EFFECT OF PRESSURE DECREASE ON THE BELOUSOV–ZHABOTINSKII OSCILLATION REACTION

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The decrease of pressure from 101.3 kPa to 5.25 kPa has an effect on the parameters of the Belousov–Zhabotinskii reaction in batch system in the atmosphere of N_2, O_2, and CO_2. Under the anaerobic conditions, the difference in the form of the reduced phase of oscillatory cycle persists even at vigorous stirring. The role of nucleation, supersaturation, atmosphere, and rate of stirring in these effects is discussed.

The parameters of oscillating systems, e.g., of the Belousov–Zhabotinskii (BZ) reaction, are influenced by the rate of stirring even in a closed (batch) system[1 – 4]. These effects have been explained: (i) by the phase exchange and supersaturation[5], (ii) by statistical fluctuations[6], (iii) by adsorption processes of molecular bromine on the walls of reaction vessel[7], (iv) by superficial catalytic processes on the platinum electrode[8], (v) by the effect on the rate constant of diffusion-controlled reactions[9], (vi) by the bromine phase exchange[10].

We are aware of only two works in which the effects of pressure changes on the homogeneous oscillation reactions are marginally mentioned[5,11]. Botré and coworkers[11] report that the decrease of CO_2 partial pressure results in the increase of oscillation amplitude, and D'Alba and DiLorenzo[5] connect the effect of decrease in pressure with the decrease in the minimum stirring rate needed for periodical oscillations for the phase exchange of CO_2 is increased. Unfortunately, the data on the atmosphere, pressure value, stirring rate, experimental procedure, and others are not given.

It is necessary to emphasize that the phase exchange of gaseous products of oscillation reaction or the adsorption mechanisms on the walls or electrode principally differ from the imperfect stirring in CSTR because in the first two cases, the material balance is influenced, and thus the operation point in the concentration space is shifted whereas the imperfect stirring acts on the chemical behaviour at a constant material balance even though even in this case it is not possible to eliminate the bromine adsorption and superficial catalysis. Therefore it is difficult to interpret the effects of stirring exclusively as the effects in the phase-homogeneous solution.

In our opinion, the study of pressure influence on the oscillation behaviour could help to clear up the nature of heterogeneities in the oscillating system. In the strictly homogeneous reactions in solution, the needed pressures would amount to several hundred MPa to change substantially the rate constants for the activation volumes are generally small. In case of the BZ type oscillation reaction with organic substrates, gaseous products with substantially higher partial molar volumes are formed. It would lead to the sensitivity of these reactions in the BZ system, in which the phase-heterogeneous process takes place, to the pressure changes, and may be, it would influence the parameters of oscillation reaction. Phase exchange in the system can be of two types: (i) between a product in solution at the given temperature and pressure and a gaseous product in the space above the solution; (ii) after forming a new phase in solution by the homogeneous nucleation, between the product in the solution and its nuclei and bubbles in the solution. Even though the first type of phase exchange can be prevented by eliminating the phase boundary between the solution and the gas phase above it, the effect of stirring on the oscillation parameters of the BZ type reactions persists[12].

The gas which originates from the BZ type oscillation reactions with organic substrates is CO_2. Hitherto it is not known whether its production and phase exchange could influence the rate of the chemical process which leads to its formation.

In the present work, the effect of decrease in external pressure on the parameters of the oscillation BZ reaction with malonic acid in a batch system is studied. To be able to study this effect experimentally, it was not possible to eliminate the phase boundary in reaction vessel. The requirement of pressure constancy in the system in which gaseous products are formed does not enable us to work under the conditions which would justify to call the system closed.

EXPERIMENTAL

Common chemicals of A.R. grade and redistilled water were used. After preliminary experiments in which the conditions were sought for the effects of pressure decrease to be well reproducible, the following initial reactant concentrations were chosen: 0.0412 M BrO_3^-, 0.075 M malonic acid, 1 . 10^{-3} M Mn(II), 1.5 M H_2SO_4.

The influence was investigated of the pressure decrease from 101.3 kPa to 5.25 kPa on the induction period (IP), period (PO) and amplitude (AO) of the BZ reaction oscillations in atmospheres of N_2, O_2, CO_2, and air at revolutions 100 – 1 000 min^{-1}. The mean error of IP was 3%, PO 5%, and AO 6%.

The experiments were carried out in a thermostatted cylindrical glass reaction vessel (diameter 3.5 cm, height 7.2 cm). It always contained 40 ml of reaction solution and was closed with a rubber stopper through which a commercial indication platinum macroelectrode (0.5 × 0.8 cm) and a reference mercurous sulfate electrode were inserted into the solution. In the stopper was also a hole for exhausting tube (diameter 0.5 cm) which was connected via a mercury manometer to a water vacuum aspirator enabling to reach the pressure of 5.25 kPa in the reaction vessel during 20 – 30 s. It is necessary to remark that about twentyfold reduction of pressure is the maximum one which can be reached at 25 °C without bringing the solution into boiling.

The potentiomentric measurements were carried out on using a Radelkis OH-105 polarograph. The solution was stirred magnetically with a Teflon-coated stirrer (length 2.5 cm, diameter 0.85 cm). The required atmosphere was reached by 20 min bubbling (600 ml min^{-1}) of the solutions of reactants with a gas from a pressure vessel. The reactants were added into the reaction vessel in the order: aqueous solution of H_2SO_4, of malonic acid, of Mn(II) ions and finally solution of BrO_3^- ions with which the oscillation reaction was started (t = 0).

It was verified that, at a fixed concentration of Mn(III) and Mn(II), the potential of the Pt indication redox electrode, E, did not depend on the used atmosphere, revolutions, and pressure.

RESULTS

The effect of pressure decrease on the oscillation parameters can be observed even in the reaction solution saturated with air. Since the O_2 contents in air is about 21%, it was assumed that the change in the concentration of this component was responsible for the changes of oscillation parameters. The experiments in the pure O_2 atmosphere showed that at the normal pressure, the oscillations were completely suppressed whereas under reduced pressure, the oscillations were observed with parameters similar to those measured in the N_2 or CO_2 atmosphere. Further experiments were therefore carried out under strictly anaerobic conditions.

Typical changes of potential of the platinum redox electrode, E, during the BZ oscillation reaction in N_2 atmosphere with pressure are plotted in Figs 1 and 2. The effect of reduced pressure is in Fig. 1 at revolutions 100 min^{-1} while Fig. 2 was

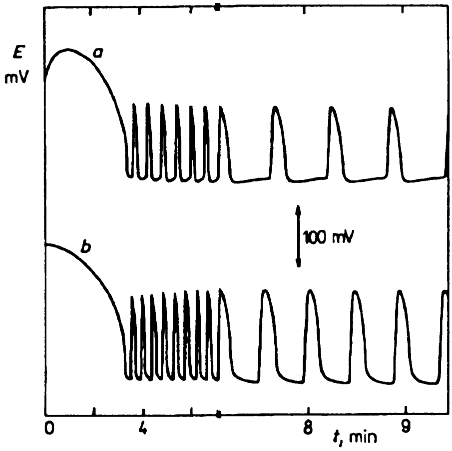

FIG. 1

Effect of decrease in pressure from 101.3 kPa (a) to 5.25 kPa (b) on the BZ reaction in N_2 atmosphere at revolutions 100 min^{-1}. Concentrations of reactants are given in text

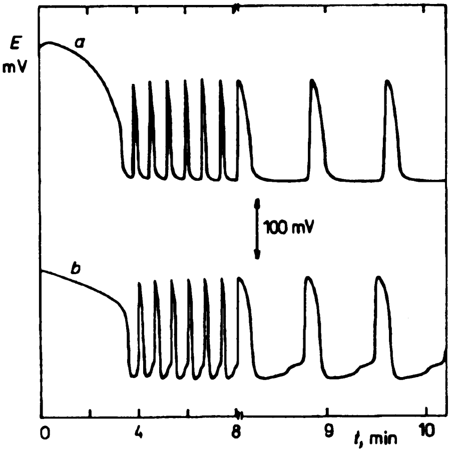

FIG. 2

Effect of decrease in pressure from 101.3 kPa (a) to 5.25 kPa (b) on the BZ reaction in N_2 atmosphere at revolutions 1 000 min^{-1}

recorded at 1 000 min^{-1}. With vigorous stirring, there are no substantial differences in PO (42 s) and AO (165 mV), however, the form of phase of the reduced stationary state changed considerably on reducing pressure.

The differences in the form of reduced phase of oscillatory cycle were observed also at slower stirring (Fig. 1), moreover, the reduced pressure leads to a smaller PO (27.5 s vs 35 s) and larger AO (148 mV vs 127 mV). These results in the nitrogen atmosphere showed that increasing the amplitude with increasing the rate of stirring was more conspicuous at the normal pressure of 101.3 kPa than at the reduced pressure of 5.25 kPa.

The results of experiments in CO_2 atmosphere are illustrated in Figs 3 and 4. The main parameters of the BZ oscillation reaction, PO (41 s) and AO (171 mV) at revolutions 1 000 min^{-1}, are the same at normal and reduced pressure, but the difference in the form of reduced phase of oscillatory cycle (Fig. 4) persists which is identical with the behaviour in the nitrogen atmosphere (Fig. 2).

The trend of decreasing PO (27 s vs 32.5 s) and increasing AO (156 mV vs 147 mV) owing to the reduced pressure at revolutions 100 min^{-1} (Fig. 3) is similar to that in N_2 atmosphere (Fig. 1) but the difference in the character of reduced stationary state is not apparent. It was verified even in CO_2 atmosphere that the increased rate of stirring increased both the amplitude and period of oscillations in the BZ oscillating reaction under normal and reduced pressure.

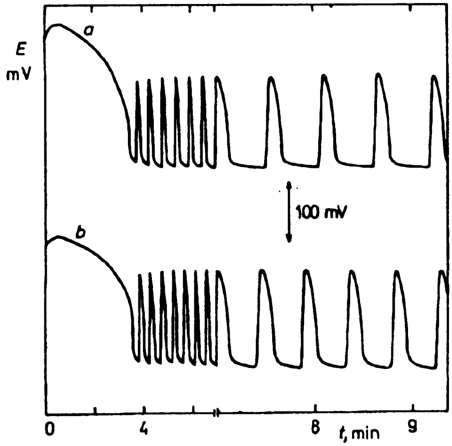

FIG. 3

Effect of decrease in pressure from 101.3 kPa (*a*) to 5.25 kPa (*b*) on the BZ reaction in CO_2 atmosphere at revolutions 100 min^{-1}

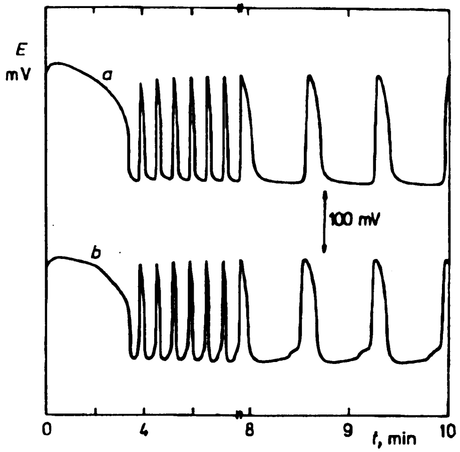

FIG. 4

Effect of decrease in pressure from 101.3 kPa (*a*) to 5.25 kPa (*b*) on the BZ reaction in CO_2 atmosphere at revolutions 1 000 min^{-1}

DISCUSSION

Our results are not at variance with the results obtained by D'Alba and DiLorenzo[5] and Botré with co-workers[11]. It is well-known that the behaviour of the gas-evolution oscillators (GEO)[13] is critically dependent on the parameters which in the perfectly homogeneous solution will not play a more significant role dependent on the stirring rate and pressure. However, GEO are explained[13] by a periodical release of the solution oversaturation by a gas (homogeneous nucleation, formation of bubbles, their subsequent enlargement and escaping from the solution).

The pressure decrease in oscillating systems in different atmospheres, however, influences not only the processes of nucleation and supersaturation. Such as it has already been discussed, the decrease in concentration of gases will take place which were used to ensure the more unique definition of the medium in which the reactions took place. The equilibrium solubilities of gases (0.00064 mol N_2 and 0.00126 mol O_2 at their pressure of 101.3 kPa and 25 °C) decreased twentyfold in the experiments at the pressure of 5.25 kPa. However, we cannot imagine the way in which the change in concentration of dissolved N_2 could influence the course of BZ reaction. The dramatic effect of decreasing pressure in the oxygen atmosphere (evocation of oscillations which do not exist at 101.3 kPa O_2) does not surprise so much; it may be connected with the decrease in oxygen concentration under the critical value which is insufficient for inhibiting the oscillations[14]. The effects of different atmosphere eliminate to a considerable degree each other under reduced pressure when there are no substantial differences in the oscillation parameters in the atmosphere of N_2, O_2, or CO_2.

The decrease in pressure in each of atmospheres used at the same stirring would lead even to the increase in rate of phase exchange of molecular bromine. It is experimentally difficult to evaluate this potential drop and differentiate from the possible removing of bromine from the solution owing to escaping the bubbles of CO_2, and therefore it is not possible to exclude that even this effect can take part in the changed parameters of the oscillation BZ reaction under reduced pressure.

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