Effect of a Gas Bubbling and Stirring on the Oscillating Bray−Liebhafsky Reaction

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A sufficient stream of nitrogen or oxygen bubbled into the oscillating Bray−Liebhafsky (BL) reaction system can suppress oscillations at ambient pressure. A significant stirring effect is observed, and it is confirmed that rapid stirring can cause the oscillatory state to be inhibited. It is shown that the rate of interphase transport of I_2 can be greatly influenced by both bubbling and stirring changes. The total iodine concentration in the solution can be significantly depleted in such a way, and the value of the pseudo rate constant $k_{obs} = 3.2 \times 10^{-4}$ s^{-1} for the I_2 removal is determined to be crucial in our set up at 50 °C. This critical value of the rate constant corresponds to the mass-transfer coefficient $k_{tr} = 1.60 \times 10^{-3}$ cm s^{-1}. We suggest that the rate of transport of volatile iodine from the BL solution to the gas phase may be a significant component of the overall mechanism of the BL oscillations.

Introduction

The oscillating Bray−Liebhafsky reaction is the decomposition of hydrogen peroxide to oxygen and water catalyzed by aqueous iodate.[1,2] The reaction can be described by process 1:

$$2H_2O_2\,(aq) \rightarrow 2H_2O + O_2(g) \qquad (1)$$

The rate of formation and comsumption of elementary iodine can alternate and the concentrations of I_2 and various other intermediates exhibit oscillations during the BL reaction. The research groups of H. Liebhafsky, of R. M. Noyes, of G. Schmitz, of S. Anič and L. Kolar-Anič and others have devoted serious attention to the mechanism of this reaction.[3] An up-to-date list of at least 50 papers that have been published on the BL reaction is offered in ref 4. Although the mechanism of the BL reaction is still incompletely understood, it is generally recognized[5−7] that oscillations in both I_2 and I^- concentrations result from the alternating dominance of the oxidation and reduction of H_2O_2 by IO_3^- to I_2 and by I_2 back to IO_3^-, respectively.

Recently, Treindl and Noyes[4] proposed a new explanation of the oscillations in the BL reaction. They believe that transport of oxygen from the supersaturated solution to the surrounding atmosphere must be included in any detailed mechanism. Because the decomposition of relatively concentrated hydrogen peroxide produces oxygen irreversibly, the total system must contain the two phases: gas and aqueous solution. The gas in contact with the atmosphere will contain O_2 molecules and at the elevated temperature at 50 °C, it also will contain some I_2 molecules, although according to ref 4, escape of this species to the gas phase should not significantly deplete the total iodine in the solution. Peard and Cullis[8] confirmed oscillatory O_2 evolution, which had been reported at 60 °C by Bray,[1] but they ascribed the oscillations to a very unusual combination of chemical and physical factors, including volatilization of iodine.

In our earlier paper on the effect of a pressure decrease and stirring on the oscillating BL reaction, we showed[9] that the rate of interphase transport of I_2 was not negligible at 50 °C and could be significantly influenced by both stirring and pressure changes. It was indicated that the external pressure could be considered to be the bifurcation parameter that determines the stability of the BL system. The high-pressure study of the BL reaction of Laurenczy and Beck[10] suggests that the oscillations dramatically change because of the different pressure dependence of the rate constants of the elementary steps. The authors also seem to feel that if oxygen is bubbled through the solution and the rate of mixing is enough to prevent supersaturation, then the oxygen concentration is constant, but the partial removal of elemental iodine certainly occurs.[10]

We do not regard the observation that rapid stirring can suppress oscillations in the BL system[4,9] as unequivocal evidence that this occurs because of rapid removal of only oxygen. We show that the rate of escape of another important species, elementary iodine, I_2, can be significantly increased by rapid stirring or by a pressure decrease and that in such a way the oscillatory parameters can be changed or even that oscillations can be inhibited at least under some conditions. However, we do not claim that dissolved oxygen does not deserve to be considered as a species that should be involved in the mechanism of the BL reaction. Study of effects of the gas stream and stirring rate on the BL reaction deserves to be made,[4] and the results of such a study are in this paper described.

Experimental Section

Freshly prepared solutions of reagent grade chemicals and redestilled water were used. Solutions of H_2O_2 were made from 30% aqueous material without stabilizer obtained from Merck. We usually obtained similar results from Fluka reagent grade material that contains a stabilizer, but stabilizer-free material was used to obtain the results reported here. The following initial reactant concentrations were used: 0.36 M KIO_3, 0.05 M $HClO_4$, and 0.32 M H_2O_2. In our earlier work on the BL reaction[9] we used 0.39 M H_2O_2; however, this slightly increased value did not bring about substantial effects in comparison with the concentration used here.

The experiments were performed in a well-thermostated (50.0 ± 0.1 °C) cylindrical glass reaction vessel (diameter of 3.5 cm, height of 7.2 cm). The volume of the reaction mixture was 40 mL with a free surface area of 7.98 cm^2 above it. The reaction vessel was closed with a rubber stopper through which a

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commercial platinum indicator macroelectrode (0.5 cm × 0.8 cm) and a reference mercury (I) sulfate electrode were inserted into the solution. There were 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) through which the gas was bubbled into the reaction vessel, and the second hole was for a glass tube (diameter 0.5 cm), which was connected via a ca. 2-m-long tubing by means of a three-way glass stopcock leading either to the atmosphere or to a water-vacuum aspirator and which enabled outflow of gas and/or iodine vapor. The rate of flow of the gas was measured by flow meter, and the value of 50 mL min^{-1} N_2 and/or O_2 was used. Various ways of physical removal of I_2 from the reaction vessel were used. At a particular gas flow rate, we immersed the end of the glass capillary tube into the reaction vessel in three locations: (1) just above a rotating stir bar at the bottom of the reaction vessel; (2) 1 mm below the interface; (3) 1 mm above the reaction solution. The substitution of a fritted disk glass (0.4 cm × 0.5 cm) for the glass capillary tube also was done.

The potentiometric measurements were carried out using a Radelkis OH-105 polarograph. The solution was stirred magnetically with a Teflon coated stir bar (polygon shaped 2 cm × 0.8 cm). The stirring rates could be varied continuously and in these experiments were from 100 to 1000 rpm. The reactants were added into the reaction vessel in the following order: aqueous solution of $HClO_4$, KIO_3, and finally H_2O_2 upon which the oscillation reaction was started. The required atmosphere at the beginning of the reaction was reached by bubbling (600 mL min^{-1}) of the gas from a pressure vessel through the reactant solution containing water, $HClO_4$, and KIO_3 for at least 10 min and through the separate concentrated solution of H_2O_2 for at least 10 min. Just before starting the oscillation reaction, the rate of gas flow was adjusted to the required value. It was verified that at given reactant concentrations the potential of the platinum indicator electrode did not depend on the common intensity of light in the laboratory, and induction periods (IP), amplitude (AO), and period of oscillations (PO) were the same in the dark.

The rates of escape of I_2 molecules from a standard solution of I_2 (8.1×10^{-4} M) to the gaseous phase above the liquid solution caused by gas-bubbling and/or stirring in the same reaction vessel were determined spectrophotometrically (Zeiss Jena Specord UV-vis spectrophotomer). The time dependence of the iodine concentration was monitored by measurement of its optical absorbance A at the I_2/I_3^- isosbestic point of 470 nm and molar absorbance coefficient ϵ equal to 740 M^{-1} cm^{-1} at both different gas-bubbling and stirring rates. The volume of the gas phase (actually, it is the volume of the laboratory) is very much greater than the volume of the liquid phase, and therefore, the infinite value of $[I_2]_{aq}$ will be negligible. Then the following equation for the rate of I_2 escape can be obtained:

$$v_{esc} = -\frac{d\,[I_2]_{aq}}{dt} = k_{obs}[I_2]_{aq} \qquad (2)$$

where $[I_2]_{aq}$ is the iodine concentration in the solution and k_{obs} depends on the bubbling and stirring rates. Values of k_{obs} were obtained from at least three measurements and calculated from plots of $\ln A_o/A$ versus time. Each run showed good pseudo-first-order kinetics. The value of k_{obs} can be expressed using the convention for interphase transfer kinetics as a mass-transfer coefficient in units of cm s^{-1}: $k_{tr} = k_{obs}V_{sol}$/surface area.

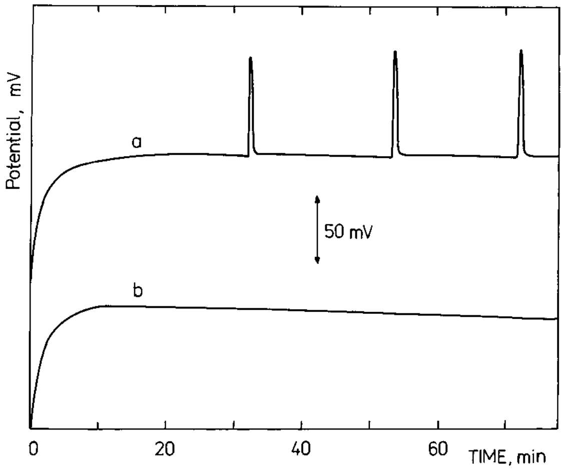

Figure 1. Potentiometric traces of the Bray−Liebhafsky oscillatory reaction obtained by a platinum redox electrode in the initial N_2 atmosphere at 100 revolutions min^{-1}, 101.3 kPa, and 50 °C: (a) without bubbling of N_2 or O_2 into reaction solution; (b) with sufficient bubbling or stirring (see details in Table 1). The initial concentrations are 0.36 M KIO_3, 0.32 M H_2O_2, and 0.05 M $HClO_4$.

Results

Effect of Bubbling on the BL Reaction. Typical changes in the potential of the platinum redox electrode during the BL reaction are plotted in Figure 1. The oscillatory trace 1a can be observed in the BL system at slow stirring (100 rpm) without bubbling or under bubbling with the capillary located above the reaction solution (the third location described in the Experimental Section). It can be observed that the concentration of I_2 rises to a maximum (4.13×10^{-4} M) during IP (32 min). Suddenly, d$[I_2]$/dt changes sign and I_2 is more rapidly consumed. After an iodine-consumption period, the process abruptly shifts to iodine production, and oscillations continue (PO ≈ 20 min). Usually, 12−13 oscillations can be recorded. Oxygen evolution from the supersaturated solution is greatest during the phase when I_2 is decreasing and corresponds to the oscillation peak in the positive potential of the platinum redox electrode, as can be seen in Figure 1a. Trace b in Figure 1 clearly shows that bubbling N_2 or O_2 gas into the reaction solution (the first and the second location of the capillary as described in the Experimental Section) suppressed oscillations even at slow stirring (100 rpm). In this arrangement no oscillations were observed when the method for removal of volatile species was changed by means of a substitution of a fritted-disk glass for the capillary. In the case of the immersed capillary, the escape of large 2−3 gas bubbles per second can be observed, while by use of the frit, the amount of small bubbles can be arranged in tens at the same gas flow rate. However, it was found that at the same flow rate of N_2 or O_2, the same rate of I_2 transport from the standard I_2 solution to the gas phase was determined.

Effect of Stirring Rate on the BL Reaction. We were familiar with previous observations that oscillations in the batch BL system can be suppressed by rapid stirring.[4,9] Therefore, we tried to find the limit above which oscillations dissappear. It was observed that under given experimental conditions a stirring rate above 200 rpm is sufficient to suppress oscillations at ambient pressure with no gas-bubbling at 50 °C. The stirring rate can be varied from 100 to 150 rpm and from 175 to 200 rpm while oscillations similar to those in Figure 1a can be found. At 250, 300, or 1000 rpm a trace similar to that in Figure 1b can be observed.

Measurements of the Rate of Transport of Iodine from Standard Solution of I_2 to the Gas Phase. We were able to

TABLE 1: Calculated Rate Constant k_{obs} of Iodine Removal from 8.1×10^{-4} M Standard I_2 Solution in 0.05 M $HClO_4$ at 50 °C for Various Rates of Stirring, Pressure, and Rates and Methods of Bubbling of N_2 or O_2 (see Experimental Section for the Method Described Here as 1, 2, and 3)[a]

no./symbol	rate of stirring, rpm	pressure, kPa	rate and method of bubbling	k_{obs}, s^{-1}
1. □	no stirring	101.3	no bubbling	8.30×10^{-5}
2. □	no stirring	13.3	no bubbling	1.84×10^{-4}
3. □	100	101.3	no bubbling	2.74×10^{-4}
4. ◐	150	101.3	no bubbling	2.85×10^{-4}
5. ◑	175	101.3	no bubbling	3.05×10^{-4}
6. ▲	200	101.3	no bubbling	3.11×10^{-4}
7. ×	100	101.3	50 mL O_2 min^{-1}, 3	3.11×10^{-4}
8. ●	100	101.3	50 mL N_2 min^{-1}, 3	3.22×10^{-4}
9. ⦶	250	101.3	no bubbling	3.20×10^{-4}
10. ⊖	300	101.3	no bubbling	3.33×10^{-4}
11. □	1000	101.3	no bubbling	4.14×10^{-4}
12. □	100	13.3	no bubbling	5.11×10^{-4}
13. ◬	100	101.3	50 mL O_2 min^{-1}, 2	5.12×10^{-4}
14. ⊙	100	101.3	50 mL N_2 min^{-1}, 2	5.25×10^{-4}
15. □	1000	13.3	no bubbling	8.23×10^{-4}
16. △	100	101.3	50 mL O_2 min^{-1}, 1	8.66×10^{-4}
17. ○	100	101.3	50 mL N_2 min^{-1}, 1	1.06×10^{-3}

[a] The rate constants of 1−3, 11, 12, and 15 were taken from ref 9 for comparison.

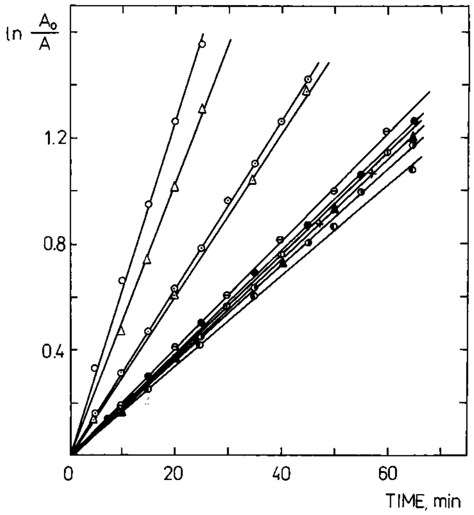

Figure 2. "Pseudo-first-order" kinetics of the removal of iodine from the standard 8.1×10^{-4} M I_2 solution (the verification of eq 2) for different bubbling and stirring rates at 50 °C. The lines correspond to the conditions 4−10, 13, 14, 16, and 17 as described in Table 1 and Figure 3.

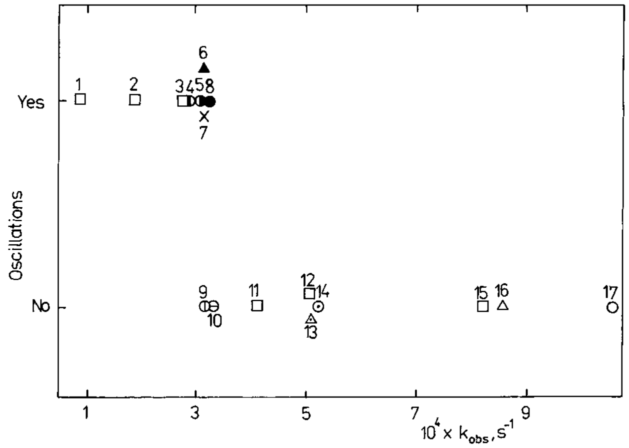

Figure 3. Influence of the obtained values of the rate constant k_{obs} for iodine removal on the behavior (oscillatory or not) of the BL system. The initial concentrations are given in the text of Figure 1 except for the □ symbols, where 0.39 M instead of 0.32 M H_2O_2 was used. Other experimental conditions and symbols are shown in Table 1.

measure the rate of transport of I_2 between the solution and the gas above it in the same experimental setup as used in the study of the BL reaction. We prepared a few standard solutions of 8.1×10^{-4} M I_2 in 0.05 M $HClO_4$ and measured the absorbance decrease at 470 nm at different gas-bubbling and stirring rates. Good pseudo-first-order kinetics were obtained for six runs with different methods of N_2 and O_2 bubbling at 100 rpm and also for five runs with different stirring rates under no bubbling (Figure 2). The corresponding rate constants k_{obs} calculated by use of eq 2 are presented in the Table 1, together with the values obtained in the earlier work.[9] In Figure 3 we can see that the changes of the rate parameter k_{obs} can cause the steady state to be stable or oscillatory. This behavior is consistent with the experimental effects of changing gas-bubbling and stirring rates (both in this work) or pressure[9] and suggests that the value of $k_{obs} = 3.2 \times 10^{-4}$ s^{-1} for transport of I_2 is critical under our given conditions. This value of the rate constant corresponds to the mass-transfer coefficient $k_{tr} = 1.60 \times 10^{-3}$ cm s^{-1}. No oscillations are observed above this estimated value. The minimal rate constant k_{obs} for transport of I_2 observed at no stirring at 101.3 kPa without gas bubbling can be increased at a stirring rate of 100 rpm at 101.3 kPa with a flow rate of 50 mL N_2 min^{-1} at the capillary immersed at the bottom of the reaction vessel by a factor of 12.8 under a given experimental setup. In agreement with the results in Figure 3, a flow rate of N_2 or O_2 higher than 50 mL min^{-1} through the BL reaction solution or through the standard solutions of I_2 caused a higher rate of iodine escape and no oscillations were observed in our set up.

Discussion

The simplest interpretation of the experimental results is that sufficient bubbling of gas into the BL system or sufficient stirring rate increases the rate of transport of volatile iodine from solution to the gas phase. Loss of I_2 changes the chemical kinetics and can take the oscillatory BL system into a regime without oscillations. This conjecture is advanced partly through analogy to the oscillatory Belousov−Zhabotinsky (BZ) system, where loss of Br_2 as vapor affects the BZ system.[11−13] In the BL system, equilibrium (eq 3)

$$HOI + I^- + H^+ \Leftrightarrow I_{2(aq)} + H_2O \qquad (3)$$

is established very quickly and through step 4

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

the concentrations of other important species, HOI and I^-, can be significantly influenced. We demonstrated that an increase of the rate of iodine escape (as described by eq 4) caused by gas bubbling at constant stirring rate can have the same effect as an increase of the stirring rate at constant slow gas flow or in the BL system without gas bubbling.

Nevertheless, we should discuss whether alternative interpretations are possible. The one obvious is a removal of oxygen by gas flow and stirring. It was found[14] that the concentration of dissolved oxygen can reach 0.04−0.06 M at 35 °C at 101.3 kPa. At 25 °C, the critical supersaturation seemed to be somewhat higher and was pushed to 0.068 M.[14] These values were estimated from a study of oxygen supersaturation, using the iodide-catalyzed decomposition of H_2O_2. At 25 °C and atmospheric pressure a maximum dissolved oxygen concentration of 0.12 M, or about 100 times the equilibrium solubility, was found.[15,16] The equilibrium solubility at this temperature is 0.001 26 M.[15] Of course, supersaturation can be easily removed by rapid stirring, sonication, or, probably, intensive gas flow. But no experimental evidence for this alternative were developed, and we do not know the rate of escape of O_2 gas from the BL solution under our experimental conditions, although increased flux of O_2 with increased stirring rate and bubbling can be expected. On the other hand, the nature of the gas bubbled into the BL system (N_2 or O_2) is certainly not the only important issue, although it can have some role. In addition, the bubbles of oxygen are formed in the BL reaction and then escape. That is the reason the rate of phase exchange of I_2 molecules in the real BL system at a given gas-bubbling or stirring rate could be a little higher than was measured in the standard I_2 solutions.

Experimental studies of the influence of the stirring rate mainly on the batch oscillating BZ system have been quite extensive. It has been suggested that it may be related to (a) supersaturation and/or phase exchange,[17−19] (b) concentration fluctuations,[20−23] (c) catalysis, e.g., at the platinum electrode,[21] (d) the effect on the rate constant of diffusion-controlled reaction,[24] (e) formation of nuclei,[25] or (f) oxygen under aerobic conditions in the BZ system.[26] Both the BL and classical BZ system have many similarities; however, the observed oscillations apparently involve distinctly different mechanisms. Despite the fact that both are based on oxyhalogen chemistry, CO_2 evolution in the BZ system and O_2 in the BL reaction can be observed. Owing to the irreversibility of process 1, oxygen must be permanently present in the BL system and, unfortunately, strictly anaerobic and closed conditions cannot be arranged.

Finally, we have shown that gas bubbling, sufficiently rapid stirring, or a pressure decrease greatly increases the rate of transport of iodine from solution, and we believe that in such a way the oscillations in the BL system can be inhibited.

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