BELOUSOV–ZHABOTINSKII TYPE OSCILLATION REACTION WITH GLYCEROL AND KINETICS OF REACTIONS BETWEEN THE SYSTEM COMPONENTS

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Glycerol causes chemical oscillations in Belousov–Zhabotinskii reaction in a closed system as well as in a reaction solution bubbled with nitrogen. Since the oxidation of glycerol with bromate ions does not proceed autocatalytically and bromine in the oxidation state 0 or $+1$ in the absence of light does not react with glycerol, hydrolysis of bromine is the probable source of bromide ions in the studied oscillation system.

The present views on the formation of Br^- ions in BZ type oscillation systems are mentioned in our preceding communication[1]. Since this question is still open for discussion, we turned our attention to glycerol as a new substrate, which is non--brominatable and moreover does not react with hypobromous acid or aqueous solution of bromine in the dark.

EXPERIMENTAL

The kinetics of oxidation of glycerol with bromate ions were studied polarographically by recording the time dependence of the limiting diffusion current of BrO_3^- ions at -1.0 V against saturated Hg_2SO_4 electrode (MSE). Glycerol is polarographically inactive in the potential region under study. The reaction solution was placed in a Kalousek polarographic cell protected from light and provided with a thermostated mantle-piece. The rate constant for the reaction of bromine with glycerol was determined from the time dependence of the limiting diffusion current of Br_2 at -0.6 V *vs* MSE on the dropping Hg electrode illuminated either by day light or by a lamp IR 2. The reaction was also followed spectrophotometrically at 400 nm, the absorption maximum of Br_2 ($\varepsilon = 166 \, l \, mol^{-1} \, cm^{-1}$).

Oxidation of glycerol with Mn(III) ions was measured at 480 nm, the absorption maximum of Mn(III). When this reaction was followed in the presence of Br_2, the drop in Mn(III) concentration was determined from the absorption at 300 nm ($\varepsilon = 1\,160 \, l \, mol^{-1} \, cm^{-1}$). The absorption measurements were carried out in 0.5—5 cm thick quartz glass cuvettes tempered at 25°C. The values of rate constants given below are averages from three independent measurements. We used a Specord UV VIS type spectrophotometer and an OH-105 type polarograph (Radelkis, Budapest).

The oscillation reactions took place in a tempered cell with a Pt electrode and a salt bridge filled with a solution of $NaHSO_4$, which led to a calomel reference electrode. The time course

of the Pt electrode potential was followed during agitation of the solution with a magnetic stirrer or by bubbling nitrogen at a rate of 0.6 dm^3 min^{-1}, the polarograph being used as a millivolt-meter. The oscillation reaction was also followed spectrophotometrically at various wave lengths (282—555 nm) in quiet solution.

The chemicals used were of reagent grade and solutions were prepared from redistilled water. A solution of Mn(III) was prepared by reaction of MnO_4^- ions with a 25-fold excess of Mn(II) in the medium of 2M-H_2SO_4.

RESULTS

Oxidation of Glycerol (1,2,3-*propanetriol*) *with* BrO_3^- *Ions*

The time course of the decrease of bromate ions in the presence of an excess of glycerol is shown in Fig. 1, curve 2. The limiting diffusion current of bromate does not decrease to zero. After addition of allyl alcohol (in a concentration twice as large as that of bromate) the decrease of bromate is governed by first-order reaction kinetics up to 95% of the extent of reaction without indication of complicating effects (Fig. 1, curve 1). Allyl alcohol is an efficient agent for capturing hypobromous acid through rapid addition to the C=C bond[2]. On adding a bromine capturing agent, 0.02 mol l^{-1} methacrylic acid amide, to the solution of bromate with glycerol, the course of the time dependence is the same as in Fig. 1, curve 2, only the residual current is somewhat lower. Similarly, if the solution is bubbled with nitrogen, whereby the bromine formed is removed, the time dependence of the bromate concentration does not correspond to a kinetic equation of the first order.

The rate constant for oxidation of glycerol with bromate in the presence of allyl alcohol was determined from the slope of the linear dependence of $\ln (I_0/I)$ on the
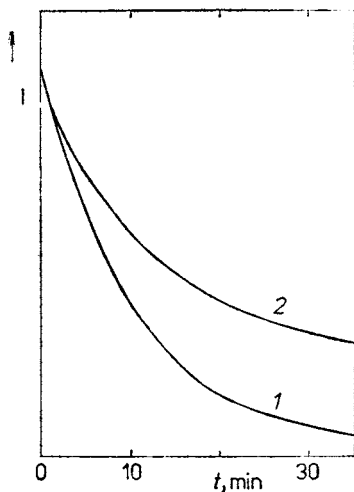

FIG. 1

Time change of the limiting diffusion current of bromate ions. *1* 1 mol l^{-1} H_2SO_4, 0.5 mol l^{-1} glycerol, $1 . 10^{-3}$ mol l^{-1} NaBrO$_3$, and $2 . 10^{-3}$ mol l^{-1} allyl alcohol at 25°C; *2* as *1* but without allyl alcohol

time; it increases linearly with the excess concentration of glycerol. Further it increases with the concentration of hydrogen ions; logarithmic analysis revealed that the reaction is of the second order with respect to hydrogen ions (in the presence of H_2SO_4 or $HClO_4$; Table I). The measurements were carried out also with $HClO_4$ to permit accurate adjustment of the ionic strength.

The rate equation for the oxidation of glycerol with bromate ions has, according to the above findings, the form

$$-d[BrO_3^-]/dt = k[BrO_3^-][C_3H_8O_3][H_3O^+]^2, \qquad (1)$$

with $k = 2\cdot6 \cdot 10^{-3} \, l \, mol^{-1} \, s^{-1}$ in $1 \, mol \, l^{-1} \, H_2SO_4$ at 25°C.

The pH dependence indicating the exchange of two protons and the analogy with the results of oxidation of secondary alcohols with bromates[3] enable us to propose a probable mechanism as follows:

$$BrO_3^- + 2\,H^+ \underset{}{\overset{K}{\rightleftharpoons}} H_2BrO_3^+ \qquad (A)$$
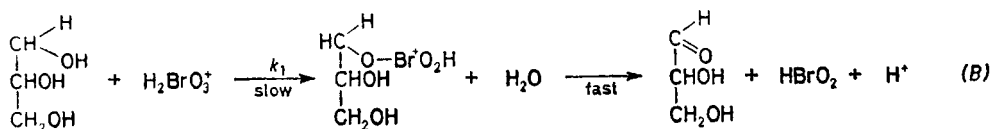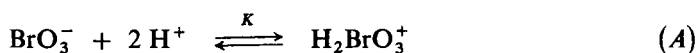
The rate equation derived on this basis is in accord with that found experimentally; the measured rate constant is equal to k_1K.

TABLE I

Influence of hydrogen ions on oxidation of glycerol with bromate. Reaction solution: $1 \cdot 10^{-3}$ mol $\cdot l^{-1}$ $NaBrO_3$, $0\cdot2$ mol l^{-1} glycerol at 25°C. The ionic strength was 2 mol l^{-1} with H_2SO_4 and 3 mol l^{-1} with $HClO_4$

H^+ mol l^{-1}	H_2SO_4 k, s^{-1}	$HClO_4$ k, s^{-1}
0·2	—	$5\cdot66 \cdot 10^{-6}$
0·5	$8 \cdot 10^{-5}$	—
0·6	—	$3\cdot33 \cdot 10^{-5}$
0·75	$1\cdot86 \cdot 10^{-4}$	—
1·0	$3\cdot0 \cdot 10^{-4}$	$9\cdot33 \cdot 10^{-5}$
1·5	$9\cdot5 \cdot 10^{-4}$	$2\cdot1 \cdot 10^{-4}$
2·0	$1\cdot5 \cdot 10^{-3}$	$3\cdot33 \cdot 10^{-4}$
2·5	—	$6\cdot0 \cdot 10^{-4}$
3·0	—	$9\cdot53 \cdot 10^{-4}$

The assumed mechanism involves the slow formation of glycerol ester of bromic acid, which decomposes rapidly in the further step, giving bromous acid. This in turn reacts with another glycerol molecule to give hypobromous acid. The bromic acid ester may form a cyclic ester with the neighbouring OH group as considered by several authors[4]. Such reactions are accompanied by a high negative value of the activation entropy. The activation parameters of the reaction were determined from the temperature dependence of the rate constant as $\Delta H^{\ne} = 54.9 \text{ kJ mol}^{-1}$ and $\Delta S^{\ne} = -132.6 \text{ J K}^{-1} \text{ mol}^{-1}$ in favour of the envisaged formation of a cyclic ester.

Oxidation of Glycerol with Mn(III) *Ions*

The decrease in absorbancy of Mn(III) ions in the presence of an excess of glycerol does not satisfy a first-order kinetic equation in the whole extent of the reaction course. The rate constant k_{obs} was evaluated by the method of initial rate; it increases toward a limit with increasing concentration of glycerol (Table II). The reaction is not influenced by light, by the addition of bromine up to $5 . 10^{-4} \text{ mol l}^{-1}$ and bromide ions up to $1 . 10^{-3} \text{ mol l}^{-1}$.

Oxidation of Glycerol with Bromine in Aqueous Solution

The reaction was followed with an excess of glycerol; it does not proceed in the dark. It is not accelerated by Mn(III) ions in a concentration up to $2 . 10^{-3} \text{ mol l}^{-1}$. From the reaction proceeding in a solution of $0.2 \text{ mol l}^{-1} \text{ C}_3\text{H}_8\text{O}_3$, $2 . 10^{-3} \text{ mol l}^{-1} \text{ Br}_2$, and $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ on the day light after an induction period, the rate constant was evaluated from the slope of the linear dependence $\ln(I_0/I) = kt$ as $k = 8.8 . 10^{-4} \text{ s}^{-1}$. When the reaction solution was irradiated with a lamp IR 2, then $k = 2.3 . 10^{-3} \text{ s}^{-1}$.

Oscillation Reaction of BZ *type with Glycerol During Bubbling with Inert Gas*

A typical course of a heterogeneous oscillation reaction is shown in Fig. 2a. Both the induction and oscillation periods are independent of the concentration of bromate ions from $9 . 10^{-3}$ to $6 . 10^{-2} \text{ mol l}^{-1}$ (in a solution of $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, $2 . 10^{-3} \text{ mol}$

TABLE II
Dependence of the rate constant for oxidation of glycerol with Mn(III) ions on the concentration of glycerol. Reaction solution: $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, $2 . 10^{-3} \text{ mol l}^{-1}$ Mn(III) at 25°C

Glycerol, mol l^{-1}	0·5	0·2	0·1	0·05	0·02
$k_{obs} . 10^2, \text{s}^{-1}$	1·74	1·06	0·57	0·23	0·12

. l^{-1} MnSO$_4$, 0·06 mol l^{-1} glycerol bubbled with 0·6 dm^3 nitrogen *per* minute at 25°C). However, both periods diminish with increasing concentration of glycerol from 0·02 to 0·28 mol l^{-1} (in a solution of 1 mol l^{-1} H$_2$SO$_4$, 2 . 10^{-3} mol . . l^{-1} MnSO$_4$, and 0·03 mol l^{-1} NaBrO$_3$ bubbled as before). The system oscillated when the concentration of H$_2$SO$_4$ changed from 0·1 to 1·6 mol l^{-1} (in a solution of 2 . 10^{-3} mol l^{-1} MnSO$_4$, 0·06 mol l^{-1} C$_3$H$_8$O$_3$ and 0·03 mol l^{-1} NaBrO$_3$ bubbled as before) and both periods decreased with increasing concentration of the acid.

With increasing concentration of Mn(II) ions, the induction period increases, while the oscillation period and the number of oscillations pass through their maximum. Oscillations were observed from 2 . 10^{-3} to 2 . 10^{-2} mol l^{-1} MnSO$_4$ in a solution of 1 mol l^{-1} H$_2$SO$_4$, 0·06 mol l^{-1} glycerol, and 0·03 mol l^{-1} NaBrO$_3$ bubbled with 0·6 dm^3 N$_2$ *per* min. The highest number of oscillations was observed at 0·01 mol l^{-1} MnSO$_4$. No oscillations took place in the presence of 0·03 mol l^{-1} allyl alcohol.

Oscillation Reaction of BZ type with Glycerol in Closed Homogeneous System

This type of oscillation reaction is illustrated in Figs 2*b* and 3. Oscillations in a closed homogeneous system were observed if the bromate ions were in excess against
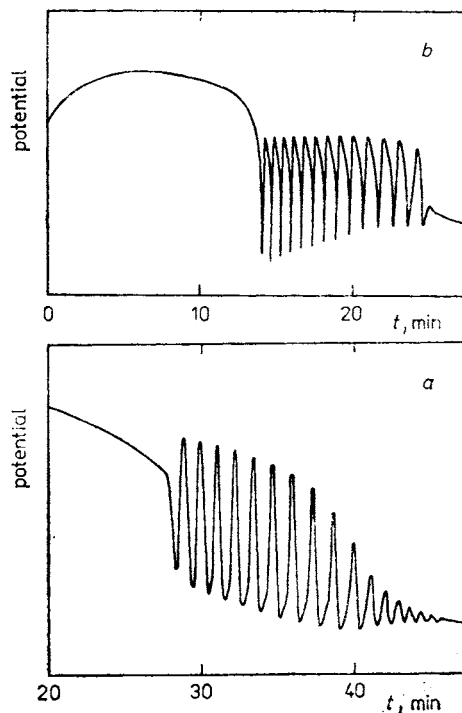

Fɪɢ. 2

Time change of the potential of Pt redox electrode. *a* 1 mol l^{-1} H$_2$SO$_4$, 0·06 mo, l^{-1} glycerol, 0·03 mol l^{-1} NaBrO$_3$, and 8 . . 10^{-3} mol l^{-1} Mn(II) at 25°C; solution volume 10 ml, bubbling rate 0·6 dm^3 N$_2$ *per* min; *b* 1 mol l^{-1} H$_2$SO$_4$, 0·2 mol l^{-1} NaBrO$_3$, 0·06 mol l^{-1} glycerol and 8 . . 10^{-3} mol l^{-1} Mn(II) at 25°C; solution volume 30 ml, stirring rate 300 rpm

glycerol. The system oscillated if the concentration of glycerol was in the range $0.06 - 0.16$ mol 1^{-1} in the presence of 1 mol 1^{-1} H_2SO_4, 0.2 mol 1^{-1} $NaBrO_3$, and $8 \cdot 10^{-3}$ mol 1^{-1} $MnSO_4$; further in a narrow concentration region of the acid, $0.7 - 1.1$ mol 1^{-1} (0.2 mol 1^{-1} $NaBrO_3$, 0.1 mol 1^{-1} glycerol, and $8 \cdot 10^{-3}$ mol 1^{-1} $MnSO_4$) and at concentrations of $NaBrO_3$ from 0.12 to 0.5 mol 1^{-1} (1 mol 1^{-1} H_2SO_4, 0.1 mol . 1^{-1} glycerol, $8 \cdot 10^{-3}$ mol 1^{-1} $MnSO_4$).

The parameters of both homogeneous and heterogeneous oscillation systems were the same when the oscillation reaction took place in the dark as when it proceeded during illumination with the IR 2 lamp.

DISCUSSION

Glycerol is a suitable substrate for BZ type oscillation reactions. Periodic changes of the potential of a Pt electrode were observed when bromine was removed from the reaction solution by bubbling with nitrogen (Fig. 2*a*), as well as in closed homogeneous system during stirring (Fig. 2*b*); oscillations were also observed spectrophotometrically in a closed cuvette without stirring (Fig. 3), where no bubbles appeared. The oscillation amplitude (the difference between the maximum and minimum absorbance) corresponded to a change in the concentration of Mn(III) ions equal to $3 \cdot 10^{-4}$ mol 1^{-1}.

With glycerol as substrate of oscillation reactions, the question about the origin of Br^- ions as controlling intermediate product is especially interesting. Varga and Körös[5,6] brought evidence that the source of bromide ions are bromate ions rather than organic bromo derivatives. Oxidation of glycerol with bromate does not proceed autocatalytically as with most other substrates suitable for BZ oscillators. The reaction is not a source of Br^- ions, hence it is not disturbed by the interaction of Br^- with BrO_3^- ions. The reduction product of the latter is in this case hypobromous acid, which must be captured with allyl alcohol (Fig. 1, curve *1*), since
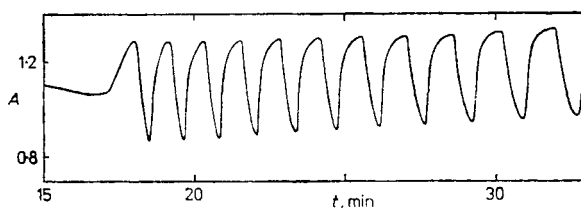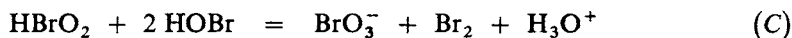
FIG. 3

Time dependence of absorbance at 300 nm for a solution of 1 mol 1^{-1} H_2SO_4, 0.06 mol 1^{-1} glycerol, 0.2 mol 1^{-1} $NaBrO_3$, and $8 \cdot 10^{-3}$ mol 1^{-1} Mn(II)

otherwise the follow-up reaction[7]

$$HBrO_2 + 2\,HOBr = BrO_3^- + Br_2 + H_3O^+ \qquad (C)$$

would take place with the result that the limiting diffusion current would not drop to zero (Fig. 1, curve 2). The residual diffusion current corresponds to BrO_3^- and Br_2 formed by reaction (C) as polarographically active products. Since neither bromine nor hypobromous acid react with glycerol, and bromous acid is produced continually as an intermediate, the rapid reaction (C) can proceed.

The time dependence of the concentration of bromine formed during oxidation of an excess of glycerol with bromate (Fig. 4, curve 1), or of glycerol with an excess of bromate (Fig. 4, curve 2) shows that bromine does not react with intermediate products formed from glycerol. The reaction of bromate with hydrazoic acid[7] is analogous. Försterling[8] in his study of reactions of aliphatic alcohols with bromate ions came to the conclusion that the main reaction step is a direct attack of the alcohol, e.g. CH_3OH with $HBrO_3$. The reaction gives HOBr and a small quantity of bromine formed by a side reaction, which however was not studied in detail.

Bromine and bromide ions cannot be formed in this system by reaction of HOBr with glycerol, since this reaction does not proceed under the given conditions and is not accelerated even by Mn(III) ions which have a positive effect, e.g., in the reaction with oxalic acid[9]. Since Br^- ions are not formed in this system by oxidation of the substrate with HOBr, as assumed in the revised[10] and amplified[11] Oregonator model, we assume that they are formed by hydrolysis of bromine formed in the reaction. Field[12] considers the hydrolytic equilibrium of bromine as an important source of bromide ions, although not the only one; the other is the reaction of HOBr with the substrate.

The concentration of Br_2 was determined spectrophotometrically under the conditions of the homogeneous oscillation reaction without catalyst $(1 \text{ mol } l^{-1}$
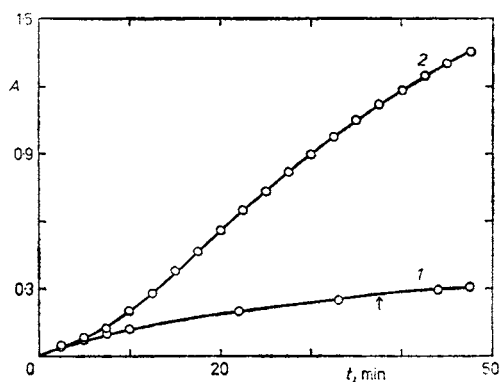

Fig. 4

Time dependence of absorbance corresponding to bromine in the oxidation of glycerol with bromate ions. 1 $1 \text{ mol } l^{-1}$ H_2SO_4, $0.5 \text{ mol } l^{-1}$ glycerol, and $5 . 10^{-3} \text{ mol } l^{-1}$ $NaBrO_3$ at 25°C; 2 $1 \text{ mol } . l^{-1}$ H_2SO_4, $2 . 10^{-3} \text{ mol } l^{-1}$ glycerol, and $0.5 \text{ mol } l^{-1}$ $NaBrO_3$ at 25°C

H_2SO_4, $0·2$ mol l^{-1} BrO_3^-, and $0·06$ mol l^{-1} glycerol) and with the catalyst ($8 .$ $. 10^{-3}$ mol l^{-1} $MnSO_4$) 17 min after mixing the solution components (*i.e.* after the induction period). The concentration of bromine was $7·23 . 10^{-3}$ mol l^{-1} in the first case and $1·68 . 10^{-2}$ mol l^{-1} in the second. From the hydrolytic equilibrium constant of bromine, $K_h = 1·37 . 10^{-8}$ mol dm^{-3} (ref.[13]), corresponding to the reaction

$$Br_2 + H_2O \overset{K_h}{\rightleftharpoons} HOBr + Br^- + H^+ , \qquad (D)$$
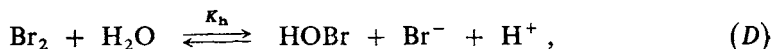
the concentration of Br^- ions corresponding to the mentioned concentrations of bromine was calculated as $9·9 . 10^{-6}$ mol l^{-1} in the system without catalyst and $1·51 . 10^{-5}$ mol l^{-1} with catalyst.

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