

# ROLE OF RADICALS IN THE BRAY-LIEBHAFSKY REACTIONS

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## ABSTRACT

The explanation of the Bray-Liebhafsky oscillations does not involve radical reactions. On the other hand, the oxygen produced oxidizes the iodide and its mechanism involves radical reactions. This oxidation can have a significant effect on the oscillations. The proposed model also explains the complicated kinetics of iodine oxidation by hydrogen peroxide.

## RADICAL AND NON-RADICAL EXPLANATIONS OF OSCILLATIONS

The Bray-Liebhafsky (BL) reaction is the decomposition of hydrogen peroxide catalyzed by iodate and iodine in acidic solutions [1, 2]. This decomposition is the sum of reaction (R) where hydrogen peroxide acts as a reducing agent and reaction (O) where it acts as an oxidant. These reactions can alternately be dominant and give rise to the oscillations discovered by Bray. The mechanism of reaction (R) seems more or less well known and involves several intermediates such as HOIO, HOI and I<sup>-</sup>. On the other hand, the mechanism of reaction (O) has remained controversial for a century.



Richard Noyes made a detailed study of the BL reaction kinetics [3, 4]. He showed that light and the oxygen produced have a significant effect on the kinetics and deduced from this that the mechanism of reaction (O) involves radicals. He proposed several possible reactions and a mechanism suggested by his experimental results, but this mechanism did not make it possible to simulate the oscillations. Treindl and Olexova [5, 6] have also suggested the importance of radical reactions. The effect of light can be explained by radical reactions initiated by  $\text{I}_2 + h\nu \rightarrow 2 \text{I}^*$  but the effect of oxygen is more difficult to explain. We will discuss only the reaction in the dark and will try to clarify the role of radical reactions. We will discuss more particularly the works of Stanisavljev et al. They published important studies of the reaction (O) [7 - 9] and proved by EPR (electron paramagnetic resonance spectroscopy) that radicals are indeed formed [10 - 12]. They concluded, like other researchers, that the explanation of the oscillations must involve radical reactions. Another explanation is however possible.

Liebhafsky has always been convinced that the oscillations must be explained by a nonradical mechanism. The reactions (R) and (O) involving several intermediates, he studied the kinetics of their subsystems [13, 14 and references therein]. Liebhafsky explained his results by non-radical reactions and proposed a non-radical model to explain the oscillations [15, 16]. However, this model involves unlikely iodine compounds. Our model published in 1987 [17] is based on the formation of the hypoiodous acid dimer noted  $\text{I}_2\text{O}$ , analog of  $\text{Cl}_2\text{O}$ , by reaction (1). It is probably hydrated and a more exact writing of its formula could be  $\text{H}_2\text{O-I-O-I}$ . The

formation of  $I_2O$  was an assumption but it was later shown [18] that it can be prepared in concentrated sulfuric acid and extracted in dichloromethane [19]. It is not observed in aqueous solutions because the equilibrium (1) is shifted to the left. The proposed model states that hydrogen peroxide reduces hypiodous acid according to reaction (2) and oxidizes its dimer according to reaction (3). The other reactions are deduced from the works of Liebhafsky.



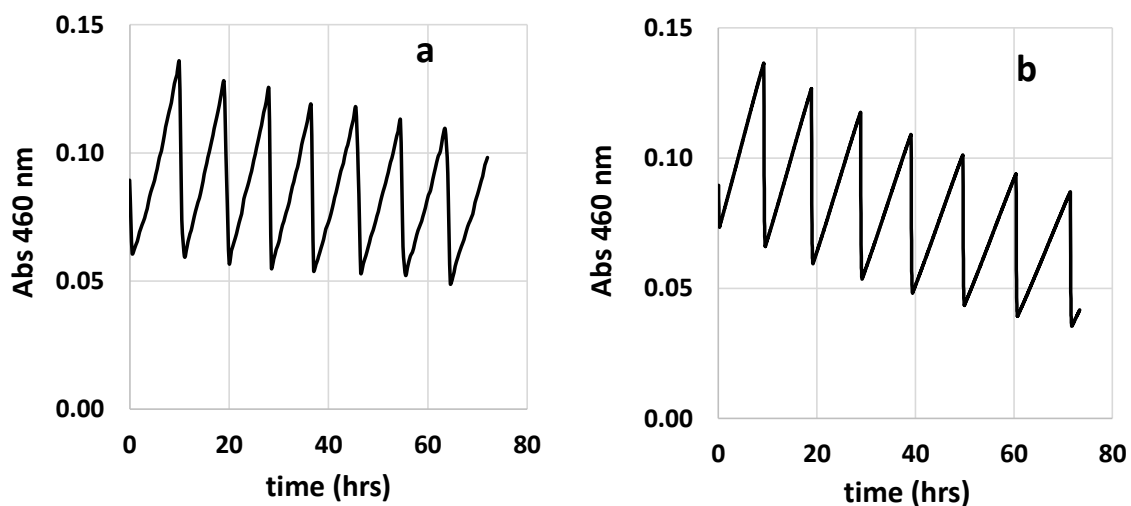
The properties of this model and some variants have been studied in collaboration with the University of Belgrade [20 – 24] and we have shown that it explains very well the oscillations. Its analysis by the SNA method (Stoichiometric Network Analysis) confirmed that the reactions (1) to (3) and the hydrolysis of iodine (4) give a current destabilizing the catalytic steady state [25, 26].



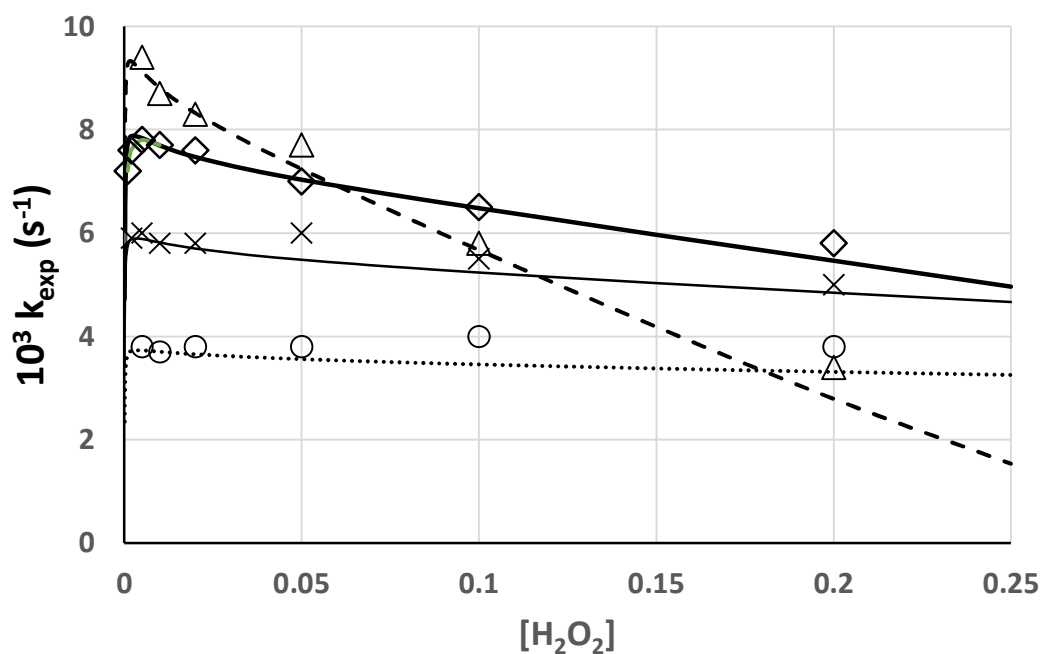
The instability of the catalytic steady state results from the competition between reaction (2) whose rate is proportional to the concentration  $[HOI]$  and reaction (3) whose rate is proportional to the concentration of its dimer, therefore to  $[HOI]^2$ . When the HOI concentration is small, reaction (2) is faster than reaction (3).  $H_2O_2$  mainly acts as a reductant and the overall reaction (R) is obtained. When the HOI concentration is large,  $H_2O_2$  mainly acts as an oxidant and the overall reaction (O) is obtained. The other reactions give the feedback creating the oscillations. Many experimental observations are explained by noting that, reaction (4) being reversible, the concentration  $[HOI]$  is small when that of iodide is large and vice versa [27]. Let us only mention the role of iodate in the study of the kinetics of reaction (O). Iodine and hydrogen peroxide do not react directly and the concentration of iodine can remain almost constant in an acid solution of these two reagents. If iodate is added, it oxidizes the iodide, increases the concentration  $[HOI]$ , thus the ratio between the rates of reactions (3) and (2) and reaction (O) can start.

The initial model was improved by the studies of the kinetics of BL subsystems made by Furrow [28 – 31] and the study of the kinetics of reaction (O) in the presence of iodate [32]. Its latest version was published recently [31]. It allows excellent simulations of oscillations at  $50^\circ\text{C}$  and explains a large number of experimental facts without involving radical reaction [33]. Furrow [34] also studied the oscillations at  $25^\circ\text{C}$ , a temperature where the periods are much longer and difficult to reproduce. Figure 1 gives an example of simulation of his results.

Figure 2 shows the values of the apparent kinetic constant of reaction (O) in the presence of small amounts of iodate. It decreases if the concentration of  $H_2O_2$  increases, although it is a reagent, and the effect of acidity is very different depending on whether the concentration of  $H_2O_2$  is small or large. The explanation of this very unusual kinetics is one of the major arguments supporting the proposed model.



**Fig. 1:** BL oscillations at 25°C.  $[\text{HClO}_4] = 0.030 \text{ M}$ ,  $[\text{KIO}_3] = 0.048 \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 0.080 \text{ M}$ . Experimental [34] (a) and calculated with the proposed model [31] (b).



**Fig. 2.** Rate constant of the iodine oxidation by hydrogen peroxide with a small initial concentration of iodate. Experimental values [32] when  $[\text{HClO}_4] = 0.04 (\Delta)$ ,  $0.10 (\diamond)$ ,  $0.20 (\times)$  and  $0.40 \text{ M} (\text{O})$ . Values calculated with the proposed model [31] when  $[\text{HClO}_4] = 0.04 (- - -)$ ,  $0.10 (\text{—})$ ,  $0.20 (\text{—})$  and  $0.40 \text{ M} (\dots)$ .

## OXYGEN REACTIONS

Oxygen can have a strong effect on the shape or even the existence of oscillations [3, 4, 35, 36]. We explain this effect by the oxidation of iodide by oxygen. The initial version of our model included the global reaction  $O_2 + 2 I^- + 2 H^+ \rightarrow 2 HOI$  with an empirical kinetic law resulting from an unknown radical mechanism. New results give some information about this mechanism. Studies of the kinetics of the reduction of HOI by  $H_2O_2$  [37, 38] have shown that reaction (2) involves the peroxide HOOI and must be split into (5) and (6).



The existence of the HOOI intermediate was confirmed by the appearance of a radical pathway during the  $IO_3^- + H_2O_2$  reaction when the concentration of  $H_2O_2$  is high [29]. Radicals formed by reaction (7) explain this new reaction path and also the formation of radicals during the Briggs-Rauscher reaction without a metal ion as a catalyst [39].



The sum (5) + (7) gives reaction (8) with  $\Delta_r G(8) = -23$  kJ/mol.



Reaction (8) is the very first reaction proposed for the formation of radicals in the dark giving a decrease in Gibbs energy. The effect of oxygen on the BL reaction is explained by the reversibility of (6) followed by (7) giving  $I^- + H^+ + O_2 + H_2O_2 \rightarrow HOO\cdot + IO\cdot + H_2O$ .

The reactions of the  $HOO\cdot$  and  $IO\cdot$  radicals in the studied solutions are unknown. Several possible reactions can lead to a reaction path thermodynamically and kinetically likely making it possible to explain, at least qualitatively, the experimental observations. Oxidation of iodide by oxygen not only explains its effects on oscillations, it also explains the interesting EPR signals obtained by Stanisavljev et al. using EPR spin trapping with BMPO, they detected oxygen-centered free radicals,  $HOO\cdot$  or  $HO\cdot$ , in acidic solutions of iodide and hydrogen peroxide at 25°C [10]. Then, using EPR spin trapping with DEPMPO, they showed that the formation of  $HOO\cdot$  is much more important than that of  $HO\cdot$  [11]. Reaction (7) explains this result. These authors also measured the spectrum of TEMPONE, a spin probe giving a stable free radical, during the BL reaction at 67°C [12] and observed that the concentration of radicals is greater after reaction (O). Reaction (7) explains also this observation. The rate of oxygen production being greater during reaction (O) than during reaction (R), its concentration and therefore that of HOOI is maximal after reaction (O). These authors also recorded the spectrum of DEMPO during the BL reaction and observed that a detectable amount of EPR-active DEPMPO adduct is formed only after an accumulation period larger than 10 min. The concentration of oxygen in the solution is initially in equilibrium with that in the atmosphere and increases during the oscillations. The observed accumulation time may be that required for the oxygen concentration to become large enough. In addition, their DEMPO adduct splitting constants being markedly different from those reported in the literature for oxygen-centered radicals, they deduce the formation of iodine radicals and propose  $OIO\cdot$ . However, the formation of  $IO\cdot$  by reaction (7) can also explain their results.

### INDUCTION OF REACTION (O)

Stanisavljev et al studied the induction period of the oxidation of iodine by hydrogen peroxide in the absence of iodate and found that it seems stochastic [7]. We discussed this induction period at our previous conference [27] by analyzing the properties of nullclines calculated with the proposed model. Without iodate initially, or with a very small initial concentration, the projection of nullclines in the concentration space onto the  $[I^- - I_2]$  plane has the shape shown in Figure 3. The gray part of the concentration space does not exist because the concentration of iodine cannot be greater than half of the total concentration of iodine atoms  $I_{tot} = 2 [I_2]_0 + [IO_3^-]_0$ . If the dissolved oxygen concentration is small, there are three quasi-steady states. The SS1 state is the one around which the oscillations occur when they exist. The SS2 state is an unstable saddle point. The SS3 state is a stable node towards which the system evolves. The concentration of iodine is constant there and the only reaction is a slow decomposition of hydrogen peroxide. What appears to be an induction period of reaction (O) is actually a quasi-steady state. Nullclines depend on acidity and concentrations including that of oxygen which increases in the state SS3 because hydrogen peroxide decomposes slowly. The calculations of the nullclines show that, under the conditions of Figure 3, this results in a displacement of the right extremum to the left. For a critical oxygen concentration between  $3.0 \times 10^{-4}$  and  $3.5 \times 10^{-4}$  M, the quasi-steady states SS2 and SS3 meet. It is a saddle-node bifurcation. The system which was in the SS3 state is now attracted by the lower branch of the nullcline and we obtain reaction (O).

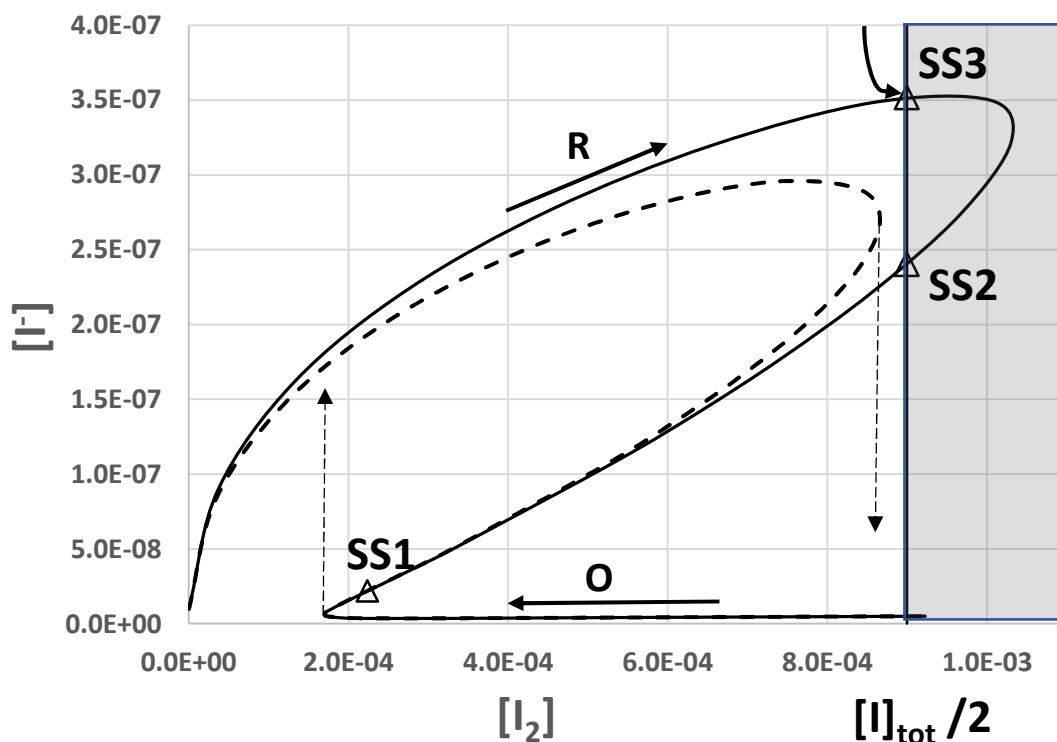


Fig.3: Nullcline calculated with the proposed model.  $[H^+]_0 = 0.050$ ,  $[H_2O_2]_0 = 0.20$ ,  $[I_2]_0 = 9 \times 10^{-4}$  M, no iodate initially.  $[O_2] = 3.0 \times 10^{-4}$  (—) and  $[O_2] = 3.5 \times 10^{-4}$  M (- - -). The arrows show the directions of the trajectories.

The concentration of oxygen in solution depends on its rate of formation and its rate of transfer to the gas phase, either by transfer through the gas-solution interface, or by the formation of bubbles. These transfer phenomena determine the induction period of reaction (O), the time required for the oxygen concentration to reach a critical value giving a saddle-node bifurcation and the start of reaction (O). If bubbles form more slowly, the supersaturation of the solution with oxygen increases faster, the critical concentration is reached earlier and the so-called induction period of reaction (O) is shorter. Figure 4 shows the evolution of iodine calculated by the proposed model for two values of the global oxygen transfer coefficient to the gas phase. A detailed discussion of this coefficient is beyond the scope of this work but we note that small change in the rate of transfer of oxygen to the gas phase can give a large change in the induction period. If this rate of transfer is too large, the critical concentration of oxygen is not reached and reaction (O) is not obtained without iodate.

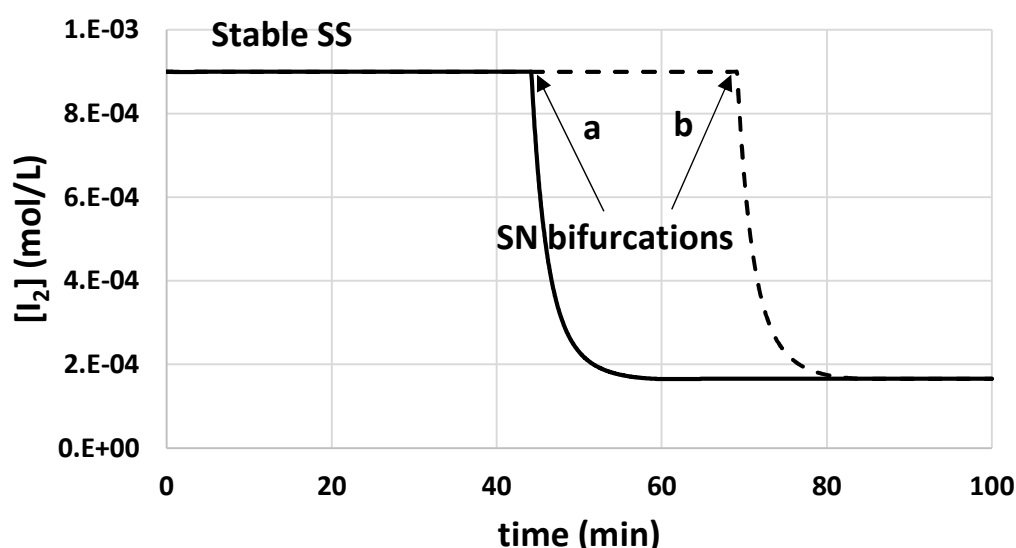


Fig.4: Time evolution calculated with the proposed model [31].  $[H^+]_0 = 0.050$ ,  $[H_2O_2]_0 = 0.20$ ,  $[I_2]_0 = 9 \times 10^{-4}$  M, no iodate initially.  $[O_2]_0 = 2.5 \times 10^{-4}$  M, global oxygen transfer coefficient  $k_{14} = 6 \times 10^{-4} \text{ s}^{-1}$  (a) or  $8 \times 10^{-4} \text{ s}^{-1}$  (b).

Stanisavljev et al recently presented an interesting discussion of oxygen bubbles germination - growth phenomena [9]. The model they propose explains neither the oscillations (Fig.1), nor the kinetics of reaction (O) (Fig.2), nor the effect of iodate or additions of  $Ag^+$ , nor the kinetics of subsystems such as the reactions of  $H_2O_2$  with HOI and HOIO. However, they are right in proposing an effect of these phenomena on the oscillations and on the induction period of reaction (O). These phenomena are difficult to control and not reproducible explaining that the induction period seems stochastic. A phenomenon seems stochastic when it depends on parameters that we ignore or do not control.

## CONCLUSIONS

The Bray-Liebhafsky oscillations were never explained by radical reactions but they are very well explained by a model based on the idea of Liebhafsky who was convinced that their origin is not radical. On the other hand, radical reactions can modify the frequency and the amplitude of the oscillations and even suppress them. The initial version of our model [17] included an empirical reaction of oxidation of iodide by oxygen with an unknown radical mechanism. Its recent version [31] proposes for the first time a thermodynamically very likely source of radicals and explains quantitatively many experimental results. For others, the explanation is only qualitative because the oxidation mechanism of iodide by oxygen remains poorly understood and because it is very difficult to model the phenomena of transfer of oxygen to the gas phase.

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