J. Phys. Chem. A **2000,** *104,* 3958−3963

Oxygen Production in the Oscillatory Bray−Liebhafsky Reaction

Peter Ševčík,* Katarína Kissimonová, and L'ubica Adamčíková

Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic

Received: September 7, 1999; In Final Form: February 4, 2000

The volume of gaseous oxygen produced during the Bray−Liebhafsky (BL) oscillating reaction was measured. The rates of oscillatory O_2 evolution were calculated and the geometrical effects of the Pt electrode surface, stirring rate, and addition of the surfactant on the oscillatory behavior were studied. A significant stirring rate and detergent effect is observed. The oxygen evolution results obtained are in satisfactory agreement with oscillatory behavior of the BL reaction monitored by potentiometric measurements. The idea that physical and chemical processes might couple in the gas evolving oscillators and similar systems was first suggested over fifteen years ago by Bowers and Noyes. The possibility that chemical processes may couple with both oxygen and iodine nucleation and evolution in order to cause, enhance, or suppress oscillations in the BL system is indicated.

Introduction

A large number of oscillating chemical reactions have been investigated both experimentally and theoretically. It is usually assumed that at least two different conditions are necessary for the occurrence of chemical oscillations: (1) the system should be far from thermodynamic equilibrium and (2) the corresponding kinetic equations must be nonlinear. Although these conditions are not sufficient they are necessary for ideal homogeneous chemical systems described by the mass-action law. However, an assumption used in many oscillating chemical reactions, i.e., homogeneity of concentration and the absence of the nucleation of gaseous products leading to the formation, growing, and escaping of bubbles, is obviously not fulfilled in every case.

The acidic hydrogen peroxide and iodate ion system is known as the Bray−Liebhafsky (BL) oscillator.[1] The overall chemical change in the BL system is described by a process (1)

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(aq)} + O_{2(g)} \qquad (1)$$

It can be presented by two summarized processes

$$5H_2O_2 + 2IO_3^- + 2H^+ \rightarrow I_2 + 6H_2O + 5O_2 \qquad (2)$$

$$5H_2O_2 + I_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \qquad (3)$$

which alternately dominate over each other, resulting in iodine oscillations and periodic oxygen gas evolution. In the BL reaction a continuous production of oxygen occurs, and its concentration in the solution can be much higher than under normal conditions because of supersaturation.[2] The chemical potential of the supersaturated oxygen solutions (formed, e.g., in iodide catalyzed decomposition of H_2O_2) at 101.3 kPa external pressure is the same as that of a solution saturated conventionally at about 10 MPa pressure. However, Bowers and Noyes[2] have shown that dissolved molecular oxygen is not a particularly vigorous oxidizing agent, and increasing its concentration by a factor of 100 increases the oxidation potential by only 0.06 V, and, therefore, kinetic effects could be much more important. The possibility that dissolved oxygen might build up as an important intermediate in the BL reaction should be considered.[2−4] An additional factor is the physical instability of the supersaturated solutions.[2]

Peard and Cullis[5] confirmed oscillatory O_2 evolution in the BL reaction but they ascribed oscillations to a very unusual combination of chemical and physical factors, including volatilization of iodine. An investigation of the effect of high pressure on the BL reaction by Laurenczy and Beck[6] indicated that the escape of oxygen from the liquid phase is not vital for the oscillations.

In our earlier papers on the effects of a pressure decrease, stirring rate, and the gas stream on the BL reaction, we showed[7,8] that the influence on the rate of interphase transport of I_2 can cause the oscillatory state to be inhibited. A recent simulation,[9] based on the models proposed by Kolar-Anic and Schmitz with co-workers,[10,11] complemented by the physical process of iodine interphase transport

$$I_{2(aq)} \rightarrow I_{2(g)} \qquad (4)$$

shows very good semiquantitative agreement with experiments. Buchholtz and Broecker[12] could show that in their CSTR experiments, when there was no gas phase above the solution, no oscillations could be observed in the BL system at a high flow rate. At a flow rate above 4.3×10^{-4} s^{-1}, oscillations led to a steady state at 60 °C.[12] The suppression of the BL oscillations has been observed for a critical value of iodine interphase transport equal to 4.6×10^{-4} s^{-1} at 60 °C under our batch conditions.[9] The essential role of iodine evaporation is extremely important also for the iodate−hydroxylamine oscillator in a CSTR, and this physical process must be taken into consideration to simulate oscillations.[13] According to Shaw and Pritchard,[14] it is clear that the evolution of a gas (O_2 in the iodate−peroxide reaction) cannot in any case be regarded as homogeneous when considered from the point of view of microscopic reversibility.

Oscillations in the BL system have been observed in several laboratories and have been followed[3,15] visually, calorimetrically, manometrically, spectrophotometrically, and potentiometrically with electrodes specific to hydrogen ion, iodide ion, and oxygen. The monitoring of the BL reaction using spectrophotometric or potentiometric methods is made difficult at higher concentra-

10.1021/jp993156y CCC: $19.00

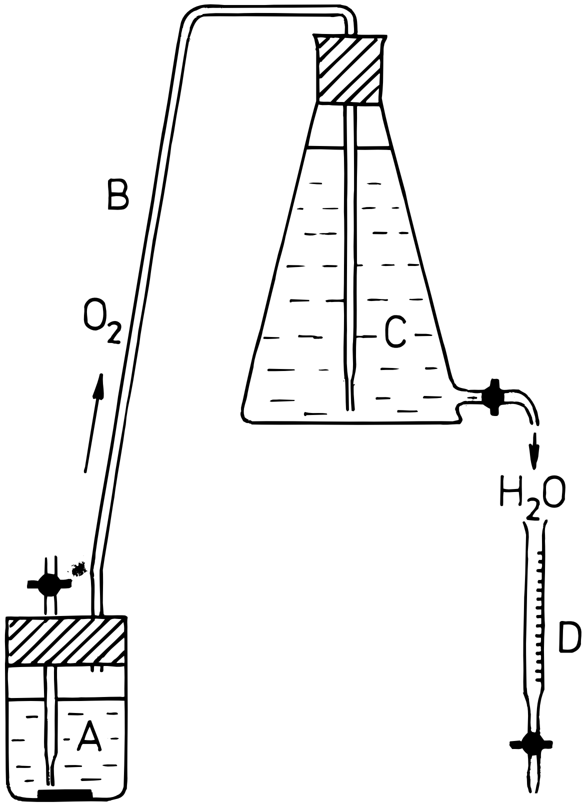

Figure 1. Experimental arrangement for measuring the production of oxygen in the BL system without the immersed electrodes into the reaction mixture A. Evolved oxygen escapes through tubing B to the flask water reservoir C. The volume of water replaced by oxygen in C is measured with a buret D.

tion of hydrogen peroxide because of bubbles of O_2 formed and the presence of another iodine species.[16,17] We are not aware of any example of measurement of exact dissolved oxygen concentration during the BL reaction, although potentiometric traces (without absolute calibration) with a Beckman Oxygen Macro Electrode were obtained.[18] Sharma and Noyes[18] report that the BL solutions become grossly supersaturated with oxygen during part of each cycle and that dissolved oxygen can affect the kinetic behavior of the system.

Our attempt to follow the concentration changes of dissolved oxygen in the batch BL system at 60 °C under given concentrations was unsuccessful, and our commercial oxygen macroelectrode was unfortunately destroyed. Therefore, an increase in the volume of the produced gaseous oxygen with the time in the BL reaction is in this work reported. From this information we were able to calculate rates of gaseous oxygen evolution and to study the effects of various physical processes on the rate of oxygen production and on oscillations in the BL reaction. We preferred another way of measuring rates as described in refs 1 and 11, where the gas buret and the mass flowmeter were used.

Experimental Section

Materials and Methods. Freshly prepared solutions of common reagent-grade chemicals and redistilled water were used. Solutions of H_2O_2 were made from 30% aqueous material without stabilizer obtained from Merck. The following initial reactant concentrations were used: 0.34−0.36 M KIO_3, 0.05 M $HClO_4$, and 0.32 M H_2O_2. The experiments (a scheme can be seen in Figure 1) were carried out in a well thermostated (50.0 or 60.0 ± 0.1 °C) cylindrical glass reaction vessel (diameter 3.5 cm; height 7.2 cm) in the dark. The volume of the reaction mixture was 40 mL with a free surface area from 7.98 cm^2 to 9.62 cm^2 above it, which was varied depending on experimental setup. The lower value corresponds to the experiments when the reaction vessel was closed with a rubber stopper through which a commercial platinum indicator macroelectrode and a reference mercury (I) sulfate electrode were inserted into the solution. The higher value was calculated for experiments performed without inserted electrodes. There were also two other holes in the stopper. One was for a glass capillary tube (diameter of 0.3 cm in the stopper, but 0.1 cm at the end) immersed into the reaction solution, through which the O_2 gas was bubbled into the reaction vessel before starting the BL reaction. The second hole was for a glass tube (diameter 0.5 cm), which was connected via tubing to a 250 mL closed Erlenmeyer-like flask reservoir containing 220 mL of water, placed above the level of the reaction vessel.

The O_2 used for saturating both the reaction mixture and the water reservoir at 101.3 kPa before starting reaction and for O_2 evolution in the BL reaction was introduced into the bottom of the water container with a glass capillary. The required atmosphere at the beginning of the reaction was reached by bubbling (600 mL min^{-1}) oxygen from a pressure vessel through both the reaction solution and water reservoir for at least 10 min. It was allowed to escape the oxygen gas stream used for saturation by opening of the top of the water reservoir. Then the water container was closed and the entire amount of oxygen evolved during the BL reaction could enter into the oxygen saturated water reservoir and accumulate only in the space above the water. The Erlenmeyer flask was also equipped with a tap at the bottom which (when opened) enabled outflow of water. It was verified that in this experimental arrangement the constant atmospheric pressure both in the reaction vessel and water reservoir is kept and the volume of the replaced water corresponds to the volume of the produced oxygen. The time dependence of the exact volume of water flowed out was measured point-by-point by reading the water level usually every 3−5 s in a calibrated buret.

The time dependent change of the platinum redox potential was also monitored by the potentiometric measurements that were carried out using a Radelkis OH−105 polarograph. The reaction solution was stirred magnetically with a Teflon-coated stirrer (polygon shaped 2 cm × 0.8 cm). The stirring rate of the magnetic stirrer was kept constant at the rate of 50 rpm up to 1000 rpm. The reactants were added into the reaction vessel in the following order: aqueous solution of $HClO_4$, KIO_3 (then saturated by oxygen), and finally a small amount of H_2O_2 (saturated by oxygen) was quickly added, after which the oscillation reaction was started. In experiments with addition of gelatine it was verified that there is no observable chemical reaction between gelatine and any of the reactants under given conditions during 80 min.

Results and Discussion

Geometrical Effect of the Electrode. It was suggested[20] that surface processes can contribute to stirring effects, since a change in stirring will change the coupling between the surface and the bulk reaction zones. Another possibility is that the surface has a catalytic activity; the rates of certain reactions could then be different when measured near the surface or in the bulk. A platinum surface would be a good candidate on which to observe such effects since the platinum surface could also work as an electrode in monitoring the oscillatory behavior. Geometric effects factors seem to play different roles in different

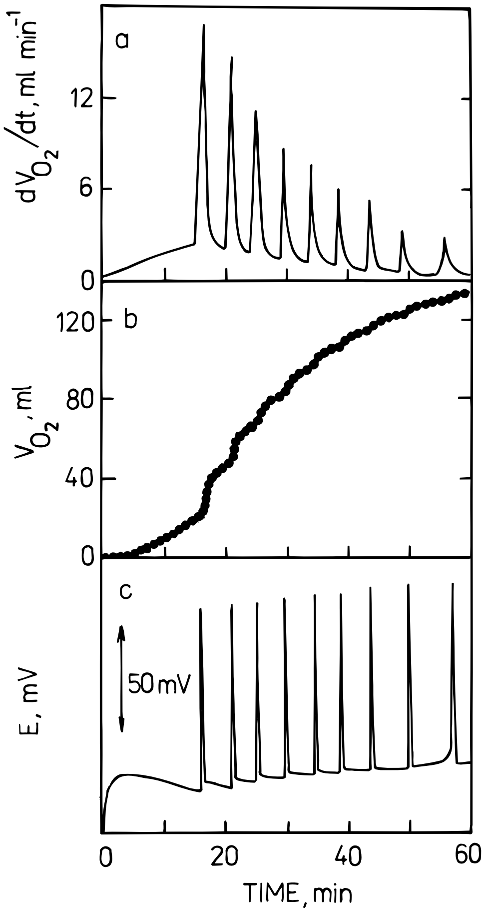

Figure 2. Time evolution of the BL solution initially containing 0.36 M KIO_3, 0.32 M H_2O_2, and 0.05 M $HClO_4$ at 100 revolutions min^{-1} and 60 °C. The changes in (a) the rate of oxygen evolution, (b) the oxygen volume, and (c) the Pt redox potential are shown.

systems. Li and co-workers[21] have found geometrical effects of the electrode during the oscillatory reduction of iodate in alkaline solution. Therefore, we first tried to find to the importance of the size and the quality of the platinum surface on the BL oscillations. We used four different types of the Pt redox electrodes: (a) a commercial smoother large size electrode (0.85 cm × 0.5 cm), (b) a smaller size (a rougher surface 0.7 cm × 0.5 cm), (c) a platinum wire electrode (1 cm long with a diameter 0.5 mm, and (d) a platinum point electrode (the smallest free surface less than 1 mm^2). For comparison, the fifth set of experiments was conducted without any electrodes inserted into the BL reaction solution.

Figure 2 represents a typical experiment and shows changes in the potential of the Pt redox electrode (curve c), the volume of the oxygen evolved and simultaneously measured (curve b; for transparency some readings were omitted, the best fit was done), and the rate of O_2 evolution (curve a; calculated from curve b) during the BL reaction. No apparent changes in oscillatory behavior are observed by varying only the size and the quality of the Pt electrode surface, although a large and rougher Pt surface could facilitate the gas evolution by providing more nucleation sites. The observed oscillations were also insensitive to the presence of small glass or porcelain balls in the bottom of the reaction vessel. The standard deviation of an individual IP measurement was 8−11% and that of PO was 9−14%. The oscillatory parameters varied within these experimental errors. The similar results were also obtained at 50 °C. However, the induction periods (IP = 40.2 min) and the first period of oscillations (PO_1 = 24 min) are lengthened if no electrodes are used, in comparison to the experiments with electrodes inserted into the BL solution (IP = 32 min and PO_1 = 13 min) at 50 °C and 100 rpm.

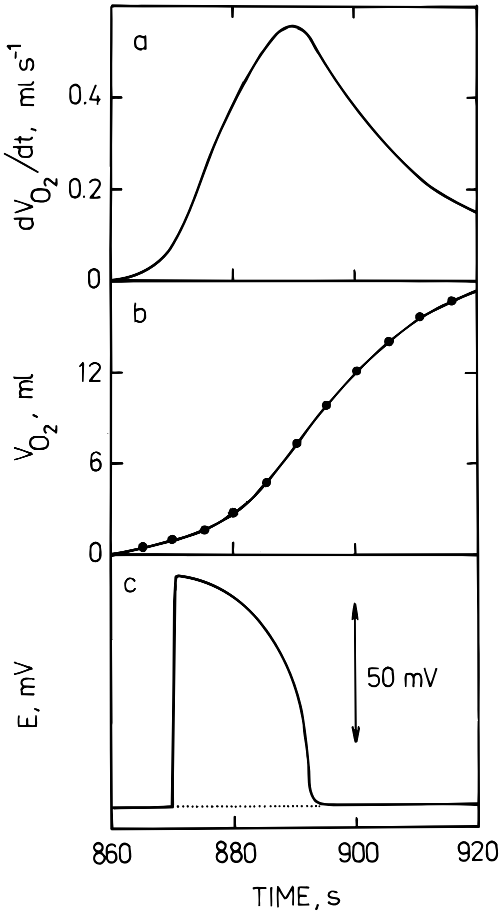

Figure 3. The detailed shape of the single BL oscillation and relationship of (a) the rate of O_2 evolution, (b) the O_2 volume, and (c) the Pt redox potential. Other constraints as in Figure 2.

The detailed relationship of the Pt potential and both volume and rate oxygen evolved during one oscillation is shown in Figure 3. We can see that the positive Pt potential suddenly rises, while the amount of oxygen evolved increases slowly at that time. Just after the Pt potential suddenly drops, the maximum in the rate of oxygen evolution is reached. Colorimetric and in some cases visual observations indicate that the maximum in O_2 rate evolved is reached at about the same time when iodine concentration in reaction solution is minimal. In other words, oxygen evolution is greatest during that phase when I_2 is oxidized. But we realize that the oxygen volume measurement could include the effect of delayed oxygen evolution, and the rate of oxygen production in the BL reaction solution may be different at the same time. Because transport processes in gases are much faster than in liquids, an excess of O_2 in the gas phase will be reduced to the equilibrium value much more rapidly than will an excess of oxygen in a comparable volume of liquid. If both gas and liquid phases are present then supersaturated solutions can persist much longer than will supersaturated vapors. Because of this persistence of supersaturation (if it occurs), it is possible in principle to observe that many bubble nuclei will be created virtually discontinuously. Those bubbles of oxygen will then grow rapidly and deplete the supersaturation as the equilibrium state is approached.

Effect of Stirring Rate. Rubin and Noyes[22] found that the apparent critical supersaturations of dissolved oxygen were in the range 0.04−0.06 M at 35 °C at 101.3 kPa and 0.05−0.06

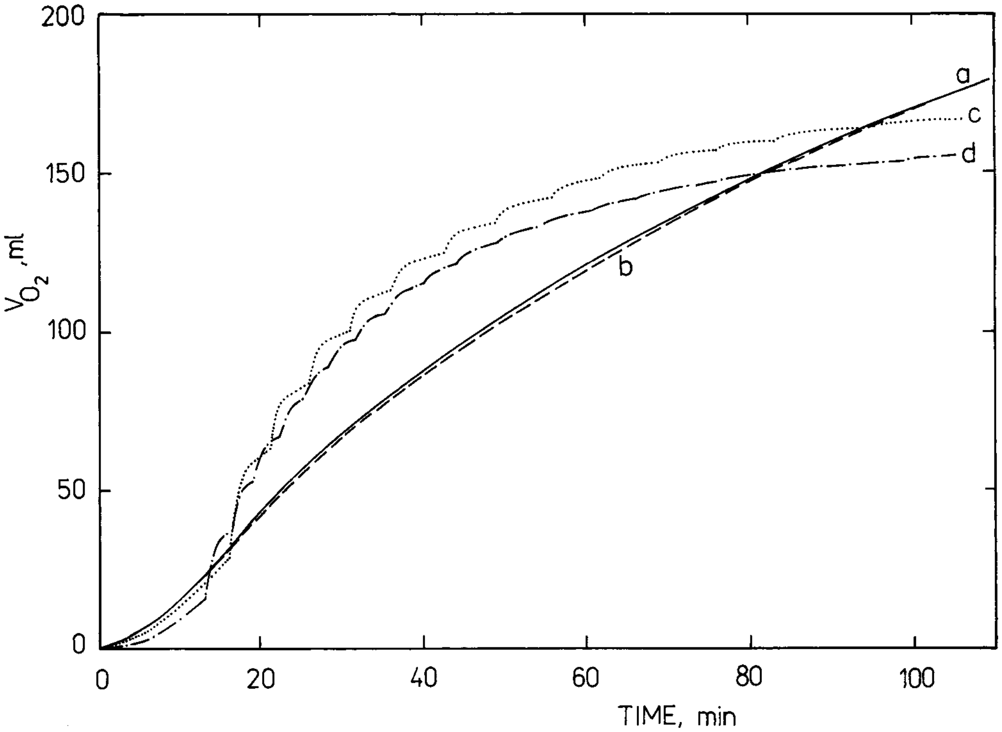

Figure 4. Time dependence of the oxygen volume evolved at various stirring rates. (a) 1000 rpm, (b) 800 rpm, (c) 300 rpm, and (d) 100 rpm. Other constraints as in Figure 2.

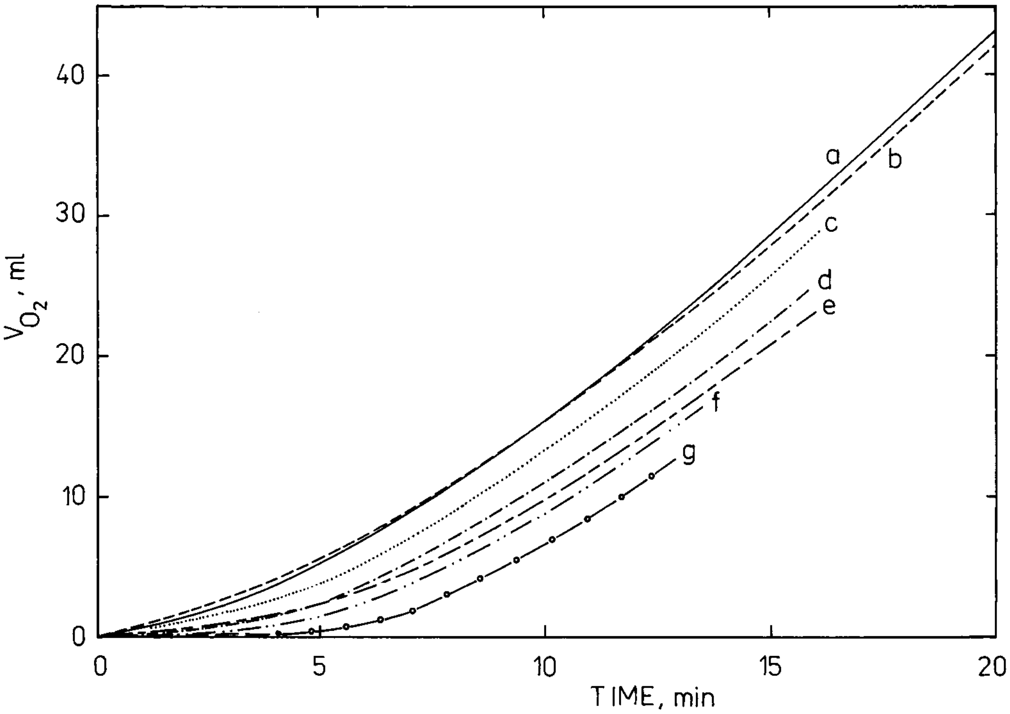

Figure 5. Time dependence of the oxygen volume evolved during the induction period in the BL reaction at various stirring rates. (a) 1000 rpm, (b) 800 rpm, (c) 300 rpm, (d) 150 rpm, (e) 100 rpm, (f) 50 rpm, and (g) without stirring. Other conditions are those in Figure 2.

M when supersaturation was released by rapid stirring or by sonication. At 25 °C and atmospheric pressure a maximum dissolved oxygen concentration of 0.12 M, or about 100 times equilibrium solubility, was found.[2,23] The equilibrium solubility of oxygen at this temperature is 0.00126 M.[2]

We were familiar with previous observations that oscillations in the batch BL system monitored potentiometrically can be suppressed by rapid stirring.[3,7−9]

Therefore, we tried to find the limit of stirring above which oscillations in the rate of oxygen evolution disappear (Figure 4). The number of oscillations ranged from 15 to 17 at stirring rate from 50 to 300 rpm. It was observed that under given experimental conditions a stirring rate above 300 rpm is sufficient to suppress oscillations also in the rate of O_2 evolved at 60 °C. This result is in agreement with that in reference 9. It can be observed that not only oscillatory behavior is dependent on the stirring rate.

There is also an effect of the stirring rate on the volume of O_2 evolved during induction periods or evolution of oxygen at rapid stirring when no oscillations are found (Figures 5 and 6).

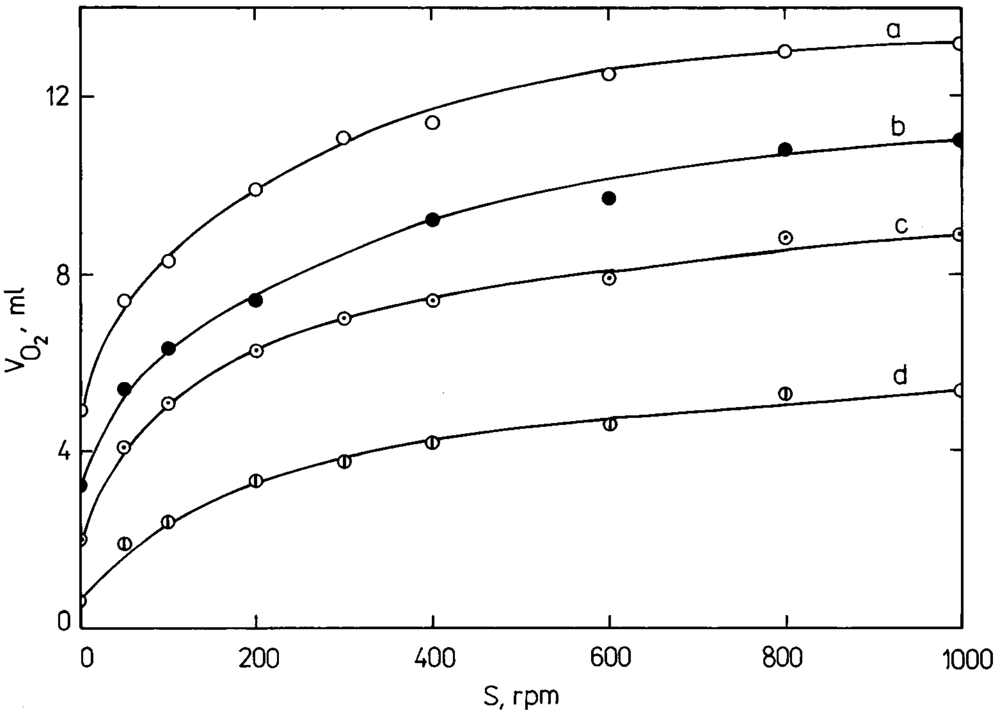

Figure 6. Dependence of the amount of the oxygen evolved on the rate of stirring at various times during the induction periods in the BL reaction. (a) at 9 min, (b) at 8 min, (c) at 7 min, (d) at 5 min. Other conditions are those in Figure 2.

Curves a–g in Figure 5 and a–d in Figure 6 were obtained for the same initial reactant concentrations and temperature. Therefore, the rate of formation of dissolved oxygen in the BL system should also be the same if only homogeneous chemical reactions are considered. It seems that the different traces in Figures 5 and 6 could be attributed to the various rates of transport of oxygen from the BL solution to the gas phase above it. The rate of oxygen transport can be only roughly estimated. Taking into consideration the measured value of the rates of O_2 transport between gas phase and solution in the Belousov–Zhabotinsky reaction[24] and works 9 and 25, the value of order ca. 10^{-4} s^{-1} can be expected in our experimental set up. This value corresponds to the mass-transfer coefficient ca. 10^{-3} cm s^{-1}. It can be concluded that not only the rate of iodine transfer but also the rate of oxygen transport from solution increases with the rate of stirring and the volume of O_2 evolved as well.

Effect of Surfactant. Addition of detergent lengthens the time period of the oscillations and the total time of the oscillatory phase for gas evolving oscillators.[26] The sensitivity of the gas evolution kinetics to surface tension changes is considered to be another indicator of the physical origin of the oscillations. Both the rate of nucleation and bubble radius are actually influenced by surface tension.

We can demonstrate that addition of gelatine to the BL system can substantially change the oscillatory behavior of the Bray–Liebhafsky reaction as well (Figure 7). The oscillatory parameters are influenced; e.g., IP = 15.4 min and PO_1 = 4.4 min measured without gelatine were shortened to IP = 11.9 min, PO_1 = 2.7 min, to IP = 8.5 min, PO_1 = 1.9 min, to IP = 8.5 min, PO_1 = 1.4 min, to IP = 11.8 min, PO_1 = 1.9 min, and then changed to IP = 19.8 min, PO_1 = 2.9 min for 0.2%, 0.5%, 1%, 2% and 3% gelatine, respectively. The oscillations are suppressed in the BL solution containing more than 3% gelatine. The values of the surface tension of the oxygen–water BL system with addition of gelatine were changed from 0.0755 N m^{-1} (in the absence of gelatine) through 0.0571 N m^{-1} (0.2% gelatine), 0.0548 N m^{-1} (0.5% gelatine) to 0.0511 N m^{-1} (1% gelatine) at 60 °C. The exact values of the surface tension of the solution with more concentrated gelatine were not determined because of the changes in the viscosity of the BL solution. The change of the viscosity from 0.60 cP (without gelatine) through 0.64 cP (1% gelatine), 0.72 cP (2% gelatine), 0.96 cP (3% gelatine) to 1.48 cP (5% gelatine) was measured at 60 °C.

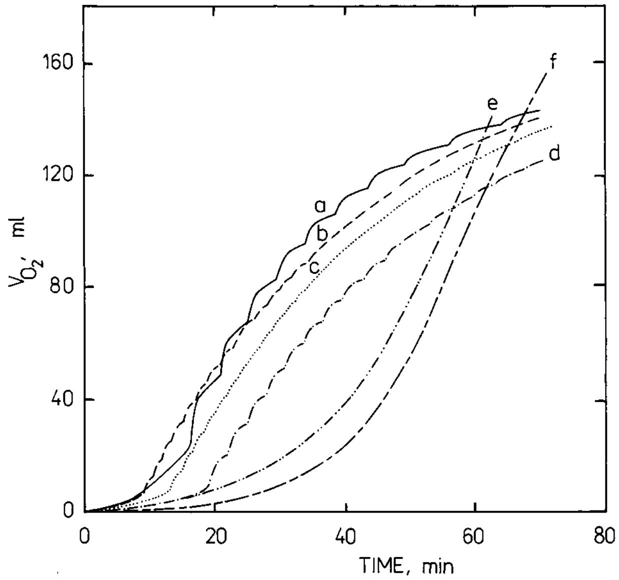

Figure 7. The volume of oxygen evolved as a function of time for the BL system with addition of gelatine. (a) a reference trace without gelatine, (b) 1%, (c) 2%, (d) 3%, (e) 4%, and (f) 5% gelatine. Initial concentrations were: 0.34 M KIO_3, 0.32 M H_2O_2, and 0.05 M $HClO_4$ at 60 °C and 100 rpm.

Conclusions

In the gas evolving oscillators, the rhythmic gas evolution occurs as a result of the natural release of supersaturation. We do not expect that nucleation and supersaturation processes are the major factors responsible for oscillatory behavior in the

Bray−Liebhafsky system. However, we do not exclude the possibility that chemical processes may couple with both oxygen and iodine nucleation and evolution in order to cause, enhance, or suppress oscillatory behavior in the BL system. Such a coupling of physical and chemical processes in the gas evolving oscillators and similar systems, which was first suggested over fifteen years ago by Bowers and Noyes,[26,27] is an area that is mostly unexplored, and systematic study of such effects for various oscillators deserves to be made.

Acknowledgment. This work was supported by Grant No. 1/4009/97 from the Scientific Grant Agency of MESR.

References and Notes

(1) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262.

(2) Bowers, P. G.; Hofstetter, Ch.; Letter, C. R.; Toomey, R. T. *J. Phys. Chem.* **1995**, *99*, 9632.

(3) Treindl, L'.; Noyes, R. M. *J. Phys. Chem.* **1993**, *97*, 11354 and references therein.

(4) Noyes, R. M.; Kalachev, L. V.; Field, R. J. *J. Phys. Chem*. **1995**, *99*, 3514.

(5) Peard, M. G.; Cullis, C. F. *Trans. Faraday Soc*. **1951**, *47*, 616.

(6) Laurenczy, G.; Beck, M. T. *J. Phys. Chem*. **1994**, *98*, 5188.

(7) Ševčík, P.; Adamčíková, L'. *Chem. Phys. Lett*. **1997**, *267*, 307.

(8) Ševčík, P.; Adamčíková, L'. *J. Phys. Chem. A* **1998**, *102*, 1288.

(9) Valent, I.; Adamčíková, L'.; Ševčík, P. *J. Phys. Chem. A* **1998**, *102*, 7576.

(10) Kolar-Anić, L.; Mišljenovic, D.; Anić, S.; Nicolis, G. *React. Kinet. Catal. Lett.* **1995**, *54*, 35.

(11) Kolar-Anić, L.; Cupić, Z.; Anić, S.; Schmitz, G. *J. Chem. Soc., Faraday Trans*. **1997**, *93*, 2147.

(12) Buchholtz, F. G.; Broecker, S. *J. Phys. Chem. A* **1998**, *102*, 1556.

(13) Rabai, G.; Epstein, I. R. *J. Phys. Chem*. **1990**, *94*, 6361.

(14) Shaw, D. H.; Pritchard, H. O. *J. Phys. Chem*. **1968**, *72*, 2693.

(15) Sharma, K. R.; Noyes, R. M. *J. Am. Chem. Soc*. **1976**, *98*, 4345 and references therein.

(16) Noszticzius, Z.; Noszticzius, E.; Schelly, Z. A. *J. Am. Chem. Soc*. **1982**, *104*, 6194.

(17) Noszticzius, Z.; Noszticzius, E.; Schelly, Z. A. *J. Phys. Chem*. **1983**, *87*, 510.

(18) Sharma, K. R.; Noyes, R. M. *J. Am. Chem. Soc*. **1975**, *97*, 202.

(19) Matsuzaki, I.; Alexander, R. B.; Liebhafsky, H. A. *Anal. Chem.* **1970**, *42*, 1690.

(20) Noszticzius, Z.; Horsthemke, W.; McCormick, W. D.; Swinney, H. L. In *Spatial inhomogenities and transient behaviour in chemical kinetics*; Gray, P., Nicolis, G., Baras, F., Borckmans, D., Scott, S. K., Eds.; Manchester University Press: Manchester and New York, 1990.

(21) Li, Z.; Cai, J.; Zhou, S. *J. Phys. Chem. B* **1998**, *102*, 1539.

(22) Rubin, M. B.; Noyes, R. M. *J. Phys. Chem*. **1987**, *91*, 4193.

(23) Bowers, P. G.; Bar-Eli, K.; Noyes, R. M. *J. Chem. Soc., Faraday Trans*. **1996**, *92*, 2843.

(24) Wang, J.; Hynne, F.; Sörensen, P. G.; Nielsen, K. *J. Phys. Chem*. **1996**, *100*, 17593.

(25) Noyes, R. M.; Rubin, M. B.; Bowers, P. G. *J. Phys. Chem*. **1992**, *96*, 1000.

(26) Bowers, P. G.; Noyes, R. M. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985.

(27) Bowers, P. G.; Noyes, R. M. *J. Am. Chem. Soc.* **1983**, *105*, 2572.