

## OSCILLATION REACTIONS OF BELOUSOV-ZHABOTINSKII TYPE WITH HYDROXY ACIDS IN CLOSED SYSTEMS WITHOUT REMOVAL OF BROMINE

Eubica ADAMČÍKOVÁ and Peter ŠEVČÍK

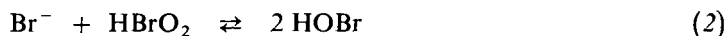
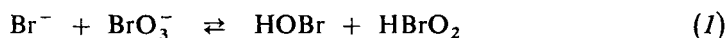
*Department of Physical Chemistry, Comenius University, 842 15 Bratislava*

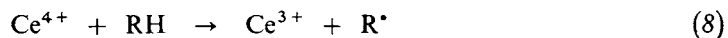
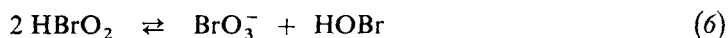
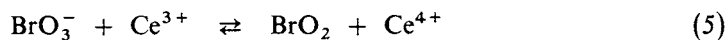
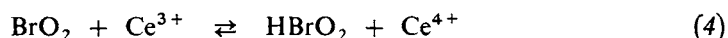
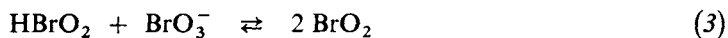
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Hydroxy acids such as tartaric, mandelic, lactic, and glycolic acids generate chemical oscillations in Belousov-Zhabotinskii reactions even in closed systems if the solution is not bubbled with an inert gas. Reduction of Ce(IV) ions with hydroxy acids is accelerated by bromine, whose reaction with them is sensitive to illumination.

The oscillation reaction of Belousov-Zhabotinskii (BZ) type (in a mixture of NaBrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, Mn(II) or Ce(III), and a substrate solution) with oxalic acid as nonbrominatable substrate was discovered by Noszticzius and Bódiss<sup>1</sup>. It has been assumed that the system with such a substrate shows oscillations if the generated bromine is removed by an inert gas stream, or chemically by using mixed substrates<sup>2</sup>, or in a continuously stirred tank reactor<sup>3</sup>. Blume and Bader<sup>4</sup> measured oscillations in BZ reactions with ascorbic, oxalic, glyceric, and pyruvic acids in a closed system. We described oscillation systems of BZ type with hydroxy acids<sup>5-8</sup>, which are not or not well brominatable substrates; these systems oscillated under the given conditions only when the solution was bubbled with an inert gas. After some concentration changes, we measured oscillations in BZ reaction with tartaric, mandelic, lactic, and glycolic acids in a closed system without removing bromine by streaming nitrogen.

Since the question which of the proposed mechanisms of BZ type oscillation reactions<sup>9-11</sup> produce Br<sup>-</sup> ions is still open, we studied the kinetics of redox reactions of Ce(IV) ions with hydroxy acids, bromine with hydroxy acids, and reduction of Ce(IV) ions with them in the presence of bromine. Varga, Györgi and Körös<sup>12</sup> proposed a so-called mechanistic model of oscillation reactions which does not involve production of Br<sup>-</sup> ions by reaction of the oxidized form of the catalyst with bromomalonic acid:





## EXPERIMENTAL

Reagent grade chemicals were dissolved in redistilled water. The reduction kinetics of Ce(IV) ions with hydroxy acids were followed polarographically at  $-0.1 \text{ V}$  against saturated  $\text{Hg}_2\text{SO}_4$  electrode (MSE), *i.e.* by measuring the limiting diffusion current of Ce(IV) ions in dilute sulphuric acid, and spectrophotometrically at a wave length of  $317 \text{ nm}$  corresponding to Ce(IV) ions. Their concentration was recorded as function of the time at an excess of hydroxy acids. The rate constant of the reaction of  $\text{Br}_2$  with glycolic acid was determined from the time dependence of the limiting diffusion current of  $\text{Br}_2$  at  $-0.6 \text{ V}$  (MSE) on a dropping mercury electrode. The reaction was also followed spectrophotometrically at  $400 \text{ nm}$ ; the concentration of  $\text{Br}_2$  was calculated by using the absorption coefficient  $\epsilon_{400} = 165 \text{ l mol}^{-1} \text{ cm}^{-1}$ . The kinetics of reduction of Ce(IV) ions with hydroxy acids in the presence of bromine were measured at a wave length of  $317 \text{ nm}$ , the molar absorption coefficient being equal to  $5470 \text{ l mol}^{-1} \text{ cm}^{-1}$  for Ce(IV) and  $44 \text{ l mol}^{-1} \text{ cm}^{-1}$  for  $\text{Br}_2$ , *i.e.* only the time dependence of Ce(IV) concentration was measured. We used a spectrophotometer Specord UV VIS with  $0.5$  and  $5 \text{ cm}$  quartz glass cuvettes and a polarograph OH-105 (Radelkis, Budapest).

The oscillation reactions took place in a thermostated cell with a Pt electrode; a salt bridge filled with a solution of  $\text{NaHSO}_4$  and agar connected the indicator electrode with a saturated calomel reference electrode. The time changes of the potential of the Pt electrode or a  $\text{Br}^-$  ion selective electrode were measured during stirring the solution with a magnetic stirrer. The same oscillations were observed when a polarographic Kalousek cell with a separated  $\text{Hg}_2\text{SO}_4$  reference electrode was used. The reaction solution with a Pt indicator electrode was stirred by bubbling nitrogen (1 bubble *per* 2 s); the OH-105 polarograph was used as a millivoltmeter.

## RESULTS

Solutions containing  $\text{BrO}_3^-$ ,  $\text{H}_2\text{SO}_4$ , a hydroxy acid, and  $\text{Mn(II)}$  or  $\text{Ce(III)}$  as catalyst show periodic potential changes of the Pt or  $\text{Br}^-$  ion selective electrode even when the excess bromine is not removed from the solution. The oscillations are formed in a closed system and  $\text{CO}_2$  bubbles escape during the reaction. Typical results obtained with tartaric, lactic, and mandelic acids are shown in Fig. 1. The parameters of the oscillation reactions, namely the induction period IP (time after which the system begins to oscillate) and the oscillation period PO (time between the first and second or second and third oscillation) at the same initial concentrations of the reactants are given in Table I. With  $3 \cdot 10^{-3} \text{ mol l}^{-1}$   $\text{Mn(II)}$  or  $\text{Ce(III)}$  as catalyst, the initial conditions were:  $0.125 \text{ mol l}^{-1} \text{ BrO}_3^-$ ,  $0.06 \text{ mol l}^{-1}$  substrate,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ,  $25^\circ\text{C}$ , 10 ml reaction volume. Oscillations were observed with all substrates and both catalysts except for mandelic acid with  $\text{Ce(III)}$  ions, which formed a precipitate of insoluble salt. Oscillations with the mentioned substrates were recorded also without bubbling nitrogen if the concentration of bromate was an order of magnitude higher than with bubbling nitrogen.

The influence of individual reactants (other conditions being kept constant) on the oscillation parameters was studied in the presence of glycolic acid as substrate. The induction period increased with the concentration of bromate ions whereas the oscillation period did not change in the interval  $0.03\text{--}0.2 \text{ mol l}^{-1}$  bromate (in a solution of  $0.06 \text{ mol l}^{-1}$  glycolic acid,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ , and  $0.003 \text{ mol l}^{-1} \text{ Mn(II)}$  ions at  $25^\circ\text{C}$ ). Further the induction period decreased with increasing concentration of glycolic acid, whereas the oscillation period did not change in the interval  $0.06$  to  $0.14 \text{ mol l}^{-1}$  (in a solution of  $0.12 \text{ mol l}^{-1}$  bromate,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ , and  $0.003 \text{ mol l}^{-1} \text{ Mn(II)}$  ions at  $25^\circ\text{C}$ ).

The system oscillated when the concentration of  $\text{H}_2\text{SO}_4$  changed from 1 to 3  $\text{mol l}^{-1}$ . The values of IP and PO decreased with increasing concentration of the acid. The highest number of oscillations was obtained in  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ . The character of the measured dependences was the same as during bubbling with nitrogen<sup>5-8</sup>. The system oscillated in a narrow interval of  $\text{Mn(II)}$  concentrations, namely from  $2 \cdot 10^{-3}$  to  $4 \cdot 10^{-3} \text{ mol l}^{-1}$ . When  $\text{Ce(III)}$  was used as catalyst, the corresponding interval was wider, from  $3 \cdot 10^{-3}$  to  $0.015 \text{ mol l}^{-1}$ .

The oscillation reaction with glycolic acid was observed not only in the presence of light but also in the dark (Fig. 2).

The reaction products of the oscillation reaction with glycolic acid were analysed by the method of capillary isotachopheresis. Organic acids were identified by comparing the conductivities of the corresponding zones with standards. The reaction mixture ( $0.12 \text{ mol l}^{-1} \text{ BrO}_3^-$ ,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ,  $0.06 \text{ mol l}^{-1} \text{ CH}_2\text{OH.COOH}$ , and  $3 \cdot 10^{-3} \text{ mol l}^{-1} \text{ MnSO}_4$ ) was analysed immediately after preparation, after 20 min during oscillations, and when the oscillations stopped. Only glycolic acid was detected

TABLE I

Parameters of oscillation reactions.  $0.06 \text{ mol l}^{-1}$  substrate,  $0.125 \text{ mol l}^{-1} \text{ BrO}_3^-$ ,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ,  $0.003 \text{ mol l}^{-1}$  catalyst,  $25^\circ\text{C}$

Substrate	IP, s		PO, s	
	Mn(II)	Ce(III)	Mn(II)	Ce(III)
Oxalic acid	30	45	60	23
Tartaric acid	375	300	45	45
Glycolic acid	360	345	75	45
Lactic acid	300	825	68	150
Mandelic acid	150	—	30	—

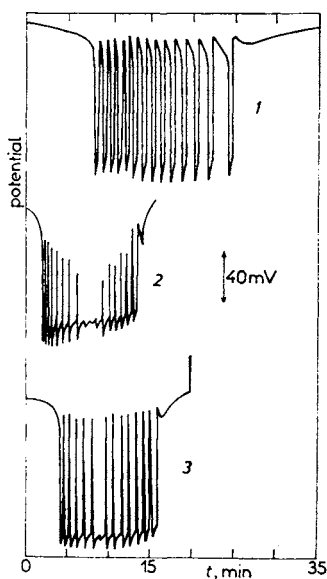


FIG. 1

Potentiometric record with a Pt indicator electrode in a solution of  $0.2 \text{ mol l}^{-1} \text{ BrO}_3^-$ ,  $0.003 \text{ mol l}^{-1} \text{ MnSO}_4$ ,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$  at  $25^\circ\text{C}$ . Added  $0.06 \text{ mol l}^{-1}$  of 1 tartaric, 2 mandelic, 3 lactic acid

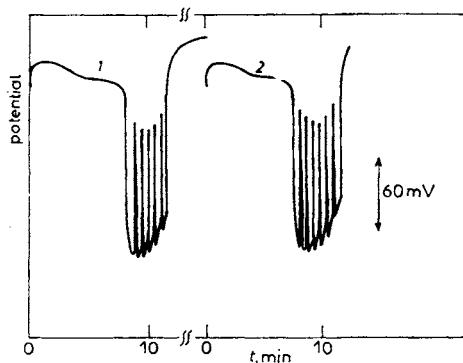


FIG. 2

Time dependence of Pt electrode potential in a solution of  $0.12 \text{ mol l}^{-1} \text{ BrO}_3^-$ ,  $0.06 \text{ mol l}^{-1}$  glycolic acid,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ , and  $0.005 \text{ mol l}^{-1} \text{ Ce(III)}$  ( $30 \text{ cm}^3$ ); stirring at 100 r.p.m.; 1 on light, 2 in the dark

at the beginning, glycolic and formic acids at the medium stage, and formic acid at the end of the reaction. Neither glyoxylic nor oxalic acid was detected, which could have originated from the oxidation of glycolic acid.

### Results of Kinetic Measurements

The reduction of bromate ions with all the mentioned substrates in excess proceeds autocatalytically<sup>5-8</sup>. The redox reactions of Ce(IV) ions with hydroxy acids in excess yielded dependences of  $\ln(c_0/c)$  on  $t$ , which permitted to evaluate the rate constants (Table II). These are independent of illumination and the presence of oxygen. The reaction of Ce(IV) ions with hydroxy acids is accelerated by bromine and is autocatalytic in character. The rate constants found after the induction period had elapsed (again from the dependence of  $\ln(c_0/c)$  on  $t$ ) are also given in Table II. A decoloration of the solution was observed after the reaction had finished. Bromide ions do not accelerate the reaction of Ce(IV) with hydroxy acids. The reactions of bromine with hydroxy acids are very slow but are strongly accelerated by illumination. For example, bromine practically does not react with glycolic acid in the dark ( $0.05 \text{ mol} \cdot \text{l}^{-1}$  glycolic acid,  $10^{-3} \text{ mol l}^{-1} \text{ Br}_2$ ,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ), the absorbancy being constant during two hours, but on illumination the solution turns colourless during several minutes. The reaction of bromine with glycolic acid was also studied polarographically (on the day light) to obtain  $k = 1.42 \cdot 10^{-4} \text{ s}^{-1}$  ( $0.05 \text{ mol l}^{-1}$  glycolic acid,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ,  $5 \cdot 10^{-4} \text{ mol l}^{-1}$  bromine,  $25^\circ\text{C}$ ). Bromine with lactic acid ( $0.05 \text{ mol l}^{-1}$  lactic acid,  $10^{-3} \text{ mol l}^{-1} \text{ Br}_2$ ,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ) in the dark reacts also very slowly, the concentration of bromine drops by 5% during 8 min, whereas under illumination the reaction is complete. Similar kinetic results were obtained with other hydroxy acids.

TABLE II

Kinetic parameters for reactions of substrates with Ce(IV) in the absence or presence of bromine.  $5 \cdot 10^{-4} \text{ mol l}^{-1}$  Ce(IV),  $0.05 \text{ mol l}^{-1}$  substrate,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ,  $20^\circ\text{C}$ ; concentration of  $\text{Br}_2$   $3.6 \cdot 10^{-4} \text{ mol l}^{-1}$

Substrate	$k, \text{s}^{-1}$	
	Ce(IV)	Ce(IV) + $\text{Br}_2$
Tartaric acid	$2.1 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$
Glycolic acid	$5 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$
Lactic acid	$4.1 \cdot 10^{-4}$	$7.8 \cdot 10^{-4}$
Mandelic acid <sup>a</sup>	$2.6 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$

<sup>a</sup>  $0.02 \text{ mol l}^{-1}$  substrate.

## DISCUSSION

Bromide ions are considered<sup>9,10,13</sup> as the rate-controlling intermediate product in the BZ reaction. Their exhaustion is expressed by the steps 1, 2, and 7. A more complicated and still open question is how the  $\text{Br}^-$  ions are produced. According to the FKN mechanism<sup>9</sup>, they are generated by a reaction between the oxidized form of the catalyst and bromomalonic acid, which accumulates in the solution during the induction period. In the revised Oregonator<sup>10</sup>, it is assumed that  $\text{Br}^-$  ions can be formed, in addition, by a reaction of  $\text{HBrO}$  with the substrate. In a recently published article, the authors<sup>12</sup> came to the conclusion that  $\text{BrO}_3^-$  ions rather than bromomalonic acid (or other organic bromo derivative) are the source of  $\text{Br}^-$  ions in BZ systems. Accordingly,  $\text{Br}^-$  ions are generated by a reaction between bromate and an oxidation product of malonic acid (ROH). The authors<sup>12</sup> proposed a reaction mechanism, which should be applicable to the BZ systems in the present work using prevailingly nonbrominatable substrates. The reduction of  $\text{Ce(IV)}$  ions with hydroxy acids is accelerated by adding bromine into the solution (Table II). For example, when  $3.6 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Br}_2$  is added to the reaction solution of  $\text{Ce(IV)}$  ions with glycolic acid ( $k = 5 \cdot 10^{-5} \text{ s}^{-1}$ ), the rate constant increases to  $k = 1.22 \cdot 10^{-3} \text{ s}^{-1}$ , and with twice the quantity of bromine we obtain  $k = 3.18 \cdot 10^{-3} \text{ s}^{-1}$  (Fig. 3). These results suggest that the formation of  $\text{Br}^-$  ions should be expressed not only by steps 7 and 10 but also by the steps

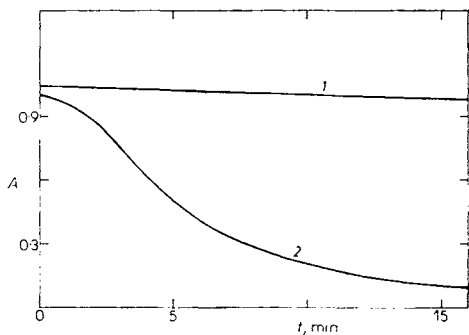
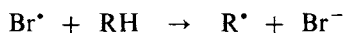
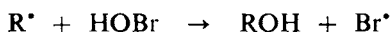
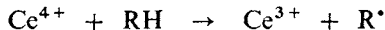
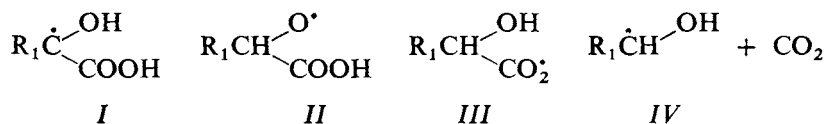


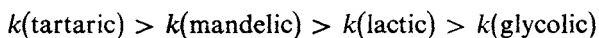
FIG. 3

Time dependence of absorbancy of  $\text{Ce(IV)}$  ions during their reduction with 1 glycolic acid, 2 glycolic acid in the presence of  $7.3 \cdot 10^{-4} \text{ mol l}^{-1}$  bromine.  $5 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Ce(IV)}$ ,  $1.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ ,  $0.05 \text{ mol l}^{-1}$  glycolic acid;  $20^\circ\text{C}$

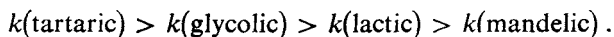
whereby the rate of formation of  $\text{Br}^-$  ions can be strongly enhanced. The following radicals can be considered<sup>14</sup> in the oxidation of hydroxy acids of the type  $\text{R}_1\text{CH}(\text{OH})\cdot\text{COOH}$ :



When hydroxy acids are oxidized with  $\text{Ce(IV)}$  ions, some authors consider more probable the formation of the radical *II*, others consider splitting of the C—C bond with the formation of the radical *IV*, especially if the oxidizing species are  $\text{Mn(III)}$  ions. The rate of oxidation of hydroxy acids (without  $\text{Br}_2$ ) with  $\text{Ce(IV)}$  or  $\text{Mn(III)}$  ions decreases in the order

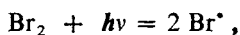


as expected if the stabilization of the radical  $\text{R}\dot{\text{C}}\text{HOH}$  is significant. The rate constants for the oxidation with  $\text{Mn(III)}$  ions are an order of magnitude higher than those for  $\text{Ce(IV)}$ . If bromine is added into the solution, the oxidation rate with  $\text{Ce(IV)}$  decreases in the changed order

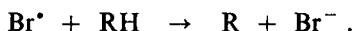


The same sequence applies for the rate of formation of the organic radical under oscillation conditions, where the concentration of  $\text{Br}_2$  in the system without bubbling is high, increasing during the oscillations<sup>15</sup>. In agreement with this, the induction period is shortest for tartaric acid, longer for glycolic, and longest for lactic acid (Table I). Oxalic acid confirms to this behaviour, since its reaction with  $\text{Ce(IV)}$  is most rapid and the induction period is clearly the shortest. These results suggest that chemical oscillations in the BZ system start only if the concentration of the organic radical attains a certain value. Thus, if the BZ system is not bubbled with nitrogen, a higher concentration of bromine is attained, causing an increase in the reduction of  $\text{Ce(IV)}$  ions with the substrate and in the formation of  $\text{Br}^-$  ions. This is the reason why we did not obtain oscillations in the presence of lactic or glycolic acid and  $\text{Ce}$  catalyst<sup>5</sup> during bubbling with nitrogen. We attributed this to the low rate of the step  $\text{Ce(IV)} + \text{glycolic or lactic acid}$ . Since bromine was removed, it could not accelerate the mentioned redox step and thus no oscillations occurred.

The reactions of bromine with hydroxy acids are strongly influenced by illumination, being very slow in the dark. The probable photoreaction is



where the  $\text{Br}^\bullet$  radical subsequently reacts with the hydroxy acid



However, the reduction of Ce(IV) ions with hydroxy acids in the presence of bromine is not sensitive to illumination, and the parameters of the oscillation reaction are not influenced by light either (Fig. 2).

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