The Effect of Light on the Bray−Liebhafsky Reaction

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The effect of light on the Bray−Liebhafsky oscillatory reaction was studied at 55 °C. It was found that both the induction time and period decreased with the increasing light intensity, and at a critical value of intensity, dependent on the initial concentration of the reactants, oscillation disappeared. The reaction scheme proposed by Schmitz was extended with a direct reaction of I_2 with H_2O_2. By taking into account the latter reaction, the oscillations were numerically calculated and good agreements with the experimental data were found.

Introduction

Although the oscillatory Bray−Liebhafsky reaction is known[1] since 1921, there is still no detailed explanation for its behavior under different conditions. This is because the mechanism of this fascinating reaction have not been explored completely. At the very beginning of the studies on the Bray-reaction it was concluded and later confirmed that H_2O_2 can both oxidize and reduce the iodine species in acidic medium.[2,3] The overall results of the processes can be formulated by the following two equations:

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

$$5H_2O_2 + I_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O$$

The final result of the above two reactions is the decomposition of H_2O_2 into water and oxygen, i.e.,

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

It was shown by Bray and Liebhafsky and later by Degn and Higgins[1,2,4,5] that the reaction was sensitive to light, and according to their investigations oscillations occurred in the absence of light. Shaw and Pritchard reported[6] that the oscillations disappeared in the absence of light. The most extensive studies on the effect of light on the Bray-reaction were performed by Noyes et al.[7−9] According to their observations light can promote or inhibit the oscillations depending on the initial concentration of the reactants, but the effect of light on the reaction was not explained quantitatively. To our best knowledge, no report on the effect of light on the Bray reaction has been published since Noyes' s works appeared, although the effect of another parameters such as pressure on the reaction has been investigated.[10,11]

Experimental Section

Materials. H_2O_2, $NaIO_3$, $HClO_4$, and $KMnO_4$ were purchased from Reanal (Hungary) and were used as received. The concentration of H_2O_2 was determined permanganometrically.

Experimental Setup and Measurements. The experiments were carried out in a double-walled glass reactor of 110 mL thermostated at 55 °C. The reactor was charged with KIO_3 and $HClO_4$ solutions, and the reaction was started by adding H_2O_2 solution to the reaction mixture. The total volume of the reaction mixture was 60 mL. The reaction was monitored with a Radelkis OP-I-0711P type iodide selective electrode in conjunction with an Orion 90-02 type double-junction reference electrode. To avoid the effect of light, the reactions were performed in a dark room. A tungsten lamp of 100 W was used to study the effect of light on the reaction by changing the distances between the reactor and the lamp. The light intensity was measured with a Se-type photoelement. To eliminate direct heating of the reaction mixture, a glass container filled with water was placed between the reactor and the light source.

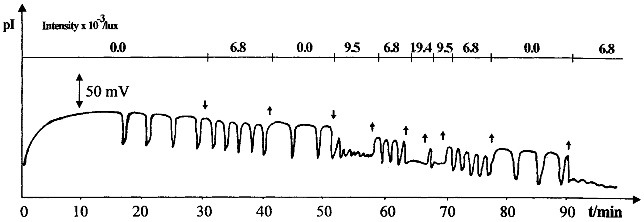

Figure 1. The effect of the light on the Bray−Liebhafsky reaction monitored by iodide ion-selective electrode. Experimental conditions: $[NaIO_3] = 0.43$ mol/dm^3, $[H_2O_2] = 0.46$ mol/dm^3, $[HClO_4] = 0.054$ mol/dm^3, $T = 55$ °C.

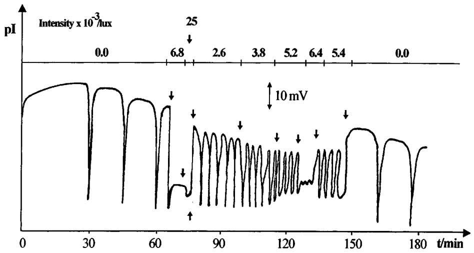

Figure 2. The effect of the light on the Bray−Liebhafsky reaction monitored by iodide ion-selective electrode. Experimental conditions: $[NaIO_3] = 0.011$ mol/dm^3, $[H_2O_2] = 0.09$ mol/dm^3, $[HClO_4] = 0.085$ mol/dm^3, $T = 55$ °C.

Results and Discussion

The effect of light intensity on the Bray−Liebhafsky reaction was studied by varying the distance between the reactor and light source. Figures 1 and 2 show two typical oscillatory curves obtained under different light intensities.

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SCHEME 1: Proposed Model for the Bray−Liebhafsky Reaction

$$IO_3^- + H_2O_2 + H^+ \longrightarrow HIO_2 + O_2 + H_2O \qquad (r1)$$

$$HIO_2 + H_2O_2 \longrightarrow HOI + O_2 + H_2O \qquad (r2)$$

$$HOI + H_2O_2 \longrightarrow I^- + H^+ + O_2 + H_2O \qquad (r3)$$

$$IO_3^- + I^- + 2H^+ \rightleftharpoons HIO_2 + HOI \qquad (r4)$$

$$HIO_2 + I^- + H^+ \longrightarrow 2\,HOI \qquad (r5)$$

$$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O \qquad (r6)$$

$$2\,HOI \longrightarrow I_2O + H_2O \qquad (r7)$$

$$I_2O + H_2O_2 \longrightarrow HIO_2 + HOI \qquad (r8)$$

$$I_2 + H_2O_2 \longrightarrow I_2O + H_2O \qquad (r9)$$

Figures 1 and show that by increasing the light intensity the period of oscillation decreased, and at a critical light intensity oscillations disappeared. By turning the light intensity back to the previous value, the period of oscillations also return to its previous time (except for the case when the concentration of the reactants, e.g., H_2O_2 is decreased strongly). The critical light intensity at which the oscillations disappeared strongly depended on the initial concentrations of the reactants.

For a successful modeling of the oscillatory Bray−Liebhafsky reaction, the following reactions and considerations should be taken into account: (i) the reactions taking place between the iodine species and its derivatives, (ii) the reactions between hydrogen peroxide and various iodine species such as IO_3^-, HIO_2, HOI, I^- etc.; and (iii) the knowledge of the rate constants of the above-mentioned reactions. Our efforts to simulate the oscillatory behavior of the Bray reaction was successful for by extending the model proposed by Schmitz.[12,13]

Scheme 1 shows our proposed model for the oscillatory Bray−Liebhafsky reaction, and Table 1 summarizes the rate constants.

The reactions r1−r3 include the reactions of iodate and its derivatives with H_2O_2, and the reactions r4−r8 is the core of the model originally proposed by Schmitz. The reaction r9 is the direct reaction of iodine with H_2O_2 that produces I_2O and water. In the presence of light homolytic cleavage of I_2 can take place according to eq 1.

$$I_2 \xrightarrow{h\nu} 2I \qquad (1)$$

It was assumed in our model calculations that light can effect via reaction r9 according to eqs 2 and 3.

$$k_9 = k_9' + k_9'' \qquad (2)$$

$$k_9'' = aI \qquad (3)$$

The rate constant of r9, i.e., k_9, is the sum of k_9' and k_9'', where k_9' is the rate constant of r9 in the absence of light and k_9'' is the rate constant of r9 in the presence of light which is directly proportional with the light intensity I, i.e., $k_9'' = aI$. Therefore k_9 can be written as $k_9 = k_9' + aI$, where a is the proportionality factor.

The calculated oscillatory curves with different light intensities are plotted in Figures 3 and Figure 4.

As it appears from Figures 3 and 4, the effect of light on Bray−Liebhafsky reaction can be semiquantitatively described. Although Cupic and Kolar-Anic[14] could describe the oscillatory behavior of the Bray−Liebhafsky reaction without assuming I_2O as an intermediate, and Lanova and Vrest'al[15] could not detect I_2O by on-line mass spectrometry, we think that this molecule is an important species. According to our model calculations, the concentration of I_2O is lower by 6 orders of magnitude than those of HIO_2 and HOI, which may explain how the detection of I_2O has failed.[15]

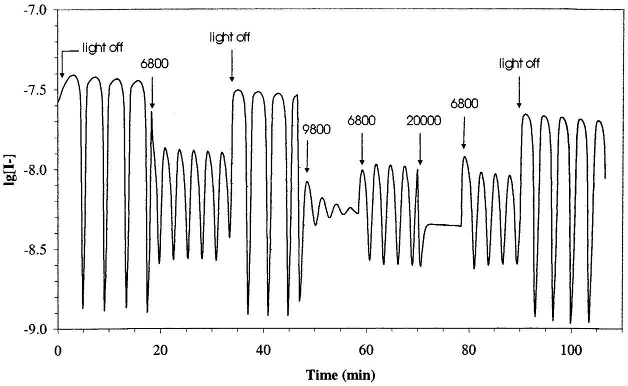

Figure 3. Oscillatory curve for the Bray−Liebhafsky reaction calculated with the proposed model. The initial concentrations of the reactants are the same as those in Figure 1.

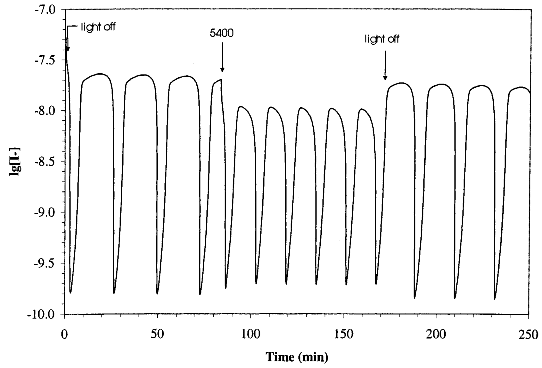

Figure 4. Oscillatory curve for the Bray−Liebhafsky reaction calculated with the proposed model. The initial concentrations of the reactants are the same as those in Figure 2.

TABLE 1: Rate Constants Used for Modeling the Bray−Liebhafsky Reaction

rate constants	value
k_1	$1 \times 10^{-6}\ M^{-2}\ s^{-1}$
k_2	$0.05\ M^{-1}\ s^{-1}$
k_3	$0.25\ M^{-1}\ s^{-1}$
k_4	$4 \times 10^{4}\ M^{-3}\ s^{-1}$
k_4	$3000\ M^{-1}\ s^{-1}$
k_5	$4 \times 10^{10}\ M^{-2}\ s^{-1}$
k_6	$1 \times 10^{12}\ M^{-2}\ s^{-1}$
k_6	$1000\ s^{-1}$
k_7	$700\ M^{-1}\ s^{-1}$
k_8	$1 \times 10^{7}\ M^{-1}\ s^{-1}$
k_9'	$1 \times 10^{-4}\ M^{-1}\ s^{-1}$
a	$6.6 \times 10^{-6}\ M^{-1}\ s^{-1}\ lux^{-1}$

Conclusions

The effect of light on the oscillatory Bray−Liebhafsky reaction is described, and additional reactions, such as the reaction of I_2 with H_2O_2 are added to the main subset of the oscillatory model proposed by Schmitz. The extended model for the Bray−Liebhafsky reaction is capable of rendering the main features of the reaction under different light intensities.

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