

## OSCILLATIONS OF BROMINE IN BELOUSOV-ZHABOTINSKII TYPE REACTION WITH OXALIC ACID

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The authors studied the influence of the concentrations of reactants and catalysts on the parameters of the catalysed oscillation reaction of bromate ions with oxalic acid in the medium of sulphuric acid. Ce(IV) and Mn(III) ions induce the reaction of bromine in the oxidation state either +1 or 0 with oxalic acid. In the presence of bromate ions, the induced reaction can lead to the formation of the same quantity of bromine as in the first oscillation cycle of the oscillation reaction.

Recently Noszticzius, Farkas and Schelly<sup>1</sup> proposed a new scheme of the Belousov-Zhabotinskii oscillation reaction, called Explodator. Based mainly on their arguments, Noyes<sup>2</sup> elaborated a revised model of the well-known Oregonator<sup>3</sup>. In six irreversible steps, he considers reactions of three important intermediate products, namely HBrO<sub>2</sub>, HOBr, and Br<sup>-</sup> ions. Explodator<sup>1</sup> is a five-step model with two autocatalytic reactions and three important intermediate products. HBrO<sub>2</sub>, HOBr, and bromine.

Both models can also be applied to systems with bromate ions, a catalyst, and nonbrominatable organic substrates, such as oxalic acid. Here, the oscillating behaviour is shown by the catalyst and bromine, if the latter is removed from the reaction solution by bubbling an inert gas<sup>4,5</sup>.

At constant concentration of the reactants, the period of oscillations in the system with oxalic acid is determined by the rate of removal of bromine from the reaction solution<sup>6</sup>. Nevertheless, it may be assumed that the quantity of Br<sub>2</sub> formed during the oscillation cycles and the oscillation period will depend on the reactant concentration. The present work deals with the influence of the concentration of BrO<sub>3</sub><sup>-</sup>, (COOH)<sub>2</sub>, Ce(III), Mn(II), and H<sub>2</sub>SO<sub>4</sub> on the quantity of bromine formed and on the oscillation period. The quantity of Br<sub>2</sub> produced during the oscillation cycles is compared with that formed in either catalysed or noncatalysed redox reaction of BrO<sub>3</sub><sup>-</sup> and Br<sub>2</sub> with (COOH)<sub>2</sub> under nonoscillating conditions, *i.e.* without bubbling an inert gas.

### EXPERIMENTAL

Freshly prepared solutions of reagent grade chemicals in redistilled water were used. The oscillation reaction was followed as described earlier<sup>5</sup> except that the time dependence of the polaro-

graphic current of bromine (formed in the reaction cell and transferred by a stream of nitrogen into the polarographic cell) was recorded on an LP 7e type polarograph (Laboratorní přístroje, Prague). The quantity of  $\text{Br}_2$  formed during the oscillation cycle was determined from calibration experiments, where the area delimited by the polarographic curve of bromine in the second cell, i.e.  $\int I_{\text{Br}_2} dt$ , was measured as function of the quantity of  $\text{Br}_2$  in the first cell. We used 10–30 ml of  $0.3\text{--}8 \cdot 10^{-4}\text{M-Br}_2$  solution which was prepared by reaction of bromate with bromide ions in the medium of  $1.5\text{M-H}_2\text{SO}_4$ ; one of the reactants was in excess to accelerate the reaction. The bromine thus prepared was transferred by nitrogen streaming at a rate of 600 ml/min into the polarographic cell. Solutions of a known bromine concentration prepared in either way gave calibration straight lines of an equal slope.

During the oscillation reaction, the reactant concentration decreases and the quantity of bromine produced in individual cycles is lowered. We therefore evaluated the area of the first peak as the quantity of bromine in the first cycle ( $n_{\text{Br}_2}$ ) corresponding to the initial concentrations of the reactants. Accordingly, we measured the first oscillation period ( $PO_1$ ) as the time elapsed between the first and second current maximum. The volume of the reaction solution was 10 ml and the temperature was  $25^\circ\text{C}$ .

Both the initial (maximum) and instantaneous concentrations of bromine at a known rate of its removal ( $t_{1/2} = 19\text{ s}$ ) were determined in the calibration experiments. In the oscillation reaction with Ce(III) catalyst, the bromine concentration in the first cycle decreases from the rapidly attained maximum similarly to the calibration experiments, i.e. the form of the curve  $I_{\text{Br}_2} = f(t)$  is very similar. This suggests that the concentration of bromine between the two maxima is controlled by the rate of flow of nitrogen. However, in the case of the Mn(II) catalyst, at the same rate of flow of nitrogen, the decrease of the bromine concentration after its rapid increase is slower. This suggests that a certain quantity of bromine is formed simultaneously with its physical removal and its concentration in the system cannot be described by the same kinetic equation as in the case of Ce(III).

The reaction of bromate ions and bromine with oxalic acid in  $1.5\text{M-H}_2\text{SO}_4$  was also followed spectrophotometrically without bubbling nitrogen. We measured the time dependence of the absorbancy of bromine at 400 nm in 2–5 cm cuvettes. The concentration and quantity of bromine were calculated by using the molar absorption coefficient  $\epsilon_{400} = 165\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  (ref.<sup>7</sup>). The same procedure was used in studying the catalysis with Ce(IV) and Mn(III) ions. A solution of Mn(III) was prepared by rapid reaction of  $\text{MnO}_4^-$  with a 20-fold excess of  $\text{Mn}^{2+}$  ions in  $3\text{M-H}_2\text{SO}_4$ .

## RESULTS

The concentration of  $\text{BrO}_3^-$  ions influences the quantity of the produced bromine and the oscillation period (Fig. 1). In the case of Ce(III), it is possible to estimate the critical concentration of bromine,  $c_k$ , after whose attainment there is a rapid formation of Ce(IV) and  $\text{Br}_2$ :

$$c_k = (n_{\text{Br}_2}/V) \exp(-PO_1 \ln 2/t_{1/2}). \quad (1)$$

Here,  $n_{\text{Br}_2}$  denotes the number of moles of  $\text{Br}_2$  in the first cycle (we assume its rapid increase to a maximum and then only physical removal),  $V$  denotes the reaction volume,  $PO_1$  period of the first oscillation cycle, and  $t_{1/2}$  time after which the  $\text{Br}_2$  concentration drops to one half by bubbling nitrogen. Since the latter two quantities

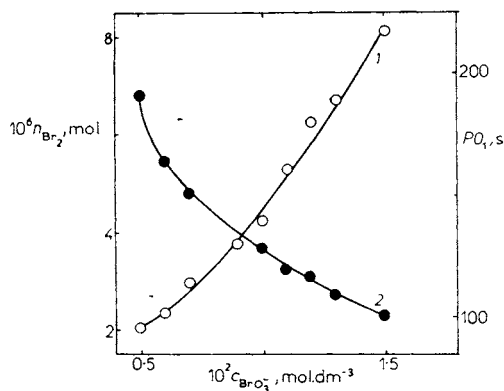


FIG. 1

1 Quantity of  $\text{Br}_2$  in the first cycle, 2 first oscillation period as function of the bromate concentration. 10 ml of a solution of  $2.5 \cdot 10^{-2} \text{M} (\text{COOH})_2$ ,  $10^{-3} \text{M} \text{Ce(III)}$ , and  $1.5 \text{M} \text{H}_2\text{SO}_4$  at  $25^\circ\text{C}$ ; rate of flow of nitrogen  $600 \text{ cm}^3 \text{ min}^{-1}$

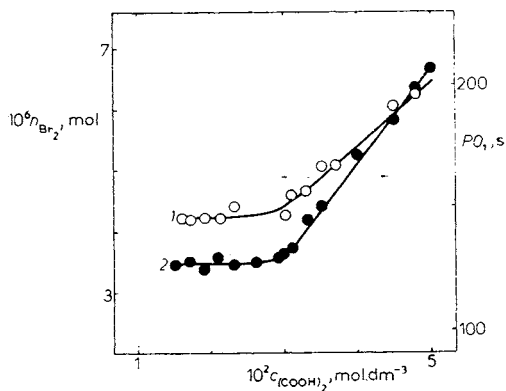


FIG. 2

Dependence of 1  $n_{\text{Br}_2}$  and 2  $PO_1$  on the concentration of  $(\text{COOH})_2$ . Solution of  $10^{-2} \text{M} \text{BrO}_3^-$  and  $10^{-3} \text{M} \text{Ce(III)}$ ; other data as in Fig. 1

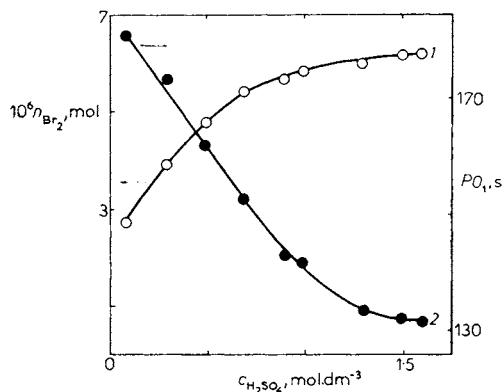


FIG. 3

Dependence of 1  $n_{\text{Br}_2}$  and 2  $PO_1$  on the concentration of  $\text{H}_2\text{SO}_4$ .  $10^{-2} \text{M} \text{BrO}_3^-$ ,  $2.5 \cdot 10^{-2} \text{M} (\text{COOH})_2$ , and  $10^{-3} \text{M} \text{Ce(III)}$ ; ionic strength  $1.7 \text{ mol dm}^{-3}$ , other data as in Fig. 1

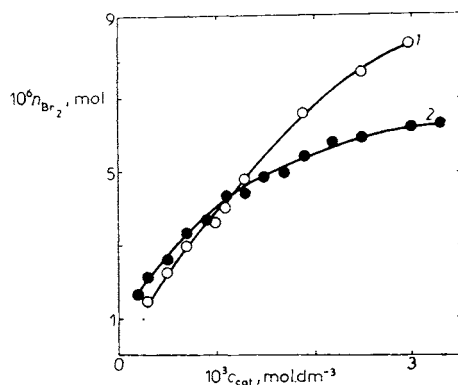


FIG. 4

Dependence of  $n_{\text{Br}_2}$  on the concentration of 1  $\text{Mn(II)}$  and 2  $\text{Ce(III)}$ .  $10^{-2} \text{M} \text{BrO}_3^-$ ,  $2.5 \cdot 10^{-2} \text{M} (\text{COOH})_2$ ; other data as in Fig. 1

were subject to an error of 11% on the average, the error in  $n_{\text{Br}_2}$  being 23%, the value of  $c_k$  is rather inaccurate. Nevertheless, we determined the dependence of  $c_k$  on the concentration of reactants. The value of  $c_k$  increases exponentially with the concentration of  $\text{BrO}_3^-$  ions. For  $0.01 \text{ mol dm}^{-3} \text{ BrO}_3^-$ ,  $0.025 \text{ mol dm}^{-3} (\text{COOH})_2$ , and  $0.001 \text{ mol dm}^{-3} \text{ Ce(III)}$  in  $1.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  we found  $c_k = (4.1 \pm 2.2) \cdot 10^{-6} \text{ mol dm}^{-3}$ .

The other reactant, oxalic acid, beginning from a concentration of about  $0.03 \text{ mol dm}^{-3}$ , increases the quantity of  $\text{Br}_2$  in the first cycle as well as the period (Fig. 2). It seems that  $n_{\text{Br}_2}$  is the lowest at the stoichiometric concentration, i.e.  $0.025 \text{ mol dm}^{-3} (\text{COOH})_2$ . The calculated dependence of  $c_k$  on the concentration of oxalic acid is roughly constant in the range  $0.015\text{--}0.031 \text{ mol dm}^{-3}$ , namely equal to  $(3.9 \pm 2.4) \cdot 10^{-6} \text{ mol dm}^{-3}$ , then decreases. With increasing concentration of oxalic acid, the curve  $I_{\text{Br}_2} = f(t)$  deviates still more and more from that in the calibration experiments. The ratio of  $n_{\text{Br}_2}/V$  is then not equal to the maximum (initial) concentration of bromine and Eq. (1) cannot be used.

With increasing concentration of sulphuric acid, at constant ionic strength equal to  $1.7 \text{ mol dm}^{-3}$ , both the quantity of bromine and the critical concentration  $c_k$  increases, while  $PO_1$  decreases (Fig. 3).

If the  $\text{Ce(III)}$  catalyst is replaced with  $\text{Mn(II)}$ , the first oscillation period in the entire concentration range increases. The dependence of the quantity of bromine on the catalyst concentration is shown in Fig. 4. The calculated critical concentration of bromine is independent of the concentration of  $\text{Ce(III)}$ ,  $c_k = (4.2 \pm 2.7) \cdot 10^{-6} \text{ mol dm}^{-3}$ , in the entire concentration range. The dependence of  $c_k$  on the concentration of  $\text{Mn(II)}$  could not be evaluated for the reasons mentioned above (Fig. 5).

The noncatalysed reaction of  $\text{BrO}_3^-$  with oxalic acid in  $1.5\text{M-H}_2\text{SO}_4$  without bubbling gas is slow. Although its autocatalytic character implies a more rapid reaction of  $\text{Br}_2$  (or  $\text{HOBr}$ , ref.<sup>11</sup>) with oxalic acid than with bromate ions, the reac-

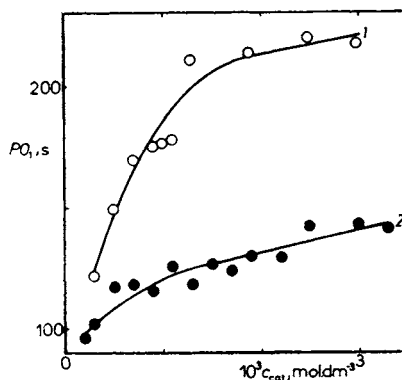


FIG. 5  
Dependence of  $PO_1$  on concentration of 1  $\text{Mn(II)}$  and 2  $\text{Ce(III)}$ . Same conditions as in Fig. 4

tion of  $\text{Br}_2$  or  $\text{HOBr}$  with oxalic acid is relatively slow, however it can be substantially accelerated by  $\text{Ce(IV)}$  or  $\text{Mn(III)}$ . (In such a case,  $\text{Ce(IV)}$  and  $\text{Mn(III)}$  can be called inductors rather than catalysts, since they are consumed in the reaction). These rapid reactions lead to  $\text{Br}^-$  ions and, in the presence of bromate, to bromine.

The dependence of absorbancy at 400 nm on the time cannot be described by a simple kinetic equation. We therefore determined the concentration of bromine during the catalysed reaction of bromate with oxalic acid in  $1.5\text{M-H}_2\text{SO}_4$  after 150 s (*i.e.* approximately the first oscillation period during bubbling) and after 660 s (at such a long time we were able to determine with a sufficient accuracy the concentration of bromine during the slow noncatalysed reaction). The results are given in Table I.

### DISCUSSION

It has been shown<sup>6</sup> that the oscillation period at constant concentration of the reactants and  $\text{Ce(III)}$  depends on the rate of removal of bromine from the solution. Besides the method used in the present work, the oscillations can be initiated in the presence of oxalic acid by a suitable chemical reaction of  $\text{Br}_2$  (*e.g.* with acetone or malonic acid) or by using a flow-through reactor<sup>6</sup>. This seems to be particularly suited for the study of numerous oscillation systems<sup>8,9</sup>.

TABLE I

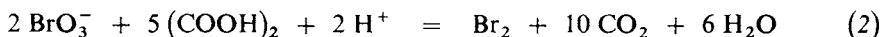
Influence of catalysts on reaction of  $\text{BrO}_3^-$  and  $\text{Br}_2$  with  $(\text{COOH})_2$  in  $1.5\text{M-H}_2\text{SO}_4$ . A stands for  $0.01\text{M-BrO}_3^- + 0.025\text{M-(COOH)}_2$ ; B stands for  $3.97 \cdot 10^{-4}\text{M-Br}_2 + 2.5 \cdot 10^{-2}\text{M-(COOH)}_2$

No	System	$10^4 c_{\text{Br}_2}$ after 150 s mol dm <sup>-3</sup>	$10^4 c_{\text{Br}_2}$ after 660 s mol dm <sup>-3</sup>
1	A	—	1.02
2	A + $10^{-3}$ mol dm <sup>-3</sup> Ce(III)	2.86	5.27
3	A + $2 \cdot 10^{-3}$ mol dm <sup>-3</sup> Ce(III)	4.06	7.0
4	A + $10^{-3}$ mol dm <sup>-3</sup> Mn(II)	4.23	11.7
5	A + $2 \cdot 10^{-3}$ mol dm <sup>-3</sup> Mn(II)	8.28	21.1
6	A + $2.5 \cdot 10^{-2}$ mol dm <sup>-3</sup> $(\text{COOH})_2$	—	1.73
7	As 6 + $10^{-3}$ mol dm <sup>-3</sup> Ce(III)	2.1	8.58
8	As 6 + $10^{-3}$ mol dm <sup>-3</sup> Mn(II)	3.46	15.06
9	A + $10^{-3}$ mol dm <sup>-3</sup> Ce(IV)	1.65	5.12
10	A + $10^{-3}$ mol dm <sup>-3</sup> Mn(III)	3.61	14.1
11	B	3.97	3.9
12	B + $10^{-3}$ mol dm <sup>-3</sup> Ce(III)	3.7	3.6
13	B + $10^{-3}$ mol dm <sup>-3</sup> Mn(II)	3.8	3.7
14	B + $10^{-3}$ mol dm <sup>-3</sup> Ce(IV)	1.9	1.38
15	B + $10^{-3}$ mol dm <sup>-3</sup> Mn(III)	0	0
16	As 14 + $10^{-2}$ mol dm <sup>-3</sup> $\text{BrO}_3^-$	6.81	13.8

The induction period of the autocatalytic reaction of Ce(III) with  $\text{BrO}_3^-$  (i.e. the time,  $IP$ , after which Ce(IV) begins to be formed) significantly decreases with increasing concentration of  $\text{BrO}_3^-$  and  $\text{H}^+$  ions, increases with the concentration of  $\text{Br}_2$  and  $\text{Br}^-$ , and is practically independent of the catalyst concentration<sup>10</sup>. The dependences of the oscillation parameters in the reaction with oxalic acid on the concentration of  $\text{BrO}_3^-$  and  $\text{H}_2\text{SO}_4$  in the presence of Ce(III) are in accord with the influence of bromine on the induction period  $IP$  of the reaction of Ce(III) with  $\text{BrO}_3^-$ . It seems that at higher concentrations of  $\text{BrO}_3^-$  or  $\text{H}^+$  ions more bromine is necessary to inhibit the oxidation of Ce(III) with  $\text{BrO}_3^-$  ions. In the studied range of (0.5 to 3.5) · 10<sup>-3</sup>M Ce(III), the increase of  $PO_1$  and  $n_{\text{Br}_2}$  compensate each other and  $c_k$  remains constant. Hence, as soon as the concentration  $c_k$  is reached (independent of the concentration of Ce(III)), the inhibition of the oxidation of Ce(III) with bromate ions stops. For example, for the reaction of 0.01M- $\text{BrO}_3^-$  with 10<sup>-3</sup>M-Ce(III) in 1.5M- $\text{H}_2\text{SO}_4$  in the presence of 4.35 · 10<sup>-4</sup>M- $\text{Br}_2$   $IP$  equals 126 s. Although the concentrations used by Barkin and coworkers<sup>10</sup> are different from those in the present work, it seems that the critical concentration of bromine and the oscillation period are both related to the concentration of bromine which controls (may be *via* its hydrolysis) the induction period in the oxidation of Ce(III) with bromate ions.

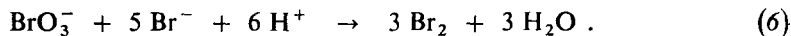
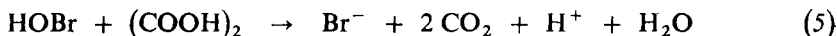
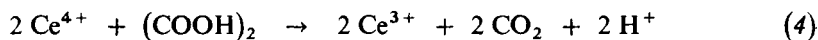
The results in Table I show that the catalysed reaction of bromine in the oxidation state +1 or 0 with oxalic acid produces after 150 s such a quantity of  $\text{Br}_2$  as observed in the first cycle of the oscillation reaction. Mn(III) is a more efficient catalyst than Ce(IV); this may be due to different stability of the complex formed by the catalyst in its higher oxidation state and oxalate ions, or perhaps to its different dissociation rate<sup>12</sup>. Since the rate of the catalysed reaction depends on the (instantaneous) concentration of the catalyst, the concentration of  $\text{Br}_2$  after 150 s depends on the initial concentration of the catalyst. A comparison of experiments 2 and 9 (Table I) shows that more  $\text{Br}_2$  is formed after 150 s if the catalyst is added in its lower oxidation state, Ce(IV) being formed by rapid oxidation with bromate ions and then consumed by reaction with oxalic acid. It is the latter reaction the intermediate products of which lead finally to a rapid formation of  $\text{Br}_2$ . The instantaneous catalyst concentration, however, is a function of the concentrations of all components of the system, hence the same applies to the quantity of bromine formed in the oscillation cycle.

The stoichiometry of the reaction



is in accord with the following system of reactions which qualitatively elucidates the oscillations:





Analogous equations are valid for the case with Mn(III).

The catalyst of reaction (5) is formed by the autocatalytic reaction (3) and is consumed by reaction (4). The oxidized form of the catalyst causes a rapid increase of the bromine concentration by reactions (5) and (6). Since bromine acts as inhibitor of reaction (3), it must be removed from the reaction solution to start reaction (3) again and repeat the cycle.

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