

OSCILLATING HETEROGENEOUS REACTION WITH OXALIC ACID

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Catalysed oxidation of oxalic acid with bromate ions at constant flow of nitrogen was investigated. Oscillations of the catalyst and bromine and the stepwise decrease of the concentration of bromate ions were followed by the polarographic method. Optimum conditions for the oscillations are at the stoichiometric ratio of the reactants. Oscillations of the concentration of bromine are enabled by the Ce(III) or Mn(II) catalyst. The oscillating behaviour of oxalic and malonic acids at heterogeneous conditions is compared.

In the classical Belousov-Zhabotinskii (BZ) oscillating reaction with malonic acid, Br^- ions formed by the reaction of Ce(IV) with bromomalonic acid (BrMA) are considered to be the key intermediate product^{1,2}. Noszticius and Bódiss³ found that oxalic acid (OA) produces oscillations of the concentrations of CO_2 and Br_2 when the gaseous products are removed from the reaction system by a constant flow of hydrogen. Heterogeneous oscillations are formed also with glyoxylic⁴ and tartaric⁵ acids. A model of heterogeneous reactions with OA controlled by bromine⁴ and Br^- ions⁶ was proposed. If the organic substrate cannot form brominated derivatives analogous to BrMA and its redox reaction with bromine in the oxidation state +1 or 0 is slow, the source of Br^- ions in the oscillating system remains unclear.

The present work deals with the oscillating behaviour of the system BrO_3^- , OA, H_2SO_4 with Ce(IV)—Ce(III) or Mn(III)—Mn(II) as catalyst. Gaseous or volatile products were removed from the reacting mixture with a constant stream of nitrogen. The polarographic method enabled us to follow the time changes of the concentrations of the catalyst, Br_2 and BrO_3^- .

EXPERIMENTAL

Chemicals. Freshly prepared solutions of KBrO_3 , $(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$, and H_2SO_4 , all of reagent grade, in distilled water were used. The reaction mixture was bubbled with chemically pure nitrogen.

Measuring apparatus. The concentrations of the catalyst, bromine, and bromate ions were determined polarographically. Two polarographs, LP 7 type (Laboratorní Přístroje, Prague) and OH 105 type (Radelkis, Budapest) with two polarographic cells were used. The oscillating reaction with OA proceeded in a Kalousek type polarographic cell with a thermostated mantle piece at 25°C and the polarographic cathodic current I_1 was measured at -0.15 V against 1M- HgSO_4 electrode; this was even in the presence of BrO_3^- , OA, and catalyst dependent mainly

on the concentration of the oxidised form of the latter. It cannot be considered as a limiting diffusion current, however, either of Ce(IV) or Mn(III), with respect to the continuous bubbling with nitrogen and to a small residual current measured at the same potential even in the presence of the sole bromate. Nevertheless, the increase of the current at -0.15 V vs 1M MSE was accompanied with the appearance of a coloration characteristic for Ce(IV) or Mn(III) ions.

The concentration of bromine was measured in the other Kalousek cell. Bromine-containing volatile products were from the first cell transferred into the second one with a constant stream of nitrogen. Since bromine was the only polarographically active component of these at -0.5 V vs 1M MSE in $1.5\text{M-H}_2\text{SO}_4$, the current in the second cell, I_2 , was proportional to the concentration of Br_2 ; besides it depended on the rate of flow of nitrogen, which was measured with a capillary flow meter. The polarographic current was well reproducible at rates of flow 300–800 ml/min. The quantity of bromine formed in the reaction cell was determined by calibration experiments. A known volume of a solution of bromine or Br^- ions with an excess of BrO_3^- in $1.5\text{M-H}_2\text{SO}_4$ was injected into the first cell and the bromine was transferred into the second one by means of nitrogen. The area delimited by the dependence of I_2 on time corresponded to the total quantity of Br_2 formed during the reaction. By injecting a solution of Br_2 into 10 ml of $1.5\text{M-H}_2\text{SO}_4$ in the first cell at a rate of flow 600 ml/min it was found that the concentration of Br_2 in the first cell decreased with a constant half-time of 32 s. The value of I_2 began to increase practically immediately after the injection and the highest concentration of Br_2 in the second cell was attained after 40 s; after another 44 s this concentration dropped to one half of its maximum value.

It is remarkable that when a quantity of Br_2 solution was injected into 10 ml $1.5\text{M-H}_2\text{SO}_4$ in the first cell at 3 min intervals to make its concentration 10^{-4} mol/dm³, the time changes of its concentration in the second cell had a similar course as in the case of an oscillating reaction of 0.01M-BrO_3^- with 0.025M OA catalysed with 10^{-3}M Ce(IV) in $1.5\text{M-H}_2\text{SO}_4$.

The concentration of BrO_3^- ions could be measured in the reaction cell at -1.00 V vs 1M MSE. Bromine and Ce(IV) or Mn(III) are also polarographically active at this potential, but the effect of BrO_3^- prevails with respect to their six-electron reduction even at equal concentrations of bromate, bromine, and catalyst. The current in the first reaction cell at -1.00 V will be denoted as I_3 .

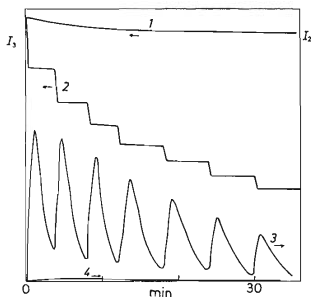
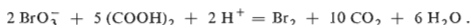


FIG. 1

Time changes of polarographic current during reaction with OA. 1 and 4 0.01M-BrO_3^- , 0.025M-OA , $1.5\text{M-H}_2\text{SO}_4$; 25°C , 600 ml N_2/min , reaction volume 10 ml; 2 and 3 as above, with addition of $7 \cdot 10^{-3}\text{M-Ce(III)}$ (final concentration)

It was found that one Br_2 molecule per 2 consumed BrO_3^- ions was produced in the catalytic oscillating reaction in accord with the overall reaction scheme³



The reaction components were added in the order H_2SO_4 , OA, catalyst; the reaction was started by adding BrO_3^- ions. The volume of the solution in both polarographic cells was 10 ml.

RESULTS

Noncatalysed oxidation of OA with bromate ions in the medium of 1.5M- H_2SO_4 proceeds relatively slowly and has an autocatalytic character⁷. If the formed bromine is removed from the reaction mixture of 0.01M- BrO_3^- + 0.025M-OA + 1.5M- H_2SO_4 with nitrogen flowing at 600 ml/min, the initial concentration of BrO_3^- drops after 40 min by 6%. The quantity of formed bromine is under these conditions very small. The addition of the catalyst causes an oscillating formation of bromine and a stepwise decrease of BrO_3^- (Fig. 1). The oscillating reaction shows no induction period. A sudden decrease of the current I_3 (Fig. 1, curve 2) is manifested by evolution of Br_2 (curve 3) whose highest concentration is recorded after 30–40 s. At the same time, Ce(IV) is formed, which partially compensates the decrease of the current at the mentioned potential. After its reduction with oxalic acid, the current attains a stationary value corresponding to the concentration of BrO_3^- ions, which takes 10–15 s. This effect was taken into account and the curve 2 in Fig. 1 is drawn so that the current I_3 follows the changes in the concentration of BrO_3^- ions.

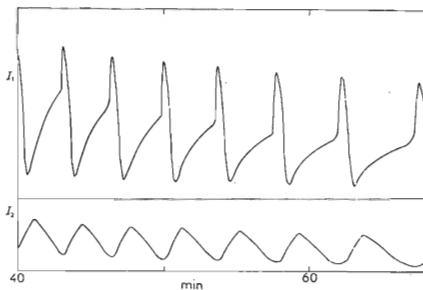


FIG. 2

Oscillations of catalyst and bromine in reaction with OA after 40 min. 0.02M BrO_3^- , 0.05M-OA, 1.5M- H_2SO_4 , 10^{-3} M-Ce(IV); 25°C, 600 ml N_2 /min, reaction volume 10 ml

Synchronous oscillations of the catalyst and Br_2 are shown in Fig. 2. The abrupt increase of the current I_1 is due to a sudden increase of the concentration of Ce(IV) . The decrease of I_1 was accompanied by decoloration of the solution. A slow exponential increase of the current I_1 in the interval between two oscillations of the catalyst can be attributed to the fact that bromine, which has an inhibiting effect on the electroreduction of BrO_3^- ions, is removed from the solution by the bubbling nitrogen. Thus, the contribution of these ions to the current measured at -0.15 V increases.

Further we sought conditions at which the system BrO_3^- , OA, $\text{Ce(IV)}-\text{Ce(III)}$ in $1.5\text{M-H}_2\text{SO}_4$ at constant flow of nitrogen (600 ml/min) oscillates. In the presence of 10^{-3}M Ce(III) and with the initial concentration 0.01M BrO_3^- the system oscillates if

$$0.25 < [\text{BrO}_3^-]_0/[\text{OA}]_0 < 1.1$$

and with the initial concentration $[\text{OA}]_0 = 0.025$ mol/dm³ if

$$0.36 < [\text{BrO}_3^-]_0/[\text{OA}]_0 < 1.2.$$

The optimum ratio of $[\text{BrO}_3^-]_0/[\text{OA}]_0$ is equal to 0.4 , i.e., the initial concentrations of the reactants are in a stoichiometric ratio. In a solution of $0.01\text{M-BrO}_3^- + 0.025\text{M-OA}$, 31 peaks of Br_2 with gradually decreasing amplitudes and frequency of 0.25 min⁻¹ were recorded (Fig. 3, curve 3). When the catalyst concentration is de-

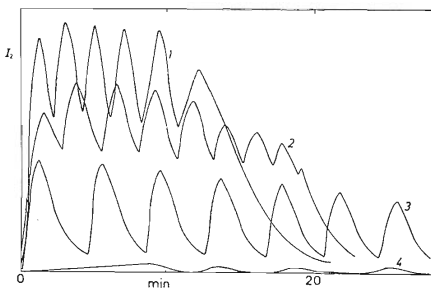


FIG. 3

Oscillations of bromine. 1 0.02M-BrO_3^- , 0.025M-OA , 10^{-3}M-Ce(III) ; 2 0.02M-BrO_3^- , 0.025M-OA , 10^{-3}M-Mn(II) ; 3 0.01M-BrO_3^- , 0.025M-OA , 10^{-3}M-Ce(III) ; 4 0.02M-BrO_3^- , 0.025M-OA , 10^{-3}M-Ce(III) ; 25°C , $1.5\text{M-H}_2\text{SO}_4$, 600 ml N_2/min , reaction volume 10 ml

creased, the number of oscillations increases. Regardless of the catalyst concentration, the oscillating formation of bromine persists at a stoichiometric ratio of the reactants until all bromate ions are reduced. For example, after 36 oscillations (during 100 min) in the system $0.02\text{M-BrO}_3^- + 0.05\text{M-OA} + 10^{-3}\text{M-Ce(IV)}$, it was found that 96% of bromate underwent reaction.

The concentration of bromate influences both the amplitude and the frequency of the oscillations at constant concentrations of OA and catalyst. The oscillating reaction proceeds faster when the concentration of bromate is increased (Fig. 3, curves 1 and 3). For comparison, the curve 4 in Fig. 3 is shown which was obtained in the classical system with malonic acid. During the induction period, the concentration of bromine increases and attains its maximum value 40 s after the coloration of the solution with Ce(IV). When the gaseous products are not removed by nitrogen, the induction period is 7 min and the frequency of oscillations is about twice as large, other conditions being the same.

As seen from curve 2 in Fig. 3, replacement of Ce(III) with Mn(II) as catalyst in oscillating reaction with OA is possible. The catalyst influences more the number and amplitude of the oscillations than their frequency; the mean difference between the highest and lowest Br_2 concentration during the first three oscillations is larger in the case of Ce(III) than with Mn(II) (Fig. 4).

If silver nitrate is added to the classical BZ system, the concentration of Br^- ions is lowered in accord with the solubility product of AgBr and the potential of a Pt redox electrode begins to oscillate, whereas the potential of a Br^- ion selective electrode changes monotonously⁸. According to our experiments, the oscillations of Br_2 in the system with OA are not suppressed by the addition of mercurous acetate or oxide in a concentration of 10^{-4} mol/dm^3 , or silver nitrate in a concentration of $5 \cdot 10^{-4}\text{ mol/dm}^3$.

Oscillations in the system with OA can be entirely suppressed by adding bromine to the streaming gas³. We added bromine or Br^- ions into the reacting solution so that the quantity of bromine formed by the reaction of Br^- with BrO_3^- ions was the same as the quantity of bromine added in the other case. As seen from Fig. 5, there is no essential difference between the effects of Br_2 and Br^- ions. In both cases, the oscillations after some time attain their normal character with frequency and amplitude determined by the concentrations of the reactants and catalyst at constant flow of nitrogen.

DISCUSSION

The classical substrate of the BZ reaction, malonic acid (MA), differs from oxalic acid by its reactions with Br in the oxidation state +1 or 0: it reacts rapidly and gives a bromo derivative, whereas the redox reaction of OA with bromine is much slower under the same conditions. For the oscillations in the system with MA to

take place, a certain quantity of BrMA must be accumulated so that it can be oxidised with the catalyst to give Br^- ions⁹. According to calculations¹⁰, the concentration of Br^- ions oscillates from 10^{-9} to 10^{-4} mol/dm³ in 0.25M-MA, 0.063M- BrO_3^- , 0.001M-Ce(III), and 1.05M- H^+ , their initial concentration being $3 \cdot 10^{-5}$ mol/dm³. Oscillations of bromine were calculated¹⁰ under the same conditions in the range 10^{-6} – 10^{-4} mol/dm³. In the case of the heterogeneous oscillation reaction with OA studied by us, the oscillations of bromine were without the induction period in the range $7 \cdot 10^{-4}$ – $1.1 \cdot 10^{-3}$ mol/dm³ for 0.02M- BrO_3^- + 0.025M-OA + 0.001M-Ce(III) + 1.5M- H_2SO_4 and flow of nitrogen 600 ml/min. Experiments with MA under the same conditions led to oscillations of bromine after an induction period from an unmeasurably low concentration to $4 \cdot 10^{-5}$ mol/dm³. Thus, in the system with OA a substantially higher concentration of bromine is maintained and the amplitude of its oscillations is about by an order of magnitude larger.

Since the reduction of BrO_3^- ions can give only Br_2 and Br^- in analytically significant amounts, a relatively high production of Br_2 in the oscillating reaction with OA means a low level of Br^- , whereas with MA, in which case also BrMA is formed, the opposite is true. Br^- ions produced by reactions of HOBr or Br_2 with OA cannot

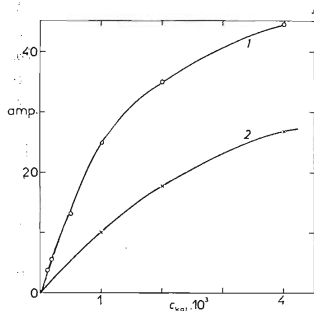


FIG. 4

Dependence of amplitude of oscillations of bromine in reaction with OA on concentration of catalyst. 1 Ce(III); 2 Ce(IV). 0.01M- BrO_3^- , 0.025M-OA, 1.5M- H_2SO_4 ; 25°C, 600 ml N_2 /min, reaction volume 10 ml

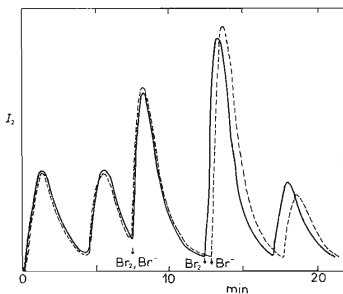
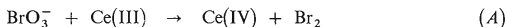


FIG. 5

Influence of addition of Br_2 or Br^- ions on oscillations of Br_2 in reaction with OA. Full curve: added $5 \cdot 10^{-4}$ M- Br_2 ; dashed curve: $8.3 \cdot 10^{-4}$ M- Br^- . Instant of addition denoted by arrow. Conditions as in Fig. 3, curve 3

inhibit the oxidation of Ce(III) or Mn(II) with bromate at the chosen concentrations of BrO_3^- and H^+ ions. However, the induction period of the oxidation of Ce(III) with BrO_3^- ions is equally increased by Br^- and bromine¹¹. In the case of OA, the effect of bromine prevails. When bromine is removed by nitrogen from the reaction system with OA, its concentration can be lowered to a "critical" value at which the reaction



begins to proceed at a higher rate (with respect to the increase of Ce(IV)) than the regenerative reaction



The critical concentration of bromine depends on the concentration of BrO_3^- ions: for 0.01M BrO_3^- is $c_{\text{crit}} = 6 \cdot 10^{-5} \text{ mol/dm}^3$, for 0.02M- BrO_3^- is $c_{\text{crit}} = 7 \cdot 10^{-4} \text{ mol/dm}^3$. During the oscillating reaction, the concentration of BrO_3^- ions decreases and a decrease of c_{crit} is also observable. By changing the rate of flow of nitrogen the time necessary to attain the critical concentration and hence the frequency of the oscillations change also. By a choice of the rate of flow of nitrogen the reaction of BrO_3^- with OA and the catalyst can attain a rapid, nonoscillating course.

In the extremely complicated kinetics of reaction (A), Ce(IV) ions have a small influence on the induction period, but they decrease exponentially the maximum oxidation rate of Ce(III) with bromate ions^{11,12}. The larger amplitude of the oscillations with Ce(III) than with Ce(IV) in the reaction with OA reflects probably a higher "starting" rate of reaction (A) and a larger quantity of produced bromine. At certain concentrations of the formed bromine and Ce(IV), the rates of the simultaneous reactions (A) and (B) become equal. In a subsequent phase, the rate of reaction (B) prevails. The concentration of Br_2 must be physically lowered below c_{crit} to enable the new start of (A).

On adding Br_2 and Br^- ions to the oscillating system with OA it turned out that their influence is essentially the same. Their addition to the oscillating system at a time when reaction (A) is still inhibited causes an increase of the time necessary for its initiation. It is necessary to remove bromine (either added or formed by the rapid reaction of BrO_3^- with Br^- ions) below the critical concentration. Addition of Br_2 or Br^- ions during the formation of Ce(IV) leads to a similar result, only the concentration of the recorded Br_2 is increased by the quantity produced in the oscillation cycle by reaction (A).

The calculated time dependence of the concentration of a reactant in the classical BZ system with malonic acid at an initial concentration of 0.125 mol/dm^3 shows that phases of more rapid and slower decrease of MA concentration alternate¹⁰. Experimental results with our heterogeneous system show that also the concentration of

BrO_3^- ions in the BZ system with OA undergoes a stepwise decrease. This is in accord with the finding that phases of more rapid and slower evolution of bromine alternate in the oscillating reaction. When the concentration of Br^- ions is not significant analytically, the rapid formation of Br_2 corresponds to an abrupt decrease of the concentration of BrO_3^- ions.

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