

OXIDATION OF Mn(II) IONS WITH BROMATE

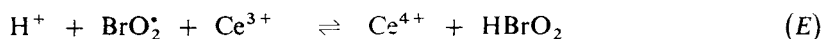
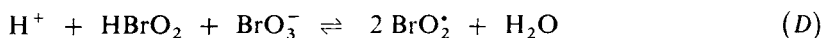
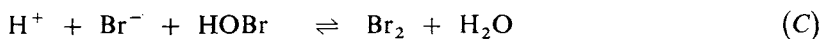
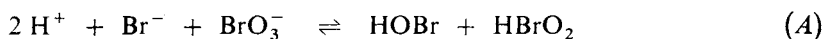
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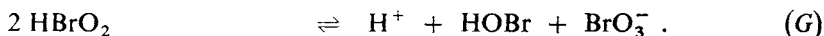
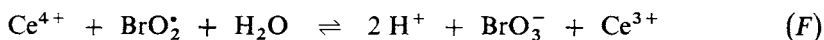
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Received October 3rd, 1984

Oxidation of Mn(II) with bromate ions was studied in the medium of aqueous sulphuric acid. The induction period as well as the maximum rate of formation of Mn(III) ions depend on the concentration of reactants, Br_2 , Br^- , H_3O^+ , and Mn(III) ions. The results are compared with kinetic data on oxidation of Ce(III) with bromate ions.

Oxidation of Mn(II) or Ce(III) ions with bromate is one of the most important steps of the Belousov–Zhabotinskii oscillation reaction, which is in a solution of BrO_3^- , MnSO_4 or $\text{Ce}_2(\text{SO}_4)_3$, substrate, and H_2SO_4 manifested by oscillations of the concentrations of Mn or Ce in either oxidation state. The kinetics of oxidation of their ions with bromate in acidic medium is complicated and of basic importance for elucidation of the Belousov–Zhabotinskii reaction. Oxidation of Ce(III) ions with BrO_3^- was studied by many authors^{1–9}. Noyes, Field and Thompson² proposed its mechanism, but they determined the reaction rate at an excess of Ce(III), whereas in the oscillation system mentioned the opposite is true: bromate is in excess and the concentration of Ce(III) is relatively low. Barkin and coworkers⁴ compared the experimental results concerning oxidation of Ce(III) ions with bromate under various conditions with those calculated on the basis of the Noyes–Field–Thompson mechanism and found a good agreement for most of the data. The mechanism consists of seven reversible reaction steps²





A different mechanism of oxidation of Ce(III) ions with bromate was proposed by Herbo, Schmitz and Van Glabbeke⁸, and still another by Zhabotinskii⁹. Little attention has been paid to oxidation of Mn(II) ions with bromate^{1,7}, which is assumed to be analogous to the oxidation of Ce(III) ions with bromate. Geiseler¹⁰ studied the autocatalytic oxidation of Mn(II) with bromate in the presence of bromide as inhibitor in a flow-through reactor. The author found some differences between the flow-through systems with Mn(II) and Ce(III).

Since Mn(II) is a more efficient catalyst than Ce(III) in the oscillation reaction with a nonbrominatable substrate, we studied the oxidation of Mn(II) ions with bromate during the oscillation reaction in the presence of bromine as inhibitor in a closed system.

EXPERIMENTAL

Oxidation of Mn(II) ions with bromate was followed spectrophotometrically by recording the absorbancy at 300 nm (corresponding to Mn(III) ions) as function of the time. The corresponding molar absorption coefficient is $1160 \text{ l mol}^{-1} \text{ cm}^{-1}$. A Specord UV VIS apparatus with 2 and 5 cm quartz glass cuvettes was employed. The concentration of bromine was measured at 400 nm by using the absorption coefficient value $165 \text{ l mol}^{-1} \text{ cm}^{-1}$.

The chemicals used were of reagent grade and were dissolved in redistilled water. The induction period was reproducible if the bromate solution was freshly prepared every day. All measurements were repeated at least three times, the mean error in the measurement of the induction period was $\pm 11\%$ and that for the maximum rate of formation of Mn(III) ions $\pm 7\%$. The solutions were pipetted into the measuring cuvette always in the same sequence: water, sulphuric acid, MnSO_4 , Br_2 , and NaBrO_3 . A solution of Mn(III) was prepared by reduction of permanganate with a 20-fold excess of MnSO_4 in $3\text{M-H}_2\text{SO}_4$. Its concentration was determined from absorption measurement in $1.5\text{M-H}_2\text{SO}_4$ at 480 nm (molar absorption coefficient $85 \text{ l mol}^{-1} \text{ cm}^{-1}$). The reaction was followed at $24.5 \pm 0.2^\circ\text{C}$.

RESULTS

Oxidation of Mn(II) ions with bromate is a complicated reaction, which is illustrated in Fig. 1. The curve can be divided into three parts: A induction period, during which the concentration of Mn(III) is close to zero, B rapid reaction period, during which Mn(III) ions are rapidly produced, and C slow reaction period, during which the concentration of Mn(III) approaches slowly a stationary value. In the absence of bromine under the conditions usual for the oscillation reactions, the induction period is shorter than 2 s. For this reason, the oxidation of Mn(II) ions with bromate was followed in the presence of bromine, which caused the induction period to incre-

ase. The time dependence of the absorbancy of Mn(III) ions (Fig. 1) enabled us to evaluate the induction period (IP) and the maximum rate of formation of Mn(III), $v_{\max} = \Delta c/\Delta t$, as the maximum slope of the rapid reaction course (corresponding to the inflexion point of the curve). The influence of the reaction species on these quantities is discussed below.

Influence of BrO_3^- Ions

It can be seen from Fig. 2 that the induction period decreases markedly with increasing concentration of bromate; in log-log coordinates we obtain a straight line with a slope -2.1 . The concentration of Mn(II) ions has no influence on this dependence: we obtained the same results in the presence of $8 \cdot 10^{-4}\text{M-Mn}^{2+}$ as in the presence of $3 \cdot 10^{-3}\text{M-Mn}^{2+}$. The rate of formation of Mn(III) ions, v_{\max} , increases with the bromate concentration (is proportional to the square root of the initial bromate concentration (Fig. 3).

Mn(II) Ions

The induction period is independent of the concentration of Mn(II) ions in the range $0.5-6 \text{ mmol l}^{-1}$; the induction period was 197 s. The reaction rate v_{\max} is directly proportional to the concentration of Mn(II) ions (Fig. 4).

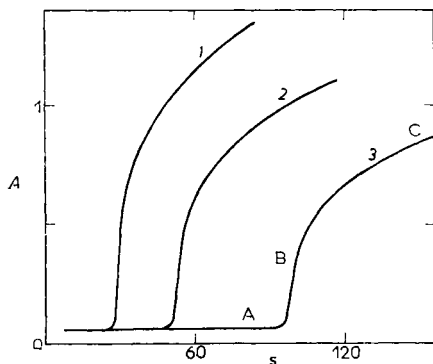


FIG. 1

Time dependence of absorbance of Mn(III) during oxidation of Mn(II) with bromate. Solution containing 0.01M-BrO_3^- , 10^{-3}M-Mn(II) , $3.9 \cdot 10^{-4}\text{M-Br}_2$ and $1.2.4\text{M-H}_2\text{SO}_4$, $2.2.1\text{M-H}_2\text{SO}_4$, $3.1.8\text{M-H}_2\text{SO}_4$. A induction period, B rapid reaction period, C slow reaction period

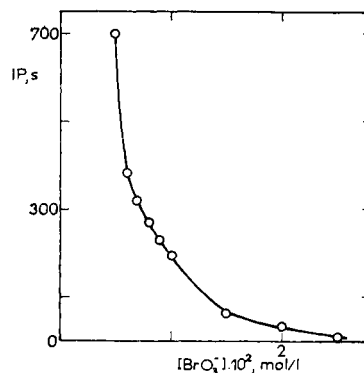


FIG. 2

Dependence of IP on concentration of BrO_3^- in a solution containing $1.5\text{M-H}_2\text{SO}_4$, $8 \cdot 10^{-4}\text{M-Mn(II)}$, and $3.9 \cdot 10^{-4}\text{M-Br}_2$

Hydrogen Ions

The induction period decreases with increasing concentration of H_3O^+ ions (Fig. 5); the slope of the dependence in log-log coordinates is equal to -4 . The dependence of $\log v_{\max}$ on $\log [\text{H}_3\text{O}^+]$ is also linear and its slope is 3.15 (Fig. 6).

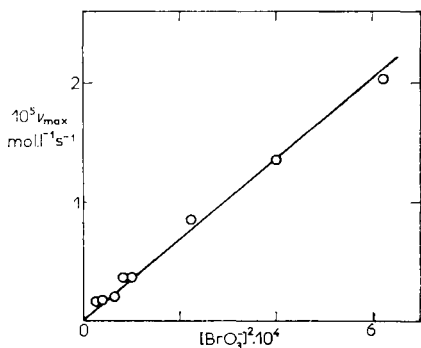


FIG. 3

Dependence of v_{\max} on concentration of BrO_3^- . Concentration of reactants as in Fig. 2

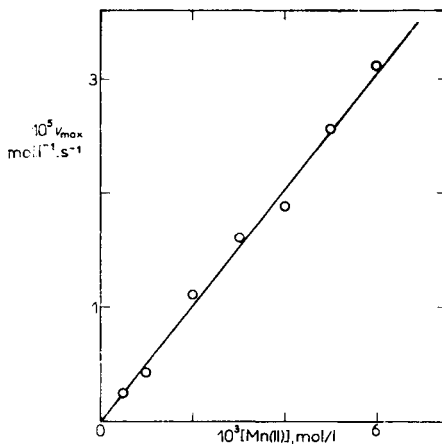


FIG. 4

Dependence of v_{\max} on concentration of Mn(II) in a solution containing 1.5M - H_2SO_4 , 0.01M - BrO_3^- , and $3.6 \cdot 10^{-4}\text{M}$ - Br_2

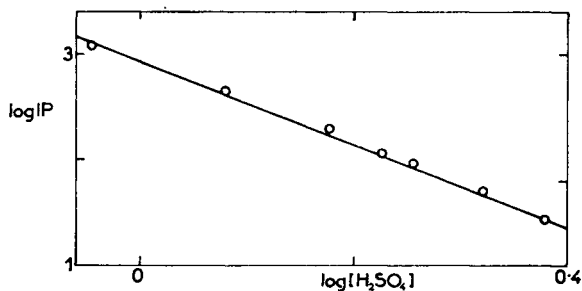


FIG. 5

Dependence of IP on concentration of H_3O^+ in a solution of 0.01M - BrO_3^- , 10^{-3}M -Mn(II), and $3.9 \cdot 10^{-4}\text{M}$ - Br_2

Mn(III) Ions

Addition of Mn(III) ions has no influence on the length of the induction period, however the concentration of Mn(III) did not exceed 0.5 mmol l^{-1} . The rate of formation of Mn(III), *i.e.* the rate of oxidation of Mn(II) is decreased by the addition

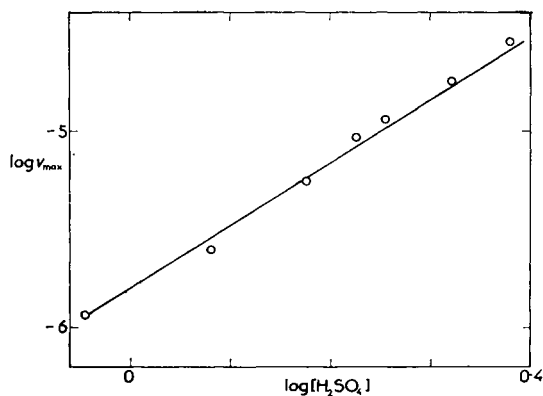


FIG. 6
Dependence of $\log v_{\max}$ on $\log [\text{H}_3\text{O}^+]$; concentration of reactants as in Fig. 5

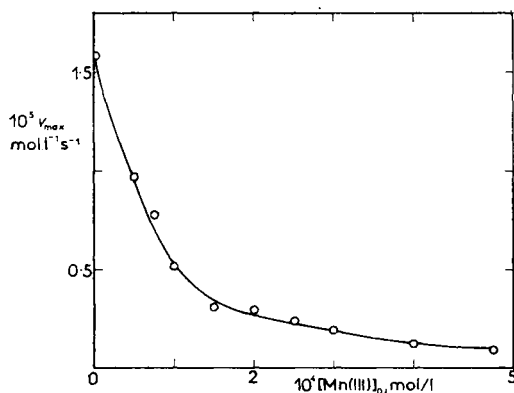


FIG. 7
Dependence of v_{\max} on initial concentration of Mn(III) in a solution of 0.01 M-BrO_3^- , $3 \cdot 10^{-3} \text{ M-Mn(II)}$, $1.5 \text{ M-H}_2\text{SO}_4$, and $4 \cdot 10^{-4} \text{ M-Br}_2$

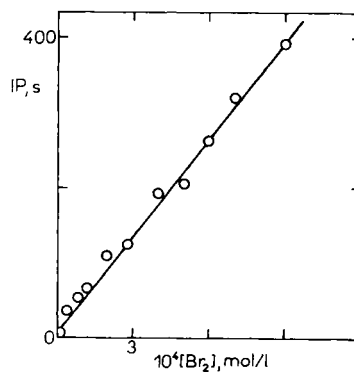


FIG. 8
Dependence of IP on concentration of Br_2 in a solution of 0.01 M-BrO_3^- , 10^{-3} M-Mn(II) , and $1.5 \text{ M-H}_2\text{SO}_4$

of Mn(III) (Fig. 7): the dependence of $\log v_{\max}$ on $\log [\text{Mn(III)}]_0$ is a straight line with a slope equal to -1 .

Bromine

The induction period increases with the concentration of bromine added in the range $0.04 - 0.9 \text{ mmol l}^{-1}$ (Fig. 8) and the value of v_{\max} decreases slightly.

Bromide Ions

If $0.666 \text{ mmol l}^{-1}$ bromide ions are added to a solution containing 10^{-3} M-Mn(II) , 0.01 M-BrO_3^- and $1.5 \text{ M-H}_2\text{SO}_4$, they react rapidly with bromate ions to give 0.4 mmol l^{-1} bromine, whereby the concentration of bromate decreases by 1.3% . The induction period was measured as 210 s and $v_{\max} = 4.14 \cdot 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$. In another experiment, where only one half of the quantity of bromide was employed, the induction period was only 114 s and $v_{\max} = 4.58 \cdot 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$. The same values of IP and v_{\max} were measured when bromine in a resulting concentration 0.4 or 0.2 mmol l^{-1} was added into the solution (Fig. 8). Changes of the measured quantities due to the slight decrease of the concentration of bromate by reaction with bromide are negligible. Hence, the influence of the concentration of Br^- ions is equivalent to that of bromine added.

Oxalic Acid

A nonbrominatable substrate, *e.g.* oxalic acid, inhibits the oxidation of Mn(II) by bromate in the oscillation reaction under study. For example, a solution containing 10^{-3} M-Mn(II) , 0.01 M-BrO_3^- and $2 \cdot 10^{-4} \text{ M-Br}_2$ was made 25 mmol l^{-1} with respect to oxalic acid. No Mn(III) ions were formed even after 10 min , while the concentration of bromine increased moderately. The induction period was only 90 s in the absence of oxalic acid.

TABLE I

Dependence of the yield $\eta = [\text{Mn(III)}]/[\text{Mn(II)}]_0$ on the concentration of H_2SO_4 (mol l^{-1}) and Mn(II) (mmol l^{-1}) in a solution containing 0.01 M-BrO_3^- and $3.9 \cdot 10^{-4} \text{ M-Br}_2$ (for the first dependence) or $3.6 \cdot 10^{-4} \text{ M-Br}_2$ (for the second)

H_2SO_4	0.9	1.2	1.5	1.68	1.8	2.1	2.4	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Mn(II)	1	1	1	1	1	1	1	0.5	1	2	3	4	5	6
Yield	0.048	0.059	0.084	0.10	0.11	0.14	0.17	0.077	0.077	0.0625	0.062	0.059	0.053	0.049

We determined also the concentration of Mn(III) 24 s after the inflexion point on the curve $A = f(t)$ had been reached at various concentrations of hydrogen ions and Mn(II). The yield η was defined as the ratio of the actual concentration of Mn(III) to the initial concentration of Mn(II), $\eta = [\text{Mn(III)}]/[\text{Mn(II)}]_0$, (Table I). The oxidation of Mn(II) was not quantitative even after a long time: the value of $\eta = 0.48$ was attained after 6 days in a solution of $1.5\text{M-H}_2\text{SO}_4$, 0.01M-BrO_3^- , 10^{-3}M-Mn(II) , and $4.2 \cdot 10^{-4}\text{M-Br}_2$. Afterwards, the concentration of Mn(III) slowly decreased and a precipitate appeared, probably manganese dioxide. The yield $\eta = 0.64$ was attained in a solution containing $2.1\text{M-H}_2\text{SO}_4$, 0.01M-BrO_3^- , 10^{-3}M-Mn(II) , and $4.2 \cdot 10^{-4}\text{M-Br}_2$ after 6 as well as 14 days.

DISCUSSION

In the oxidation of Mn(II) with bromate ions in dilute sulphuric acid in a closed system in the presence of bromine, bromide ions are initially formed by hydrolysis. These are consumed in the process^{2,4,10} consisting of steps (A)–(C) and no increase of the Mn(III) concentration is observed (IP in Fig. 1). As soon as the bromide concentration drops below a certain critical level, the rate of step (B) decreases and another process, composed of steps (D)–(G), comes into play. Step (D) gives rise to the formation of BrO_2^\cdot radicals which oxidize Mn(II) ions to Mn(III). At the same time, HBrO_2 is formed autocatalytically and its concentration rises exponentially. Accordingly, the concentration of Mn(III) increases causing a rapid growth of absorbance (Fig. 1). Bromide ions are further exhausted according to step (B). Step (G) controls the increase of the concentration of HBrO_2 ; Mn(III) formed in the reaction can be reduced with BrO_2^\cdot and HBrO_2 causing inhibition of the oxidation of Mn(II) with increasing concentration of Mn(III) (Fig. 1, part C). Simulation calculations based on the Noyes–Field–Thompson mechanism for oxidation of Ce(III) ions with bromate explain satisfactorily most of the experimental data⁴. The form of the dependences of IP and v_{max} on the concentration of reactants for the oxidation of Mn(II) with bromate is in most cases in agreement with the results of Barking and coworkers⁴, only the dependence of v_{max} on the concentration of bromate is different. The dependence found by us is in agreement with the work of Yoshida⁵, who discussed his results in terms of the elementary steps (D), (E), and (G) of the mechanism mentioned. He found that the slope of the kinetic curve at the inflexion point is directly proportional to $[\text{BrO}_3^-]^2$. Oxidation of Mn(II) with bromate is more sensitive toward pH changes than that of Ce(III), as can be seen from the dependence of both IP and v_{max} on the concentration of hydrogen ions. The experimental value of the slope of the first dependence is -4 compared with -2.33 for cerium⁴, and of the second 3.15 compared with 2.2 for cerium according to Barkin⁴ or 1 according to Vavilin and Zhabotinskii⁶. The induction period of the reaction increases with the concentration of Br_2 or Br^- ions added (Fig. 8). This is due

to the fact that reaction (B) generates a significant amount of HOBr resulting in a decrease of the concentration of HBrO_2 , from which BrO_2^\bullet radicals are formed, which in turn are responsible for the oxidation of Mn(II). The Noyes–Field–Thompson mechanism is also supported by simulation calculations of bistability (existence of two stable stationary states for the same parameter values) in a flow-through reactor, which are in accord with experiments^{10,11}. However, the deviations between the measured and calculated regions of multiplicity and oscillations are somewhat higher in the case of oxidation of Mn(II) with bromate¹⁰ than in the case of cerium¹¹. Geiseler¹⁰ attributed the difference to steps (E) and (F); especially the ratio of k_E/k_{-E} is important since it is influenced by the difference between the reduction potentials of Mn(III) and Ce(IV). Of the manganese ions, which could change the concentration of the ions mentioned, only Mn^{2+} and Mn^{3+} were taken into account in the calculations.

The study of the oxidation of Mn(II) ions with bromate revealed a qualitative accord between the dependences of IP and v_{\max} on the concentration of reactants, Mn(III), Br_2 , and Br^- on one hand and those for the oxidation of Ce(III) with bromate on the other. A more pronounced dependence on the concentration of BrO_3^- and H_2SO_4 may be related to different hydrolytic and complexation equilibria of the Mn(III) and Ce(IV) ions. Disproportionation of Mn(III) results in incomplete oxidation of Mn(II) with bromate even after a long time.

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Translated by K. Micka.