Influence of oxygen on the Belousov—Zhabotinskii oscillating reaction
II. Liberation of gaseous reaction products and concentration oscillations of oxygen

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The average rate of malonic acid oxidation as a function of flow and method of oxygen bubbling may increase as well as decrease. At a low efficiency of bubbling, the curves describing the evolution of CO_2 in N_2 and O_2 twice intersect each other. At a high efficiency of bubbling, the amount of CO_2 evolved in O_2 is considerably greater than in N_2 in spite of the fact that the consumption of bromate is decreased. The participation of O_2 in oxidation of malonic acid can exceed 70 %. During the induction period the liberation of bromine in the presence of O_2 is retarded, but its overall liberated quantity is increased. For one oscillation, more bromine is released in O_2 though the average rates of its liberation in the course of oscillations in N_2 and O_2 are comparable. If the solution is bubbled through with O_2, two types of concentration oscillations of dissolved O_2 may arise, either in the region of low or high concentration. The second type is conditioned by the effective removal of bromine from the reaction system.

Средняя скорость окисления малоновой кислоты в зависимости от скорости тока и способа пробулькивания кислородом может повышаться и понижаться. При низкой действенности пробулькивания кривые зависимостей выделения CO_2 от времени в N_2 и O_2 два раза пересекаются. При высокой действенности пробулькивания количество выделенного CO_2 в O_2 значительно более высоко, чем в N_2, несмотря на то, что потребление бромата понижается. Доля O_2 в окислении малоновой кислоты может

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превышать 70 %. Во время индукционного периода под действием O_2 выделение брома в присутствии O_2 замедляется, но его общее выделенное количество возрастает. На одну осцилляцию в O_2 выделяется больше брома, хотя средние скорости его выделения за время осцилляций в N_2 и O_2 сравнимы по величине. При пробулькивании раствора кислородом могут возникнуть два вида концентрационных осцилляций растворенного O_2, в области низкой или высокой концентрации. Второй вид определяется эффективным отводом брома из реакционной системы.

This study is a continuation of the preceding part [1] dealing with the influence of gas flow, temperature, and stirring on the Belousov—Zhabotinskii (BZ) oscillating system. The variation of parameters of oscillating reaction accompanying the bubbling through with an inert gas cannot be explained by mechanical stirring only. This fact stimulated us to study the liberation of gaseous reaction products (CO_2, Br_2). The investigation of CO_2 evolution reveals to which extent oxygen changes not only the character of the oscillation regime but also the rate of oxidation of organic substrate. What happens with oxygen introduced in the reaction mixture is explained by measurements with a Clark oxygen probe.

Experimental

The experiments were performed in the same reaction vessel, with equal concentrations of reactants and under equal reaction conditions as described in the preceding part [1] (0.47 M-MA, 2×10^{-3} M-MnSO$_4$, 6×10^{-2} M-KBrO$_2$, 1.5 M-H$_2$SO$_4$, 80 cm^3 of solution, 16 °C, stirring frequency 350 min^{-1}). The use of other indication electrodes (especially of other geometrical dimensions than in [1]) slightly altered the hydrodynamic conditions in the reaction vessel during bubbling and stirring. Consequently the number of oscillations has been a little changed. However, the dependence of oscillatory parameters on the gas flow remained of the same character.

Measurement of CO_2

The evolution of CO_2 was measured by the absorption method. The bubbling gas was led from the reaction vessel through a U-tube filled with granulated anhydrous $Mg(ClO_4)_2$ for capture of moisture. For control, there was a layer of dried silica gel in the end of $Mg(ClO_4)_2$ column. Further, the gas was led through a three-way stopcock by means of which the gas flow was switched over into one of two absorption apparatuses. The half of the absorption apparatus was packed with granulated soda asbestos. Afterwards, an $Mg(ClO_4)_2$ column for absorption of water formed in the reaction between CO_2 and NaOH succeeded. The quantity of liberated CO_2 was determined by weighing the absorption apparatuses. By

switching over the stopcock in time intervals of 2—5 min the flowing gas alternately passed through the first or second apparatus. When the gas passed through one apparatus, the second one was weighed and *vice versa*. Thus the time dependence of CO_2 evolution was obtained. The precision of CO_2 determination by weighing is high provided all CO_2 is captured and other substances are not absorbed. It is suitable to measure the kinetics of CO_2 evolution only in a certain interval of flows. At flows under $100 \text{ cm}^3 \text{ min}^{-1}$, the delay increases too much. At flows over $400 \text{ cm}^3 \text{ min}^{-1}$, the capture of CO_2 is not quantitative any more. Higher flows require rather long absorption tubes the precise weighing of which is problematic.

Measurement of Br_2

The liberation of bromine was followed polarographically in the solution placed in a separated vessel through which the gas passing the reaction vessel bubbled [2]. The Kalousek polarographic cell was filled with 10 cm^3 of $1.5 \text{ M-H}_2\text{SO}_4$ and thermostated to the temperature of the reaction vessel. According to concentration of the dissolved bromine and to its content in carrier gas, bromine was either dissolving in this solution or carried out from it. The concentration of dissolved bromine was followed polarographically using a static Pt-electrode at the potential of $+0.2$ V against a 1.5 M-mercurosulfate electrode. The area under the curve describing the time dependence of bromine concentration is proportional to the amount of bromine liberated from the reaction vessel. This linear relationship was verified experimentally and confirmed by theoretical reasoning [3]. The calibration was performed for both F- and T-bubbling [1] and for all values of flows at which Br_2 oscillations were recorded.

Measurement of O_2

For measuring the concentration of dissolved oxygen, the Clark probe (Yellow Springs Instrument) with teflon membrane was placed closely over the bottom of the reaction vessel in order to prevent the sticking of bubbles on the sensitive part of its surface. The probe was connected with a polarograph (Radelkis, type OH-102 or OH-105) and the potential of -0.7 V was imposed on it.

Results

Evolution of CO_2

The variations of the amount of CO_2 liberated from 80 cm^3 of the reaction mixture with time, flow of O_2 or N_2, and method of bubbling are represented in Figs. 1—3. Carbon dioxide starts to produce immediately after mixing the reactants. Owing to a certain volume of gas above solution and in inlet tubes to absorbers as well as to solubility of CO_2 in the reaction mixture the recording of

CO_2 by the absorption method is delayed with respect to processes occurring in the reaction mixture (~ 2 min).

At T-bubbling the curves expressing CO_2 evolution in N_2 and in O_2 twice intersect each other (Fig. 1). The rate of CO_2 production is the highest in the course of induction period, slows down during oscillations and attains its lowest value in the stationary state after the end of oscillations. The arrows in Fig. 1 denoting the end of oscillations are corrected for the delay. In the course of induction period and oscillations the rate of CO_2 evolution is higher in oxygen than in nitrogen. But the number of oscillations in O_2 is smaller and these oscillations terminate earlier. Thus the production of CO_2 in O_2 is slowed down and the curves intersect each other for the first time. After oscillations finished, the production of CO_2 during the stationary state in N_2 is about ten-times lower than in O_2 owing to which the curves of CO_2 evolution intersect each other for the second time. The quantity of CO_2 liberated in equal reaction times at T-bubbling decreases with increasing flow of O_2. This decrease is due to reducing number of oscillations caused by increasing flow of O_2. The rate of CO_2 production changes periodically during the oscillation regime of the reaction [4, 5]. The absorption method allows to record the average rate of CO_2 evolution only.
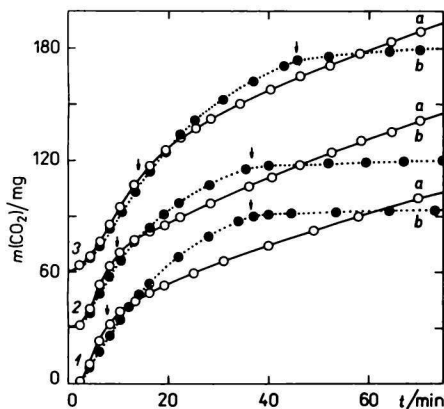

Fig. 1. Time dependence of CO_2 evolution; T-bubbling; a) O_2; b) N_2; flow of gas: 1. 375 cm³ min⁻¹, 2. 230 cm³ min⁻¹ (origin shifted by 30 mg), 3. 120 cm³ min⁻¹ (origin shifted by 60 mg).
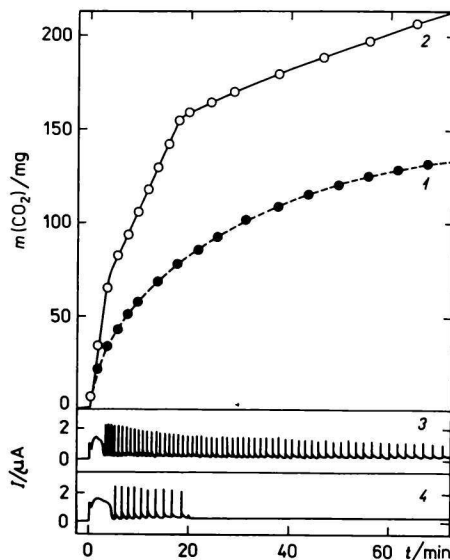
Fig. 2. Time dependence of CO_2 evolution (corrected for delay) (1, 2) and parallel polarographic record of the reaction (3, 4). Flow of gas 375 cm³ min⁻¹; F-bubbling; N_2 (1, 3); O_2 (2, 4).

As for F-bubbling and flows over 80 cm^3 min^{-1}, the curve of CO_2 evolution in O_2 is situated over the curve of CO_2 evolution in N_2 (Fig. 2). A parallel polarographic record follows the changes occurring in the reaction solution. In oxygen, distinct difference in the rate of CO_2 evolution during the induction period, in the course of oscillations and after their termination is observed. As for F-bubbling, the quantity of CO_2 liberated in equal reaction times changes monotonously with increasing flow. In the range of oxygen flow from 80 to 200 cm^3 min^{-1} the quantity of CO_2 evolved during 30 min of reaction increases with flow (Fig. 3) because the number of oscillations also increases. At flows over 200 cm^3 min^{-1} the induction as well as oscillation period is nearly independent of oxygen flow and thus the rate of CO_2 evolution is also independent of it. If the oscillation regime is changed to the stationary state, the production of CO_2 significantly slows down. Therefore the overall amount of liberated CO_2 depends only on the number of oscillations. As the number of oscillations at flows over 200 cm^3 min^{-1} decreases, the amount of liberated CO_2 also decreases. For bubbling with N_2, the rate of CO_2 evolution during oscillations gradually decreases (Fig. 2). That is due to prolongation of oscillation period and to the decrease in oscillation amplitude.

Liberation of Br_2

The presence of bromine in the carrier gas after passing through the reaction vessel was analytically proved by fluorescein. The liberation of Br_2 was followed polarographically at flows over 500 cm^3 min^{-1}. At lower gas flows, the response is
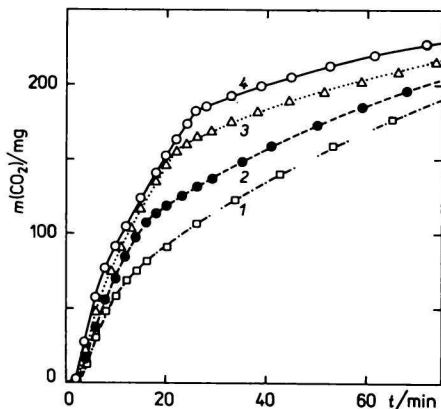

Fig. 3. Time dependence of CO_2 evolution. F-bubbling; flow of oxygen/(cm^3 min^{-1}): 1. 80; 2. 100; 3. 125; 4. 200.
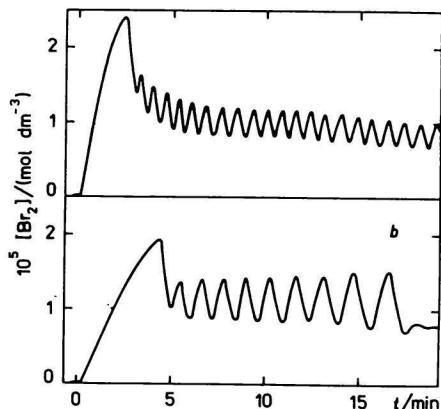
Fig. 4. Time dependence of Br_2 liberation. Concentration changes of Br_2 in a separated Kalousek cell (see Experimental); flow of gas 0.5 dm^3 min^{-1}; F-bubbling; a) N_2; b) O_2.

too delayed and the changes in the rate of Br_2 production are suppressed and averaged. The kinetics of Br_2 liberation at F-bubbling with N_2 and O_2 is represented in Fig. 4. The highest rate of Br_2 liberation is to be observed in the course of induction period. During oscillations in the system, the rate of Br_2 liberation periodically varies whereby the highest rate appears during the autocatalytic oxidation of Mn^{2+} As for T-bubbling with O_2, the reaction system does not oscillate after the induction period, the stationary state is established, which corresponds to a constant rate of Br_2 liberation.

The overall quantity of Br_2 liberated during the induction period increases with flow of gas and is greater for F-bubbling than for T-bubbling (Fig. 5). Though the overall quantity of bromine liberated during the induction period is greater in O_2 than in N_2, the rate of bromine liberation in O_2 is smaller. The dependence of the slope of the Br_2 curve in origin on the flow of N_2 or O_2 is represented in Fig. 6. The
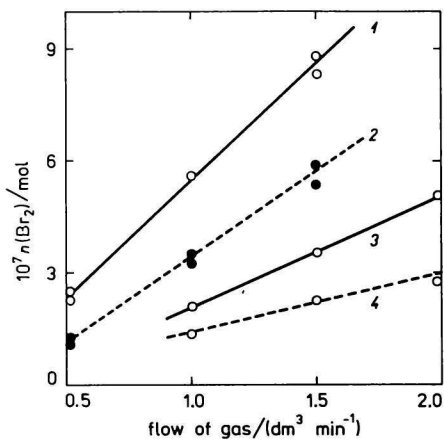

Fig. 5. Dependence of total amount of liberated Br_2 during the induction period on gas flow. F-bubbling: 1. O_2, 2. N_2; T-bubbling: 3. O_2, 4. N_2.
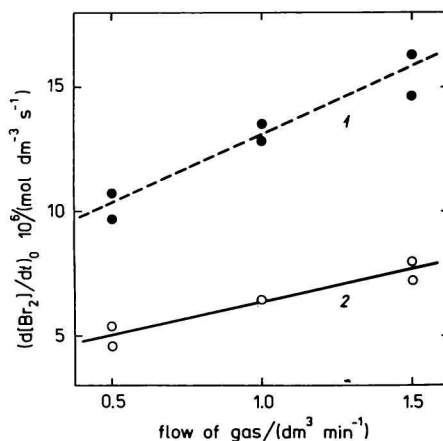
Fig. 6. Slope of the curve expressing Br_2 liberation at the beginning of induction period as a function of gas flow. F-bubbling: 1. N_2, 2. O_2.

amount of Br_2 liberated during one oscillation increases with flow, is greater in O_2 than in N_2 and greater for F-bubbling than for T-bubbling (Fig. 7). The amplitude of the Br_2 oscillations is also greater in O_2, but the average rates of Br_2 liberation during oscillations in N_2 or O_2 are comparable. The overall quantities of Br_2 liberated in the course of 10 min of reaction in N_2 or O_2 are nearly equal, but they are much greater for F-bubbling than for T-bubbling.

Bromine present in the carrier gas may be captured on CO_2 absorbent. In 10 min of reaction and at the flow of 500 cm^3 min^{-1} about 0.1 mg of bromine is liberated

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and the rate of its liberation still decreases in later stages of reaction. It results from this fact that the presence of bromine in this system has no influence on the absorption determination of CO_2 (in the scope of experimental error).
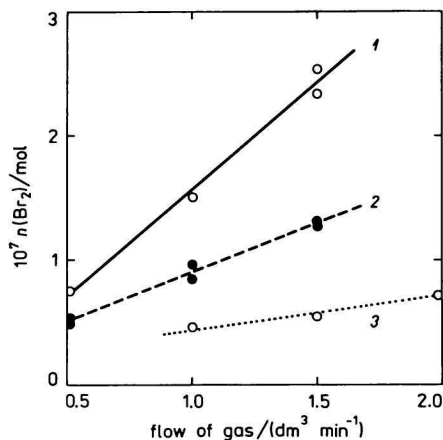

Fig. 7. Dependence of the amount of Br_2 liberated in the course of the fifth oscillation on gas flow. F-bubbling: 1. O_2, 2. N_2; T-bubbling: 3. N_2.
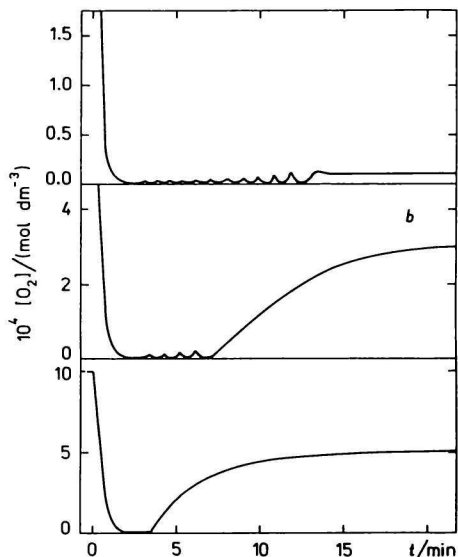
Fig. 8. Variation of the concentration of dissolved oxygen in the course of reaction with flow. T-bubbling; flow of oxygen/(cm³ min⁻¹): a) 100; b) 200; c) 375.

Oscillations of O_2

A Clark probe was used for following the concentration of dissolved oxygen in the reaction mixture under constant bubbling. The dependence of concentration of dissolved oxygen on time in the course of reaction enables us to calculate even the amount of oxygen which has reacted in the solution. At a constant flow, dissolving of oxygen follows the first-order kinetics. The saturation rate constants for the solution of malonic acid, $MnSO_4$, and H_2SO_4 at F- and T-bubbling have been given in Part I — Fig. 3. The saturation rate at constant flow depends on the concentration of dissolved oxygen according to the relation

$$v(O_2) = k([O_2]_s - [O_2]) \qquad (1)$$

where $[O_2]_s$ is the concentration of O_2 in the saturated solution and k is the

saturation rate constant. The amount of oxygen consumed in the time interval from t_1 to t_2 is given by the equation

$$n(O_2) = V \int_{t_1}^{t_2} v(O_2)dt + V \, \Delta[O_2] \qquad (2)$$

where V is the volume of solution and $\Delta[O_2]$ has the meaning of difference between oxygen concentrations in the time moments t_1 and t_2.

$$\Delta[O_2] = [O_2]_1 - [O_2]_2 \qquad (3)$$

By solving these equations, we obtain

$$n(O_2) = Vk \left[[O_2]_s(t_2 - t_1) - \int_{t_1}^{t_2} [O_2]dt \right] + V \, \Delta[O_2]$$

$$n(O_2) = V(kP + \Delta[O_2]) \qquad (4)$$

The amount of oxygen consumed in the time interval from t_1 to t_2 is given by eqn (4) where P corresponds to the area over the curve of concentration changes of oxygen up to the line of the saturated solution between the time moments t_1 and t_2.

The concentration changes of dissolved O_2 in the course of oscillating reaction at different flows and methods of bubbling are represented in Figs. 8 and 9. The solutions are saturated with oxygen before reaction. After mixing of reactants a rapid consumption of oxygen occurs and its concentration in the solution falls to zero. The highest consumption appears in the course of induction period. During the oscillation regime the rate of O_2 consumption depends on the instantaneous concentration of Mn^{3+}. At high concentration of Mn^{3+} the rate of O_2 consumption increases and thus the concentration of dissolved oxygen decreases. At a low concentration of Mn^{3+}, the rate of oxygen consumption is also low and the concentration of dissolved oxygen increases owing to bubbling. The result of these processes are the concentration oscillations of dissolved oxygen. After the oscillations finished, a stationary state is established in the system and a stationary value of oxygen concentration is attained.

During oscillations with T-bubbling the concentration of oxygen is maintained at a low value and decreases after each oscillation down to zero (Fig. 8). After the oscillations finished, the oxygen consumption decreases, owing to which its concentration in the system increases and is stabilized at a constant value. The amplitude of O_2 oscillations increases with flow but the number of oscillations decreases (Part I, Fig. 9). The system does not oscillate any more at flows exceeding 200 cm^3 min^{-1} and a stationary state is established immediately after the induction period.

The reaction course at low flows (up to 30 cm^3 min^{-1}) with F-bubbling resembles the course observed for T-bubbling. The amplitude of oscillations increases with oxygen flow, but the number of oscillations decreases. The system does not
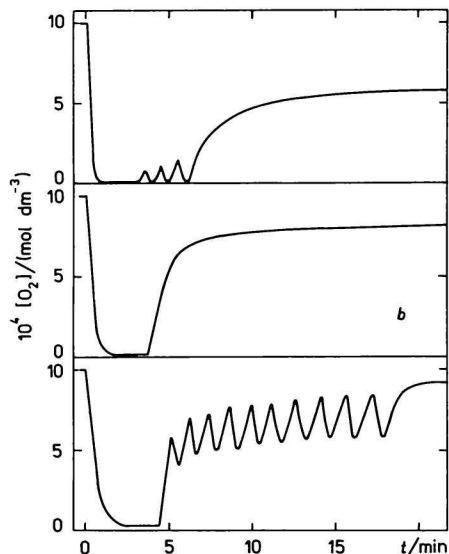
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Fig. 9. Variation of concentration of dissolved oxygen in the course of reaction with flow. F-bubbling; flow of oxygen/(cm³ min⁻¹): a) 23; b) 46; c) 100.
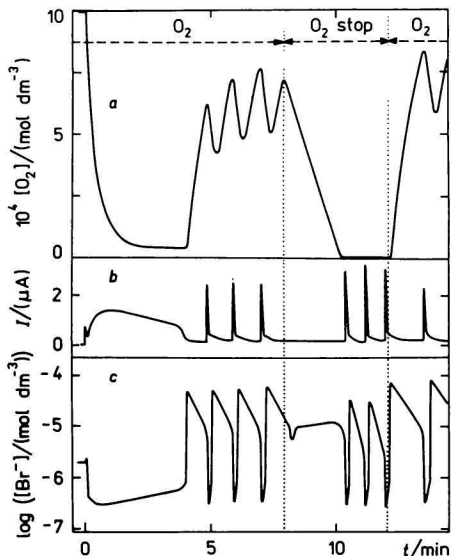
Fig. 10. Effect of the stoppage of oxygen flow on the oscillation regime at a high concentration of dissolved oxygen. Oxygen flow 200 cm³ min⁻¹; F-bubbling; a) concentration of dissolved oxygen; b) polarographic record of reaction; c) record by a Br⁻-sensitive electrode.

oscillate in the interval of flow between $30 \text{ cm}^3 \text{ min}^{-1}$ and $100 \text{ cm}^3 \text{ min}^{-1}$ and a stationary state is established after the induction period. The system oscillates again at flows exceeding $100 \text{ cm}^3 \text{ min}^{-1}$, but the concentration of dissolved oxygen oscillates on a considerably higher level (Fig. 9). If the oxygen inlet is stopped during these oscillations (flow over $100 \text{ cm}^3 \text{ min}^{-1}$), they instantaneously terminate and the concentration of dissolved oxygen decreases linearly because of the constant rate of oxygen consumption in the stationary state (Fig. 10). If the oxygen concentration falls to zero, the oscillation regime is restarted, but the period of oscillations is diminished and corresponds to the course of oscillations in N_2. By restoring the oxygen inlet, the period of oscillations increases and the oxygen concentration in the solutions rises again and starts to oscillate. The parallel registration with a Br⁻ selective electrode indicates the concentration change of Br⁻ in the course of reaction (for more detail see Part III).

The rate of oxygen consumption during the induction period linearly depends on the rate constant of saturation and is independent of the method of bubbling (Fig. 11). The overall oxygen quantity consumed during the induction period increases nonlinearly because its length also increases (Fig. 12). The rate of oxygen
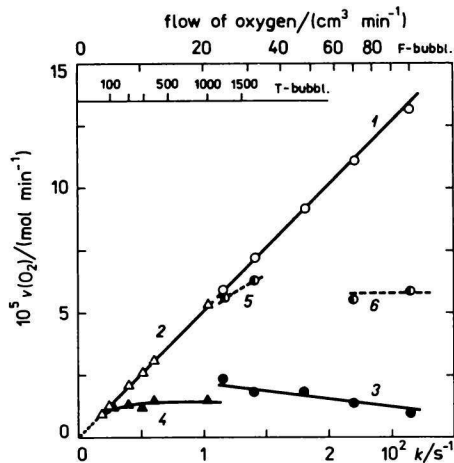
Fig. 11. Rate of oxygen consumption as a function of the saturation rate constant and of the oxygen flow. In the course of the induction period at F-bubbling (*1*) and T-bubbling (*2*); during the stationary state at F-bubbling (*3*) and T-bubbling (*4*); during the oscillation regime at F-bubbling and low oxygen concentration (*5*) or high oxygen concentration (*6*), at T-bubbling (curve *2* up to flow 200 cm³ min⁻¹).
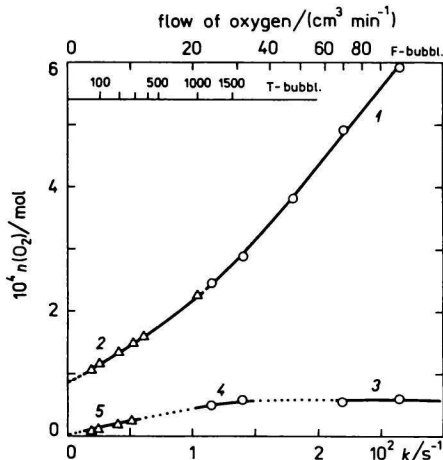
Fig. 12. Variation of the total amount of consumed oxygen with the saturation rate constant and with oxygen flow. In the course of the induction period at F-bubbling (*1*) and T-bubbling (*2*); during one oscillation at F-bubbling and high oxygen concentration (*3*) or low oxygen concentration (*4*), at T-bubbling (*5*).

consumption during oscillations as well as the amount of oxygen consumed for one oscillation increases with flow up to the limiting value and afterwards it is independent of flow (Figs. 11 and 12). After the end of oscillations, the rate of oxygen consumption reaches its lowest value and is only little dependent on oxygen flow. Figs. 11 and 12 point out the different efficiency of saturation of the solution with oxygen for different methods of bubbling. For instance, the T-bubbling with the flow of 1000 cm³ min⁻¹ has equal effect on the induction period as the F-bubbling with the flow of 20 cm³ min⁻¹.

The efficiency of absorption of oxygen introduced in the reaction system is higher at F-bubbling than at T-bubbling and decreases with increasing flow. The highest efficiency of oxygen absorption is in the induction period (for F-bubbling up to 8 %) and the lowest one is after the end of oscillations (for T-bubbling ≈ 0.05 %).

Substance balance

The parallel registration of CO_2 evolution and concentration of dissolved oxygen enables us to determine the participation of O_2 in the oxidation of MA. Provided

the final products of catalytic oxidation of MA are CO_2 and bromomalonic acid (BrMA), the resulting stoichiometry is given by the following equation

$$2BrO_3^- + 3MA + 2H^+ \xrightarrow{Mn^{2+}} 2BrMA + 3CO_2 + 4H_2O \qquad (A)$$

Oxygen functions in this system as a four-equivalent oxidizing agent like bromate. It means that 2/3 of mol BrO_3^- or O_2 are necessary for the formation of 1 mol CO_2 from MA. The fraction of MA oxidized by oxygen is given by the equation

$$x_{MA}/\% = 150n(O_2)/n(CO_2)$$

where $n(O_2)$ is the quantity of oxygen consumed and $n(CO_2)$ is the quantity of CO_2 liberated in the same interval of time. The participation of oxygen in oxidation of MA during the induction period at the flow of 100 cm³ min⁻¹ and F-bubbling is greater than 70 %. During oscillations and after their end the participation of oxygen in oxidation of MA decreases approximately to 50 %. The participation of oxygen in oxidation of MA at T-bubbling increases from 15 % to 30 % at flows from 100 cm³ min⁻¹ to 400 cm³ min⁻¹. This participation increases to 50 % after the end of oscillations in the course of stationary state. The calculated amount of reduced bromate is smaller in O_2 than in N_2. For instance, at the flow of 100 cm³ min⁻¹ and F-bubbling the concentration of BrO_3^- decreases by 27 % in N_2 and by 23 % in O_2 in the first twenty minutes of reaction. The decrease in BrO_3^- concentration after 20 min is equal to 44 % in N_2 and only 36 % in O_2. In the same time interval the concentration of MA decreases by 2.8 % in N_2 and 4.7 % in O_2 (before reaction MA is in stoichiometric excess).

Discussion

Influence of bubbling on the rate of MA oxidation

According to the flow and method of bubbling through the reaction system with oxygen or nitrogen, the rate of MA oxidation may be changed. The highest rate is during the stationary state at the high concentration of Mn^{3+} (induction period) while the lowest rate appears during the stationary state at the low concentration of Mn^{3+} (after the end of oscillation regime). In the course of oscillations the rate periodically varies between these limiting values. As the bubbling changes the parameters of oscillating reaction (especially the number of oscillations), the average rate of MA oxidation is also altered. Oxygen participates in MA oxidation, increases its rate and is irreversibly consumed in the system. Nevertheless, a direct oxidation of MA with oxygen is not possible. Oxygen reacts with the malonyl radicals which are formed in the first step of the reaction of MA with the Mn^{3+} ions

[6, 7]. The higher is the concentration of the Mn^{3+} ions, the greater is the consumption of oxygen and the rate of oxidation is also higher.

Varying the flow and method of oxygen bubbling the average rate of MA oxidation may be either increased or decreased. The amount of evolved CO_2 is a result of combination of two effects, *i.e.* the influence of O_2 on the parameters of oscillating reaction and the influence of O_2 on the rate of MA oxidation. At T-bubbling especially the first effect dominates. The quantity of oxidized MA (in one hour) decreases with increasing oxygen flow owing to rapid decrease in the number of oscillations. The amounts of CO_2 liberated in O_2 or N_2 are comparable and the curves expressing evolution of CO_2 twice intersect each other. As for F-bubbling and flows exceeding 100 cm³ min⁻¹, the system oscillates for sufficiently long time even in oxygen and thus the second effect, acceleration of MA oxidation by the influence of O_2, predominates. Therefore the amount of CO_2 liberated in O_2 is always greater than that liberated in N_2.

Liberation of Br_2

The concentration of dissolved Br_2 has significant influence on the course of oscillating reaction. Bromine is in close relation with the Br^- ions which are the key-intermediate. In an oscillation system with high concentration of MA, bromine may be removed by bubbling in spite of the fact that MA rapidly reacts with it. Bubbling accounts for a decrease in concentration of dissolved Br_2 owing to which the concentration of the Br^- ions decreases too [6]. The stationary concentration of Br^- after the end of the oscillation regime is only a little higher than the critical concentration $[Br^-]_{crit, U}$, the consequence of which is a high sensitivity of the system to its change. If Br_2 is removed, the concentration of Br^- decreases under the critical value and next oscillation is started. Thus the bubbling significantly affects the duration of the oscillation regime as well as the overall number of oscillations analogously as observed in the systems with substrates which cannot be brominated [2, 8, 9].

During oscillation, in the state of autocatalytic oxidation of the Mn^{2+} ions, a greater amount of Br_2 is liberated in O_2 than in N_2. As the frequency of oscillations is lower in O_2, the average amounts of liberated Br_2 (*e.g.* after 10 min of reaction) in O_2 and N_2 are comparable irrespective of the fact that approximately twofold amount of MA is oxidized in O_2 in equal time interval.

If the reaction mixture is not bubbled through, the evaporation of Br_2 from the surface and diffusion of O_2 into the solution cause that conditions in the surface layer of the reaction mixture are different from those inside the solution. It has been demonstrated by the experiment, in which chemical waves spreading from the surface inside the solution were observed after stoppage of stirring and oxygen bubbling.

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Oscillation of O_2

In the reaction solution such concentration of dissolved oxygen is established at which the rate of saturation is equal to the rate of oxygen consumption. In addition the saturation rate linearly increases with decreasing concentration of dissolved oxygen (eqn (1)). The concentration oscillations of dissolved oxygen are a consequence of changes in the ratio of the rate of saturation of the solution with oxygen to the rate of its irreversible consumption. The condition for origination of the oxygen oscillations is the fact that the maximum rate of saturation at a given flow must be greater than the minimum rate of oxygen consumption during the oscillation regime. The rate of oxygen consumption depends on malonyl radical concentration which is determined by the concentration of the Mn^{3+} ions [6]. Therefore it is the highest during the induction period and the lowest during the stationary state after the end of oscillations.

The length of the induction as well as oscillation period is dependent on oxygen flow as long as the maximum rate of saturation with oxygen does not exceed the rate of its consumption. It means that at these conditions the concentration of oxygen never falls to zero during the whole reaction. The upper limit of the rate of oxygen consumption during the induction period was never reached in our measurements because it would require flows exceeding $200 \ cm^3 \ min^{-1}$ at which the changes in oxygen concentration were too fast with respect to the response of the Clark probe (the saturation rate constant cannot be determined).

There are two types of concentration oscillations of oxygen which may be observed in the region of low or high concentrations if oxygen bubbles through the reaction solution. At low rates of saturation ($k < 1 \times 10^{-3} \ s^{-1}$, T-bubbling or small flows at F-bubbling), the concentration of oxygen oscillates on a low level and periodically falls to zero (Fig. 8). If the oxygen inlet is stopped, the system continues to oscillate like in nitrogen. The BZ system can oscillate even at higher concentrations of dissolved oxygen but only at a simultaneous intensive bubbling, owing to which the concentration of bromine is reduced (Fig. 10).

The high rate of irreversible oxygen consumption indicates the importance of surface interfaces solution—gaseous oxygen. The concentration of dissolved oxygen may be increased only be perfect dispersion of introduced oxygen because the consumption of oxygen is greater than the rate of its diffusion from the interface (surface of bubble) inside the solution. For this reason, the parameters of oscillating reaction are so significantly dependent on flow and method of oxygen introduction into the solution. Thus at T-bubbling and oxygen flows lower than $100 \ cm^3 \ min^{-1}$ the concentration of dissolved oxygen in the course of oscillations approximates to zero.

Substance balance

The participation of oxygen in MA oxidation approaches to 80 % at higher concentration of the Mn^{3+} ions (induction period) and sufficiently intensive saturation of the solution with oxygen. As oxygen is a four-equivalent oxidant, it holds for the stoichiometric ratio $n(Mn^{3+}):n(O_2) \approx 1:1$ as supposed in paper [7]. At low values of Mn^{3+} concentration and especially at insufficiently intensive saturation with oxygen, the participation of oxygen in MA oxidation decreases. As the consumption of the Mn^{3+} ions in oxygen is retarded [6] the rate of their regeneration by bromate is reduced. In addition, the oscillation period is longer in O_2 than in N_2 and so the autocatalytic oxidation of the Mn^{2+} ions (which substantially raises the consumption of BrO_3^-) does not occur so frequently as it does in N_2. For these reasons, the amount of bromate reduced in the presence of O_2 is smaller in spite of the fact that much more MA is oxidized.

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