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KINETIC MODEL FOR THE BRAY-LIEBHAFSKY PROCESS WITHOUT THE REACTION $IO_3^- + I^- + 2H^+ \rightleftarrows HIO + HIO_2$

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Abstract

Oscillations in the concentration of intermediates were obtained when a model without reaction $IO_3^- + I^- + 2H^+ \rightleftarrows HIO + HIO_2$ was used for the simulation of the Bray-Liebhafsky process.

Keywords: Oscillatory reactions, Bray-Liebhafsky system, modeling of chemical processes, chemical kinetics, nonlinear dynamics

INTRODUCTION

The mechanism of the Bray-Liebhafsky reaction [1,2], the decomposition of hydrogen peroxide into water and oxygen in the presence of KIO_3 and H_2SO_4:

$$2H_2O_2 \xrightarrow{IO_3^-, H^+} 2H_2O + O_2$$

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is known to be complex [3-11]. Since in that reaction system many species *e.g.*, HIO_2, HIO, I_2, I^- are present, the reactions among all of them, as well as between them and hydrogen peroxide have to be considered when building up a model.

Since the Bray-Liebhafsky reaction is an oscillatory one, the corresponding model should exhibit the characteristics of a nonlinear system [12-14].

One model satisfying oscillatory evolution of the given reaction has been proposed by Schmitz [7]. Later it has been extended to include additional reactions [15,16]. Analyzing the recently suggested variant of the model [16]:

$IO_3^-+I^-+2H^+$	$\rightleftharpoons$	$HIO+HIO_2$	(R1,R-1)
$HIO_2+I^-+H^+$	$\longrightarrow$	I_2O+H_2O	(R2)
I_2O+H_2O	$\rightleftharpoons$	$2HIO$	(R3,R-3)
$HIO+I^-+H^+$	$\rightleftharpoons$	I_2+H_2O	(R4,R-4)
$HIO+H_2O_2$	$\longrightarrow$	$I^-+H^++O_2+H_2O$	(R5)
$I_2O+H_2O_2$	$\longrightarrow$	$HIO+HIO_2$	(R6)
$HIO_2+H_2O_2$	$\longrightarrow$	$IO_3^-+H^++H_2O$	(R7)
$IO_3^-+H^++H_2O_2$	$\longrightarrow$	$HIO_2+O_2+H_2O$	(R8)

which oscillates, we found that the model exhibits oscillatory behavior even if the first reaction is omitted. The following questions await answers: what is the role of reactions [(R1)(R-1)] in the overall model, and how the model behaves if this reaction is neglected? The answers require a careful analysis not only of the complete model consisting of reactions (R1)-(R8) [16], but also of the reduced model with reactions (R2)-(R8).

MODEL CONSISTING OF REACTIONS (R2)-(R8)

Using the Stoichiometric Network Analysis [14], which is an appropriate method for the examination of nonlinear systems, such as the reduced model [(R2)-(R8)], we have found that the overall process of hydrogen peroxide decomposition into water and oxygen, can be realized by two steady-state reaction pathways. They are:

$$HIO_2+I^-+H^+ \longrightarrow I_2O+H_2O \quad \text{(R2)}$$

$$HIO+H_2O_2 \longrightarrow I^-+H^++O_2+H_2O \quad \text{(R5)}$$

$$I_2O+H_2O_2 \longrightarrow HIO+HIO_2 \quad \text{(R6)}$$

$$\text{net:} \quad 2H_2O_2 \longrightarrow 2H_2O+O_2$$

$$HIO_2+H_2O_2 \longrightarrow IO_3^-+H^++H_2O \quad \text{(R7)}$$

$$IO_3^-+H^++H_2O_2 \longrightarrow HIO_2+O_2+H_2O \quad \text{(R8)}$$

$$\text{net:} \quad 2H_2O_2 \longrightarrow 2H_2O+O_2$$

The steady-state concentrations of the intermediates as functions of the hydrogen peroxide concentration are the following:

$$[\mathbf{I^-}]_s = \frac{k_3 k_5^2 k_7}{k_2 k_{-3} k_6 k_8}[\mathbf{H_2O_2}]$$

$$[\mathbf{HIO}]_s = \frac{k_3 k_5}{k_{-3} k_6}$$

$$[\mathbf{HIO_2}]_s = \frac{k_8}{k_7}$$

$$[\mathbf{I_2}]_s = \frac{k_3^2 k_4 k_5^3 k_7}{k_2 k_{-3}^2 k_{-4} k_6^2 k_8}[\mathbf{H_2O_2}]$$

$$[\mathbf{I_2O}]_s = \frac{k_3 k_5^2}{k_{-3} k_6^2}$$

The concentrations of iodate and hydrogen ions are taken as constant since they are relatively large compared to the concentrations of the intermediates and they are incorporated into the rate constants: $k_2 = k_2^0[\mathbf{H}^+]$, $k_3 = k_3^0$, $k_{-3} = k_{-3}^0$, $k_4 = k_4^0$, $k_{-4} = k_{-4}^0/[\mathbf{H}^+]$, $k_5 = k_{5'} + k_5''[\mathbf{H}^+]$, $k_6 = k_6^0$, $k_7 = k_7^0$ and $k_8 = (k_{8'} + k_8''[\mathbf{H}^+])[\mathbf{IO_3^-}]$. The true rate constants are denoted by superscript "^{0}".

The model under consideration [reactions (R2)-(R8)] simulates the oscillatory evolution of the intermediates. The instability condition is given by the following relation between the rate constants and hydrogen peroxide concentration:

$$2\frac{k_3k_5^2}{k_{-3}k_6k_8} > 7 + \frac{k_2k_{-3}k_6k_8}{k_3k_4k_5k_7} + 4\frac{k_6}{k_3}[\mathbf{H_2O_2}]$$

The dependence of instability condition on the iodate and hydrogen concentrations becomes obvious when explicit forms of rate constants are included in the expression.

The numerical simulations of the Bray-Liebhafsky reaction based on models (R2)-(R8) and (R1)-(R8) are performed by integration of the system of ordinary differential equations using the Gear's method [17].

DISCUSSION AND CONCLUSION

By analytical calculations and numerical simulations it was shown that the model consisting of reactions (R2)-(R8) has the general characteristics of an oscillatory chemical reaction. Moreover, oscillations in the concentration of the intermediates appear approximately in their real domains (Fig.1). However, the temporal evolution of the system is closer to that obtained experimentally when reactions (R1,R-1) are included into the model [5,8]. In other words, in the experiments and in the case of model (R1)-(R8), after an oscillatory period, the system exhibits monotonic (non-oscillatory) catalysis, whereas in the case of model (R2)-(R8) the system is confined to the region of instability.

Also, considering the instability condition of the reduced model (R2)-(R8), it can be seen (by explicit calculation of hydrogen peroxide concentration) that an oscillatory region exists for hydrogen peroxide concentrations between zero and some positive value, which is a function of the rate constants. This upper limit is

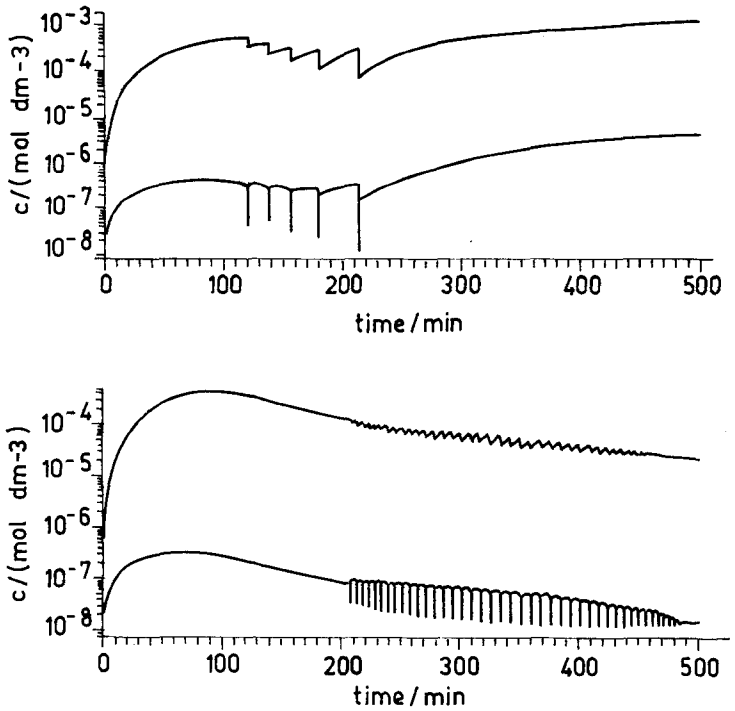

Fig.1. Numerical simulation of iodine and iodide concentration during hydrogen peroxide decomposition in the Bray-Liebhafsky system based on the models (R2)-(R8) and (R1)-(R8), upper and lower figures, respectively. In both cases: $[H_2O_2]_0$ = 0.35 mol/dm^3; $[IO_3^-]_0$ = 0.0733 mol/dm^3; $[H^+]_0$ = 0.049 mol/dm^3. Rate constants used in numerical calculations were taken from ref.16

in accordance with experiments [5,8]. However, in the experiments there is a lower limit too {predictable by the instability condition of complete model (R1)-(R8) [16]}. Notwithstanding that the reduced model (R2)-(R8) generates oscillations, the model that contains also reactions (R1) and (R-1) simulates the experiments much better.

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