Influence of oxygen on the Belousov—Zhabotinskii oscillating reaction
III. Release of bromides, kinetics of malonic acid oxidation by manganese(III), and simulating calculations

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Bromide ions are released by the effect of oxygen more rapidly in the reaction of the Mn^{3+} ions with a mixture of malonic acid (MA) and bromomalonic acid (BrMA) of low summary concentration, but the overall released quantity is smaller. At a high summary concentration of MA and BrMA the quantity of released Br^- ions in the presence of oxygen is substantially greater. To follow the concentration of the Br^- ions during oscillations the polarographic method with Pt-electrode may be used. Oxygen enhances the rate of Mn^{3+} consumption in the reaction with MA of a low concentration, but reduces it at a high concentration of MA. In addition, the oxygen consumption increases with MA concentration. A new mechanism has been proposed for the influence of oxygen on the oxidation of MA by Mn^{3+} Its essence is an acceleration of Mn^{3+} consumption by the reaction with glyoxylic acid at low MA concentration and regeneration of Mn^{3+} by oxidation of Mn^{2+} with hydroperoxide (MAOOH) at high MA concentration.

При реакции ионов Mn^{3+} со смесью малоновой (МА) и броммалоновой (BrMA) кислот с низкой суммарной концентрацией под действием кислорода выделяются бромид-ионы быстрее, однако их общее выделенное количество меньше. При высокой суммарной концентрации [МА] + [BrMA] количество выделенных Br^- ионов в присутствии O_2 значительно больше. Для наблюдения концентрационных изменений бромид-ионов за время осцилляций можно использовать полярографию с платиновым электродом. Кислород повышает скорость потребления Mn^{3+} при реакции

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с МА с низкой концентрацией, но при высокой концентрации МА снижает ее. Потребление O₂ повышается при росте концентрации МА. Предложен новый механизм воздействия O₂ на окисление МА ионами Mn³⁺ Сущностью его является ускорение потребления ионов Mn³⁺ реакцией с глиоксалевой кислотой при низкой концентрации МА и регенерация Mn²⁺ в результате окисления Mn²⁺ гидроперекисью МАOOH при высокой концентрации МА.

This paper is a continuation of preceding Parts I and II which deal with the influence of gas flow, temperature, and stirring on the parameters of oscillating reaction [1], with the liberation of CO_2 and Br_2, and concentration oscillations of dissolved O_2 [2]. It is concerned with investigation of Br^- concentration in the course of oscillating reaction and release of the Br^- ions in oxidation of the mixture of malonic acid (MA) and bromomalonic acid (BrMA) by Mn^{3+} ions. The kinetics and mechanism of this reaction are significantly affected by the presence of oxygen [3, 4]. The simulating calculations concerning the influence of oxygen on the parameters of oscillating reaction [5] do not correspond to all experimental observations. The most expressive disproportion appears in explanation of the oxygen influence on the period of oscillations. The mechanism proposed by *Barkin et al.* [3] does not account for the kinetics of the reaction of MA with Mn^{3+} at a high MA concentration in the solution saturated with oxygen. On the basis of calculation of the relative rates of radical interactions and oxygen consumption, we have proposed a new (modified) mechanism of this reaction.

Experimental

Reaction conditions and chemicals

The oscillating reactions were investigated at the same conditions (16 °C, stirring frequency 350 min⁻¹) and with the same concentrations of reactants as described in Part I (0.47 M-MA, 2×10^{-3} M-MnSO₄, 6×10^{-2} M-KBrO₃, 1.5 M-H₂SO₄).

The stock solution of the Mn^{3+} ions was prepared by mixing KMnO₄ with stoichiometric excess of MnSO₄ in 4.5 M-H₂SO₄ so that the concentration of produced Mn^{3+} did not exceed the value of 3×10^{-3} mol dm⁻³. Before measurements, the solution was diluted three-times with redistilled water.

The mixture of MA with 10 mole % of BrMA was prepared by the reaction of MA with Br_2 which was formed directly in 1.5 M-H₂SO₄ by the reaction of bromate with Br^- The ratio of initial concentrations was $[BrO_3^-]:[Br^-] = 1:2$. By mixing the formed solution with the solution of MA in H₂SO₄, the solutions of MA with required concentration of BrMA (0.5—10 mole %) were prepared.

Methods

The concentration of Br⁻ ions was followed potentiometrically by means of Br⁻ selective electrode and polarographically by means of a static Pt-electrode with moving solution. In polarographic measurements, the anodic current of Br⁻ was recorded at the potential of $+0.72$ V against a 1.5 M-mercurosulfate reference electrode. The concentration of Br⁻ was determined by means of calibration curves.

The kinetics of MA oxidation by the Mn^{3+} ions was investigated polarographically by means of a static Pt-electrode at the potential of $+0.2$ V against the 1.5 M-mercurosulfate reference electrode. The concentration of dissolved oxygen was measured with a Clark probe equipped with a teflon membrane. The electrochemical measurements were carried out with a polarograph Radelkis OH-102.

Results

Concentration changes of the Br⁻ ions during oscillations

In respect to certain critical comments [6] on quantitative determination of the Br⁻ concentration in oscillation system by means of a Br⁻ selective electrode, the concentration of Br⁻ was followed by two independent methods. The effect of oxygen on concentration changes of Br⁻ in the course of oscillating reaction measured polarographically and by Br⁻ selective electrode is represented in Figs. 1 and 2. The results obtained by these methods are semiquantitatively consistent.

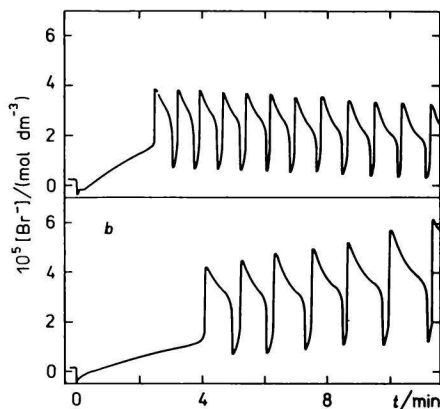Fig. 1. Concentration changes of the Br⁻ ions during oscillating reaction measured polarographically.
Flow of gas 500 cm³ min⁻¹; F-bubbling; a) N₂; b) O₂.

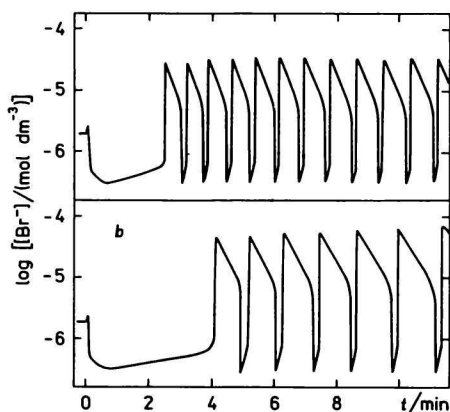Fig. 2. Concentration changes of the Br⁻ ions during oscillating reaction measured by means of a Br⁻-selective electrode.
Flow of gas 500 cm³ min⁻¹; F-bubbling; a) N₂; b) O₂.

In the course of induction period the rate of Br$^-$ release in the presence of oxygen is slowed down (at F-bubbling almost two-times). Lower critical concentrations of bromides [Br$^-$]$_{crit, L}$ (passing of which stops the autocatalytic oxidation of Mn^{2+} by bromate) in O$_2$ and N$_2$ are comparable. However, both methods gave different absolute values: [Br$^-$] = (1—2) × 10^{-5} mol dm^{-3} by polarography and [Br$^-$] = (6—8) × 10^{-7} mol dm^{-3} by Br$^-$ selective electrode. The upper critical concentration of bromides [Br$^-$]$_{crit, U}$ (the decrease under this value starts the autocatalytic oxidation of Mn^{2+}) is in O$_2$ higher than in N$_2$ and decreases with increasing gas flow. The selective electrode gives the values [Br$^-$] = (0.7—1.5) × 10^{-5} mol dm^{-3} while the values given by polarography are approximately two-times greater. The value of [Br$^-$]$_{crit, U}$ always decreases during the reaction.

The maximum concentration of bromides in the course of oscillations is greater in O$_2$ than in N$_2$ (in the first oscillation by 50 % — measured by selective electrode and by 30 % — measured polarographically). As for bubbling with N$_2$, the maximum concentration of Br$^-$ almost does not change or merely slightly decreases. On the other hand, in the presence of oxygen the maximum concentration of Br$^-$ increases during oscillations, it means that the amplitude of the Br$^-$ concentration oscillations enhances. If the concentration of Br$^-$ exceeds a certain critical value, the oscillations vanish and a stationary state is established. The stationary concentration of bromides [Br$^-$]$_s$ is always much greater in O$_2$ than in N$_2$. According to gas flow, it is (2—4) × 10^{-5} mol dm^{-3} in O$_2$ and less than 1 × × 10^{-5} mol dm^{-3} in N$_2$.

The rate of concentration decrease of Br$^-$ during oscillations (from [Br$^-$]$_{max}$ to [Br$^-$]$_{crit, U}$) is greater in N$_2$ than in O$_2$. At flows exceeding 100 cm^3 min^{-1} and F-bubbling, the rate constant of concentration decrease of Br$^-$ in oxygen is by 40 % lower (the slope of semilogarithmic record by selective electrode). Its value for the first oscillation in nitrogen is 2.3 × 10^{-2} s^{-1} and in oxygen it decreases to 1.5 × 10^{-2} s^{-1}.

Kinetics of MA oxidation by the Mn^{3+} ions

The influence of oxygen on the kinetics of MA oxidation by the Ce^{4+} and Mn^{3+} ions was studied earlier [3, 4, 7]. However, it has been revealed that the known kinetic data cannot be extrapolated to higher MA concentrations (0.5 mol dm^{-3}) at which the oscillation system was studied. The reaction was investigated at 16 °C in 1.5 M-H$_2$SO$_4$ in the presence of an excess of the Mn^{2+} ions (c = 1.5 × 10^{-3} mol dm^{-3}). The initial concentrations of reactants were as follows: [Mn^{3+}] = 5 × 10^{-4} mol dm^{-3} and [MA] = (1 × 10^{-2}—5 × 10^{-1}) mol dm^{-3}. Before reaction, the reactants were bubbled through with nitrogen for 20 min or they were

saturated with oxygen. Though MA was present in a stoichiometric excess, the decrease in Mn^{3+} concentration did not exactly obey the first-order kinetics. The rate constant of the reaction in N_2 had the tendency to decrease a little and contrary it increased in O_2. Fig. 3 shows the dependence of the experimental pseudofirst-order rate constant on initial MA concentration. For evaluating the experimental rate constants, the average values of rate constants determined in the first three half-lives of the reaction were used. The dependence of $1/k_{exp}$ vs. $1/[MA]$ for the reaction under nitrogen atmosphere is linear [8], which indicates the formation of an intermediary complex [MA—Mn(III)]. Under given experimental conditions, the value of the maximum rate constant is $k_{max} = 0.165$ s^{-1} and that of the Michaelis constant is $K = 0.11$ mol dm^{-3}. Provided the concentration of MA is less than 10^{-2} mol dm^{-3}, the rate constant of the reaction is about two-times higher in O_2 than in N_2. The ratio of the rate constants in O_2 and N_2 decreases with increasing concentration of MA. For an initial MA concentration exceeding 0.2 mol dm^{-3}, the rate constant of Mn^{3+} concentration decrease is greater in N_2 than in O_2.
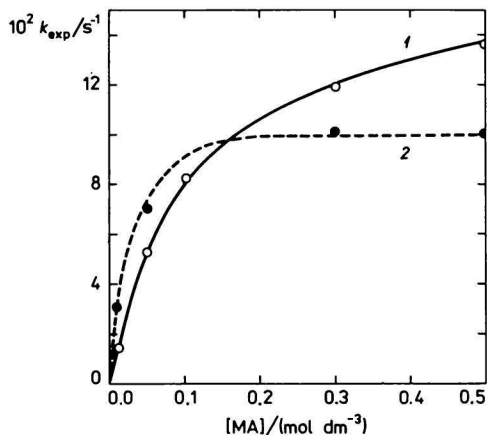

Fig. 3. Variation of the experimental rate constant with initial concentration of MA for the reaction of MA with Mn^{3+} ions under N_2 (1) or O_2 (2).

The oxygen consumption in this reaction was also measured under equal experimental conditions. As the reaction is too rapid at higher MA concentrations with respect to the response of the Clark probe, we measured only the difference of concentrations between the initial state (solution saturated with oxygen) and the final value. The dependence of oxygen consumption on MA concentration is represented in Fig. 4. It is possible to determine from this dependence, that the amount of oxidized substrate was seven-times increased by the effect of oxygen at the concentration of MA 0.5 mol dm^{-3} (since oxygen is a four-equivalent oxidant).

Kinetics of Br⁻ release in oxidation of MA—BrMA mixture by Mn³⁺ ions

Kinetics of Br^- release in oxidation of MA—BrMA mixture by Mn^{3+} ions

The kinetics of Br^- release was investigated polarographically in 1.5 M-H_2SO_4 in excess of Mn^{2+} ($c = 1.5 \times 10^{-3}$ mol dm^{-3}) at 16 °C. The initial concentration of Mn^{3+} was equal to 5×10^{-4} mol dm^{-3}. The summary concentration [MA] + [BrMA] and percentage of BrMA in MA have been changed. In order to make the calibration more precise, a standard quantity of Br^- was added into the reaction mixture immediately after the end of reaction.

At a low summary concentration ([MA] + [BrMA]) = 1×10^{-2} mol dm^{-3} with 2 mole % of BrMA, the release of Br^- ions in oxygen is more rapid, but the total released quantity is approximately by 20 % smaller (Fig. 5) which was confirmed by means of a Br^- selective electrode as well. The rate constants for concentration decrease of Mn^{3+} and concentration increase of Br^- in O_2 are consistent, but the rate constant of Br^- release in N_2 is about two-times smaller. The release of Br^- under N_2 is governed by other kinetics than Mn^{3+} consumption. The average value of the stoichiometric coefficient defined as the ratio of Br^- concentration after reaction to the initial Mn^{3+} concentration is about 0.03 in O_2 and 0.04 in N_2.
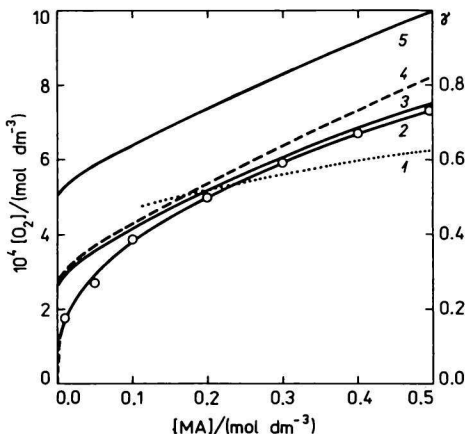

Fig. 4. Dependence of oxygen consumption on initial concentration of MA for the reaction of MA with the Mn^{3+} ions.
$[Mn^{3+}]_0 = 5 \times 10^{-4}$ mol dm^{-3}. *1.* Approximation with termination of MA· radicals; *2.* experimental curve; *3.* calculated curve; *4.* approximation with termination of MAOO· radicals; *5.* calculated dependence of γ (see the text) on MA concentration for $[Mn^{3+}] = 5 \times 10^{-4}$ mol dm^{-3}.

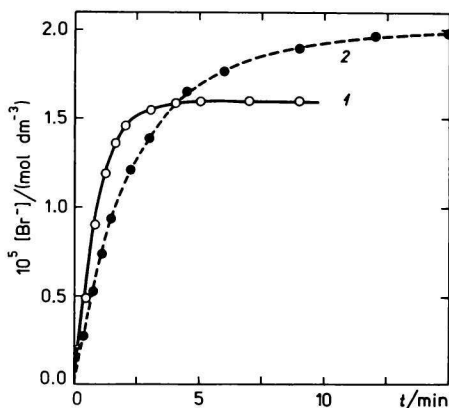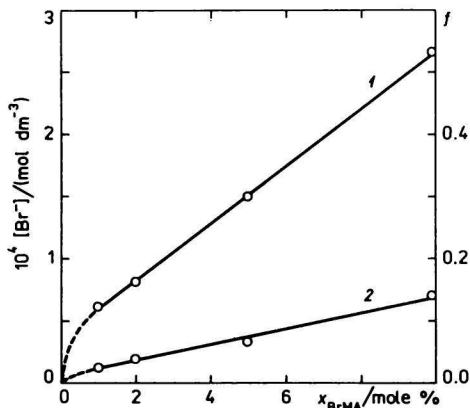*Fig. 5.* Kinetics of the Br^- release in oxidation of the MA—BrMA mixture by Mn^{3+} ions.
$([MA] + [BrMA])_0 = 1 \times 10^{-2}$ mol dm^{-3}; 2 mole % of BrMA; $[Mn^{3+}]_0 = 5 \times 10^{-4}$ mol dm^{-3}; *1.* in O_2; *2.* in N_2.

Fig. 6. Total amount of the released Br^- ions as a function of the degree of bromination of MA.
$([MA] + [BrMA])_0 = 0.5$ mol dm^{-3}; $[Mn^{3+}]_0 = 5 \times 10^{-4}$ mol dm^{-3}; stoichiometric coefficient $f = [Br^-]_\infty/[Mn^{3+}]_0$; *1.* in O_2; *2.* in N_2.

At a high summary concentration $([MA] + [BrMA]) = 0.5$ mol dm^{-3} the amount of released bromides increases with percentage of BrMA (Fig. 6) and is always greater in O_2 than in N_2 (Fig. 7). The dependence of logarithm of numerical value of Br^- concentration on time is not fully linear, but exhibits a break-point. After this break-point the rate constant decreases in N_2 and increases in O_2. The average rate constants for Mn^{3+} concentration decrease and Br^- release in O_2 are consistent, but the rate constant of Br^- formation in N_2 is approximately by one half smaller than that of Mn^{3+} decay. The consumption of O_2 is greater than in the reaction of the Mn^{3+} ions with sole MA.
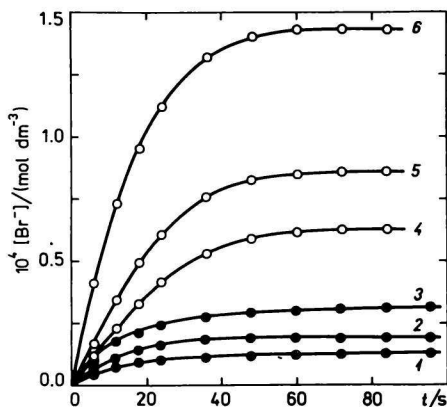
Fig. 7. Kinetics of the Br^- release in oxidation of the MA—BrMA mixture by the Mn^{3+} ions. $([MA] + [BrMA])_0 = 0.5$ mol dm^{-3}; $[Mn^{3+}]_0 = 5 \times 10^{-4}$ mol dm^{-3}; 1 mole % of BrMA *1.* in N_2, *4.* in O_2; 2 mole % of BrMA *2.* in N_2, *5.* in O_2; 5 mole % of BrMA *3.* in N_2, *6.* in O_2.

Fig. 8. Relative rates of radical interactions referred to the rate of the initiation reaction as a function of MA concentration. $[Mn^{3+}] = 5 \times 10^{-4}$ mol dm^{-3}; *1.* v_B; *2.* v_E; *3.* v_D; *4.* $0.5\ v_E + v_F$; *5.* v_C; *6.* v_F.

Analysis of mechanism of the reaction $MA + Mn^{3+} + O_2$

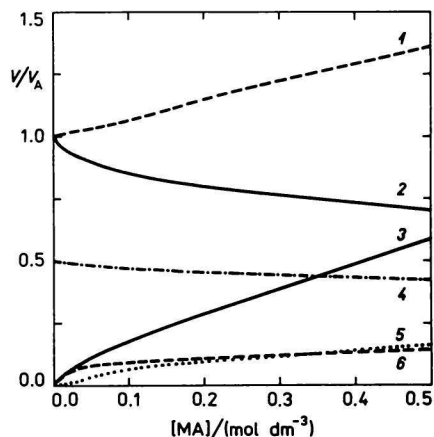On the basis of the mechanism proposed for the oxidation of MA by Ce^{4+} ions in the presence of oxygen [3], we cannot explain the retardation of Mn^{3+} decay by oxygen at high concentrations of MA and the increase in oxygen consumption with increasing concentration of MA. Therefore we searched for a model which could explain these experimental data.

On the basis of the calculations of the relative rates of radical interactions, relative rates of formation of reactive intermediates, oxygen consumption, and measured experimental results, we propose the mechanism of MA oxidation by Mn^{3+} ions in the presence of oxygen which is outlined in Scheme 1.
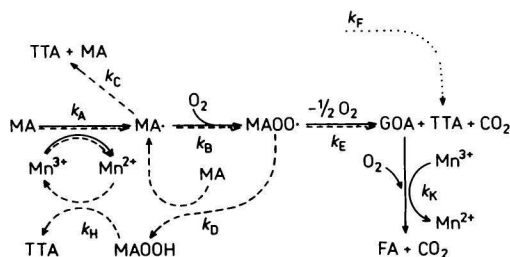
Scheme 1

The initiation reaction involves formation of the malonyl radical $\cdot CH(CO-OH)_2(MA\cdot)$ and is governed by the Michaelis—Menten kinetics

$$MA + Mn^{3+} \;\rightleftharpoons\; [MA-Mn(III)] \xrightarrow{k_{max}} MA\cdot + Mn^{2+} + H^+ \qquad (A)$$
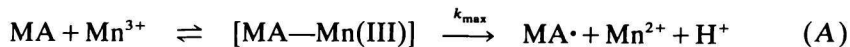
Malonyl radicals react with oxygen (reaction B) and at a higher concentration disproportionate

$$MA\cdot + O_2 \xrightarrow{k_B} MAOO\cdot \qquad (B)$$

$$2MA\cdot + H_2O \xrightarrow{k_C} TTA + MA \qquad (C)$$

where TTA denotes tartronic acid $HOCH(COOH)_2$. Peroxy radicals of malonic acid ($MAOO\cdot$) react with MA or disproportionate with simultaneous liberation of oxygen and carbon dioxide according to equations (D) and (E)

$$MAOO\cdot + MA \xrightarrow{k_D} MAOOH + MA\cdot \qquad (D)$$

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$$2MAOO\cdot \xrightarrow{k_E} GOA + TTA + O_2 + CO_2 \qquad (E)$$

where GOA denotes glyoxylic acid. The termination of radical chains is also promoted by interaction between the $MA\cdot$ and $MAOO\cdot$ radicals in which, however, no oxygen is liberated

$$MA\cdot + MAOO\cdot \xrightarrow{k_F} GOA + TTA + CO_2 \qquad (F)$$
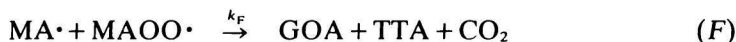
The hydroperoxide of malonic acid (MAOOH) oxidizes Mn^{2+} and glyoxylic acid reduces the Mn^{3+} ions producing formic acid (FA) and CO_2. Because of the high reactivity, the concentrations of radicals $MA\cdot$ and $MAOO\cdot$ are maintained on a pseudostationary level $(d[MA\cdot]/dt = d[MAOO\cdot]/dt = 0)$ and thus it holds true for the reaction rates

$$v_A + v_D = v_B + v_C + v_F \qquad (1)$$

$$v_B = v_D + v_E + v_F \qquad (2)$$

By expressing the rates and solving the relations we obtain

$$[MA\cdot] = \frac{k_D[MA][MAOO\cdot] + 2k_E[MAOO\cdot]^2}{k_B[O_2] - k_F[MAOO\cdot]} \qquad (3)$$

$$[MA\cdot] = \frac{[(2k_F[MAOO\cdot])^2 + 8k_C(v_A - 2k_E[MAOO\cdot]^2)]^{1/2} - 2k_F[MAOO\cdot]}{2k_C} \qquad (4)$$

which lead to an equation of the fourth order. Therefore we solved the problem by the iteration method starting from approximate solutions with one termination step. We used the calculated concentrations of the radicals $MA\cdot$ and $MAOO\cdot$ for determination of relative reaction rates referred to the initiation reaction rate. The average number of oxygen molecules which are consumed in the system for one reduced Mn^{3+} ion is given by the equation

$$\gamma = \left(v_B - \frac{1}{2}v_E\right)\bigg/ v_A \qquad (5)$$

It is valid for this model that the termination of the $MAOO\cdot$ radicals prevails at a low concentration of MA, while the termination of the $MA\cdot$ radicals predominates at a high concentration of MA. The concentration of MA at which the $MA\cdot$ termination overreaches the $MAOO\cdot$ termination is independent of the initiation reaction rate

$$[MA]_c = k_B[O_2](k_E/k_C)^{1/2}/k_D \qquad (6)$$

At low concentration of MA (only MAOO· termination), the average number of oxygen molecules consumed for one ion of Mn^{3+} is independent of oxygen concentration

$$\gamma_L = \frac{1}{2} + k_D[MA](2k_E v_A)^{-1/2} \tag{7}$$

At high concentration of MA (only MA· termination) it is valid

$$\gamma_H = k_B[O_2](2k_C v_A)^{-1/2} \tag{8}$$

The oxygen consumption for the decrease of Mn^{3+} concentration from the initial value $[Mn^{3+}]_0$ to zero may be calculated from the values of γ. It is valid for a low concentration of MA

$$d[O_2] = -\gamma \, d[Mn^{3+}] \tag{9}$$

$$\Delta[O_2] = -\int_{[Mn^{3+}]_0}^{0} \left[\frac{1}{2} + k_D[MA](2k_E k_A[Mn^{3+}])^{-1/2}\right] d[Mn^{3+}]$$

$$\Delta[O_2] = \frac{1}{2}[Mn^{3+}]_0 + \frac{2k_D[MA]}{(2k_E k_A)^{1/2}}[Mn^{3+}]_0^{1/2} = \left(2\gamma_0 - \frac{1}{2}\right)[Mn^{3+}]_0 \tag{10}$$

where k_A is the pseudofirst-order rate constant $k_A = k_{max}[MA]/([MA]+K)$ and γ_0 is the average number of oxygen molecules consumed for one ion Mn^{3+} at the concentration $[Mn^{3+}]_0$. The limit of eqn (10) for [MA] approaching zero is

$$\lim_{[MA]\to 0} \Delta[O_2] = \frac{1}{2}[Mn^{3+}]_0 \tag{11}$$

At high concentration of MA, the oxygen consumption is dependent on its concentration

$$\int_{[O_2]_0}^{[O_2]} \frac{d[O_2]}{[O_2]} = \int_{[Mn^{3+}]_0}^{0} \left[k_B(2k_C k_A[Mn^{3+}])^{-1/2}\right] d[Mn^{3+}]$$

$$\ln\frac{[O_2]}{[O_2]_0} = -2k_B[[Mn^{3+}]_0/(2k_C k_A)]^{1/2} = 2\gamma_0[Mn^{3+}]_0/[O_2]_0$$

$$\Delta[O_2] = [O_2]_0[1 - \exp(-2\gamma_0[Mn^{3+}]_0/[O_2]_0)] \tag{12}$$

Provided $\gamma_0[Mn^{3+}]_0 \ll [O_2]_0$, the function (12) may be expanded in a series. Neglecting higher terms we obtain

$$\Delta[O_2] = 2\gamma_0[Mn^{3+}]_0 \tag{13}$$

If γ increases, the $\Delta[O_2]$ approximates to $[O_2]_0$. It means that the total amount of oxygen dissolved in the solution is consumed during the reaction.

The values of the rate constants taken from the paper by *Barkin et al.* [3] lead to too high values of γ (for $[MA] > 0.1$ mol dm^{-3} $\gamma > 7$). For this reason, we fitted the constants k_C and k_D for a better agreement of the calculated oxygen consumption with experimental results (Fig. 4). Fig. 8 represents dependences of the relative rates of reactions $(A—F)$ on MA concentration at Mn^{3+} concentration 5×10^{-4} mol dm^{-3} calculated by the use of the following constants: $k_{max} = 0.165$ s^{-1}, $K = 0.11$ mol dm^{-3}, $k_B = 4 \times 10^5$ mol^{-1} dm^3 s^{-1}, $k_C = 1 \times 10^8$ mol^{-1} dm^3 s^{-1}, $k_D = 4 \times 10^2$ mol^{-1} dm^3 s^{-1}, $k_E = 6 \times 10^8$ mol^{-1} dm^3 s^{-1}, $k_F = 1 \times 10^8$ mol^{-1} dm^3 s^{-1}. The constant k_F was estimated, its value has only small effect on the character of this dependence. It reduces a little the concentration of radicals at medium concentration of MA. The relative rates of the propagation reactions (v_B and v_D) increase with MA concentration. Consequently the relative rate of formation of hydroperoxide MAOOH as well as the average number of oxygen molecules consumed for one reduced Mn^{3+} ion (γ, Fig. 4) also increases. The relative rate of GOA formation (Fig. 8, curve *4*) slows down with decreasing participation of MAOO· recombination in termination of radical chains.

At a low or high concentration of MA, γ is proportional to $[Mn^{3+}]^{-1/2}$. We have verified numerically that the linearity is also preserved in the region of medium MA concentrations. At lower MA concentrations, the termination of MAOO· radicals prevails and so the oxygen consumption can be approximated by the following equation

$$\Delta[O_2] = (2\gamma_0 - v_E/2v_A)[Mn^{3+}]_0 \qquad (14)$$

The dependence of oxygen consumption on its concentration increases with the participation of MA· recombination in termination of radical chains. Provided the recombination of MA· radicals is the only termination reaction, eqn (*12*) is valid. For a given rate constant the exact value of oxygen consumption was determined on the basis of eqn (*9*) by numerical integration. The linear dependence on $[Mn^{3+}]^{-1/2}$ was used for extrapolation of the values of γ. The calculated dependence of oxygen consumption on MA concentration is in good agreement with experimental plot. It is bounded from above by function (*14*) and from below at higher MA concentrations by function (*12*), (Fig. 4).

At a certain MA concentration, the rate of propagation reactions increases with decreasing Mn^{3+} concentration and thus γ increases, too. The portions of the MA· and MAOO· termination reactions almost do not change at lower MA concentrations, which is consistent with eqn (*6*). At high MA concentration the participation of MA· radicals in termination increases owing to concentration decrease of oxygen.

Discussion

Concentration oscillations of bromides

The measurements of concentration of the Br^- ions during oscillations by means of selective electrode and polarographic method are in relatively good agreement. The greatest discrepancy appears in determination of the lower critical concentration $[Br^-]_{crit, L}$. We assume in accord with [6] that HOBr influences the potential of selective electrode at a low concentration of bromides and thus apparently decreases the measured value of Br^- concentration. The polarographic measurements are rather sensitive to the choice of a convenient potential. The residual currents of Br_2, Mn^{3+}, and Mn^{2+} are minimal at the used potential of $+0.72$ V, but we do not rule out their presence completely. They may be responsible for small differences at a higher Br^- concentration when compared with the determinations performed by means of a selective electrode. It results that polarography with a Pt-electrode is under certain conditions a convenient method for investigating the concentration variation of Br^- during oscillating reaction.

During the oscillation regime, the rate of concentration decrease of the Br^- ions from the maximum value to the critical one is dependent on the rate of their production and consumption. The slower process is always rate-determining. It is valid at the precondition that the bromination of substrate is rapid enough. Under our experimental conditions (temperature, concentration of reactants), the rate constant (first-order) of Br^- production is smaller than the rate constant (first-order) of Br^- consumption in the reaction with bromate [9]. It means that the rate-determining process is the release of Br^- ions in oxidation of MA—BrMA mixture by Mn^{3+} ions. At a high concentration of the substrate, the rate constant of this process decreases by the effect of O_2 and thus the rate of slow concentration decrease of the Br^- ions during oscillations also decreases. The increase of stoichiometric coefficient f by the effect of oxygen causes the increase of $[Br^-]_{max}$, owing to which the time, necessary for the Br^- decrease from maximum concentration to the critical one, is prolonged. Because of these two effects, the period of oscillations in the presence of oxygen is expanded and their amplitude is increased [9].

Kinetics of oxidation of malonic acid

The mechanism of MA oxidation in the presence of oxygen proposed by *Barkin et al.* [3] takes into account only one termination reaction, *i.e.* the recombination of MA· radicals. It results from this assumption that the kinetic length of radical chains should increase with decreasing MA concentration and one molecule of

oxygen should be consumed in each propagation cycle. At low concentrations, it would result in autooxidation of the substrate, which is inconsistent with experimental observations.

Therefore we modified the equation describing the recombination of MAOO· radicals so that it might lead up to termination of radical chain (reaction (E)). We assume that tetroxide formed by combination of MAOO· radicals releases one oxygen molecule and produces two alkoxy radicals MAO· which react with each other owing to the cage effect [10]. A disproportionation of MAO· radicals gives rise to TTA and GOA, owing to decarboxylation of instable 2-oxopropanedioic acid [11, 12] (Scheme 2). It may be that the whole rearrangement proceeds synchronously in one reaction step.
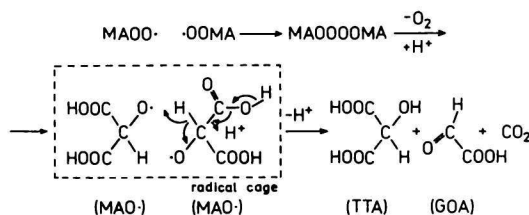
Scheme 2

The retardation of Mn^{3+} consumption at high MA concentrations cannot be explained by the reaction of produced hydroperoxide MAOOH with Mn^{3+} ions. We also took into consideration the change of rate constant of the initiation reaction by coordination of molecular oxygen to the manganese(III) sulfate complexes [13] (decrease in k_{max} and K). Nevertheless, this idea does not allow to explain the dependence of oxygen consumption on MA concentration.

For kinetic reasons, we assume that the formed hydroperoxide preferentially reacts with Mn^{2+} ions. The salts of manganese are known to be effective catalysts of the decomposition of hydroperoxides [14]. In diluted H_2SO_4 t-butyl hydroperoxide reacts more rapidly with Mn^{3+} than it does with Mn^{2+} ions. Since the peroxy group of MAOOH is on the secondary carbon atom and owing to proximity of two electron-withdrawing carboxylic groups, we may assume that the oxidative properties of MAOOH must be enhanced and so the rates of competitive reactions become comparable [15].

$$MAOOH + Mn^{3+} \quad \rightarrow \quad MAOO\cdot + Mn^{2+} + H^+ \qquad (G)$$

$$MAOOH + Mn^{2+} + H^+ \quad \rightarrow \quad MAO\cdot + Mn^{3+} + H_2O \qquad (H)$$

The arising alkoxy radicals may oxidize another Mn^{2+} ion

$$MAO\cdot + Mn^{2+} + H^+ \quad \rightarrow \quad TTA + Mn^{3+} \tag{I}$$

or react with MA

$$MAO\cdot + MA \quad \rightarrow \quad TTA + MA\cdot \tag{J}$$

As the concentration of MA is substantially higher than the concentration of Mn^{2+}, reaction (J) should be preferred.

The oxidation of glyoxylic acid by Mn^{3+} ions is by two orders faster than that of MA [12, 16]. The stoichiometry of this reaction is $n(Mn^{3+}) : n(GOA) = 2 : 1$ [17] and this ratio may decrease in the presence of oxygen. The reaction gives rise to CO_2 and formic acid.

$$GOA + 2Mn^{3+} + H_2O \quad \rightarrow \quad FA + CO_2 + 2Mn^{2+} + 2H^+ \tag{K}$$
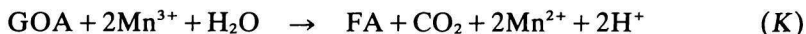
At a low concentration of MA (up to 0.01 mol dm^{-3}) a pseudostationary state is rapidly established, *i.e.* GOA is oxidized with equal rate as it is formed. As the reduction of one Mn^{3+} ion gives at most $1/2$ GOA, it results from the overall stoichiometry that the consumption of Mn^{3+} may be accelerated at most by 100%, which corresponds to experimental data. Provided the concentration of MA increases ($[MA] = (0.01—0.1)$ mol dm^{-3}), the pseudostationary concentration of GOA is reached in a later stage of reaction, which results in acceleration of the consumption of Mn^{3+} at higher half-lives. The competition between MA and GOA for the Mn^{3+} ions unambiguously shifts in favour of MA at increasing MA concentration. Moreover, the relative rate of GOA production decreases, from which it results that GOA only minimally influences the rate of Mn^{3+} consumption at high concentrations of MA.

The manganese(II) is in excess with respect to manganese(III) in the reaction system. Provided $[Mn^{2+}] = 3[Mn^{3+}]$ and $k_G = k_H[H^+]$, reaction (H) is three-times more rapid than reaction (G) and the observed rate constant of Mn^{3+} consumption is given by the expression

$$k_{obs} = k_A(1 - 0.5 v_D/v_A) \tag{15}$$

For concentration $[MA] = 0.5$ mol dm^{-3}, eqn (15) gives the value $k_{obs} = 0.1$ s^{-1} which is consistent with experimental value. The increasing participation of reaction (H) in hydroperoxide decomposition is compensated by reaction (K) owing to increasing concentration of GOA.

We do not attribute absolute validity to the rate constants k_C and k_D obtained by fitting the model on experimental data because they are dependent on the choice of other parameters in the model. Our experimental results are not sufficient for their determination. However, the simulating calculations led to modifications of the originally proposed mechanism [3] and determined the ratios which ought to be preserved between individual values of the rate constants.

Release of bromides in oxidation of the MA—BrMA mixture

The ratio of pseudostationary concentrations of the radicals $[MAOO\cdot]/[MA\cdot]$, determined by simulating calculations of the reaction $MA + Mn^{3+} + O_2$, decreases with increasing MA concentration. It results from this fact that the increase in efficiency of the Br^- release in the presence of oxygen at increasing summary concentration $[MA] + [BrMA]$ cannot be explained neither by increasing effectiveness of $MAOO\cdot$ radicals in the release of Br^- from BrMA when compared with $MA\cdot$ radicals [4] nor by competition between BrMA and O_2 for $MA\cdot$ radicals [18].

On the basis of the proposed mechanism of the influence of oxygen on the reaction between MA and Mn^{3+} ions, we may also explain the change in production of bromides in oxidation of the MA—BrMA mixture caused by presence of oxygen. At a low concentration of MA, the Mn^{3+} ions react not only with MA and BrMA but also with GOA, owing to which the efficiency of Br^- release decreases. At a high MA concentration, there are two effects that contribute to the efficiency of Br^- release. In the first place, the kinetic length of radical chains is expanded. The radical formed by reduction of one Mn^{3+} ion attacks in propagation cycle several molecules of MA or BrMA till it decays in recombination reaction. In the second place, Mn^{3+} ions are regenerated by the reaction of Mn^{2+} with hydroperoxide MAOOH and so they enter again into the reaction with MA and BrMA. Bromides are released by hydrolysis of $BrMA\cdot$ radicals formed directly in the reaction of Mn^{3+} with BrMA or in the reaction of BrMA with the primarily formed radicals [12].

Influence of oxygen on the BZ oscillation system

The results of this series of publications show that the oxygen bubbling affects the oscillation system by the three different ways. It influences the stirring of solution, carries away volatile reaction products and at the same time oxygen is a reactant which is irreversibly consumed in the system. At a high MA concentration, oxygen retards the rate of reduction of the Mn^{3+} ions and simultaneously enhances the amount of oxidized substrate as well as the stoichiometric coefficient f of the Br^- release. If the method of bubbling is changed, the proportion of the importance of individual effects is not preserved. The replacement of T-bubbling by F-bubbling emphasizes removal of Br_2, saturation with oxygen and its reaction in the solution to the detriment of stirring of the reaction mixture. The form of the curves describing the dependences of the oscillatory parameters on oxygen flow can be explained by combination of these effects.

In the course of induction period the consumption of bromate is decreased by the effect of oxygen because the rate of Mn^{3+} consumption is reduced. As the production of BrMA is slowed down and the critical concentration $[Br^-]_{crit, L}$

remains nearly unchanged the induction period prolongs. The liberation of bromine is retarded, but the production of CO_2 is considerably higher.

As the rate constant of MA oxidation by Mn^{3+} ions is decreased by the effect of oxygen, the concentration decrease of Br^- in the course of each oscillation is retarded. Consequently the oscillation period is prolonged. Oxygen increases the value of the stoichiometric coefficient f, owing to which the maximum concentration $[Br^-]_{max}$ is greater than that in N_2 and in addition it continues to increase in the course of oscillations. Moreover, the increase in f by the effect of O_2 brings about that the number of oscillations rapidly decreases to zero with increasing oxygen flow. Further increase in oxygen flow makes possible to reach the state in which the maximum saturation rate overreaches the rate of oxygen consumption. Then the concentration of dissolved oxygen is never equal to zero and the influence of oxygen as a reactant (especially on production of Br_2 and Br^- ions) becomes to be independent of flow. But the intensity of Br_2 removal continues to increase linearly with flow. Thus the system at a certain flow (provided Br_2 is removed with sufficient intensity) attains again the region of instable stationary states and convenient conditions for the formation of stable oscillations arise again. The oscillations of this type instantaneously vanish if the flow of oxygen is decreased or the bubbling is interrupted (Part II, Fig. 10).

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