

## KINETICS OF REDOX REACTION OF LACTIC ACID WITH BROMATE IONS, AND BELOUSOV-ZHABOTINSKII OSCILLATOR WITH LACTIC ACID

Lubica ADAMČÍKOVÁ and Irena HALINÁROVÁ

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

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The kinetics and mechanism of the redox reaction of bromate ions with lactic acid was studied in the medium of sulphuric acid. The reaction is of first order with respect to both reactants. The dependence of the measured rate constant on the concentration of hydrogen ions was analysed and the activation parameters of the reaction were determined. Based on the experimental kinetic data, the probable mechanism is discussed. Oscillations of bromine and catalyst are observed in the system  $\text{KBrO}_3\text{-CH}_3\text{CHOHCOOH-H}_2\text{SO}_4\text{-MnSO}_4$  if the solution is bubbled with nitrogen. The dependence of the induction period and oscillation period on the concentration of the reactants was evaluated.

The present work is a continuation of our study of Belousov-Zhabotinskii (BZ) type oscillation reactions with emphasis on hydroxy acids as nonbrominatable substrates<sup>1,2</sup>. Such systems oscillate only if the bromine formed during the reaction is removed by bubbling inert gas. A heterogeneous oscillation reaction of the BZ type with oxalic acid as nonbrominatable substrate was discovered by Noszticzius and Bódiss<sup>3</sup>, who assumed the kinetics to be influenced by bromine, although they did not consider this type of reaction to be controlled by bromide ions. The classical BZ reaction (with malonic acid, which is susceptible to bromination) was analysed by Field, Körös and Noyes<sup>4</sup>, and the mechanism proposed by them served as a basis for a simplified model, called Oregonator<sup>5</sup>. However, some experimental facts remained unexplained. Noszticzius, Farkas and Schelly<sup>6</sup> proposed another model, called Explodator. Their objections were taken into consideration by Noyes<sup>7</sup>, who therefore proposed a modified Oregonator model. This eliminates some stoichiometric inadequacies and is (by a minor modification of one of the six steps) able to describe situations, in which the final oxidation state of bromine is +1, 0, or 1.

The present work deals with an oscillation system involving another nonbrominatable hydroxy acid, *i.e.* lactic acid, and preliminary results are reported also for an analogous system with  $\alpha$ -hydroxybutyric acid. In addition, we studied the kinetics and mechanism of reduction of bromate ions with lactic acid, for which data in the literature are lacking.

### EXPERIMENTAL

The kinetics of reduction of bromate ions with lactic acid was studied polarographically by recording the time dependence of the limiting diffusion current of bromate ions at  $-1.0$  V against

saturated Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode. In the studied potential range, lactic acid is polarographically inactive. Polarographs of the type OH-102 and OH-105 (Radelkis, Budapest) were employed. The reaction course was followed during two or three half-times; the measured rate constants are mean values from 3–5 measurements, which were accurate to  $\pm 5\%$ . The polarographic Kalousek cell was tempered by means of a U 3 type ultrathermostat (Prüfgeräte-Werk, Medingen, GDR). Chemicals were of reagent grade and solutions were prepared in redistilled water. The oscillations of bromine were recorded polarographically as described earlier<sup>8</sup>. The reaction volume was 10 ml; the reactants were added in the order: H<sub>2</sub>SO<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>, MnSO<sub>4</sub>, and KBrO<sub>3</sub>. The solution was bubbled with nitrogen, the rate of flow of which was kept constant and measured with a flow meter of the type TG 400 (GDR). Thus, the reaction solution was stirred and the bromine formed during the reaction was transferred by the streaming gas into the Kalousek cell, in which its concentration was continually measured in the medium of 1.5M-H<sub>2</sub>SO<sub>4</sub> at 0.6 V against M.S.E. An analogous procedure was used in the case of  $\alpha$ -hydroxybutyric acid.

## RESULTS AND DISCUSSION

### *Reduction of Bromate with Lactic Acid*

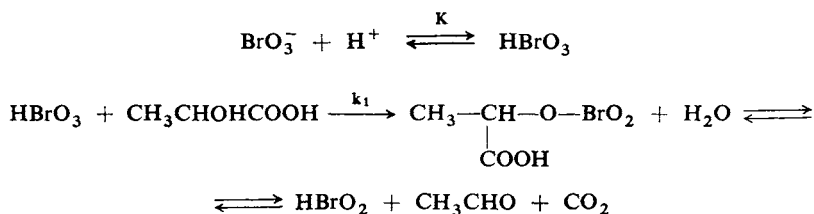
The reduction of bromate with excess lactic acid is autocatalytic in character (Fig. 1) similarly to the case of other nonbrominatable substrates showing oscillations in the BZ system. Lactic acid reacts with bromate under formation of bromine and HOBr, which are reduced further to Br<sup>-</sup> ions. The kinetics of the reaction of lactic acid with bromine was studied by Rathor and Grover<sup>9</sup>, who found that the reactive species are Br<sub>2</sub> and HOBr and that  $k_{\text{HOBr}} \gg k_{\text{Br}_2}$ . Tribromide ions are kinetically inactive. Bromate ions are consumed not only by the reaction with lactic acid but also with bromide ions. If the bromine is removed from the solution by bubbling nitrogen, it cannot take part in the follow-up reactions and the over-all reaction loses its autocatalytic character (Fig. 1). (The stream of nitrogen was stopped for about 10 s during recording the polarographic current of bromate.) The linear dependence of  $\ln(I_0/I)$  on  $t$  enables us to follow separately the reduction of bromate with lactic acid, which is of first order with respect to bromate. The rate constant increases linearly with the concentration of lactic acid. The reaction order with respect to lactic acid was found by logarithmic analysis to be equal to 1. Hence, the rate equation is

$$-d[\text{BrO}_3^-]/dt = k[\text{BrO}_3^-][\text{C}_3\text{H}_6\text{O}_3],$$

where  $k = 2.77 \cdot 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$  in 1M-H<sub>2</sub>SO<sub>4</sub> at 25°C.

The rate constant increases also with the concentration of hydrogen ions, logarithmic analysis indicating the exchange of one proton. Lactic acid dissociates slightly ( $K = 1.38 \cdot 10^{-4}$  at 25°C) and it is probable that bromate ions in the medium of H<sub>2</sub>SO<sub>4</sub> react prevailingly with its undissociated molecules. The probable

mechanism



he first step of which is rapid and the second slow, corresponds to the rate equation

$$-d[\text{BrO}_3^-]/dt = k_1 K [\text{H}^+] [\text{BrO}_3^-] [\text{C}_3\text{H}_6\text{O}_3],$$

which is in accord with the observed experimental facts. Ionic strength does not influence the rate constant  $k$  for reduction of bromate with lactic acid, since the slow step involves interaction of two neutral molecules. The assumed mechanism includes the slow formation of a lactic ester of bromic acid, which dissociates rapidly in the subsequent step. The carboxyl group of the ester may react with the bromate group to form a cyclic ester, which is considered by several authors. Natarajan and Venkatasubramanian<sup>10</sup> studied the oxidation of some  $\alpha$ -hydroxy acids such as lactic acid with bromate ions in the medium of acetic acid and they assume the formation of a cyclic ester. Cyclic esters are formed also during oxidation of lactic and

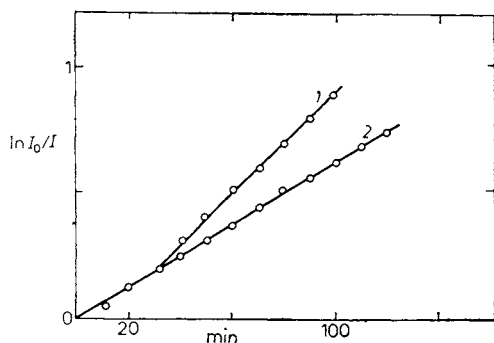


FIG. 1

Dependence of  $\ln(I_0/I)$  on time. Solution of  $5 \cdot 10^{-4} \text{M-BrO}_3^- + 0.4 \text{M-C}_3\text{H}_6\text{O}_3 + 1 \text{M-H}_2\text{SO}_4$  at  $25^\circ\text{C}$ ; 1 without bubbling; 2 bubbled with nitrogen

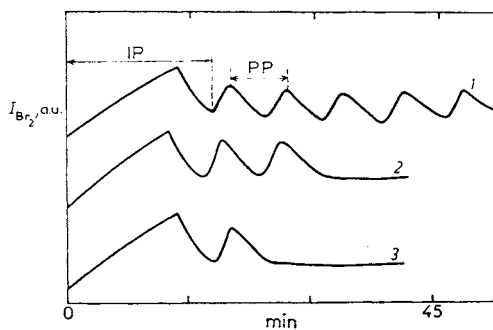


FIG. 2

Oscillations of  $\text{Br}_2$  (arbitrary units) during reaction with lactic acid. Solution of  $4 \cdot 10^{-3} \text{M-BrO}_3^- + 0.036 \text{M-C}_3\text{H}_6\text{O}_3 + 1.5 \text{M-H}_2\text{SO}_4$  at  $25^\circ\text{C}$ , rate of flow of  $\text{N}_2$   $600 \text{ ml} \cdot \text{min}^{-1}$ , solution volume  $10 \text{ ml}$ ; 1 in water; 2  $6.15 \text{ ml H}_2\text{O} + 3.85 \text{ ml D}_2\text{O}$ ; 3  $3.55 \text{ ml H}_2\text{O} + 6.45 \text{ ml D}_2\text{O}$

mandelic acid with chromate<sup>11</sup>; these reactions have a high negative value of the activation entropy ( $\Delta S^\ddagger = -156$  and  $-165 \text{ J K}^{-1} \text{ mol}^{-1}$ ). The activation entropy increases if a transition state with an open cycle is formed<sup>11</sup>. The activation parameters found by us for the reduction of bromate with lactic acid,  $\Delta H^\ddagger = 52.8 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta S^\ddagger = -135 \text{ J K}^{-1} \text{ mol}^{-1}$ , are in support of the formation of a cyclic ester.

### Oscillation System

If  $\text{Mn(II)}$  ions are added to a solution of lactic acid with bromate ions in  $1.5\text{M-H}_2\text{SO}_4$  or  $1.5\text{M-HClO}_4$ , the reaction system starts to oscillate. Oscillations of the concentration of  $\text{Mn(III)}$  ions can be observed visually and those of the bromine polarographically (Fig. 2). The time after which the system starts to oscillate is the induction period, IP. The time elapsed between the first and second or between the second and third maximum of the bromine concentration is denoted as the oscillation period. Again, it turned out that the system with a nonbrominatable substrate starts to oscillate if certain kinetic conditions are satisfied<sup>12</sup>. Both the induction and oscillation periods depend on the starting concentrations of the reactants (Fig. 3).

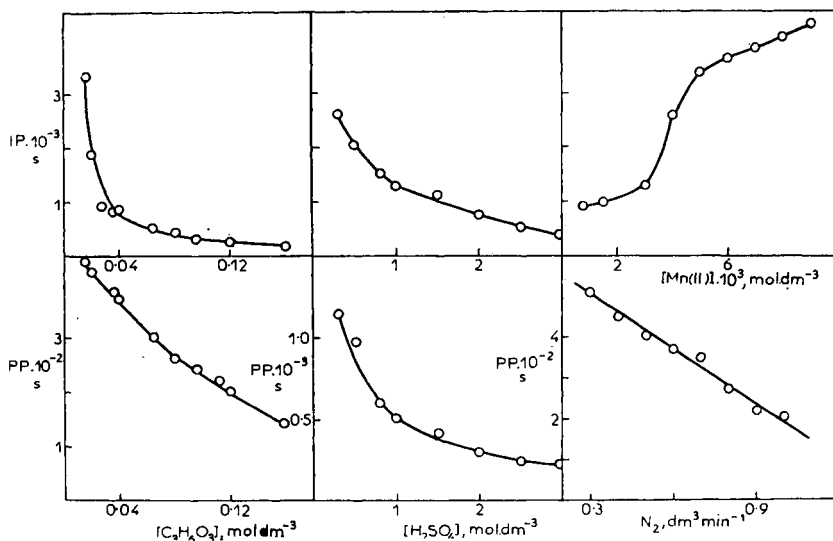
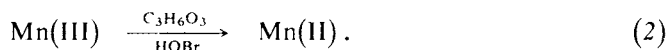
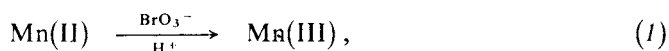


FIG. 3

Dependence of induction period (IP) and oscillation period (PP) on the concentration of reactants. Solution of  $5 \cdot 10^{-3}\text{M-BrO}_3^- + 0.036\text{M-C}_3\text{H}_5\text{O}_3 + 1.5 \cdot 10^{-3}\text{M-Mn(II)} + 1.5\text{M-H}_2\text{SO}_4$  at  $25^\circ\text{C}$ , rate of flow of nitrogen  $600 \text{ ml min}^{-1}$

During the induction period, bromine is generated at a higher rate than corresponds to its removal by bubbling nitrogen ( $k = 0.023 \text{ s}^{-1}$ ). As soon as the concentration of bromine drops below a certain critical value, the system starts to oscillate. Several seconds after mixing the system components together Mn(III) and HOBr are formed as a result of an autocatalytic reaction of bromate ions with Mn(II). Hypobromous acid then reacts with lactic acid<sup>9</sup> to form  $\text{Br}^-$  ions or, in the presence of bromine,  $\text{Br}_2$ , the concentration of which increases during the induction period. The value of IP decreases with increasing concentration of lactic acid and sulphuric acid and its dependence on the concentration of Mn(II) is shown in Fig. 3. However, it does not change on changing the concentration of  $\text{BrO}_3^-$  ions or on adding  $\text{Br}^-$  ions or bromine into the reaction solution. The value of IP slightly increases with the rate of flow of nitrogen. It is probable that the induction period is due to accumulation of bromine and organic intermediates.

Our measurements show that the system oscillates at a rate of flow of nitrogen  $600 \text{ ml min}^{-1}$  in the presence of  $1.5 \cdot 10^{-3} \text{ M-Mn(II)}$  if  $0.031 < [\text{BrO}_3^-]_0 / [\text{C}_3\text{H}_6\text{O}_3]_0 < 0.31$  for  $[\text{BrO}_3^-]_0 = 5 \text{ mmol l}^{-1}$  or if  $0.28 < [\text{BrO}_3^-]_0 / [\text{C}_3\text{H}_6\text{O}_3]_0 < 0.194$  for  $[\text{C}_3\text{H}_6\text{O}_3]_0 = 36 \text{ mmol l}^{-1}$ . The oscillation cycle can be represented schematically as



The autocatalytic reaction (1) is inhibited by bromine and Mn(III) ions in analogy to the oxidation of Ce(III) with bromate ions<sup>13</sup>. If the concentrations of  $\text{Br}_2$  and Mn(III) surpass a critical value, reaction (1) stops and reaction (2) starts to proceed. In the case of lactic acid, the oscillation period probably depends not only on the physical removal of bromine and lowering its concentration below the critical value as in the case of oxalic acid<sup>14</sup>, but also on the rate of lowering the concentration of Mn(III) ions to a limit that enables the commencement of a new cycle represented by reaction (1). Mn(III) ions namely react very rapidly with oxalic acid ( $k \approx 0.1 \text{ s}^{-1}$  for  $0.03 \text{ M-C}_2\text{H}_2\text{O}_4$  at  $20^\circ\text{C}$ ), but relatively slowly with lactic acid ( $k = 0.017 \text{ s}^{-1}$  for  $0.036 \text{ M-C}_3\text{H}_6\text{O}_3$  at  $25^\circ\text{C}$ ), and their concentration in the system is lowered by the latter reaction at a rate lower than or comparable to that of removal of bromine. This is in accord with the shortening of the oscillation period with increasing concentrations of lactic and sulphuric acids (Fig. 3), which accelerate the reaction of Mn(III) ions with lactic acid. Changes of the concentrations of bromate ions and Mn(II) catalyst have no marked influence on the oscillation period, but increasing rate of flow of nitrogen causes its shortening. If the concentration of Mn(III) decreased by reaction with lactic acid at an equal rate (at the same solution composition) and more slowly than the removal of bromine, the oscillation period would be

independent of the rate of flow of nitrogen. Since this is not the case, we assume that bromine in solution influences also the reaction of Mn(III) with lactic acid<sup>15</sup>.

Addition of D<sub>2</sub>O has no influence on the oscillation period, but changes the number of oscillations (Fig. 2). Heavy water changes the rate constants of the reaction steps in the oscillation system in a sense unfavourable for the oscillations.

If Mn(II) in the oscillation system is replaced by Ce(III), no oscillations take place, since reaction (2), by which the reduced form of the catalyst is generated, is too slow. The apparent rate constant for oxidation of lactic acid with Mn(III) and Ce(IV) ions in a solution of 0.036M-C<sub>3</sub>H<sub>6</sub>O<sub>3</sub> + 5 · 10<sup>-4</sup>M-Mn(III) or Ce(IV) + 1.5M-H<sub>2</sub>SO<sub>4</sub> were measured as 0.017 and 3.55 · 10<sup>-4</sup> s<sup>-1</sup> at 25°C, respectively.

An analogue of lactic acid is α-hydroxybutyric acid, which also can take part in the modified BZ reaction. Thus, we found an induction period of 330 s and an oscillation period of 550 s in a solution of the starting composition 1.5M-H<sub>2</sub>SO<sub>4</sub> + 0.065M-C<sub>4</sub>H<sub>8</sub>O<sub>3</sub> + 8 · 10<sup>-3</sup>M-BrO<sub>3</sub><sup>-</sup> + 3 · 10<sup>-3</sup>M-Mn(II) at 25°C and rate of flow of nitrogen 600 ml min<sup>-1</sup>.

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