

Mechanism of the Bray-Liebhafsky Reaction: Effect of the Reduction of Iodate Ion by Hydrogen Peroxide

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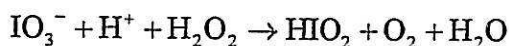
Abstract

The influence of the reduction of iodate ion by hydrogen peroxide on the mechanism of the Bray-Liebhafsky reaction introduced by Schmitz et al is analysed. The reaction of reduction is used in original form proposed by Liebhafsky, with corresponding data.

Introduction

It is known that ordinary physico-chemical systems can show complex behaviour presenting many of the characteristics usually ascribed to life (Nikolis and Prigozine 1989). The same is the case with the iodate-catalyzed disproportionation of hydrogen peroxide in acid media, known as the Bray-Liebhafsky oscillatory reaction (Bray 1921, Bray and Liebhafsky 1931). In mentioned system a variety of species can be found (Bray 1921, Bray and Liebhafsky 1931, Baxendale 1952, Liebhafsky et al 1981, Sharma and Noyes 1976, Furrow 1985, Schmitz 1974). Most of them cannot be monitored experimentally. Consequently, some of elementary reactions cannot be verified. Also, the rate constants and initial concentrations of some species are not determined. Therefore, because of existence of numerous undetermined parameters in such a complex process, the mechanism is only partially known (Liebhafsky et al 1981, Sharma and Noyes 1976, Furrow 1985, Schmitz 1974, Liebhafsky and Wu 1974, Edelson and Noyes 1974, Schmitz 1987, Schmitz 1991, Kolar-Anić and Schmitz 1992, Treindl and Noyes 1993).

Hence, there is a long list of the reactions which are considered as candidates for the model. Between them is the reduction of iodate ion by hydrogen peroxide:



examined experimentally by Liebhafsky in 1931. He found that the rate of this reaction (in mol/dm³min) at 50°C is:

$$-\frac{d[\text{IO}_3^-]}{dt} = (2.6 \times 10^{-4} + 129 \times 10^{-4}[\text{H}^+])[\text{IO}_3^-][\text{H}_2\text{O}_2]$$

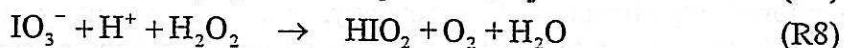
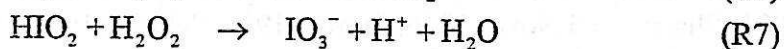
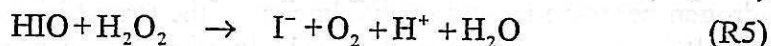
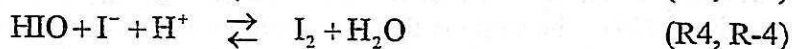
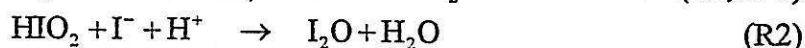
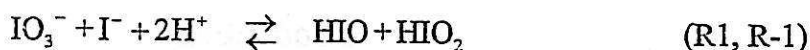
This reaction appeared later in his skeleton mechanism (Liebhafsky and Wu 1974, Lebhafsky et al 1978), but also in the mechanism proposed by Sharma, Noyes and Edelson (Sharma and Noyes 1976, Edelson and Noyes 1979). Moreover, it is analysed in other references (Furrow 1987, Furrow and Noyes 1982, De Kepper and Epstein 1982). The rate constant proposed by Liebhafsky is usually taken for the numerical simulations.

This relatively slow reaction is not always important in kinetics of overall decomposition of hydrogen peroxide. It can make a considerable contribution depending on the ratio between H₂O₂ and I⁻ concentrations. When iodide concentration is low, the pathway for hydrogen peroxide disproportionation where it take place becomes more possible than the parallel one(s). As probably slowest reaction in this pathway it is then the rate determining step (Lebhafsky 1931, Edelson and Noyes 1979).

The previous reaction is not taken into account in any variant of the model proposed by Schmitz et al (Schmitz 1974, Schmitz 1983, Schmitz 1987, Schmitz 1991, Kolar-Anić and Schmitz 1992). Thus, we are dealing with its influence on the last published variant of the model (Kolar-Anić and Schmitz 1992). For this purpose the Stoichimetric Network Analyzis proposed by Clarke (Clarke 1980) is used.

The kinetic model

The reduction of iodate ion by hydrogen peroxide in the form given by Liebhafsky is added to the model proposed by Kolar-Anić and Schmitz (Kolar-Anić and Schmitz 1992). Hence, the analysed set of chemical reactions in the present work is:



The subset of the model [reactions (R1-R6)] is enough for the simulation of the oscillatory evolution. The reaction (R7) is introduced as the experimentally found one (Furrow 1987) which gives better agreement with experiments.

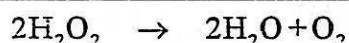
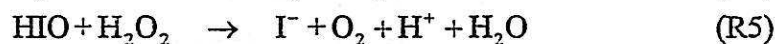
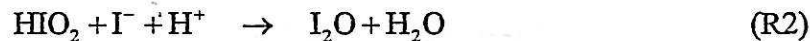
By the procedure proposed by Clarke (Clarke 1980), and more explained by Kolar-Anić and Schmitz (Kolar-Anić and Schmitz 1992), the following set of extreme currents, denoting all reaction pathways presented as the columns in the matrix **E**, is obtained.

$$E = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 \end{bmatrix}$$

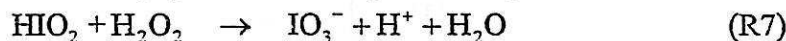
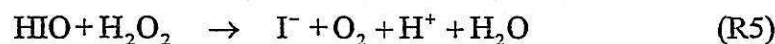
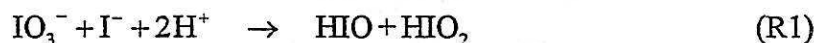
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The rows of the matrix E corresponds to the reactions in the same order as in the model, that is (R1), (R-1), (R2), (R3), (R-3), (R4), (R-4), (R5), (R6), (R7) and (R8).

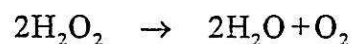
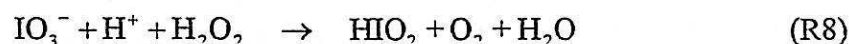
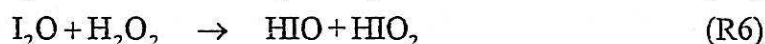
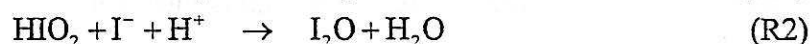
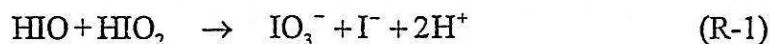
The first three extreme currents are the equilibrations of reactions (R1), (R3) and (R4), respectively. The next four, E_4 , E_5 , E_6 and E_7 , denote all possible extreme steady-state stoichimetric networks which give the product of the overall process. Thus, the extreme current E_4 correspond to:



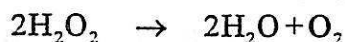
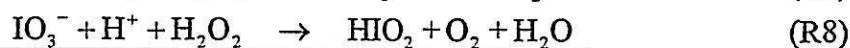
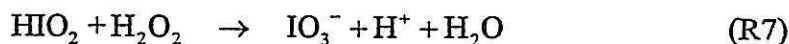
the extreme current E_5 corresponds to:



the extreme current E_6 corresponds to:



and extreme current E_7 corresponds to:



Obviously reaction (R8) take place in two last stoichiometric paths. Therefore it have certain influence on the overall kinetics. The importance of its contribution is verified by performing numerical simulations.

For this purpose we need to choose a set of parameters (the rate constants and initial concentrations). Since they are only partially known, we welcome any additional criteria for them. In this paper we use the following method. As Bray-Liebafsky reaction exhibits oscillatory evolution of intermediates with time, we perform stability analysis to find the values of undetermined parameters to satisfy the instability conditions which ensures the oscillations.

Following the method proposed by Clarke (Clarke 1980) we introduce so-called current vector \mathbf{j} which gives the relation between the matrix \mathbf{E} and steady-state velocities \mathbf{v}_s :

$$\mathbf{v}_s = \mathbf{E} \mathbf{j} \quad (1)$$

Here, the reversible reactions are presented by separate forward and reverse reactions, i.e. as two different components of \mathbf{v}_s .

From last equation we read:

$$\begin{aligned} k_1[\text{I}^-]_s &= j_1 + j_5 \\ k_{-1}[\text{HIO}]_s[\text{HIO}_2]_s &= j_1 + j_6 \\ k_2[\text{HIO}_2]_s[\text{I}^-]_s &= j_4 + j_6 \\ k_3[\text{I}_2\text{O}]_s &= k_{-3}[\text{HIO}]_s^2 = j_2 \\ k_4[\text{HIO}]_s[\text{I}^-]_s &= k_{-4}[\text{I}_2]_s = j_3 \\ k_5[\text{HIO}]_s[\text{H}_2\text{O}_2]_s &= j_4 + j_5 \\ k_6[\text{I}_2\text{O}]_s[\text{H}_2\text{O}_2]_s &= j_4 + j_6 \\ k_7[\text{HIO}_2]_s[\text{H}_2\text{O}_2]_s &= j_5 + j_7 \\ k_8[\text{H}_2\text{O}_2]_s &= j_6 + j_7 \end{aligned} \quad (2)$$

Here, k_i denotes the rate constant of reaction (Ri) and $[\text{X}]_s$ the steady-state concentration of the intermediate X. The concentrations of iodate and hydrogen ions can be regarded as constant as they are relatively large in comparison with the others. Therefore they are included in the rate constants such that

$$k_1 = k_1^0[\text{IO}_3^-][\text{H}^+]^2, \quad k_{-1} = k_{-1}^0, \quad k_2 = k_2^0[\text{H}^+], \quad k_3 = k_3^0, \quad k_{-3} = k_{-3}^0, \quad k_4 = k_4^0, \quad k_{-4} = k_{-4}^0, \\ k_5 = (k_5^1 + k_5^2[\text{H}^+])[\text{H}_2\text{O}_2], \quad k_6 = k_6^0[\text{H}_2\text{O}_2], \quad k_7 = k_7^0[\text{H}_2\text{O}_2] \quad \text{and} \quad k_8 = (k_8^1 + k_8^2[\text{H}^+])[\text{IO}_3^-].$$

Eliminating currents j_1, \dots, j_7 from last equations, the relations for the steady-state concentrations of the intermediate species as functions of the rate constants are obtained:

$$\begin{aligned}
[\text{HIO}]_s &= \frac{k_3 k_5}{k_{-3} k_6} P \\
[\text{I}^-]_s &= [\text{HIO}]_s^2 \frac{[\text{H}_2\text{O}_2]}{F} \\
[\text{HIO}_2]_s &= \frac{k_{-3} k_6}{k_2 k_3} F \\
[\text{I}_2]_s &= \frac{k_4}{k_{-4}} [\text{HIO}]_s^3 \frac{[\text{H}_2\text{O}_2]}{F} \\
[\text{I}_2\text{O}]_s &= \frac{k_{-3}}{k_3} [\text{HIO}]_s^2
\end{aligned} \tag{3}$$

where

$$F \equiv f([\text{HIO}]_s) = \frac{k_2}{k_7} \left[\frac{k_3}{k_{-3} k_6} (k_8 + k_5 [\text{HIO}]_s) - [\text{HIO}]_s^2 \right] \tag{4}$$

and

$$P = \frac{1 + \frac{k_1 k_3}{k_{-3} k_6} \frac{1}{F}}{1 + \frac{k_{-1} k_{-3} k_6}{k_2 k_3 k_5} \frac{F}{[\text{H}_2\text{O}_2]}} \tag{5}$$

In all performed simulations, in oscillatory domain, F have values between 10^{-6} and 10^{-8} , whereas P is closed to one. The steady state is unstable if there is a negative principal minor of the matrix $V(j)$ (Clarke 1980) which is:

$$V(j) = -S (\text{diag } E_j) K^t \tag{6}$$

where S denotes the matrix of the stoichiometric coefficients and K^t the transpose of matrix of the orders of reactions.

The instability condition which follows from the principal minor, where I^- , HIO , HIO_2 and I_2O are key intermediates, consists of 51 summands. Therefore, some reductions based on the experimental evidencies are necessary.

Thus, considering relations between the stationary velocities and currents, eqs.(2), we found the relations between currents j_1, \dots, j_7 and express the instability condition in the reduced (approximative) form:

$$\frac{2k_3 k_5^2}{k_{-3} k_6 k_8} (8 - 7P) > \left(7 + 4 \frac{k_6 [\text{H}_2\text{O}_2]}{k_3} \right) P^2 + 23 \frac{k_{-1} k_5}{k_2 k_8} \frac{F}{[\text{H}_2\text{O}_2]} P \tag{7}$$

where P is already given in eq (5).

Numerical Simulations

The numerical simulation of the Bray-Liebhafsky reaction with the use of the parameters listed in Table 1. is presented in the figures 1(a)-1(d). The rate constant for reaction (R8) at 60°C is taken from the paper by Liebhafsky (Liebhafsky 1931).

Table I: Rate constants used for Bray-Liebhafsky reaction
(for the sake of brevity, M means mol/dm³.)

reaction	rates	rate constants (k_i^0) at 60°C
R1	$k_1^0[I^-][IO_3^-][H^+]^2$	$3.18 \times 10^5 \text{ M}^{-3} \text{ min}^{-1}$
R-1	$k_{-1}^0[HIO][HIO_2]$	$7.91 \times 10^7 \text{ M}^{-1} \text{ min}^{-1}$
R2	$k_2^0[HIO_2][I^-][H^+]$	$5.00 \times 10^{11} \text{ M}^{-2} \text{ min}^{-1}$
R3	$k_3^0[I_2O]$	$5.00 \times 10^3 \text{ min}^{-1}$
R-3	$k_{-3}^0[HIO]^2$	$3.15 \times 10^8 \text{ M}^{-1} \text{ min}^{-1}$
R4	$k_4^0[HIO][I^-]$	$3.00 \times 10^{11} \text{ M}^{-1} \text{ min}^{-1}$
R-4	$k_{-4}^0[I_2]/[H^+]$	4.50 M min^{-1}
R5	$(k_5' + k_5''[H^+])[HIO][H_2O_2]$	$k_5' = 12 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$ $k_5'' = 30[H^+] \times 10^3 \text{ M}^{-2} \text{ min}^{-1}$
R6	$k_6^0[I_2O][H_2O_2]$	$5.00 \times 10^5 \text{ M}^{-1} \text{ min}^{-1}$
R7	$k_7^0[HIO_2][H_2O_2]$	$2.00 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$
R8	$(k_8' + k_8''[H^+])[IO_3^-][H_2O_2]$	$k_8' = 9.5 \times 10^{-4} \text{ M}^{-1} \text{ min}^{-1}$ $k_8'' = 3.92 \times 10^{-2} \text{ M}^{-2} \text{ min}^{-1}$

Fig 1(a) refers to the model formed by the first six reactions. The effect of addition of reaction (R7) to the previous model can be seen in Fig. 1(b). The effect of addition of reaction (R8) to the models presented in Figs 1(a) and 1(b) are presented in Figs 1(c) and 1(d), respectively.

The initial concentrations of potassium iodate and acidity are taken to be $[KIO_3]_0 = 0.0733$ and $[H_2SO_4]_0 = 0.0245 \text{ mol/dm}^3$. The experiments with similar initial conditions and similar oscillatory evolution are described in the paper by Anić and Kolar-Anić (Anić and Kolar-Anić 1986).

Although the rate constant of reaction (R8) is very small, it can have an important influence on the overall evolution of the system depending on the other parameters.

Also, this reaction is formally the sum of reactions (R1) and (R5), but the important prolongation of induction period caused by presence of reaction (R8) on the

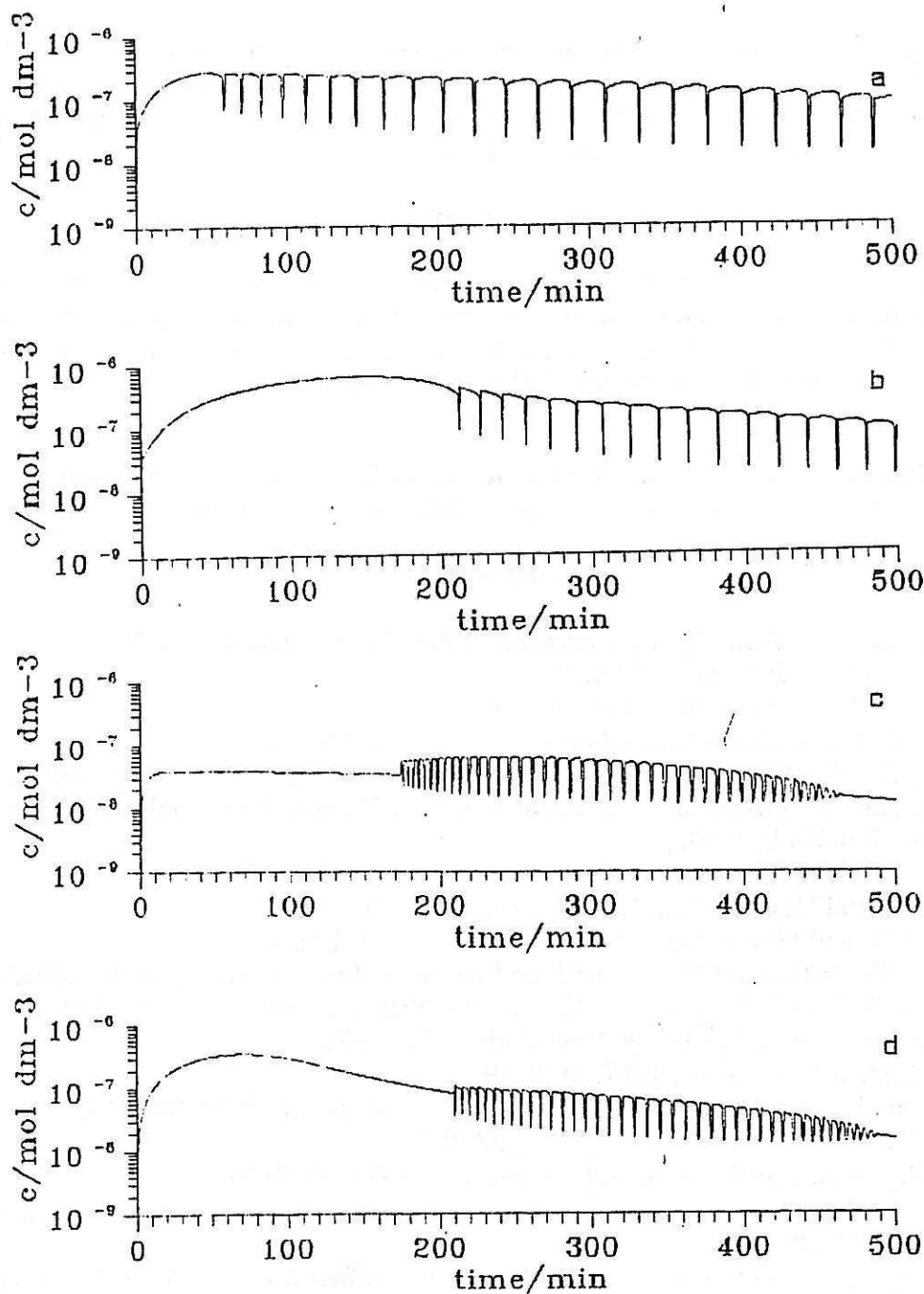


Figure 1. The numerical simulation of iodide concentration during the hydrogen peroxide decomposition in the Bray-Liebafsky system. The rate constants for reactions are listed in Table 1., $[H_2O_2]_0 = 0.35$, $[KIO_3]_0 = 0.0733$ and $[H_2SO_4]_0 = 0.0245$ (in mol/dm^3). Figure 1(a) is for the main subset of the model, reactions (R1) - (R6). Figures 1(b) and 1(c) are for main subset of the model with added single reaction (R7) and (R8) respectively. Figure 1(d) is for the complete model (R1) - (R8).

mechanism (R1)-(R6) (Fig.1(c)) could not be obtained by the model (R1) - (R6) where (R1) and (R5) are present (Fig.1(a)). This is particularly important if we know that analysed reaction (R8) in the Briggs-Rauscher mechanism is explained by the sum of radical reactions (Furrow and Noyes 1982).

Conclusion

It can be seen that the presence of reduction of iodate ion by hydrogen peroxide in the skeleton mechanism proposed by Schmitz et al. (Schmitz 1974, Schmitz 1987, Kolar-Anić and Schmitz 1992) is desirable. Even the rate constant proposed by Liebhafsky (Liebhafsky 1931) can be taken as is.

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