Influence of oxygen on the Belousov—Zhabotinskii oscillating reaction
I. Dependence of oscillatory parameters on the gas flow, method of bubbling, stirring, and temperature

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The parameters of oscillating reaction depend on the efficiency and intensity of saturation of the reaction solution with oxygen, which is given by oxygen concentration in bubbling gas, flow of gas, method of gas introduction into solution, stirring, and temperature. The increase in apparent activation energy is due to the decrease in ratio of the rate of saturation of solution with oxygen to the average rate of substrate oxidation at increasing temperature. The dependence of the number of oscillations on nitrogen flow exhibits several maxima. The concentration oscillations of manganese(II) were investigated by the circulation ESR technique.

Параметры осцилляционной реакции зависят от действенности и интенсивности насыщения реакционного раствора кислородом, определяемых концентрацией O_2 в пробулькиваемом газе, скоростью пропускания газа, способом подвода газа в раствор, перемешиванием и температурой. Рост кажущейся энергии активации вызван понижением отношения скорости насыщения раствора кислородом к средней скорости окисления субстрата при повышающейся температуре. График зависимости числа осцилляций от скорости тока N_2 имеет несколько максимумов. Концентрационные осцилляции Mn(II) наблюдались методом кругового ЭПР.

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A classical example of chemical oscillations is the Belousov—Zhabotinskii (BZ) reaction [1, 2]. The presence of oxygen significantly affects the course of this reaction. Oxygen extends the induction as well as oscillation period and shortens the lifetime of oscillations [3]. The oscillation period of the reaction in oxygen increases twice more rapidly than it does in nitrogen. But at higher values of the ratio of concentrations of catalyst to the organic substrate oxygen shortens the induction period and the apparent activation energy of the first oscillation period decreases [4]. The influence of oxygen on oscillating reaction depends on initial concentration of substrate. At a low concentration of malonic acid (MA), oxygen transforms the stable stationary state to an oscillating one. On the other hand, at higher concentration of MA oxygen inhibits the oscillation regime [5, 6] and produced stationary state is usually excitable [7]. By stopping the inlet of oxygen, the oscillations restart. The inhibition of oscillations does not mean the inhibition of oxidation reaction [8]. The sensitivity to oxygen also depends on the character of catalyst and decreases in the order $Fe(phen)_3^{2+}$, Mn^{2+}, Ce^{3+} [8].

In the course of oscillating reaction, oxygen is consumed [5, 8—10] and thus the stoichiometry of the resulting substance transformation is changed. The ratio of consumed amounts of MA to those of bromate increases in oxygen [3]. Provided the saturation of the solution with oxygen is stationary, the concentration oscillations of dissolved oxygen occur [5, 10]. Oxygen influences the kinetics of oxidation of MA by cerium(IV) [9, 11] or manganese(III) [12] ions and changes the quantity of bromides liberated during oxidation of MA and bromomalonic acid (BrMA) mixture [9, 11]. The simulating calculations based on the change in kinetics and stoichiometry of the reaction of Ce^{4+} ions with BrMA by the effect of oxygen correspond only partially to experimental observations [3].

The aim of our study has been the elucidation of the influence of oxygen on the BZ oscillating system with MA and Mn^{2+} respecting the fact that it is a heterogeneous reaction between gaseous oxygen and the liquid BZ reaction mixture. This first part deals with the influence of the character of bubbling (introduction of O_2 into the reaction mixture), temperature, and stirring on parameters of the oscillating reaction. The second part is concerned with liberation of the gaseous reaction products and concentration changes· of the dissolved oxygen. The influence of oxygen on the release of bromides and oxidation of MA by the Mn^{3+} ions as well as the simulating calculations of the consumption of oxygen is the topic of the third part.

Experimental

Chemicals

Anal. grade chemicals and redistilled water were used for the preparation of solutions. Malonic acid was recrystallized in the first step from the methanol—water mixture (volume

ratio = 1 : 1) and in the second step from water with activated carbon. The initial concentrations of reactants were as follows: 0.47 M-MA, 2×10^{-3} M-MnSO$_4$, 6×10^{-2} M-KBrO$_3$, and 1.5 M-H$_2$SO$_4$.

Reaction vessel

As a heterogeneous reaction is to be investigated, the kind of introduction of oxygen into the reaction mixture, geometry, and arrangement of the measuring apparatus are very important for reproducibility of the results. We used two kinds of oxygen introduction, *i.e.* through a tube or a glass frit. A schematic diagram of the reaction vessel with thermostated jacket is represented in Fig. 1. The inside diameter of the reaction vessel was 55 mm. A magnetic stirrer with 50—1000 revolutions per minute was used. The iron stirring rod of 5 mm diameter and of 22 mm length was coated in teflon. The bubbling gas was led into the solution through a tube at the bottom of the vessel (T-bubbling) or through a glass frit (F-bubbling). The frit diameter was equal to 18 mm and average porosity of the glass was 150 μm. The bottom side of the frit was 1 mm distant from rotating stirrer. The centre of the frit was shifted with respect to the rotation axis of the stirrer by 10 mm. The frit was removed from the vessel during T-bubbling. The bubbling gas passed through flow-meters. A set of
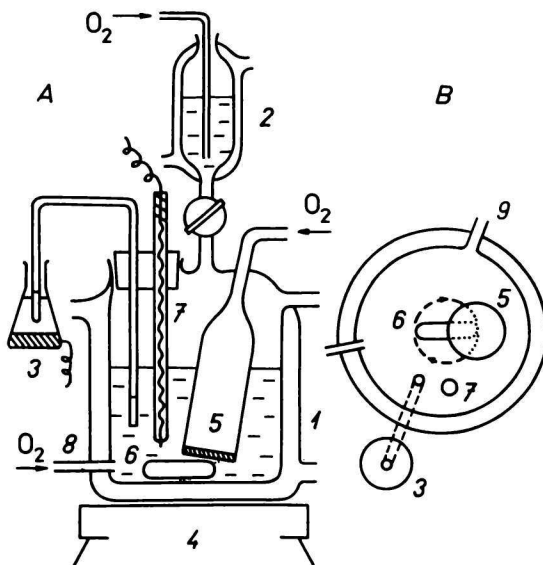

Fig. 1. Scheme of the reaction vessel.
A. Front-view, B. top-view. *1.* Proper reaction vessel; *2.* vessel for thermostating the second reaction component; *3.* reference electrode; *4.* magnetic stirrer; *5.* frit; *6.* stirrer; *7.* Pt-electrode; *8.* inlet for T-bubbling; *9.* outlet for circulation circuit.

flow-meters with accuracy of adjustment of the flow up to ± 3 % was used. An indication electrode was placed in the reaction vessel and a salt-bridge containing H_2SO_4 connected the reaction solution with a reference electrode.

Polarographic measurements

The course of oscillating reactions was followed by the polarographic method (polarograph Radelkis OH-102) applying a static Pt-electrode and moving solution. The imposed potential of 0.0 V against a separated 1.5 M-mercurosulfate electrode was used. The volume of the reaction mixture was 80 cm³. The solution of $MnSO_4$ and MA in 1.5 M-H_2SO_4 was thermostated and bubbled through with a gas directly in the reaction vessel before the reaction was started. The solution of $KBrO_3$ in 1.5 M-H_2SO_4 was thermostated and bubbled through in a vessel separated by a ground-glass cock. Opening this cock the solution of bromate was pressed into the reaction vessel and thus the reaction was started. If no other information is given, the experiments were carried out with the stirring frequency 350 min⁻¹ and at the temperature 16 °C.

ESR measurements

The concentration changes of Mn^{2+} were studied by the circulation ESR technique [13]. A spectrometer Varian E-3 operating in X-band with 100 kHz modulation frequency was used. The reaction mixture was drawn from the reaction vessel by means of a teflon gear pump ($v = 200$ cm³ min⁻¹) through a flat cell situated in the resonance cavity (Fig. 2).
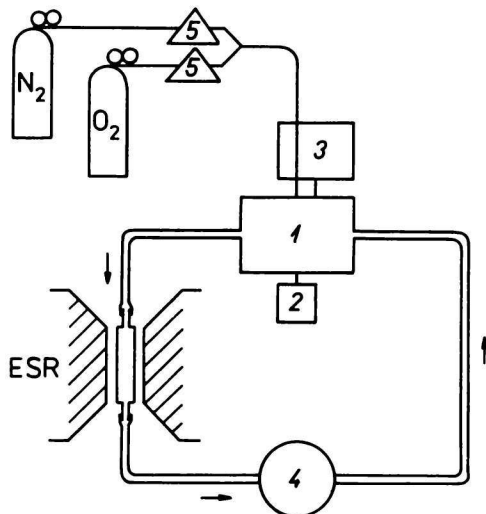

Fig. 2. Scheme of the circulation ESR technique.
1. Reaction vessel; 2. magnetic stirrer; 3. thermostat; 4. teflon gear pump; 5. flow-meter.

T-bubbling was used and the inlets of gases through flow-meters enabled us to adjust arbitrary ratio of O_2 to N_2 and to maintain overall gas flow constant ($v = 2.5$ dm^3 min^{-1}). For circulation measurements the total volume of the reaction mixture was increased to 100 cm^3 because of internal volume of the pump and hoses.

First of all, the ESR spectrum of the thermostated MnSO$_4$—MA mixture in H$_2$SO$_4$ was recorded. The manganese(II) ions give the typical six-line spectrum. Then the induction of magnetic field was adjusted to the top of the third line of the Mn^{2+} sextet. The sensitivity of spectrometer was increased ten-times because the maximum concentration changes of Mn^{2+} approximately corresponded to 30 % of manganese analytical concentration. The reaction was started by addition of the KBrO$_3$ solution. The time dependence of line intensity was recorded at constant induction of magnetic field. As the line width does not change, the signal intensity given by its height is linearly proportional to the Mn^{2+} concentration within limits of experimental errors. For low-temperature measurements cylindrical ESR cell was used.

Measurement of oxygen

The kinetics of saturation of the solution with oxygen was measured by a Clark oxygen probe equipped with teflon membrane (polarizing voltage — 0.7 V). The electrode was placed closely over the vessel bottom in order to prevent the sticking of bubbles on its surface.

Results

Saturation of the solution with oxygen

The reaction solution without bromate was bubbled through with nitrogen and subsequently with oxygen and the concentration of dissolved oxygen was monitored by means of a Clark probe. The dissolving of oxygen at constant flow follows the first-order kinetics. The dependence of the rate constant of saturation on oxygen flow and method of bubbling is represented in Fig. 3. The efficiency of saturation is many times higher provided a frit is used, *e.g.* it is ten-times greater at the flow rate of 65 cm^3 min^{-1}.

Dependence of the parameters of oscillating reaction on temperature and oxygen content in bubbling gas

Oxygen affects many parameters of the BZ reaction. Fig. 4 represents a section of the ESR record of oscillation reaction under constant bubbling through the reaction mixture with nitrogen or oxygen. Oxygen extends the induction period as
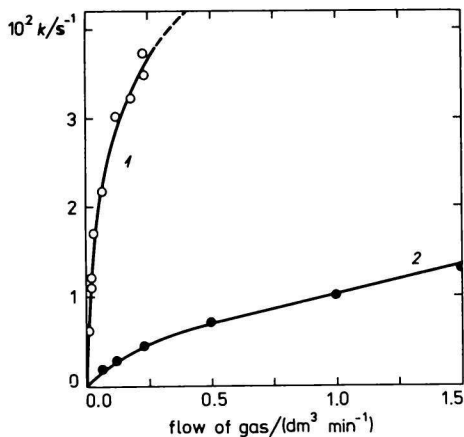
Fig. 3. Variation of the rate constant of oxygen saturation of the solution with oxygen flow.
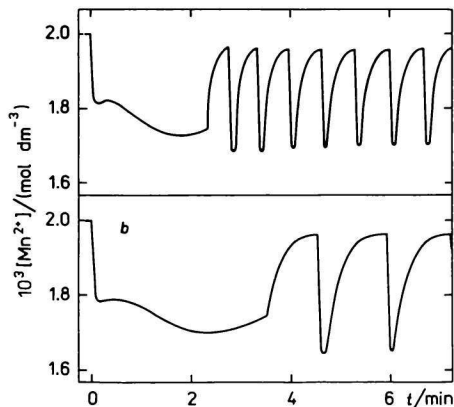1. F-Bubbling; 2. T-bubbling.

Fig. 4. Influence of oxygen on concentration change of the Mn^{2+} ions during oscillation reaction.
Circulation ESR technique, 16 °C. a) N_2; b) O_2.

well as the oscillation period, increases the amplitude of the Mn^{2+} concentration oscillations, and shortens the lifetime of oscillations. The influence of oxygen is more expressive at lower temperatures and decreases with increasing temperature. The temperature dependence of the induction and first oscillation period in N_2 and O_2 is represented in Fig. 5. The initial amplitude of Mn^{2+} oscillations decreases
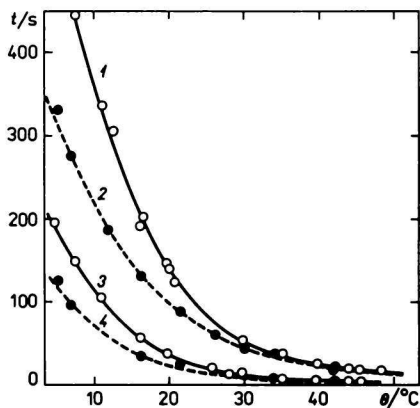

Fig. 5. Temperature dependence of induction (t_i) and first oscillation (t_{os}) period.
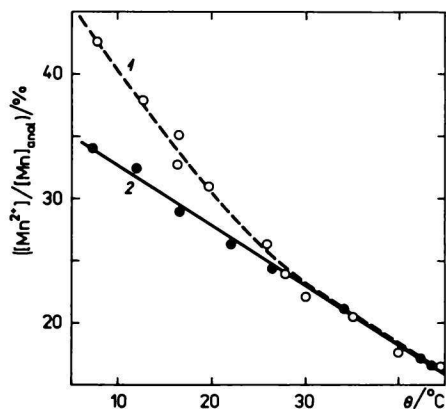ESR technique; 1. t_i, O_2; 2. t_i, N_2; 3. t_{os}, O_2; 4. t_{os}, N_2.

Fig. 6. Amplitude of the first oscillation as a function of temperature.
ESR technique; 1. O_2; 2. N_2.

with increasing temperature while it is greater in O_2 than in N_2, especially at lower temperatures (Fig. 6). The ESR records of oscillations always refer to the ESR spectrum of Mn^{2+} in the reaction mixture in the absence of bromate at a corresponding temperature because the intensity of signal in question increases with temperature. The ratio of the maximum Mn^{2+} concentration change in the course of oscillations to the analytical concentration of manganese is independent of the initial Mn^{2+} concentration in the range from 2×10^{-4} to 2×10^{-3} mol dm^{-3}. Its value in nitrogen at 25 °C is 0.25.

If the temperature and gas flow are constant, the parameters of oscillating reaction depend on oxygen content in the bubbling gas. The relationships between log $\{t_i\}$ or log $\{t_{os}\}$ and reciprocal value of temperature are linear. The slopes enable us to determine the apparent activation energies of these processes. The apparent activation energy of the induction as well as the first oscillation period nearly linearly increases with percentage of oxygen in the bubbling gas (Fig. 7). The difference between the values found in nitrogen and oxygen is approximately equal to 10 kJ mol^{-1}.

Dependence of the parameters of oscillating reaction on gas flow and method of bubbling

A polarographic record of oscillating reaction taking place in the solution bubbled through with nitrogen or oxygen is represented in Fig. 8. At the potential
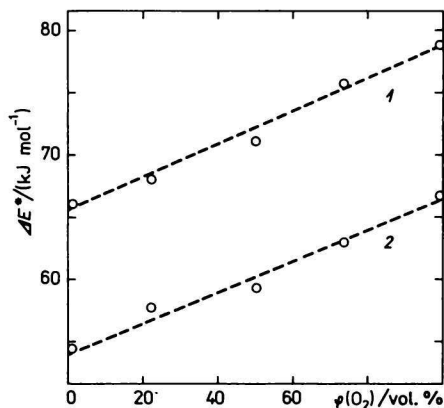

Fig. 7. Variation of the apparent activation energy evaluated from induction period (1) and first oscillation period (2) with percentage of oxygen in bubbling gas. ESR technique.
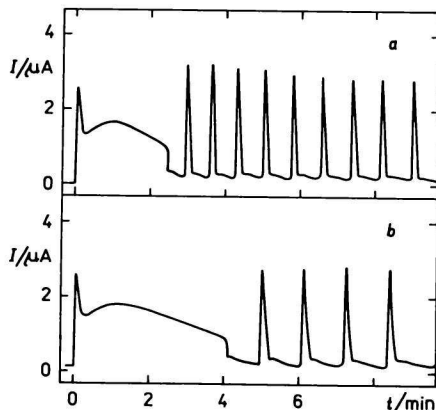

Fig. 8. Polarographic record of oscillating reaction.
Flow of gas 150 cm^3 min^{-1}; F-bubbling; a) N_2; b) O_2.

of 0.0 V against the reference electrode Mn^{3+} ions are reduced on the platinum electrode. However, the maxima on oscillation curve several times exceed the cathodic diffusion currents corresponding to the concentration changes of Mn^{3+} The shape of oscillations is also different from the Mn^{3+} concentration changes measured spectrophotometrically or by the ESR method (Fig. 4). We assume that the sharp peaks on oscillation curve correspond to kinetic currents of Mn^{3+} during autocatalytic oxidation of Mn^{2+} by bromate [14]. The low current values between the peaks are to be attributed to diffusion current of Mn^{3+} This method is convenient for exact determination of the parameters of oscillating reaction even if the concentration changes of Mn^{3+} cannot be quantitatively evaluated.

The influence of oxygen flow on the parameters of oscillating reaction at different ways of bubbling is described in Figs. 9—12. The figures also express the
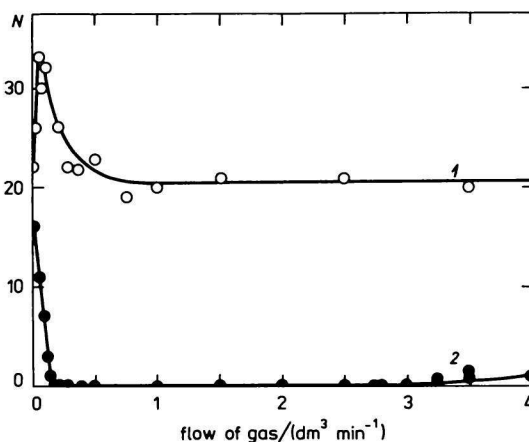

Fig. 9. Dependence of the number of oscillations on the gas flow for T-bubbling.
1. N_2; 2. O_2.

dependence on nitrogen flow because the inert gas bubbling through also affects the parameters of reaction. The influence of oxygen as a reactant is given by the difference between the courses of the reaction in O_2 and N_2 at equal gas flow. As for T-bubbling, nitrogen especially influences the number of oscillations (Fig. 9) while the induction period is less affected (Fig. 10). The number of oscillations falls to zero with increasing oxygen flow (Fig. 9). At a higher flow exceeding 3 dm^3 min^{-1} the system exhibits 1—2 oscillations again. The bubbling with oxygen significantly alters the length of the induction period as well as period of oscillations (Fig. 10).
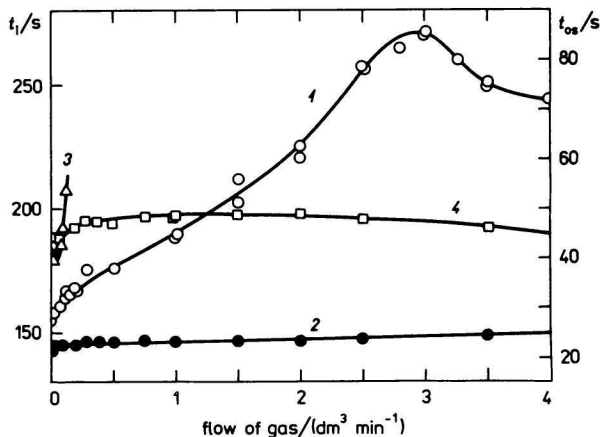
154

Fig. 10. Dependence of induction (t_i) and first oscillation (t_{os}) period on the gas flow for T-bubbling. *1.* t_i, O_2; *2.* t_i, N_2; *3.* t_{os}, O_2; *4.* t_{os}, N_2.
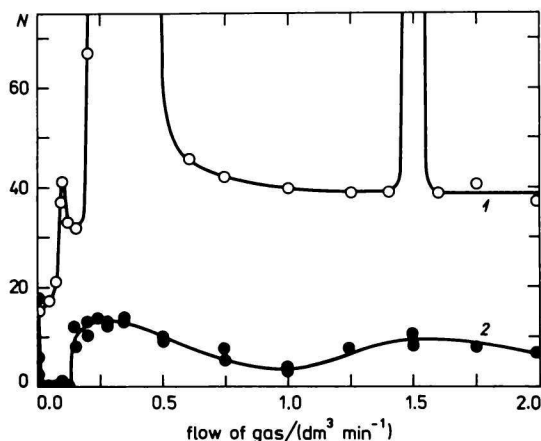

Fig. 11. Dependence of the number of oscillations on the gas flow for F-bubbling. *1.* N_2; *2.* O_2.

Since the saturation of solution with oxygen is much more effective when the frit is used, its influence on the parameters is also much stronger. The left-side part of Figs. 11 and 12 up to the flow of 150 cm³ min⁻¹ resembles Figs. 9 and 10. The induction as well as the first oscillation period rapidly increase with increasing flow of O_2 at the beginning, but their values only little change at higher flows (Fig. 12). The dependence of the number of oscillations on the flow of N_2 and O_2 is surprising
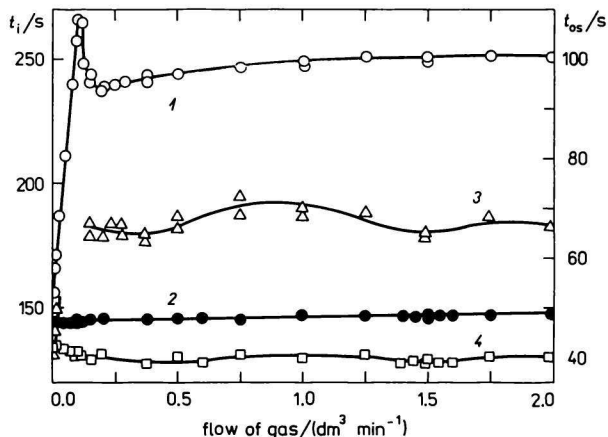
Fig. 12. Dependence of induction (t_i) and first oscillation (t_{os}) period on the gas flow for F-bubbling.
1. t_i, O_2; *2.* t_i, N_2; *3.* t_{os}, O_2; *4.* t_{os}, N_2.

(Fig. 11). The plot obtained for nitrogen exhibits three maxima. A system with O_2 does not oscillate in the flow-rate interval 30—120 cm^3 min^{-1} and an excitable stationary state is established after the induction period. At these circumstances the reaction mixture is of slight pink colour and so the stationary concentration of Mn^{3+} is not equal to zero. Sometimes the system produces one oscillation at the oxygen flow of 100 cm^3 min^{-1}. This extreme occurs exactly under the maximum of the plot for N_2. Provided the flow of O_2 exceeds 120 cm^3 min^{-1}, the plot indicating the number of oscillations exhibits two little distinct maxima which are situated under the maxima of the plot for N_2.

If the number of oscillations is less than 70, the oscillations are little damped and they terminate discontinuously. It means that the oscillation regime is abruptly transformed in a stationary state. A bistability, *i.e.* coexistence of stable oscillations and stable stationary state is to be observed in this stage of reaction. After the oscillations finished, a random larger fluctuation or convenient external impulse (stopping of the stirrer for a few seconds) may transiently bring the system into oscillation regime again. For this reason, the number of oscillations is not always precisely reproducible. If the number of oscillations exceeds 70, the amplitude of oscillations is gradually damped and the transition into stationary state is continuous. After about the 80th oscillation the system oscillates even without nitrogen bubbling.

Influence of stirring

Nitrogen not only removes volatile reaction products from the reaction system [15], but also affects the stirring of this system. Therefore we investigated the

156

dependence of the parameters of oscillating reaction in nitrogen atmosphere on stirring frequency (Fig. 13). The induction period remains nearly constant at increasing revolutions while the period of oscillations slightly increases. However, the number of oscillations rapidly decreases.
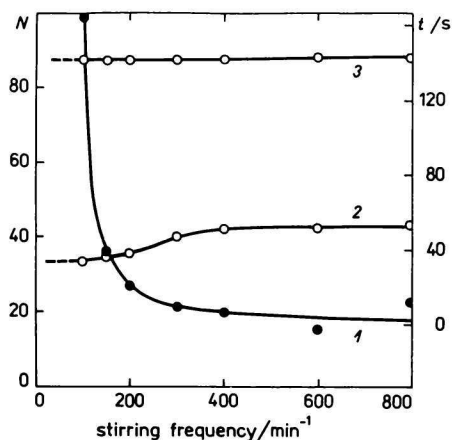

Fig. 13. Dependence of the number of oscillations (1), first oscillation period (2), and induction period (3) on stirring frequency. Flow of N_2 100 cm³ min⁻¹ over solution.

Low-temperature measurements

A part of the reaction mixture was abruptly frozen by liquid nitrogen during oscillations in the stage with the maximum or minimum concentration of Mn^{2+} Obtained ESR spectra only very little differed in intensity. Free radicals were not observed. At the temperature of $-150\,°C$, the ESR spectra consisting of three superimposed sextets belong only to the asymmetrical signal of manganese(II).

Discussion

Saturation of the solution with oxygen

The kinetic data corresponding to the dissolving of oxygen are exactly valid only for a given composition of the solution. The rate of saturation changes with MA concentration because the viscosity and surface tension of the solution is changed, which influences the size of arising bubbles. MA is in excess in the reaction system so that this effect does not influence the oscillation measurements and the saturation rate constant remains unchanged during whole reaction.

Influence of temperature

The influence of oxygen on the BZ oscillating system is dependent not only on its presence, but also on its amount and temperature. The effect of O_2 increases with its content in bubbling gas and decreasing temperature. As the rate of all reactions in the oscillating system increases with temperature, the rate of consumption of O_2 also increases [15]. However, the flow of gas was constant and its solubility decreases with temperature. Owing to these effects, the influence of O_2 decreases with increasing temperature. For this reason the activation energy of oscillations in oxygen apparently rises. For these reasons, this quantity has merely the meaning of the temperature coefficient characterizing the temperature dependence of the parameters of oscillating reaction (t_i, t_{os}) in a given medium and does not result from an increase in activation energy of some elementary process due to oxygen.

Influence of bubbling on the parameters of oscillating reaction

It follows from experimental results that the bubbling through with an inert gas especially influences the number of oscillations, moreover the dependence on the flow is not monotonous. The increase in the number of oscillations is connected with the removal of Br_2 from the system [15]. An increasing intensity of stirring of the solution (due to bubbling through) has opposite effect and reduces the overall number of oscillations. Meanwhile, we are not able to explain the presence of several maxima on the plot expressing the dependence of the number of oscillations on the flow at F-bubbling. However, we assume that the essence of this phenomenon is more of physical than chemical character and relates to hydrodynamic conditions in the reaction system (stirring, bubbling).

Oxygen significantly influences all parameters of oscillating reaction. The better is oxygen dispersed into the solution, the stronger is its effect at a given gas flow. The smaller are the arising bubbles, the greater is the liquid—gas interface and the bubbling through is more efficient. Oxygen and also nitrogen may cause either activation or inhibition of oscillations. It is dependent only on a convenient change in gas flow and reaction stage in which the change in gas flow is performed.

Influence of stirring

As for time oscillations, all volume elements of solution have to oscillate in equal phase. As not all elements are exposed to equal conditions (interface of phases, local inhomogeneities), the time oscillations of the whole solution are observed only if the solution is stirred, owing to which a phasing in the whole volume is maintained.

The concentration of the Br$^-$ ions exponentially decreases from the maximum value to a stationary one during each oscillation [16]. If the stationary concentration is below the critical value, the system cannot gain it because further oscillation spontaneously arises after reaching the critical value. Then fluctuations can influence the oscillation period only. The stationary concentration of the Br$^-$ ions gradually increases in the course of reaction until it exceeds the critical value. If the difference between these values is small, a bistability is to be observed. Under these conditions the concentration fluctuations have fundamental importance for further reaction course. A random greater fluctuation locally disturbs the stationary state, starts oscillation and this perturbation (impulse) is instantaneously extended by stirring into the whole volume. The fluctuation must be of sufficient intensity in order that the impulse may be extended. The local fluctuations are suppressed by stirring and the probability of origination of sufficiently great fluctuations decreases with increasing stirring frequency [17, 18]. Thus the overall number of oscillations decreases and the period of oscillations slightly increases with raising stirring frequency.

Circulation measurements

It results from the high rate of oxygen consumption in the reaction mixture [15] that the circulation measurements cannot be directly compared with the measurements performed in a closed reaction vessel. The concentration of dissolved O_2 in the reaction mixture passing through a circulation circuit rapidly falls to zero. Thus a modified solution returns into the reaction vessel and therefore it becomes the source of oscillations (pacemaker) for the whole reaction volume.

References

1. Field, R. J., in *Theoretical Chemistry*, Vol. 4, p. 53. Academic Press, New York, 1978.
2. Treindl, Ľ. and Tkáč, I., *Chem. Listy 77*, 698 (1983).
3. Bar-Eli, K. and Haddad, S., *J. Phys. Chem. 83*, 2953 (1979).
4. Treindl, Ľ. and Fabian, P., *Collect. Czechoslov. Chem. Commun. 45*, 1168 (1980).
5. Roux, J. C. and Rossi, A., *C. R. Acad. Sci.* (Paris) *C287*, 151 (1978).
6. Farage, J. and Janjic, D., *Chimia 35*, 289 (1981).
7. Ruoff, P., *Chem. Phys. Lett. 92*, 239 (1982).
8. Varadi, Z. and Beck, M. T., *J. Chem. Soc., Chem. Commun. 1973*, 30.
9. Barkin, S., Bixon, M., Noyes, R. M., and Bar-Eli, K., *Int. J. Chem. Kinet. 10*, 619 (1978).
10. Vidal, C., Roux, J. C., and Rossi, A., *J. Amer. Chem. Soc. 102*, 1241 (1980).
11. Ganapathisubramanian, N. and Noyes, R. M., *J. Phys. Chem. 86*, 5158 (1982).
12. Treindl, Ľ. and Mrákavová, M., *Chem. Zvesti 36*, 627 (1982).

13. Frühbeis, H. and Röder, A., *Angew. Chem. 83*, 208 (1971).
14. Treindl, Ľ., unpublished results.
15. Tkáč, I. and Treindl, Ľ., *Chem. Papers 39*, 161 (1985).
16. Tkáč, I. and Treindl, Ľ., *Chem. Papers 39*, 175 (1985).
17. Ruoff, P., *Chem. Phys. Lett. 90*, 76 (1982).
18. Ruoff, P. and Schwitters, B., *Z. Phys. Chem. Neue Folge 135*, 171 (1983).

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