KINETICS OF COMPONENT REACTIONS OF THE BELOUSOV–ZHABOTINSKII TYPE OSCILLATION SYSTEM WITH OXALIC ACID AND HYPOPHOSPHITE IONS

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The authors studied the kinetics of oxidation of oxalic acid and hypophosphite ions with bromate ions, aqueous solution of bromine, and Mn(III) ions in the medium of aqueous sulphuric and perchloric acids. The kinetics of these two-component reactions of the Belousov–Zhabotinskii type oscillation system was considerably influenced by the addition of a third component.

In various models of the Belousov–Zhabotinskii (BZ) reaction[1-6], the sequence of non-radical reactions by which the Br⁻ ions are removed from the system is generally accepted. Although bromine was originally considered in the Explodator[7] as controlling intermediate product, later the decisive role of bromide ions[8] was experimentally verified.

The main problem which must be solved if the oscillations in the BZ system are controlled by the concentration of Br⁻ ions is to find their source and reactions by which they are generated. Körös and coworkers[9] found recently that even in the classical BZ system a substantial portion of Br⁻ ions originates from bromate ions and not from bromomalonic acid. Therefore, they proposed the reaction between bromate ions and oxidation product of malonic acid to explain the formation of Br⁻ ions. In the revised[4] and amplified[6] Oregonator model, the regeneration of Br⁻ ions is attributed to the oxidation of the substrate with hypobromous acid. In Field's model[5] of the BZ reaction with oxalic acid in the presence of acetone, the hydrolytic equilibrium of bromine is considered important besides the reaction of HOBr with the substrate.

There are problems with the form of the rate equations and with the rate constants of the reactions in which Br⁻ ions are formed. The values of the rate constants involved in various models are needed for the numerical simulation of the oscillation reactions.

The present work brings the results of a kinetic study of the oxidation of oxalic acid and hypophosphite ions with bromate ions, aqueous solution of bromine, and Mn(III) ions. The two substrates can be used in oscillation reactions of BZ type[10-16]; they do not form brominated derivatives, and if Br⁻ ions are formed, they must

originate from reduced bromate ions. It will be shown below that the kinetics of these two-component reactions, which may proceed in oscillating systems, is strongly influenced by the addition of a third component.

EXPERIMENTAL

Reagent grade chemicals and redistilled water were used to prepare the reaction solutions. A solution of Mn(III) ions was prepared every day by the reaction of MnO_4^- ions with a 50-fold excess of Mn(II) ions in the medium of $3M-H_2SO_4$.

The kinetics of oxidation with bromate ions was followed polarographically from the time dependence of the limiting diffusion current of BrO_3^- at a potential of -1 V against 1 M-MSE. Under the given conditions, the dependence of the diffusion current on the concentration of BrO_3^- was linear, whereas oxalic acid and hypophosphite ions are polarographically inactive. The reactions proceeded in a blackened Kalousek polarographic cell with a thermostated mantle at $25 \pm 0.1°C$. Bubbling nitrogen at a rate of 0.6 dm^3 min^{-1} was used to remove oxygen and, in some cases, to lower the concentration of bromine, which proceeded in 10 ml of solution with a half-time of 30 s corresponding to a "rate constant" $2.3 . 10^{-2}$ s^{-1}.

The kinetics of oxidation with Br_2 and Mn(III) ions was followed spectrophotometrically; the former at 400 nm, corresponding to the absorption maximum of Br_2 ($\varepsilon = 166$ mol^{-1} l cm^{-1}). Since bromine absorbs light also at the wavelength of 480 nm corresponding to the absorption maximum of Mn^{3+} ions, their concentration was followed at $300-310$ nm (at 300 nm is $\varepsilon = 1160$ mol^{-1} l cm^{-1}, and even more in the presence of oxalic acid thanks to the formation of oxalate complexes[17]). The absorbance of the reaction solutions was measured in $0.5-5$ cm thick quartz cuvettes tempered at $25 \pm 0.1°C$.

In kinetic measurements, the substrate was in a large ($10-500$ fold) excess, nevertheless the experimental rate constant, k_{exp}, could not always be evaluated from the pseudo first-order kinetic dependences, $\ln (I_0/I) = k_{exp}t$ or $\ln (A_0/A) = k_{exp}t$. In case of deviations, k_{exp} was evaluated by the method of initial rates.

RESULTS AND DISCUSSION

Oxidation of Oxalic Acid and Hypophosphite Ions with Bromate

A characteristic feature of both these reactions is their autocatalytic course in a homogeneous medium (Figs 1 and 2, curve 1). This can be changed in the reaction with oxalic acid by bubbling nitrogen (curve 2 in Fig. 1 corresponds to a pseudo first-order reaction) causing removal of bromine. At an excess of the substrate, Br_2 is an intermediate product whose concentration in the reaction with hypophosphite ions is under the detection limit (below $1.2 . 10^{-6}$ mol dm^{-3}).

The second-order rate constants for the reaction of bromate with oxalic acid and $H_2PO_2^-$ ions were evaluated by the method of initial rates as $1.61 . 10^{-3}$ $dm^3 .$ $. mol^{-1}$ s^{-1} and $6.5 . 10^{-5}$ dm^3 mol^{-1} s^{-1} in $1M-H_2SO_4$ at 25°C, respectively. This is in accord with the values found previously in other media[17-20]. Field[5] in simulating the system $BrO_3^- + Ce(III) + (COOH)_2 + $ acetone assumed a value which was lower by the factor of 320 (at 29°C).

Oxidation of Oxalic Acid and Hypophosphite Ions with Bromine

The following equilibrium is rapidly established in aqueous bromine solutions:

$$Br_2 + H_2O \xrightleftharpoons{K_h} HOBr + Br^- + H^+, \qquad (A)$$
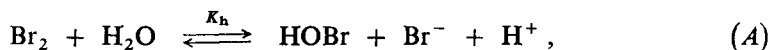
where $K_h = 1.37 . 10^{-8}$ mol dm^{-3} according to ref.[21]. Elimination of autocatalysis in the reaction of BrO_3^- with $(COOH)_2$ by bubbling nitrogen can thus be interpreted so that Br_2 or HOBr oxidizes the substrate more rapidly than BrO_3^- ions.

The drop in the concentration of Br_2 in the reaction with $(COOH)_2$ does not correspond to a first-order kinetic equation even at a large excess of the substrate. The pronounced decrease of the rate suggests an inhibition by Br^- ions. To verify this assumption, we studied the influence of added Br^- ions into the solution of Br_2 and oxalic acid at various concentrations of H^+ ions. Thus, the initial equilibrium concentration of HOBr was substantially decreased, while the concentration of Br_2 was practically unaltered and no Br_3^- ions were formed. We added $0.5 - 2.5 . 10^{-3}$ mol.
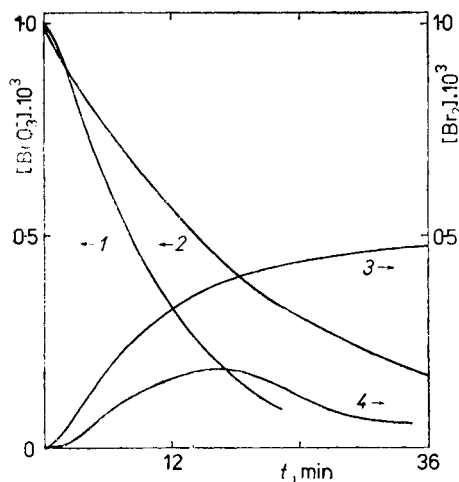

FIG. 1

Time change of the concentration of BrO_3^- ions (curves *1* and *2*) and bromine (*3* and *4*) in the reaction with $(COOH)_2$ in $1M$-H_2SO_4. Initial concentrations: *1* 0.001 mol dm^{-3} BrO_3^- and 0.5 mol dm^{-3} $(COOH)_2$; *2* as *1*, bubbling with 0.6 dm^3 nitrogen *per* min; *3* 0.5 mol dm^{-3} BrO_3^- and 0.0025 mol dm^{-3} $(COOH)_2$; *4* as *1*
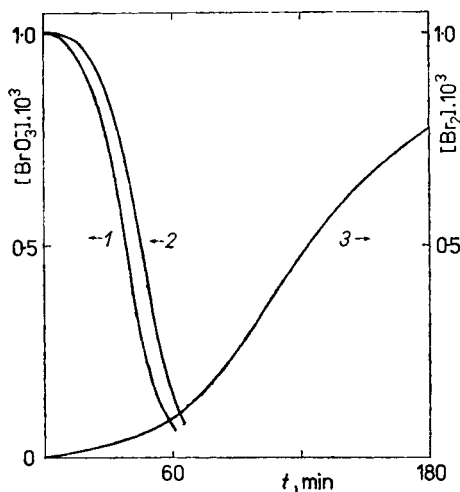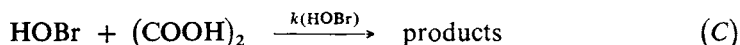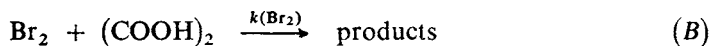
FIG. 2

Time change of the concentration of BrO_3^- ions (curves *1* and *2*) and Br_2 (curve *3*) in the reaction with $H_2PO_2^-$ ions in $1M$-H_2SO_4. Initial concentrations: *1* 0.001 mol dm^{-3} BrO_3^- and 0.5 mol dm^{-3} $H_2PO_2^-$; *2* as *1*, bubbling with 0.6 dm^3 nitrogen *per* min; *3* 0.5 mol dm^{-3} BrO_3^- and 0.0025 mol dm^{-3} $H_2PO_2^-$

. dm^{-3} Br^- to $0.3-1.26 \cdot 10^{-3}$ mol dm^{-3} Br_2 and 0.5 mol dm^{-3} $(COOH)_2$ in 0.01 to 1 M-H_2SO_4 or $0.01-1$M-$HClO_4$ at constant ionic strength.

The rate constants evaluated by the method of initial rates decreased with increasing concentration of H^+ and added Br^- ions. This can be attributed to the preceding equilibrium (A) and the parallel reactions

$$Br_2 + (COOH)_2 \xrightarrow{k(Br_2)} \text{products} \qquad (B)$$

$$HOBr + (COOH)_2 \xrightarrow{k(HOBr)} \text{products} \qquad (C)$$

leading to the rate equation

$$-\frac{d[Br_2]}{dt} = \left(k(Br_2) + \frac{k(HOBr) K_h}{[H^+][Br^-]} \right) [Br_2] [(COOH)_2] . \qquad (1)$$
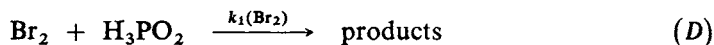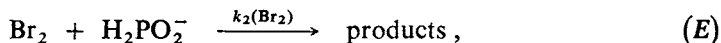
The dependence

$$-\frac{d[Br_2]_0}{dt} \cdot \frac{1}{[Br_2]_0 [(COOH)_2]_0} = f\left(\frac{1}{[Br^-]} \right) \qquad (2)$$

at an excess of H^+ and added Br^- ions was found experimentally to be linear and leads to the values of $k(Br_2)$ and $k(HOBr)$.

The mean value of the rate constant for the reaction of Br_2 with oxalic acid, $k(Br_2) = 5.5 \cdot 10^{-4}$ dm^3 mol^{-1} s^{-1}, was found from the intersection with the coordinate axis, and $k(HOBr) = 15.5$ dm^3 mol^{-1} s^{-1} for the reaction of HOBr with oxalic acid from the slope. The relatively slow reaction of Br_2 with $(COOH)_2$ in aqueous solution can be accelerated either by the action of light or by the addition of $Mn(III)$ ions. The dependence of $\log k$ on $\log [Mn(III)]_0$ was linear with a slope 0.58 from 0.1 to 0.001 mol dm^{-3} $[Mn(III)]_0$.

The reaction of Br_2 with $H_2PO_2^-$ ions is more rapid and its course is different. At constant pH and excess of $H_2PO_2^-$ ions, it is of the pseudo first order. The second-order rate constant is $k(Br_2) = 1.26$ dm^3 mol^{-1} s^{-1} in 1M-H_2SO_4 and 1.32 dm^3 . . mol^{-1} s^{-1} in 1M-$HClO_4$. Addition of Br^- ions up to the concentration 0.005 mol . . dm^{-3} has no influence on the reaction rate. This suggests that the reaction path *via* HOBr plays no role in this case. At constant ionic strength 2 mol dm^{-3}, the rate constant decreased with increasing concentration of H^+ ions ($HClO_4$) from 0.1 to 2 mol dm^{-3}. Considering the dissociation of hypophosphorous acid, $K_D = 7.95$ . . 10^{-2}, and the parallel reactions of its forms with bromine

$$Br_2 + H_3PO_2 \xrightarrow{k_1(Br_2)} \text{products} \qquad (D)$$

$$Br_2 + H_2PO_2^- \xrightarrow{k_2(Br_2)} products, \qquad (E)$$

we obtain the expression for the rate constant

$$k = \frac{k_1(Br_2) + k_2(Br_2) K_D[H^+]^{-1}}{1 + K_D[H^+]^{-1}}. \qquad (3)$$

The measured dependence of $k(1 + K_D[H^+]^{-1})$ on $[H^+]^{-1}$ (Fig. 3) led to the determination of the rate constants for both reaction paths, the reaction of the dissociated form being preferred: $k_1(Br_2) = 0.65 \, dm^3 \, mol^{-1} \, s^{-1}$ and $k_2(Br_2) = 9.76 \, dm^3 \, mol^{-1} \, s^{-1}$.

In contrast to oxalic acid, the rate constant of the reaction of Br_2 with $H_2PO_2^-$, which remains pseudo first-order, is not influenced by the presence of $0.1 - 0.001 \, mol$ . . $dm^{-3} \, Mn(III)$.

The value of $k(HOBr)$ in the reaction with $(COOH)_2$ given by Smith[22], which is similar to that found by us, had to be increased by the factor of 6 in simulating the BZ reaction[5] (nearly to $222 \, dm^3 \, mol^{-1} \, s^{-1}$ as in ref.[23]) to obtain agreement between the calculated and measured oscillation periods. The model of Ruoff and Noyes[6] implies that the rate of formation of Br^- ions is proportional to the square root of the concentration of the catalyst. This is close to our finding in the case of oxalic acid. On the other hand, the reaction order with respect to the catalyst in the reaction with $H_2PO_2^-$ ions was zero.

Influence of Bromine on the Oxidation of Oxalic Acid and
$H_2PO_2^-$ with Mn(III) Ions

Whereas Br^- ions up to $1.2 \, . \, 10^{-3} \, mol \, dm^{-3}$ concentration have no influence on the rate of the reaction of $Mn(III)$ with $(COOH)_2$, the influence of Br_2 is illustrated in Fig. 4: It causes an induction period with a length directly proportional to the concentration of added Br_2. After the IP has been finished, the rate of decrease of $Mn(III)$ ions is no more dependent on the concentration of bromine. Bromide ions have no influence on the course of the reaction of $Mn(III)$ with $(COOH)_2$ even in the presence of bromine, which always causes an induction period. Bromine is consumed in the three-component system $Mn(III) + Br_2 + (COOH)_2$ at the same rate without induction period as $Mn(III)$ after the induction period.

Still different is the influence of Br_2 on the reaction of $Mn(III)$ with $H_2PO_2^-$ ions (Fig. 5). After the initial slow phase, in which the rate of consumption of $Mn(III)$ is similar to that in the absence of bromine, the rate increases. The further course obeys the first-order kinetics and the dependence of the measured rate constant on the concentration of added bromine can be expressed as $k_{exp} = k' + k''[Br_2]$,

where $k' = 1.68 \cdot 10^{-3}\,\text{s}^{-1}$ and $k'' = 7.36\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ in $0.01\text{M-H}_2\text{PO}_2^-$. Addition of Br^- ions to the two-component system $\text{Mn(III)} + \text{H}_2\text{PO}_2^-$ causes acceleration from the beginning of the reaction. Addition of Br^- ions to the three-component system $\text{Mn(III)} + \text{Br}_2 + \text{H}_2\text{PO}_2^-$ causes shortening of the slow phase and further increase of the rate.
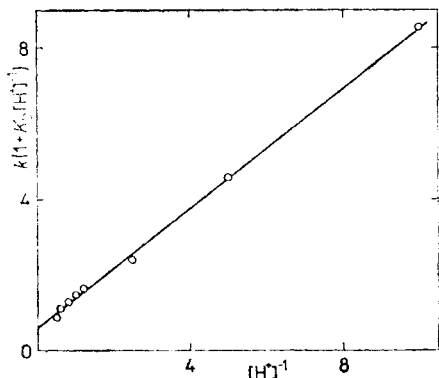

FIG. 3

Influence of H^+ ions on the rate constant for the reaction of Br_2 with H_2PO_2^- ions in HClO_4. $0.01\,\text{mol}\,\text{dm}^{-3}\,\text{H}_2\text{PO}_2^-$ and $0.001\,\text{mol}\,\text{dm}^{-3}\,\text{Br}_2$, ionic strength $2\,\text{mol}\,.\,\text{dm}^{-3}$
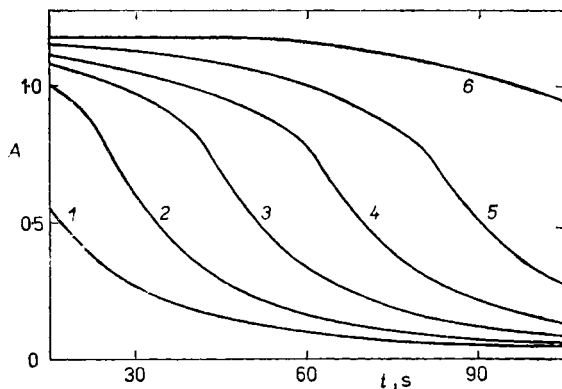

FIG. 4

Influence of bromine on the time change of absorbance of Mn(III) at 310 nm in the reaction with $(\text{COOH})_2$ in $1\,\text{M-H}_2\text{SO}_4$, $3.5 \cdot 10^{-4}\,\text{mol}\,\text{dm}^{-3}$ Mn(III), and $0.1\,\text{mol}\,.\,\text{dm}^{-3}$ $(\text{COOH})_2$. Concentration of Br_2: 1 0; 2 $3 \cdot 10^{-4}$; 3 $6 \cdot 10^{-4}$; 4 $9 \cdot 10^{-4}$; 5 $1.2 \cdot 10^{-3}$; 6 $1.5 \cdot 10^{-3}\,\text{mol}\,\text{dm}^{-3}$
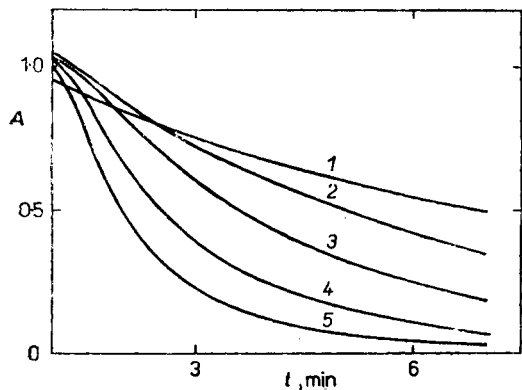

FIG. 5

Influence of bromine on the time change of absorbance of Mn(III) at 300 nm during the reaction with H_2PO_2^- in $1\text{M-H}_2\text{SO}_4$, $0.001\,\text{mol}\,\text{dm}^{-3}$ Mn(III), and $0.01\,\text{mol}\,.\,\text{dm}^{-3}$ H_2PO_2^-. Concentration of Br_2: 1 0; 2 $2.25 \cdot 10^{-4}$; 3 $4.5 \cdot 10^{-4}$; 4 $9 \cdot 10^{-4}$; 5 $1.35 \cdot 10^{-3}\,\text{mol}\,\text{dm}^{-3}$

REFERENCES

1. Field R. J., Noyes R. M.: J. Chem. Phys. *60*, 1877 (1974).
2. Field R. J. in the book: *Oscillations and Travelling Waves in Chemical Systems* (R. J. Field and M. Burger, Eds), p. 55—92. Wiley–Interscience, New York 1985.
3. Tyson J. J.: Ref. 2, p. 93—144.
4. Noyes R. M.: J. Chem. Phys. *80*, 6071 (1984).
5. Field R. J., Boyd P. M.: J. Phys. Chem. *89*, 3707 (1985).
6. Ruoff P., Noyes R. M.: J. Chem. Phys. *84*, 1413 (1986).
7. Noszticzius Z., Farkas H., Schelly Z.: J. Chem. Phys. *80*, 6062 (1984).
8. Noszticzius Z., Gaspar V., Försterling H. D.: J. Am. Chem. Soc. *107*, 2314 (1985).
9. Varga M., Györgyi L., Körös E.: J. Am. Chem. Soc. *107*, 4780 (1985).
10. Noszticzius Z., Bódiss J.: J. Am. Chem. Soc. *101*, 3177 (1979).
11. Ševčík P., Adamčíková Ľ.: Collect. Czech. Chem. Commun. *47*, 891 (1982).
12. Adamčíková Ľ., Ševčík P.: Int. J. Chem. Kinet. *14*, 735 (1982).
13. Noszticzius Z., Stirling P., Wittmann M.: J. Phys. Chem. *89*, 4914 (1985).
14. Gáspár V., Galambosi P.: J. Phys. Chem. *90*, 2222 (1986).
15. Alamgir M., Orbán M., Epstein I. R.: J. Phys. Chem. *87*, 3725 (1983).
16. Blume R., Bader H. J.: Z. Naturforsch. *39b*, 1795 (1984).
17. Adler S. J., Noyes R. M.: J. Am. Chem. Soc. *77*, 2036 (1955).
18. Reddy C. S., Laxmi V., Sundaram E. V.: Ind. J. Chem. A *19*, 544 (1980).
19. Ševčík P., Adamčíková Ľ., Gunárová D., Kováčiková D.: Acta Univ. Comen., Fac. Rerum. Nat., Chimia *31*, 17 (1983).
20. Adamčíková Ľ., Treindl Ľ.: Chem. Zvesti *23*, 321 (1969).
21. Eigen M., Kustin K. J.: J. Am. Chem. Soc. *84*, 1355 (1962).
22. Smith R. H.: Aust. J. Chem. *25*, 2503 (1972).
23. Knoller Y., Perlmutter-Hayman M.: J. Am. Chem. Soc. *77*, 3212 (1955).

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