

THE BRAY-LIEBHAFSKY AND BRIGGS-RAUSCHER OSCILLATING REACTIONS

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ABSTRACT

The common points and differences between the Bray-Liebhafsky and Briggs-Rauscher reactions are discussed. The reactants of the non-catalyzed version of the Briggs-Rauscher reaction being the same as those of the Bray-Liebhafsky reaction plus a reducing organic compound, the mechanisms of these two systems must have several common points. The marked difference between the oscillating behaviours comes from radical reactions that could be initiated by the new pathway of the iodate reduction by hydrogen peroxide at high concentrations.

FOREWORD

... to conduct my thoughts in such order that, by commencing with objects the simplest and easiest to know, I might ascend by little and little to the knowledge of the more complex...

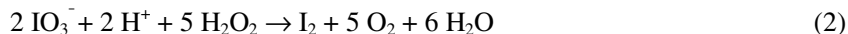
René Descartes (1596–1650). Discourse on Method.

COMPARISON OF THE BL AND BR REACTIONS

The Bray-Liebhafsky (BL) [1] reaction is the decomposition (1) of hydrogen peroxide catalyzed by iodate in acidic solutions.



Reaction (1) is the result of two reactions where hydrogen peroxide acts as a reducing (2) or as an oxidizing (3) agent. The sum of reactions (2) and (3) gives reaction (1).



Within a narrow range of concentrations, reactions (2) and (3) dominate alternately and oscillations are observed in the concentrations of iodine and iodide ions and in the rate of oxygen production. The mechanism of these reactions is complicated involving, beside IO_3^- and I_2 , numerous iodine intermediates. The main part of the mechanism proposed recently [2] is given in Table I. It explains the main features of the oscillations, but for simulating quantitatively the complex observed behaviours, it must be supplemented by reactions describing the perturbing effect of oxygen.

Table I. Main part of the mechanism of the BL reaction

$\text{IO}_3^- + \Gamma + 2 \text{H}^+ \rightleftharpoons \text{IOH} + \text{IO}_2\text{H}$	R1
$\text{IO}_2\text{H} + \Gamma + \text{H}^+ \rightleftharpoons \text{I}_2\text{O} + \text{H}_2\text{O}$	R2
$\text{I}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2 \text{IOH}$	R3
$\text{IOH} + \Gamma + \text{H}^+ \rightleftharpoons \text{I}_2 + \text{H}_2\text{O}$	R4
$\text{IOH} + \text{H}_2\text{O}_2 \rightarrow \Gamma + \text{H}^+ + \text{O}_2 + \text{H}_2\text{O}$	R5
$\text{I}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{IOH} + \text{IO}_2\text{H}$	R6
$\text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{IO}_2\text{H} + \text{O}_2 + \text{H}_2\text{O}$	R7
$2 \text{IO}_2\text{H} \rightleftharpoons \text{I}_2\text{O}_3 + \text{H}_2\text{O}$	R8a
$\text{I}_2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{IO}_2\text{H}$	R8b
$\text{I}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{IO}_3^- + \text{H}^+ + \text{IOH}$	R8c

The BL oscillations can be observed conveniently only above 40°. The oscillations at room temperature are irregular and the periods are very long (several hours). However, a modification of this system, discovered by Briggs and Rauscher [3], oscillates nicely at room temperature with a period usually shorter than one minute. The mixture contains the same compounds as the BL reaction, acid, iodate and hydrogen peroxide, and also an organic reducing compound like malonic acid (MA) and a metal-ion catalyst (Mn^{++} in the original recipe). The classical

mechanism [4] includes reactions (R1)-(R5), reactions of iodination and oxidation of the organic compound and radical reactions with the metal-ion catalyst initiated by reaction (4).



However, estimations of Gibbs energies of formation (ΔG_f) [5] indicate that the equilibrium constant of reaction (4) is so small that the recombination of OIO \cdot radicals (-4) is nearly irreversible. Thus the classical mechanism must be revised. Moreover, BR like oscillations can be observed without metal-ion catalyst.

THE NON-CATALYSED BR REACTION

An acidic mixture of iodate, hydrogen peroxide and malonic acid can show oscillations similar to the BR oscillations. This was already recognized by Briggs and Rauscher in their original paper and one of us [6] has found that the range of these oscillations is wider than originally thought. An example is given in Fig.1. These non-catalyzed oscillations are observed only at high hydrogen peroxide concentrations.

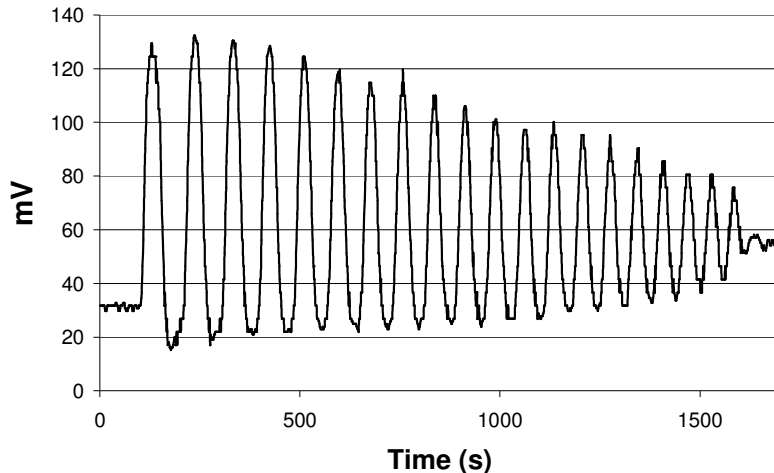


Fig.1. BR oscillations at 25° without catalyst. $[\text{HClO}_4]_0 = 0.10\text{M}$, $[\text{KIO}_3]_0 = 0.0033\text{M}$, $[\text{H}_2\text{O}_2]_0 = 1.0\text{M}$, $[\text{MA}]_0 = 0.002\text{M}$. H_2O_2 was added at 104 s. The ordinate gives the potential of an iodide selective electrode. Higher potential means lower $[\text{I}^-]$.

The oscillations in Fig.1 are important because they make a link between the BR and BL systems: the BR reaction without catalyst is also the BL system plus malonic acid. Thus, we have tried to simulate these oscillations adding malonic acid reactions to the model in Table I, but without success. The system is more complicated, is inhibited by radical scavengers and, consequently, involves radical reactions. In the example of Fig.1, addition of 2×10^{-6} mol/l of catechol stopped the oscillations for 208 s. Then oscillations resumed at about half the previous amplitude and continued for about 1480 seconds. This restart is explained by the iodination/oxidation of catechol. With 5×10^{-6} mol/l of catechol, no restart is observed. The oscillations are also inhibited by resorcinol and ferroin. Knowing that the initiation of the radical reactions is not reaction (4), the elucidation of the radical part of the non-catalyzed BR reaction mechanism remains a major challenge.

REACTIONS COMMON TO THE BL AND BR SYSTEMS

In order to understand complicated systems, it is always useful to study simpler subsystems. Independent information about reaction (R1) - (R7) was obtained previously (see references in [2]) but, apart from a mention in a pioneering document [7], nothing was known about reaction (R8). It was introduced into the model to allow good simulations of the kinetics of the component (2) of the BL reactions [2]. According to reaction (R8), the oxidation of IO_2H by hydrogen peroxide should follow a second order rate law. This rate law is obtained assuming that the concentration of the intermediate I_2O_3 is so small that we can make the steady state approximation $r_{8a} = r_{8b} + r_{8c}$.

$$k_{8a} [\text{IO}_2\text{H}]^2 = (k_{-8a} + k_{8b} [\text{H}_2\text{O}_2] + k_{8c}) [\text{I}_2\text{O}_3]$$

The sum (R8a) + (R8c) gives the IO_2H disproportionation $2 \text{IO}_2\text{H} \rightarrow \text{IO}_3^- + \text{H}^+ + \text{IOH}$ with the rate law

$$r_{8c} = \frac{k_{8a} k_{8c}}{k_{-8a} + k_{8b} [\text{H}_2\text{O}_2] + k_{8c}} [\text{IO}_2\text{H}]^2$$

The sum (R8a) + (R8b) gives the IO_2H oxidation $\text{IO}_2\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$ with the rate law

$$r_{8b} = \frac{k_{8a} k_{8b} [\text{H}_2\text{O}_2]}{k_{-8a} + k_{8b} [\text{H}_2\text{O}_2] + k_{8c}} [\text{IO}_2\text{H}]^2$$

A kinetic study of these reactions is under progress and confirms that the rate of IO_2H oxidation by low concentrations of hydrogen peroxide is proportional to

$[\text{H}_2\text{O}_2][\text{IO}_2\text{H}]^2$. Fig.2 shows an example of our results. This second order with respect to $[\text{IO}_2\text{H}]$, instead of the first order assumed previously, is important for modelling the BL and BR reactions [2].

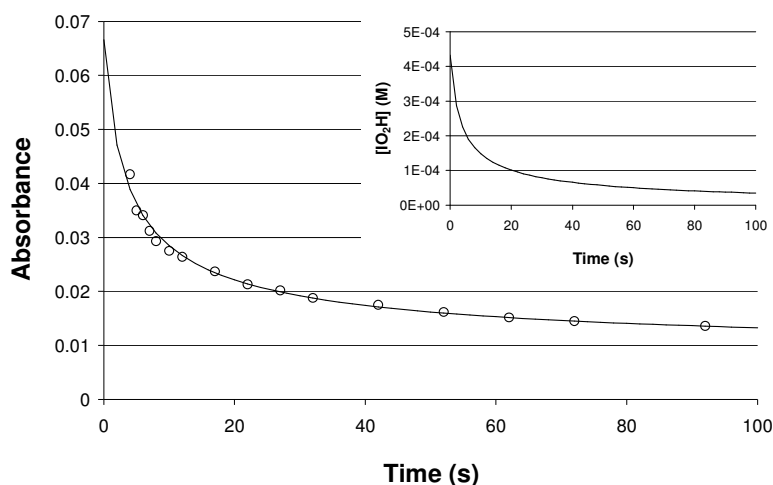


Fig.2. Time evolution of the experimental absorbance (o) and of the absorbance calculated (—) using the rate law $-d[\text{IO}_2\text{H}]/dt = 1.2 \times 10^6 [\text{H}_2\text{O}_2][\text{IO}_2\text{H}]^2$. $[\text{H}_2\text{SO}_4] = 0.26 \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 5.7 \times 10^{-4} \text{ M}$, $[\text{IO}_2\text{H}]_0 = 4.32 \times 10^{-4} \text{ M}$. The insert shows the calculated evolution of $[\text{IO}_2\text{H}]$.

Another important subsystem is the iodate reduction by hydrogen peroxide. Reaction (R7) with its associated rate law was widely accepted but a new study [5] revealed another reaction pathway. It appears at high hydrogen peroxide concentrations, has a rate more than proportional to $[\text{H}_2\text{O}_2]^2$ and is inhibited by scavengers of free radicals. The discovery of this new pathway gives a partial answer to an essential question about the BR reaction: what is the source of radicals in the absence of catalyst? Knowing that the kinetics of the iodate reduction by hydrogen peroxide changes suddenly at high peroxide concentrations and that the non-catalysed BR oscillations are observed only at high hydrogen peroxide concentrations, we suggest that the two mechanisms are closely related. They are not completely elucidated but the radical part of the mechanism is probably initiated by $\text{IOH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{IOOH} + \text{H}_2\text{O}$ and $\text{IOOH} + \text{H}_2\text{O}_2 \rightarrow \text{IO}^\cdot + \text{H}_2\text{O} + \text{HOO}^\cdot$ [5]. These reactions are also important for explaining the effect of oxygen on the BL reaction [2].

CONCLUSION

The oscillating behaviour of the BL and BR reactions are different but their essential components, acidic iodate and hydrogen peroxide, are the same and the BL reaction is a subsystem of the BR reaction. The mechanisms of these two reactions are strongly related and we propose that the mechanism of the BR oscillations should be build starting with the mechanism of the BL reaction and adding radical reactions. Progress in this direction is supported by the kinetic study of constituent reactions and of the effect of radical scavengers.

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