the concentration of Br^- ions can be calculated from that of Br_2. At the critical concentration of Br_2 we have $[Br^-] \approx 3.7 \cdot 10^{-7}$ mol/l, while the maximum concentration of Br^- ions is about $2.1 \cdot 10^{-6}$ mol/l. These values are based on experiments in which the oscillations of the bromine concentration were recorded, bromine being removed physically. In the other cases, the oscillations of the potential of the Br^- selective electrode were recorded. However, since the concentration of Br^- ions was very low, it could be expected that the potential measurements were distorted by the presence of other components of the system[16,17]. Therefore, in the experiments with acetone and MA and in the flow-through reactor the concentration of Br^- ions was not determined.

We assume that the only function of acetone and MA is the reaction with bromine, giving 1 mol Br^- per 1 mol Br_2. During the oscillation reaction, 1 mol Br^- gives 0.6 mol Br_2 by rapid reaction with BrO_3^-, causing a decrease of the rate of consumption of bromine in the reaction by a factor of 0.4. Experimentally, we found a factor of $1/2.46$ for acetone and $1/2.4$ for MA, the difference being negligible. The rate of formation of Br^- ions by the reaction of Br_2 with OA is relatively low even if we take into account the rate constant of the more reactive HOBr, which is in equilibrium with Br_2, $k_{HOBr} = 222 \, l \, mol^{-1} \, s^{-1}$ (ref.[18]).

In the absence of acetone or MA, 1 mol Br_2 gives 2 mol Br^- and in the presence of BrO_3^- there is a back reaction giving rapidly 1.2 mol Br_2. Owing to the high rate of this reaction, the concentration of bromine in the system BrO_3^-, Br_2, OA increases.

Since the reaction of Ce(IV) with OA is much more rapid than that with acetone or MA, it seems that regeneration of the reduced form of the catalyst is one of the functions of the substrate. Oxalic acid decreases the concentration of Ce(IV) to a value that has no influence on the rate of oxidation of Ce(III) with BrO_3^-. In such a case oscillations appear, the period of which is controlled by the rate of removal of bromine

from the reaction solution. Removal of bromine by bubbling gas with $k_F = 0.023 \text{ s}^{-1}$ or in a flow-through reactor with the same value of k_R is equivalent to chemical removal of bromine with 0.1M acetone of $4 \cdot 10^{-3}\text{M}$ malonic acid and causes oscillations the first period of which is equal to 150 s in the system 0.01M-BrO_3^-, 0.025M-OA, and 0.001M-Ce(III) in $1.5\text{M-H}_2\text{SO}_4$.

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