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Simulations of the Iodine Interphase Transport Effect on the Oscillating Bray−Liebhafsky Reaction

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The effect of the iodine interphase transport originated from physical processes, such as pressure decrease, vigorous stirring, and/or an inert gas bubbling, on the dynamics of the oscillating Bray−Liebhafsky reaction is studied. Some new experiments were made at 60 °C that confirmed the possibility of suppressing oscillations by means of the iodine vapor removal from the reaction solution. It has been proved that the iodine vaporization is governed by the first-order kinetics with respect to the concentration of aqueous iodine, and a critical rate constant for iodine escape causing inhibition of the oscillatory mode was determined. The experiments were confronted with the models proposed by Kolar-Anić and Schmitz with co-workers. Both the models studied reflect the observed phenomenon. A simulation based on the latest model shows very good semiquantitative agreement with experiment, needing only a minor modification of the rate constants suggested by Kolar-Anić et al.

Introduction

Over 30 years before the discovery of the most studied and best understood Belousov−Zhabotinsky (BZ) oscillating reaction,[1] Bray[2] observed oscillations during the iodate-catalyzed disproportionation of hydrogen peroxide. The overall chemical change in the Bray−Liebhafsky (BL) system is described by a process (A):

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(aq)} + O_{2(g)} \tag{A}$$

Although the overall stoichiometry of the BL reaction appears to be much more simpler than that for the BZ system, this simplicity is actually a hindrance to gaining mechanistic understanding, because there are fewer composition variables which can be varied independently in order to observe the effects of such variation. However, an internally consistent mechanism for the oscillating BL reaction should ultimately be attainable, and recently two mechanisms and models of the BL reaction appeared.[3,4] In ref 3 the mechanism involving 10 individual steps was suggested in which the transport of oxygen from the supersaturated solution was a significant component of the overall mechanism of the batch BL oscillations. Noyes et al.[5] used this skeleton mechanism and proposed a model explored both analytically and numerically. Numerical integration for certain parameter values showed oscillations, but the model does not involve a true limit cycle.[5]

The mechanism for the BL reaction:

$$I^- + IO_3^- + 2H^+ \leftrightarrow HIO + HIO_2 \tag{R1}$$

$$HIO_2 + I^- + H^+ \rightarrow I_2O + H_2O \tag{R2}$$

$$I_2O + H_2O \leftrightarrow 2HIO \tag{R3}$$

$$HIO + I^- + H^+ \leftrightarrow I_2 + H_2O \tag{R4}$$

$$HIO + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \tag{R5}$$

$$I_2O + H_2O_2 \rightarrow HIO + HIO_2 \tag{R6}$$

$$HIO_2 + H_2O_2 \rightarrow IO_3^- + H^+ + H_2O \tag{R7}$$

was suggested by Kolar-Anić and Schmitz.[4] The reduction of iodate by hydrogen peroxide

$$IO_3^- + H_2O_2 + H^+ \rightarrow HIO_2 + O_2 + H_2O \tag{R8}$$

originally postulated by Liebhafsky,[6] is also considered as a possible step in the mechanism later proposed by Kolar-Anić et al.[7,8]

Peard and Cullis[9] confirmed oscillatory O_2 evolution in the BL reaction, which had been reported at 60 °C by Bray,[2] 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[10] 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[11,12] that the rate of interphase transport of I_2 can be greatly influenced by physical processes and that such physical processes can cause the oscillatory state to be inhibited. It is found that the value of the "pseudo rate constant" $k_{obs} = 3.2 \times 10^{-4}$ s^{-1} for I_2 removal is crucial in our setup 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} above which the batch BL oscillations are suppressed at 50 °C.

Very similar results for the BL reaction were found in a continuous flow tank reactor (CSTR) by Buchholtz and Bro-

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ecker.[13] They could show that in their experimental setup, when there was no gas phase above the solution in the CSTR, no oscillations could be observed at a high flow rate. At a flow rate above 4.3×10^{-4} s^{-1}, damped oscillations lead to a steady state at 60 °C.[13]

The aim of this work was testing the possibility to model the effects of various physical processes on oscillations in the BL reaction. Furthermore, several experiments were performed for the batch BL system at 60 °C because the rate constants used in simulations were usually determined or estimated at this elevated temperature and also to compare the behavior for the batch system with that in a CSTR as described in ref 13. And finally, the ability of the reaction mechanisms described mainly in refs 7 and 8 to simulate an oscillation behavior of the batch BL system, when gas bubbling, a pressure decrease, or stirring are used to remove the volatile species from the reaction solution, was analyzed.

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 same initial reactant concentrations as in our earlier work[12] were used: 0.36 M KIO_3, 0.05 M $HClO_4$, and 0.32 M H_2O_2.

The experiments were carried out in a well-thermostated (60.0 ± 0.1 °C) cylindrical glass reaction vessel (diameter, 3.5 cm; height, 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 commercial platinum indicator macroelectrode (0.5 cm × 0.8 cm) and a reference mercury(I) sulfate electrode were inserted into the solution. 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 gas (N_2 or O_2) was bubbled into the reaction vessel before starting, and the second hole was for a glass tube (diameter 0.5 cm), which was connected via tubing to the atmosphere. This second hole enabled outflow of gas used for reaching the required atmosphere (N_2 or O_2), and also for outflow of O_2 bubbles formed during the BL reaction and of iodine vapor.

The time-dependent change of the platinum redox potential was 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 stirbar (polygon shaped 2 cm × 0.8 cm). The stirring rate of the magnetic stirrer was kept constant at the rate of 100 rpm up 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 solution for at least 10 min.

To determine 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 some physical process (in this experimental part by various stirring) in the same reaction vessel, the time dependence of 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} spectrophotometrically (Zeiss Jena Specord UV spectrophotometer).

In our experimental setup (for experimental details, see ref 12), the following equation for the rate of I_2 escape can be obtained

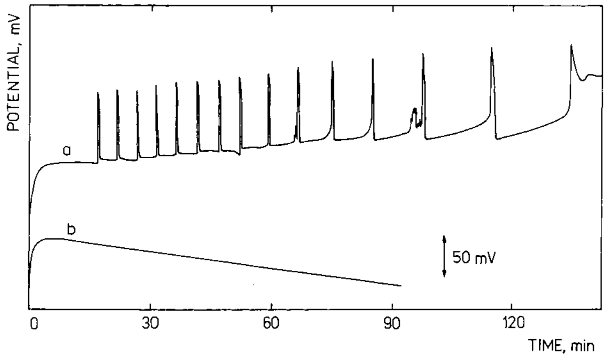

Figure 1. Potentiometric traces of the Bray−Liebhafsky oscillatory reaction obtained by a Pt redox electrode in the initial N_2 atmosphere at 60 °C: (a) at 100 rpm, (b) at 800 rpm. Curve b was shifted by some arbitrary offset. The initial concentrations are 0.36 M KIO_3, 0.32 M H_2O_2, and 0.05 M $HClO_4$.

$$v_{esc} = -d[I_2]_{aq}/dt = k_{obs}[I_2]_{aq} \tag{1}$$

where $[I_2]_{aq}$ is the iodine concentration in the solution and k_{obs} is a constant depending on the stirring rate while the other parameters are fixed. Values of k_{obs} were obtained from at least three measurements and calculated from plots of ln (A_0/A) vs time.

Simulations. Computer simulations were carried out on an HP 735 workstation by means of numerical integration of a differential equation system derived from a model under study. Concentrations of the six species I^-, HIO, HIO_2, I_2, I_2O, and H_2O_2 were set as variables. Calculations were performed using the Fortran subroutine LSODE from a systematized collection of ODE solvers—ODEPACK[14] with an absolute error tolerance of 10^{-30} and a relative error tolerance of 10^{-6}. The initial concentration values of all the species not referred to be present at the reaction beginning were set as zero.

Results and Discussion

Our experiments show that the oscillating behavior of the platinum redox electrode in the batch BL reaction depends on the stirring rates in the initial both N_2 and O_2 atmosphere at 60 °C (Figure 1). As can be seen in Figure 1a, at the relatively higher temperature of 60 °C (in comparison with 50 °C in ref 12) both the induction period (IP) and the period of oscillations (PO) are shortened at 100 rpm. The IP decreased approximately to a half, the first PO to a quarter, while amplitudes of the oscillations (AO) are not significantly sensitive to changes of the temperature from 50 to 60 °C at 100 rpm. The number of oscillations ranged from 15 to 17 and oscillations collapsed into a higher Pt redox steady state that corresponded to the colorless reaction solution. A variation of the stirring rate from 50 to 1000 rpm shows that the BL oscillations are completely suppressed when the stirring rate is increased above 300 rpm in our setup (Figure 1b).

We were able to 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 system at 60 °C. The absorbance decrease in standard iodine solutions was measured at different stirring rates, and the corresponding rate constants k_{obs} were calculated by use of eq 1 (Figure 2). The results obtained are similar to those at 50 °C. The value of the rate constant of $k_{obs} = 4.64 \times 10^{-4}$ 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 $k_{tr} = k_{obs}V_{sol}$/surface area $= 2.33 \times$

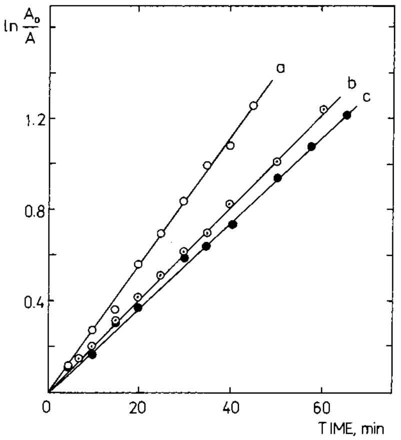

Figure 2. "Pseudo-first-order" kinetics of interphase transport of iodine from the standard 8.1×10^{-4} M I_2 solution for the BL experimental setup: (a) 60 °C and 300 rpm (corresponds to the critical value of $k_{obs} = 4.6 \times 10^{-4}$ s^{-1} at 60 °C); (b) 50 °C and 300 rpm; (c) 50 °C and 200 rpm (corresponds to the critical value of $k_{obs} = 3.2 \times 10^{-4}$ s^{-1} at 50 °C).

10^{-3} cm s^{-1}. No oscillations are observed above this value. It should be noticed that our experiments at 60 °C do not show any oscillations above 300 rpm while the stirring rate above 200 rpm is sufficient to reach a steady state in our setup at 50 °C.

Simulations. A set of reactions R1−R6 is sufficient for the simulation of the oscillatory evolution.[15] The oxidation of iodous acid by hydrogen peroxide (R7) was introduced later[4] to account for some experimental findings concerning in particular the induction period. The latest modification of the Kolar-Anic and Schmitz's model, represented by introducing the slow reaction R8, further improves agreement between the model and experimental behavior. In our simulations we checked both reaction sets R1−R7 and R1−R8 for the ability to reflect the effect of iodine interphase transport on the oscillatory dynamics of the BL reaction described in the previous works.[11,12]

A model including reactions R1−R7 complemented by the physical process of iodine interphase transport

$$I_{2(aq)} \rightarrow I_{2(g)} \qquad \text{(R9)}$$

shows strong sensitivity toward the parameter k_{obs}. Using the rate constants and initial conditions as in ref 4 at 60 °C, a simulation reveals a widening of the oscillation period for $k_{obs} = 3 \times 10^{-2}$ min^{-1} under concentration conditions as follows: $[H_2O_2]_0 = 0.005$ M; $[IO_3^-]_0 = 0.098$ M, $[H^+]_0 = 0.0733$ M (ref 4, Figure 2c), and $[I^-]_0 = 1.0 \times 10^{-8}$ M. The oscillations are completely suppressed at $k_{obs} = 4 \times 10^{-2}$ min^{-1}. This value is comparable to those used for iodine removal in the experiments,[11,12] despite the different concentration and temperature conditions. Since the rate constant of the forward reaction R3 was a subject of some uncertainty in the proposed models, we also tested variation of that parameter. A decrease of k_3 from 1×10^6 min^{-1} down to 6×10^5 min^{-1} brings about formation of an induction period under the same conditions as mentioned above without the iodine removal. Further decrease leads to suppression of the oscillations at $k_3 = 4 \times 10^5$ min^{-1}. So it may be concluded that the rate constant k_3 can significantly influence the dynamics of the studied model and its value cannot be chosen arbitrarily.

Other important information that is usually omitted when reporting kinetics simulations is the initial concentration values for species not present at the reaction beginning as was recently pointed out by Pereira and Faria.[16] To avoid a divide-by-zero condition when exact zero starting values are attributed to some concentrations, for many numerical integrators it is necessary to set an arbitrary concentration "background" of level, say 1×10^{-10} M, for all the species not initially present. This is not the case when integrators with both absolute and relative error tolerance control, such as the ODEPACK package routines, are used. Then the "background" corresponds to the absolute error tolerance that is set as 1×10^{-30} for all the species in our simulations. Dealing with the studied models of the BL reaction, the initial concentration value problem arises particularly for I^- ions. Iodide is not initially added into the reaction mixture in the experiments with the BL reaction; however, I^- ions are essential to start up the dynamics of the models. Kolar-Anić and Schmitz[4] do not refer any initial concentration values in their numerical simulations except those for H_2O_2, IO_3^-, and H^+. Our calculations show that the $[I^-]_0$ value, at least in some cases, may considerably affect the simulated time course, hence it should rather be given as well as the initial concentrations of the other reactants. While a variation of the $[I^-]_0$ value in the range from 2.5×10^{-8} M down to 1×10^{-10} M causes only a negligible shift between the time plots, a decrease of the initial iodide concentration to the value of 1×10^{-12} M brings about a significant prolongation of the induction period (ca. 100 min more), together with a change of its shape that turns to a sigmoidal one (Figure 3). It should be mentioned that at the very beginning of the reaction the iodide concentration falls from the initial value to a minimum before its autocatalytic production is started for all the $[I^-]_0$ values that have been tested.

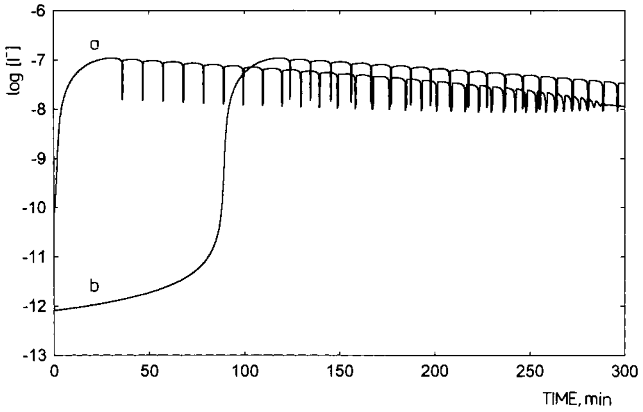

Figure 3. Effect of the initial concentration of iodide ions on simulations with the R1−R7 model. The initial concentrations are 0.098 M IO_3^-, 0.05 M H_2O_2, 0.0733 M H^+, (a) 1×10^{-10} M I^- and (b) 1×10^{-12} M I^-.

The second subject of our study was the latest model so far proposed by Kolar-Anić with co-workers,[7,8] consisting of the reactions R1−R8. The authors show an oscillatory regime for the following initial concentrations: $[H_2O_2]_0 = 0.35$ M; $[IO_3^-]_0 = 0.0733$ M; $[H^+]_0 = 0.0490$ M at 60 °C.[7,8] Addition of the iodine removal process (R9) to the model with $k_9 = 3 \times 10^{-2}$ min^{-1}, similarly as in the previous case, causes a widening of the oscillatory period and lowering of the number of oscillations. Under the given conditions, the oscillations are suppressed, increasing the iodine removal up to the value of 4×10^{-2} min^{-1} as for the previous model. The initial iodide concentration used in the simulations was $[I^-]_0 = 2.5 \times 10^{-8}$ M. An effect of the k_3 value variation on the reaction dynamics can be detected again. Our simulations show oscillations for a value of k_3 in the range from 3.5×10^3 up to 2×10^4 min^{-1} using the same initial conditions already mentioned for the second model

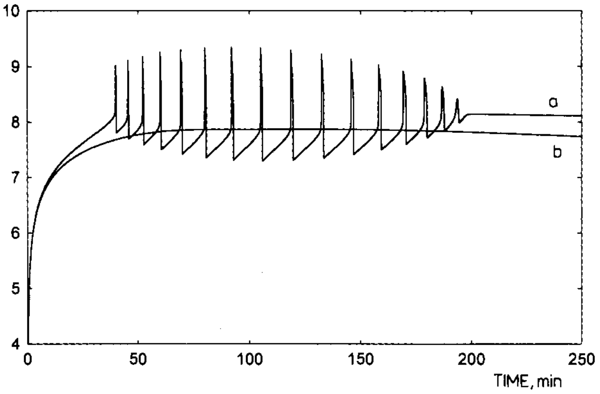

Figure 4. A simulation of the iodine interphase transport effect on the BL reaction. The initial concentrations are 0.36 M IO_3^-, 0.32 M H_2O_2, 0.05 M H^+, 1.0×10^{-8} M I^-. Model R1−R9, rate constants as in Table 1 with (a) $k_9 = 2.0 \times 10^{-2}$ min^{-1} and (b) 4.5×10^{-2} min^{-1}.

without iodine removal. The authors report a value of 5×10^3 min^{-1} (ref 7) for the rate constant of the reaction R3 in the forward direction, whereas the value $k_3 = 1 \times 10^6$ min^{-1} (ref 4) was used in the previous model (reactions R1−R7). The value of the rate constant k_6 has also been significantly decreased by 2 orders of magnitude. Other rate constants remain unchanged, except minor modification of k_{-3}. In contrast to the previous model, the initial iodide concentration has practically no effect on the dynamics of the model including reaction R8 under the conditions under study. The time dependence of the iodide concentration also initially drops to a minimum, but then rises rapidly to a trajectory that is almost the same for all the $[I^-]_0$ values tested of the range from 10^{-20} up to 10^{-7} M. Thus it may be stated that the addition of the reduction of iodate by hydrogen peroxide (R8) to the previous model of the BL reaction proposed by Kolar-Anić and Schmitz preserves the ability of the model to suppress the oscillations when iodine escapes from the system according to the first-order kinetics and that reaction R8 stabilizes the dynamics of the model toward the initial iodide concentration.

The reasonability of a model can be reliably confirmed only in confrontation with experimental reality. Since the rate constants proposed by Kolar-Anić et al. for their models studied in this paper correspond to a temperature of 60 °C, we performed new experiments of the iodine removal effect on the BL reaction at this temperature as described above. The suppression of the oscillations has been observed for a critical value of iodine interphase transport equal to 4.6×10^{-4} s^{-1} under the conditions given in Figure 1. Simulations using the latest model by Kolar-Anić et al. complemented with the iodine escape step show (Figure 4) satisfactory agreement with our experiments, needing only a minor modification of several rate constants (Table 1), which may be in part be ascribed to different ionic strengths. There is some discrepancy between the measured (ca. 16 min) and calculated (ca. 40 min) induction periods of the reaction. This is, perhaps, due to iodine compound impurities present at the beginning of the experiments. The simulated period and number of oscillations are in very good agreement with experiment. A small difference in shape of a calculated and observed oscillation may be attributed to the fact that the measured potential of the Pt electrode is a more complex quantity than the logarithm of the ratio $[I_2]/[I^-]$ used in our simulations. Finally, the most important question is if the oscillations vanish when iodine removal of a critical k_{obs} value is introduced into the studied model under conditions used in the experiment. Simulations show that the latest model by Kolar-Anić et al. with the rate constant as in Table 1 reflects this experimental finding, and a suppression of oscillatory behavior occurs at $k_9 = 7.5 \times 10^{-4}$ s^{-1} (Figure 4b). This value is somewhat higher than the experimental one (4.6×10^{-4} s^{-1}); nevertheless, agreement may be treated as satisfiable. Moreover, the value of $k_{obs} = 4.6 \times 10^{-4}$ s^{-1} has been determined as a rate of iodine escape from an I_2 solution in water under the conditions corresponding to the critical condition in the BL reaction mixture as a stirring rate and/or a nitrogen flow rate are concerned. It means that an actual rate of I_2 escape from a real BL reaction solution is a little higher than the determined value because of an oxygen gas stream evoluted during the reaction course that may accelerate vaporization of I_2 molecules.

TABLE 1: Rate Constants Used in Simulations for the BL Reaction

reaction	rate	rate constant
R1	$k_1[IO_3^-][I^-][H^+]^2$	$k_1 = 1.8 \times 10^5$ M^{-3} min^{-1}
R−1	$k_{-1}[HIO][HIO_2]$	$k_{-1} = 7.91 \times 10^7$ M^{-1} min^{-1}
R2	$k_2[HIO_2][I^-][H^+]$	$k_2 = 5.0 \times 10^{11}$ M^{-2} min^{-1}
R3	$k_3[I_2O]$	$k_3 = 5.0 \times 10^3$ min^{-1}
R−3	$k_{-3}[HIO]^2$	$k_{-3} = 3.15 \times 10^8$ M^{-1} min^{-1}
R4	$k_4[HIO][I^-]$	$k_4 = 3.0 \times 10^{11}$ M^{-1} min^{-1}
R−4	$k_{-4}[I_2]/[H^+]$	$k_{-4} = 4.50$ M min^{-1}
R5	$(k_5' + k_5''[H^+])[HIO][H_2O_2]$	$k_5' = 1.2 \times 10^4$ M^{-1} min^{-1} $k_5'' = 3.0 \times 10^4$ M^{-2} min^{-1}
R6	$k_6[I_2O][H_2O_2]$	$k_6 = 2.0 \times 10^5$ M^{-1} min^{-1}
R7	$k_7[HIO_2][H_2O_2]$	$k_7 = 6.0 \times 10^2$ M^{-1} min^{-1}
R8	$(k_8' + k_8''[H^+])[IO_3^-][H_2O_2]$	$k_8' = 2.7 \times 10^{-4}$ M^{-1} min^{-1} $k_8'' = 1.12 \times 10^{-2}$ M^{-2} min^{-1}
R9	$k_9[I_2]$	k_9 = parameter

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