



Bray–Liebhafsky oscillations at room temperature

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Abstract

Concentration ranges where Bray–Liebhafsky oscillations appear at room temperature have been explored. The periods are very long and the maxima of the iodine concentration little reproducible, most likely due to the effect of the oxygen produced by the reaction. The experimental results are compared to numerical simulations made with the model published in the same issue of this journal.

Keywords Bray–Liebhafsky · Room temperature · Stirring effects · Oxygen effects

Introduction

When Bray [1] discovered oscillations in the iodate–iodine–hydrogen peroxide system at 60 °C, he thought this was the first example of chemical oscillations in homogeneous solution. These oscillations being accompanied by the formation of oxygen bubbles, Bray wanted to prove that they are not responsible for the oscillations. He carried out experiments at 25 °C under conditions where the reaction was slow enough that oxygen left solution by diffusion without forming bubbles. In the example he published, the period of oscillations is several days. The possibility of obtaining chemical oscillations in homogeneous solution was however disputed until the discovery 37 years later of the Belousov–Zabotinsky oscillating reaction [2].

Subsequently, the Bray–Liebhafsky reaction has almost always been studied around 50–60 °C. Oscillations at 25 °C have only been mentioned in two articles [3, 4]. This work is part of our study of the reactions of iodine compounds at different degrees of oxidation with each other and with hydrogen peroxide. An update of our earlier model is proposed in the same issue of this journal [5] and is reproduced in the appendix. Many kinetic constants are only known at 25 °C and we wanted to compare experimental Bray–Liebhafsky oscillations with simulations using this

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model. Many of the same reactions are also important in the Briggs–Rauscher oscillator which is usually studied near room temperature. The periods at 25 °C are very long and the experiments take a long time, but the main problem is that the oscillations are little reproducible. Another aim of this work is to explore the reasons for this lack of reproducibility.

Experimental and calculations

Solutions were prepared from stock solutions of HClO_4 , KIO_3 , I_2 , and H_2O_2 . The reagents are of the best purity commercially available and used without further purification. The 18 M Ω water is supplied by a Barnstead Micropore ST model. A small amount of I_2 was added initially to shorten the first period of the oscillations. If the initial concentration of I_2 is larger, the oscillations begin with a decrease of the I_2 concentration. Absorbance changes were followed with an Agilent Cary 60 scanning spectrophotometer, focusing on the iodine peak near 460 nm. The cell chamber was thermostatically controlled at 25 °C. The effect of using or not using a micro-stirrer in the cell is discussed in the text.

The spectrophotometer results are transferred to a computer and the analytical calculations are done with Excel. They are compared with the numerical results obtained using the model in the appendix. Differential equations associated with this model were integrated in Reading using COPASI (<https://copasi.org>) and in Brussels using the *ode15s* function of MATLAB (www.mathworks.com) specially adapted to stiff differential equations. Simulations gave the same results. The absorbances at 460 nm are calculated from $746 \times [\text{I}_2] + 975 \times [\text{I}_3^-]$.

Results

Effect of light

The effect of light on the BL reaction is well known [6, 7] and certainly important with modern spectrophotometers using a xenon lamp. Light decreases the amplitude of oscillations and can suppress them. We minimized this effect by leaving the lamp off during the experiments except short times to measure absorbances periodically (generally every 30 min). The presence or absence of a UV filter in the light beam had no effect. The results presented can be considered as representative of the reaction in the dark.

Effect of stirring

Our first series of experiments were carried out with a mini-stirrer in the cell. Fig. 1a and c show regular oscillations obtained when this mini-stirrer remained at the surface of the solution by the effect of surface tension. However, the mini-stirrer sank frequently to the bottom giving very irregular oscillations as in Fig. 2.

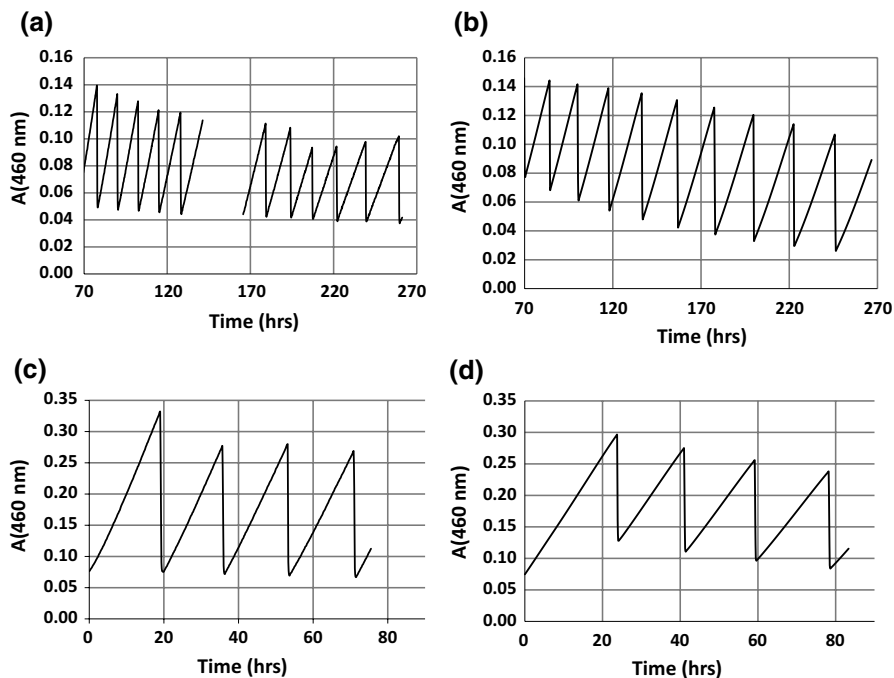
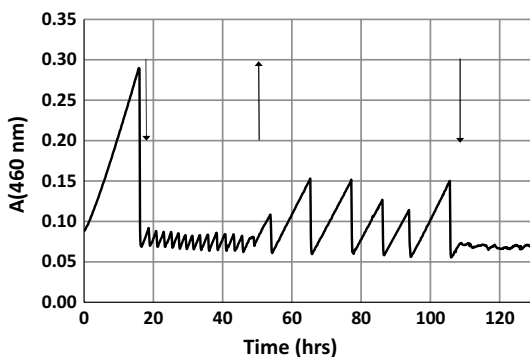


Fig. 1 **a** $[\text{HClO}_4]_0 = 0.030 \text{ M}$; $[\text{KIO}_3]_0 = 0.033 \text{ M}$; $[\text{I}_2]_0 = 1.0 \times 10^{-4} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 0.16 \text{ M}$; Stirrer at the surface of the solution; No measurement between 150 and 165 h. **c** Same concentrations as in **(a)**; stirrer at the surface of the solution with a probably slower rotation rate. **b** Simulation of the experiment **(a)** with the kinetic constants in the appendix, $k_{12a} = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{14} = 5 \times 10^{-5} \text{ s}^{-1}$ (slow oxygen escape rate). **d** Simulation of the experiment **(c)** with the kinetic constants in the appendix, $k_{12a} = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{14} = 5 \times 10^{-4} \text{ s}^{-1}$ (fast oxygen escape rate)

Fig. 2 Effect of stirrer position. $[\text{HClO}_4]_0 = 0.030 \text{ M}$; $[\text{KIO}_3]_0 = 0.033 \text{ M}$; $[\text{I}_2]_0 = 1.2 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{O}_2]_0 = 0.16 \text{ M}$. No stirrer initially. A mini stirrer was inserted after the first maximum but fell to the bottom of the cell. It was brought to the surface with an external magnet after about 50 h but fell to the bottom after about 110 h



With the stirrer on the bottom, small bubbles tended to form and be attached to the stirrer. Various methods were tried to keep the stirrer on top, but were unsuccessful. Experiments with a stirrer usually giving irregular oscillations, the following runs were made without a stirrer.

Fig. 1a and c show another problem. The amplitudes of the oscillations are very different although the initial concentrations are the same. We attribute this difference to different rates of transfer of produced oxygen to the gas phase. We suspect that the stirrer rotation rate was lower in the case of Fig. 1a but did not measure this rate to avoid the effect of outside lights. Fig. 1b and d show simulations obtained with the model in the appendix. They are obtained by changing only the value of the oxygen transfer parameter k_{14} .

Effect of oxygen

With a nearly full cell tightly stoppered, oscillations did not occur. With a stopper with a small capillary opening to control oxygen escape, oscillations usually occurred. Presumably, high oxygen pressure inhibits oscillations. One experiment with simultaneous absorbance and pressure readings showed that the rise in pressure is faster when the I_2 concentration is decreasing, in agreement with previous studies showing that most oxygen evolution is associated with oxidation of iodine to iodate after a drop in iodide concentration [8].

Without stirring and with a Teflon stopper not tightly closed, the oscillations were sometimes regular as in Fig. 3 but sometimes very irregular. In this case, it is the transition from increasing $[I_2]$ (reaction R) to decreasing $[I_2]$ (reaction O) that is most variable. Reactions R and O are discussed in [9]. The iodide concentration being maximum near the transition from reaction R to reaction O, this supports the former assumption that the uncontrolled variables are related with the iodide oxidation by oxygen. It is obvious that there are some uncontrolled variables here, even though the whole system is on automatic and untouched for days. Without stirrer and with a stopper with capillary controlling the rate of oxygen escape we suspect that the oscillations are not reproducible because the nucleation-growth phenomena of the bubbles are not. The reproducibility of the oscillations is all the less good the greater the rate of oxygen production.

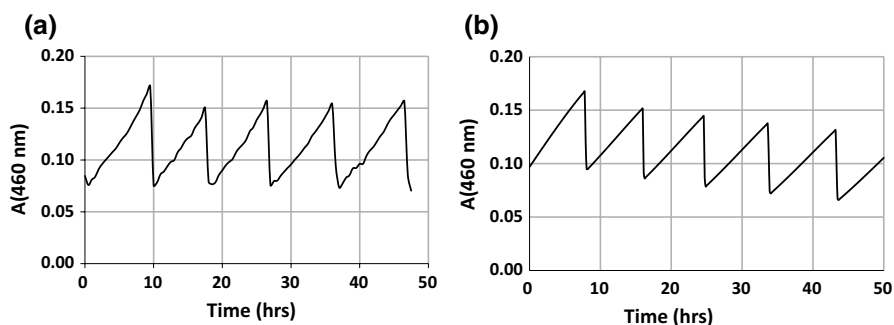


Fig. 3 a $[HClO_4]_0 = 0.030$ M, $[KIO_3]_0 = 0.048$ M, $[H_2O_2]_0 = 0.12$ M, $[I_2]_0 = 1.3 \times 10^{-4}$ M; No stirrer; Stopper with capillary. b Simulation with the kinetic constants in the appendix, $k_{12a} = 1 \times 10^7$ M $^{-1}$ s $^{-1}$; $k_{14} = 1 \times 10^{-4}$ s $^{-1}$

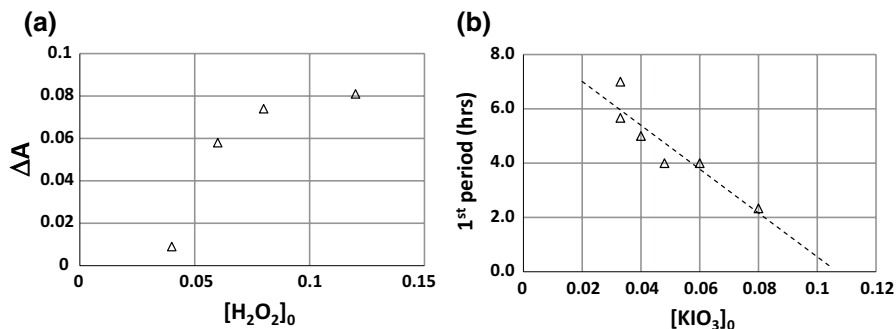
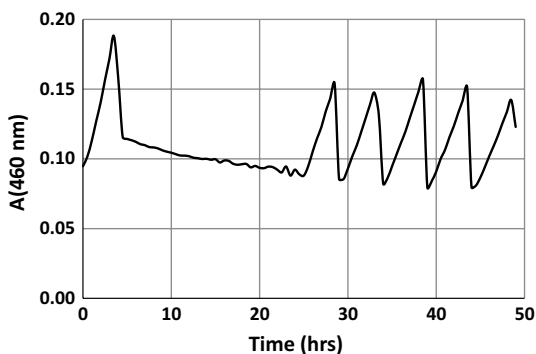


Fig. 4 **a** Effect of the H_2O_2 initial concentration on the amplitude ΔA of the first oscillation. $[\text{HClO}_4]_0=0.030$ M, $[\text{KIO}_3]_0=0.048$ M. **b** Effect of the KIO_3 initial concentration on the period of the first oscillation. $[\text{HClO}_4]_0=0.030$ M, $[\text{H}_2\text{O}_2]_0=0.16$ M

Fig. 5 Typical evolution when $[\text{H}_2\text{O}_2]$ is large. $[\text{HClO}_4]_0=0.030$ M, $[\text{KIO}_3]_0=0.048$ M, $[\text{H}_2\text{O}_2]_0=0.24$ M, $[\text{I}_2]_0=1.3 \times 10^{-4}$ M



Effect of concentrations

The effect of $[\text{H}_2\text{O}_2]$ was studied for $[\text{HClO}_4]_0=0.030$ M and $[\text{KIO}_3]_0=0.048$ M. The minimum value of $[\text{H}_2\text{O}_2]$ giving oscillations is about 0.04 M (see Fig. 4a). Then, the amplitude ΔA of the oscillations increases when $[\text{H}_2\text{O}_2]$ increases. The periods decrease from about 10 h to about 3 h. When $[\text{H}_2\text{O}_2]_0=0.20$ M, a new phenomenon appears illustrated by Fig. 5. A first peak smaller than expected is followed by a regular decrease in absorbance before oscillations reappear. We attribute this evolution to the effect of oxygen. Its production rate increases when the concentration of H_2O_2 increases. In the example of Fig. 5, the solution becomes supersaturated with oxygen, which may explain the suppression of the oscillations. Then the concentration of H_2O_2 decreases and the oscillations reappear when it becomes small enough. The model qualitatively confirms this explanation but does not make it possible to reproduce the experimental curves because the reversibility of R6 followed by R12 is clearly an over-simplification of these phenomena. Let us also recall that we have shown that a radical mechanism of reduction of iodate by H_2O_2 appears when the concentration of H_2O_2 becomes greater than about 0.2–0.3 M [10].

The effect of $[\text{KIO}_3]$ was studied for $[\text{HClO}_4]_0 = 0.030 \text{ M}$ and $[\text{H}_2\text{O}_2]_0 = 0.16 \text{ M}$. If $[\text{KIO}_3] < 0.03 \text{ M}$, one obtains large non-reproducible oscillations. Then, the period of the oscillations decreases (see Fig. 4b). If $[\text{KIO}_3] > 0.10 \text{ M}$, no more oscillations are obtained.

Regular oscillations are obtained only around $[\text{HClO}_4] \sim 0.03 \text{ M}$ when $[\text{KIO}_3]_0 = 0.048 \text{ M}$ and $[\text{H}_2\text{O}_2]_0 = 0.16 \text{ M}$. If $[\text{HClO}_4] = 0.02 \text{ M}$, large non-reproducible oscillations are obtained. One experiment with $[\text{HClO}_4] = 0.037 \text{ M}$ gave a behavior similar to Fig. 5. If $[\text{HClO}_4] = 0.04 \text{ M}$, the absorbance decreases continuously suggesting a stable steady state of slow catalytic disproportionation of H_2O_2 .

Conclusions

The BL system do oscillate at room temperature, although the oscillations are strongly dependent on light, stirring and oxygen concentration. It is difficult to obtain reproducible oscillations because it is difficult to control these factors and perhaps other unknown factors. The concentration of oxygen, a product of the reaction, is difficult to control because the solution becomes supersaturated and the formation of oxygen bubbles seems stochastic. The reaction could be studied under conditions where the production of oxygen is slow enough not to form bubbles, as in the example given by Bray in his historical article [1]. The effect of oxygen being most likely due to the oxidation of iodide by a radical mechanism, the rate of this reaction should also be controlled. We considered removing it by adding a radical scavenger, but the ones we tried react with iodine compounds and only complicate the kinetics of the system. The oxidation of iodide by oxygen deserves a new kinetic study.

The erratic nature of many of the experiments precludes a strong test of the proposed model. It has successfully depicted various sub-systems of the BL oscillator and oscillations at 50°C , but gives only semi quantitative, sometimes only qualitative, simulations of the room temperature oscillations. Moreover, the mechanism of the oxidation of iodide by oxygen remains unknown and the part of the model simulating it is an over-simplification. We had shown that an extension of this model is able to explain the Briggs–Rauscher oscillations which seem much less sensitive to oxygen. The study of the oscillations with malonic acid or other substrate and with or without metal catalyst is ongoing.

Appendix: kinetic model [5]

R1	$\text{IO}_3^- + \text{I}^- + 2 \text{H}^+ \rightleftharpoons \text{HOI} + \text{HOIO}$ $r_1 = k_1 [\text{IO}_3^-] [\text{I}^-] [\text{H}^+]^2 - k_{-1} [\text{HOI}] [\text{HOIO}]$	$k_1 = 1300$	$k_{-1} = 212$
R2	$\text{HOIO} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2\text{O} + \text{H}_2\text{O}$ $r_2 = k_2 [\text{H}^+] [\text{HOIO}] [\text{I}^-] - k_{-2} [\text{I}_2\text{O}]$	$k_2 = 5 \times 10^9$	$k_{-2} = 1.02^a$
R3	$\text{I}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2 \text{HOI}$ $r_3 = k_3 [\text{H}^+] [\text{I}_2\text{O}] - k_{-3} [\text{H}^+] [\text{HOI}]^2$	1×10^{7a}	$k_{-3} = 2.44 \times 10^8$

R4	$\text{HOI} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2 + \text{H}_2\text{O}$ $r_4 = k_4 [\text{HOI}][\text{I}^-] - k_{-4} [\text{I}_2]/[\text{H}^+]$	$k_4 = 1.7 \times 10^9$	$k_{-4} = 1.8 \times 10^{-3}$
Reactions down			
R5	$\text{HOI} + \text{H}_2\text{O}_2 \rightleftharpoons \text{HOOI} + \text{H}_2\text{O}$ $r_5 = k_5 [\text{HOI}][\text{H}_2\text{O}_2] - k_{-5} [\text{HOOI}]$	$k_5 = 6$	k_{-5} neglected
R6	$\text{HOOI} \rightleftharpoons \text{I}^- + \text{H}^+ + \text{O}_2$ $r_6 = k_6 [\text{HOOI}] - k_{-6} [\text{I}^-][\text{H}^+] [\text{O}_2]$	$k_6 = 1 \times 10^8$	$k_{-6} = 1 \times 10^5$
R7	$\text{HOIO} + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{O}_2 + \text{H}_2\text{O}$ $r_7 = k_7 [\text{HOIO}][\text{H}_2\text{O}_2]/[\text{H}^+]$	$k_7 = 0.5$	
R8	$\text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{O}_2 + \text{H}_2\text{O}$ $r_8 = (k'_8 + k''_8[\text{H}^+]) [\text{IO}_3^-] [\text{H}_2\text{O}_2]$	$k'_8 = 1.3 \times 10^{-7}$	$k''_8 = 1.5 \times 10^{-5}$
Reactions up			
R9	Net: $\text{HOIO} + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$ $r_9 = k_9 [\text{H}_2\text{O}_2] [\text{HOIO}]^2 / \{[\text{H}^+] (1 + \alpha_9[\text{H}_2\text{O}_2])\}$	$k_9 = 1.7 \times 10^5$	$\alpha_9 = 10$
R10	$\text{I}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{HOIO}$ $r_{10} = (k'_{10} + k''_{10}[\text{H}^+]) [\text{I}_2\text{O}] [\text{H}_2\text{O}_2]$	$k'_{10} = 5 \times 10^5$ ^a	$k''_{10} = 4.1 \times 10^4$ ^a
R11	$\text{I}^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{H}_2\text{O}$ $r_{11} = (k'_{11} + k''_{11}[\text{H}^+]) [\text{I}^-] [\text{H}_2\text{O}_2]$	$k'_{11} = 0.012$	$k''_{11} = 0.17$
Effect of oxygen			
R12	$\text{HOOI} + 2 \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{O}_2 + 2 \text{H}_2\text{O}$ Global radical reaction beginning with $\text{HOOI} + \text{H}_2\text{O}_2 \rightarrow \text{HOO}^* + \text{H}_2\text{O} + \text{IO}^*$ (R12a) $r_{12} = k_{12a} [\text{H}_2\text{O}_2] [\text{HOOI}]$	$k_{12a} \sim 1 \times 10^7$	
Side reactions			
R13	$2 \text{HOIO} \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+$ $r_{13} = (k'_{13}/[\text{H}^+] + k''_{13}/[\text{H}^+]^2) [\text{HOIO}]^2$	$k'_{13} = 0.045$	$k''_{13} = 0.065$
R14	$\text{O}_2 \rightleftharpoons \text{O}_2(\text{g})$ $r_{14} = \max(0; k_{14} ([\text{O}_2] - [\text{O}_2]_{\text{sat}}))$	See note ^b	$[\text{O}_2]_{\text{sat}} = 1.25 \times 10^{-3}$
R15	$\text{I}_2 \rightleftharpoons \text{I}_2(\text{g})$ $r_{15} = k_{15} [\text{I}_2]$	See note ^c	
R16	$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$ $r_{16} = 5 \times 10^9 ([\text{I}_2][\text{I}^-] - [\text{I}_3^-]/K_{16})$	$K_{16} = 713$	
R17	$\text{HIO}_3 \rightleftharpoons \text{IO}_3^- + \text{H}^+$ $r_{17} = 5 \times 10^9 (K_{17} [\text{HIO}_3] - [\text{IO}_3^-][\text{H}^+])$	$K_{17} = 0.28$	
R18	$\text{HOI} + \text{H}^+ \rightleftharpoons \text{H}_2\text{OI}^+$ $r_{18} = 5 \times 10^9 (K_{18} [\text{HOI}] [\text{H}^+] - [\text{H}_2\text{OI}^+])$	$K_{18} = 0.3$	
R19	$\text{HOIO} + \text{H}^+ \rightleftharpoons \text{H}_2\text{OIO}^+$ $r_{19} = 5 \times 10^9 (K_{19} [\text{HOIO}] [\text{H}^+] - [\text{H}_2\text{OIO}^+])$	$K_{19} \sim 0$	

^aAs indicated in our other article in this journal [5], the numerical results only depend on the ratios k_{-2}/k_3 , k'_{10}/k_3 and k''_{10}/k_3 and not on the value of k_3 if it is large enough for the concentration $[\text{I}_2\text{O}]$ being quasi-stationary. We use $k_3 = 1 \times 10^7$ giving the values of k_{-2} , k'_{10} and k''_{10} in this table. $k_3 = 1 \times 10^8$ with k_{-2} , k'_{10} and k''_{10} ten times larger give the same results

^bDepends on experimental conditions and stirring rate. Values around 1×10^{-4} usually give good simulations

^cSome iodine can be lost to the gas phase. Direct loss through the interface seems unimportant and $k_{15} = 0$ was used. Loss of iodine vapor in the oxygen bubbles could have an effect but is difficult to model

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