



A STUDY OF THE DYNAMIC OF IODINE FORMATION IN THE Mn(II) CATALYSED BRAY-LIEBHAFSKY REACTION

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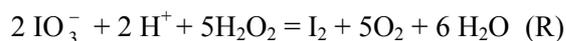
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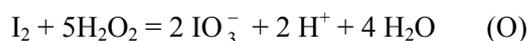
On the basis of the synergistic action of Mn(II) and iodate ions in the Mn(II) catalysed Bray-Liebhafsky system, $\{ \text{IO}_3^-, \text{H}_2\text{O}_2, \text{H}^+, \text{Mn}^{2+} \}$, that was proved previously, a reaction mechanism of iodine formation, based on the concentrations of the species: Mn(II), H_2O_2 and IO_3^- , was proposed and discussed. The evolution of the reaction model is in total agreement with Cooke's experimental data.

INTRODUCTION

The hydrogen peroxide, H_2O_2 , decomposes in water and oxygen with an appreciable rate in the presence of the Fe(II), Fe(III), complex combination like Mn(dipyril)₂ or complex ion like $[\text{MnHCO}_3]^+$.¹ The hydrogen peroxide decomposition is also catalyzed by iodate ions in acidic medium like in the case of the Bray-Liebhafsky oscillating reaction:²⁻⁶



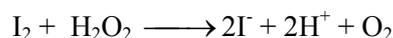
When the iodine concentration and the pH reach critical values, the oxidation reaction of iodine to iodate starts:²⁻⁶



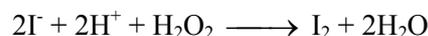
The sum of (R) + (O) gives the total reaction of the hydrogen peroxide decomposition:



In agreement with Guy Schmitz, the constraint parameter which establishes the (O) reaction is the acidity. When the acidity is low, H_2O_2 does not oxidize I_2 but reduces its to I^- :⁶



and



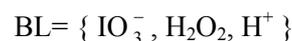
Liebhafsky studied these reactions and concluded that H_2O_2 does not react directly with I_2 .^{7,8} In order that reaction (O) takes place it must exist small amount of IO_3^- and pH=2. So, reaction (R) does not take place totally.

As I_2 is accumulating in the presence of the iodate anions, I_2 is oxidizing to IO_3^- .⁶

Cooke proved experimentally that when Mn(II) was added in the BL system, the I_2 production rate increased considerably.⁹⁻¹⁴

In this work we proposed to study the mechanism by which Mn(II) ion, added to the BL system increases the I_2 production rate.

The next notations were used:



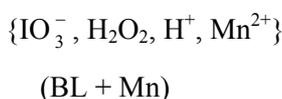
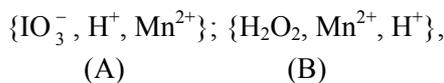
and the system obtained by adding Mn^{2+} is noted:



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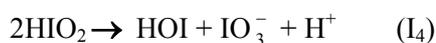
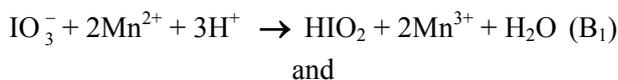
Thermodynamic aspects

The next systems were studied separately:



The system (A) $\{\text{IO}_3^-, \text{H}^+, \text{Mn}^{2+}\}$

In the system (A) $\{\text{IO}_3^-, \text{H}^+, \text{Mn}^{2+}\}$ it would be possible two consecutive reactions:

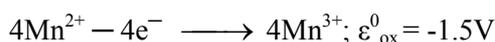


Due to the instability of HIO_2 , the standard reduction potential for the couple $\text{IO}_3^-/\text{HIO}_2$ is not known. There is known however the standard electrode potential for the couple IO_3^-/HOI .

Adding 2(B₁) to (I₄), it results:



The variation of the Gibbs energy for (B₂) can be determined from the values of the standard electrode potentials:¹⁵



With:

$$E^0 = \varepsilon_{\text{red}}^0 + \varepsilon_{\text{ox}}^0 = -0.37 \text{ V}$$

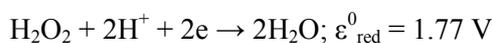
$\Delta_r G^0$ becomes:

$$\begin{aligned} \Delta_r G^0 &= -z F E^0 = -4 \times 96486 \times (-0.3) = \\ &= +1,42 \times 10^5 \text{ J} = +33.93 \text{ kcal.} \end{aligned}$$

Because $\Delta_r G^0$ of the reaction (B₂) has a large, positive value it results that the reaction (B₁) is impossible from thermodynamic point of view; reaction (I₄) would proceed spontaneously^{16,17} if reaction (B₁) would be possible. As a consequence, in the system (A), Mn(II) does not react with IO_3^- producing HIO_2 and Mn(III).

The system (B) $\{\text{H}_2\text{O}_2, \text{Mn}^{2+}, \text{H}^+\}$

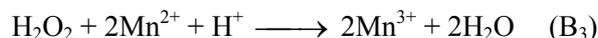
The following reduction and oxidation potentials are known:¹⁵



Consequently:

$$\Delta_r G^0 = -z F E^0 = -5.01 \times 10^4 \text{ J} = -11.98 \text{ kcal.}$$

The negative value of $\Delta_r G^0$ suggests that the reaction takes place thus:



Though, the reaction (B₃) does not take place experimentally.

From the above analysis it results that the separated action of Mn(II) on the IO_3^- , {system (A)}, and the separated action of Mn(II) on H_2O_2 , {system (B)}, does not explain the large production rate of I_2 and O_2 that takes place in the system (BL+Mn), where the Mn^{2+} and IO_3^- species are found simultaneously. It was found also that separated action of the Mn^{2+} and of α , α' dipyridil does not catalyze H_2O_2 decomposition reaction. Instead, their mixture catalyses efficiently the H_2O_2 decomposition, as it was shown in the introduction.¹

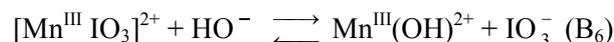
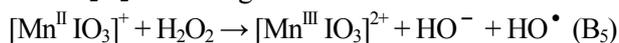
RESULTS AND DISCUSSION

The system $\{\text{IO}_3^-, \text{H}_2\text{O}_2, \text{H}^+, \text{Mn}^{2+}\}$

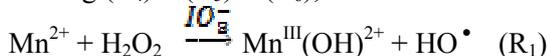
According to the theory of Pearson, the Mn^{2+} and IO_3^- acceptor-donor pair forms a complex ion:¹⁸



We took into consideration the only one iodate anion because as we will show further, the complex ion is less stable. This complex ion acts with H_2O_2 according to the reactions:



Adding (B₄) + (B₅) + (B₆), results:



Reaction (B₆) is possible because HO^- ion has a stronger nucleofilicity than IO_3^- which is substituted from $[\text{Mn}^{\text{III}} \text{IO}_3]^{2+}$. Through this mechanism initiated by $[\text{Mn}^{\text{II}} \text{IO}_3]^+$ complex ion, according to the global reaction (R₁), it appears two very reactive intermediate species, HO^\bullet and $\text{Mn}^{\text{III}}(\text{OH})^{2+}$, which both react with H_2O_2 with HO_2^\bullet formation.

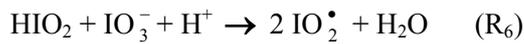
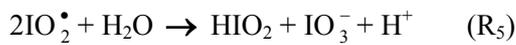
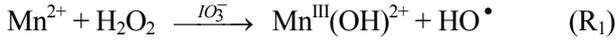
In a previous work we proved experimentally, using a kinetic method (the spectrophotometric study of iodine formation in Dushamn reaction) and cyclic voltammetry that iodate anions come

into coordination sphere of Mn(II) with the formation of a complex ion, $[\text{MnIO}_3]^+$.¹⁹

The dynamic of I₂ formation in the Mn(II) catalysed Bray-Liebhafsky Reaction

We proposed below the reaction mechanism which is initiated by HO• and Mn^{III}(OH)²⁺, according to the reaction (R₁).

Reactions set 1:



$$\frac{d[\mathbf{X}_i]}{dt} = \sum v_{ip} v_p = \sum_{i=1}^n v_{ip} k_p \prod [\mathbf{X}_{ip}]^{m_i} \quad (\rho = 1, r) \quad (1)$$

With:

\mathbf{X}_i = the concentration of the specie i ($i = \overline{1, n}$)

v_{ip} = the stoichiometric coefficient of the specie i that reacts in the reaction ρ

k_p = the rate constant of the reaction ρ

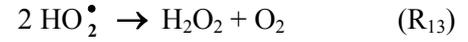
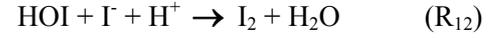
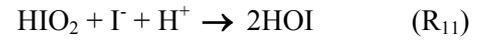
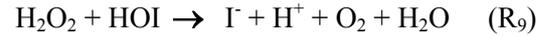
v_p = the rate of the reaction ρ

m_i = the partial order of reaction.

By numerical integration we obtained the temporal evolution of the species, that is $[\mathbf{X}_i] = f(\text{time})$. For this purpose we used the rate constants from the Table 1.

In Fig. 1 are shown the temporal evolutions of the final species: IO_3^- and I_2 when the initial concentrations of the reactants are: $[\text{IO}_3^-] = 4.4 \times 10^{-2}$ M; $[\text{H}_2\text{O}_2] = 1.2$ M; $[\text{Mn}^{2+}] = 8 \times 10^{-3}$ M and $[\text{H}^+] = 5.3 \times 10^{-2}$ M.

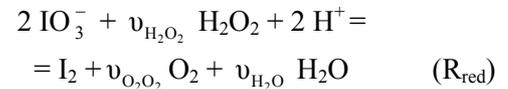
From the $[\text{IO}_3^-] = f(\text{time})$ and $[\text{I}_2] = f(\text{time})$ figures we calculated the IO_3^- disappearance rates and the I_2 appearance rates according to the global reduction reaction obtained from the set 1:



We proposed the reactions (B₄), (B₅), (B₆), (R₁). The other reactions were proposed by Furrow and Noyes.¹⁹⁻²² From this reason we kept the initial notations of these authors. $\text{HO}_2\bullet$ radical plays an important role in the $\text{IO}_2\bullet$ radical appearance, according to the (R₄) reaction. Indeed, Cooke demonstrated that $\text{IO}_2\bullet$ represents the key-intermediary in the I_2 formation mechanism.^{10,11}

We consider as variables the external species IO_3^- , H_2O_2 , I_2 and O_2 as well as the intermediate species: $\text{HO}\bullet$, $\text{Mn}(\text{OH})^{2+}$, $\text{HO}_2\bullet$, $\text{IO}_2\bullet$, HIO_2 , HOI and I^- .

For each species we write a differential equation with the next form:



Taking into consideration the definition equation of the reaction rate:

$$v = \frac{1}{v_i} \frac{d[\mathbf{X}_i]}{dt} \quad (2)$$

that is unique for the all species, we have:

$$v = \frac{1}{2} \frac{\Delta[\text{IO}_3^-]}{\Delta t} = \frac{4.4 \times 10^{-2}}{2 \times 84.615} = 2.600 \times 10^{-4} \left[\frac{\text{mol}}{\text{L} \cdot \text{s}} \right]$$

$$v = \frac{1}{1} \frac{\Delta[\text{I}_2]}{\Delta t} = \frac{2.2 \times 10^{-2}}{84.615} = 2.600 \times 10^{-4} \left[\frac{\text{mol}}{\text{L} \cdot \text{s}} \right]$$

Cooke proved¹¹ that in the Mn(II) presence, the appearance rate of I_2 is the first order with respect to Mn(II) and H_2O_2 and the zero order with respect to IO_3^- , when $[\text{IO}_3^-] > 2 \times 10^{-2}$ M.

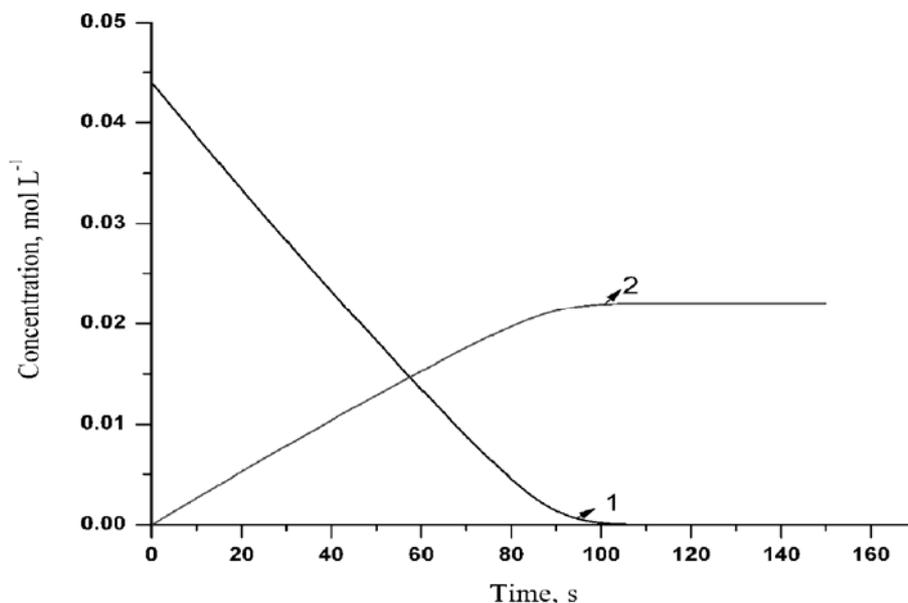


Fig. 1 – The temporal evolution of the final species: IO_3^- (curve 1) and I_2 (curve 2) when the initial concentrations of the reactants are: $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{O}_2] = 1.2 \text{ M}$; $[\text{Mn}^{2+}] = 8 \times 10^{-3} \text{ M}$ and $[\text{H}^+] = 5.3 \times 10^{-2} \text{ M}$.

We studied these aspects taking into consideration the reactions which were proposed in the reaction set 1 and, evidently, the system of differential equation (1).

a) The influence of Mn(II) concentration

The curve 1 of Fig. 2, shows the temporal evolution of the iodine concentration when $[\text{Mn(II)}] = 8 \times 10^{-3} \text{ M}$ (curve 1, Fig. 2). If the Mn(II) concentration increases two times, $[\text{Mn(II)}] =$

$2 \times 8 \times 10^{-3} \text{ M}$, the I_2 apparition rate increases also two times. (Fig. 2, curve 2).

If $[\text{Mn(II)}] = 0.5 \times 8 \times 10^{-3} \text{ M}$, the I_2 apparition rate is decreasing two times (Fig. 2, curve 3). The other concentrations of the reactants stay constants $[\text{H}_2\text{O}_2] = 1.2 \text{ M}$; $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$.

b) The influence of H_2O_2 concentration

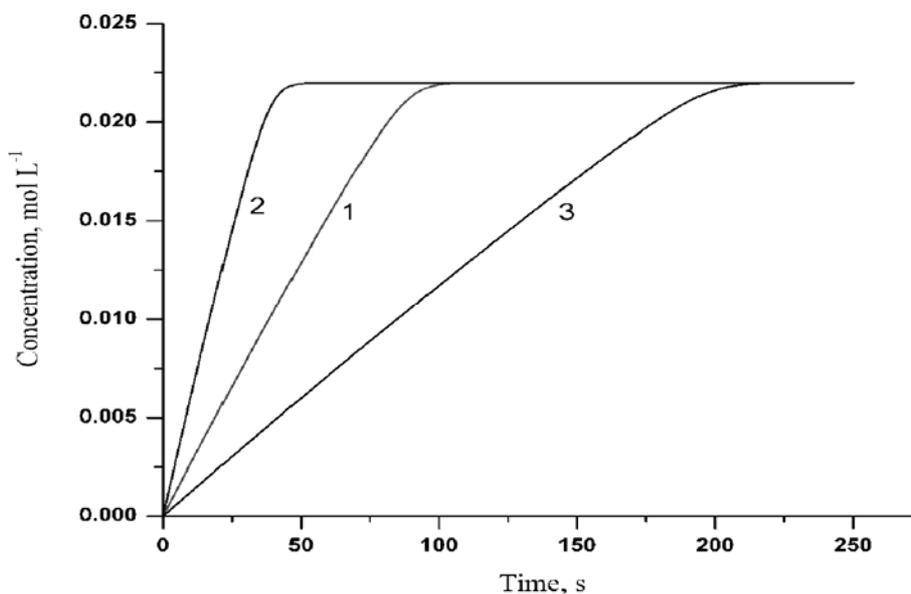


Fig. 2 – The temporal evolution of the iodine concentration with $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{O}_2] = 1.2 \text{ M}$ and: $[\text{Mn(II)}] = 8 \times 10^{-3} \text{ M}$ (curve 1), $[\text{Mn(II)}] = 2 \times 8 \times 10^{-3} \text{ M}$ (curve 2), $[\text{Mn(II)}] = 0.5 \times 8 \times 10^{-3} \text{ M}$ (curve 3).

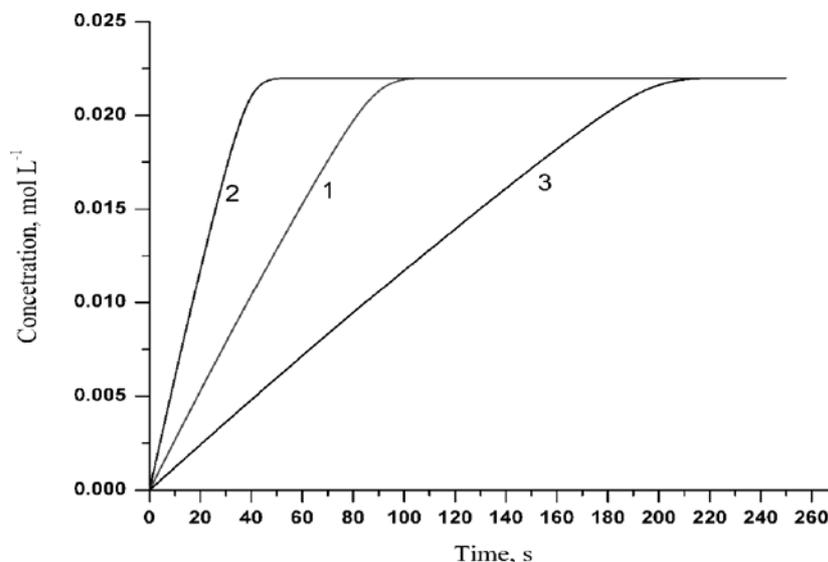


Fig. 3 – The temporal evolution of the iodine concentration with $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$, $[\text{Mn}^{2+}] = 8 \times 10^{-3} \text{ M}$ and: $[\text{H}_2\text{O}_2] = 1.2 \text{ M}$ (curve1), $[\text{H}_2\text{O}_2] = 2 \times 1.2 \text{ M}$ (curve2), $[\text{H}_2\text{O}_2] = 0.5 \times 1.2 \text{ M}$ (curve 3).

The curve 1 of Fig. 3 shows the temporal evolution of the iodine concentration when $[\text{H}_2\text{O}_2] = 1.2 \text{ M}$, $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$ and $[\text{Mn}^{2+}] = 8 \times 10^{-3} \text{ M}$.

If $[\text{H}_2\text{O}_2] = 2 \times 1.2 \text{ M}$, then I_2 appearance rate increases two times (Fig. 3, the curve 2). When $[\text{H}_2\text{O}_2] = 0.5 \times 1.2 \text{ M}$, then the I_2 appearance rate decreases two times (Fig. 3, the curve 3).

c) The influence of IO_3^- concentration

When $[\text{IO}_3^-] = 2 \times 4.4 \times 10^{-2} \text{ M}$ (Fig. 4, curve 2) or $[\text{IO}_3^-] = 0.5 \times 4.4 \times 10^{-2} \text{ M}$ (Fig. 4, curve 3), the I_2 appearance rate stays constant. The curve 1 from Fig. 4 corresponds to the $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$.

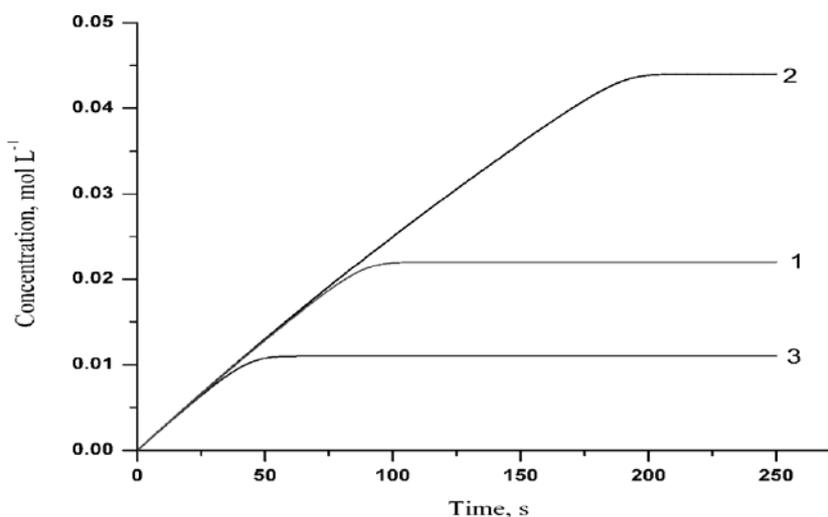
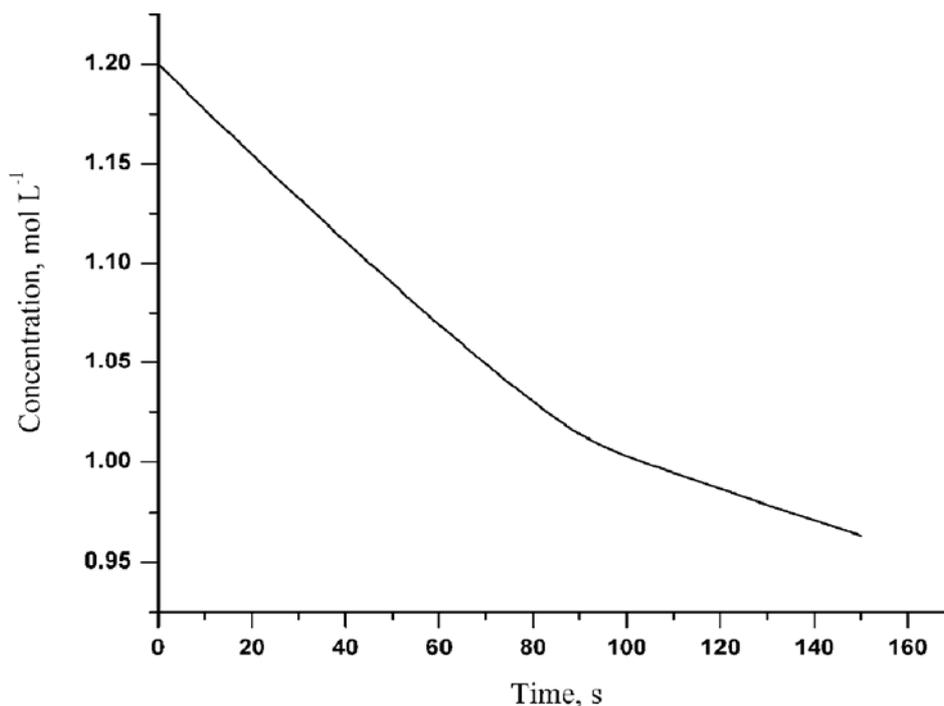
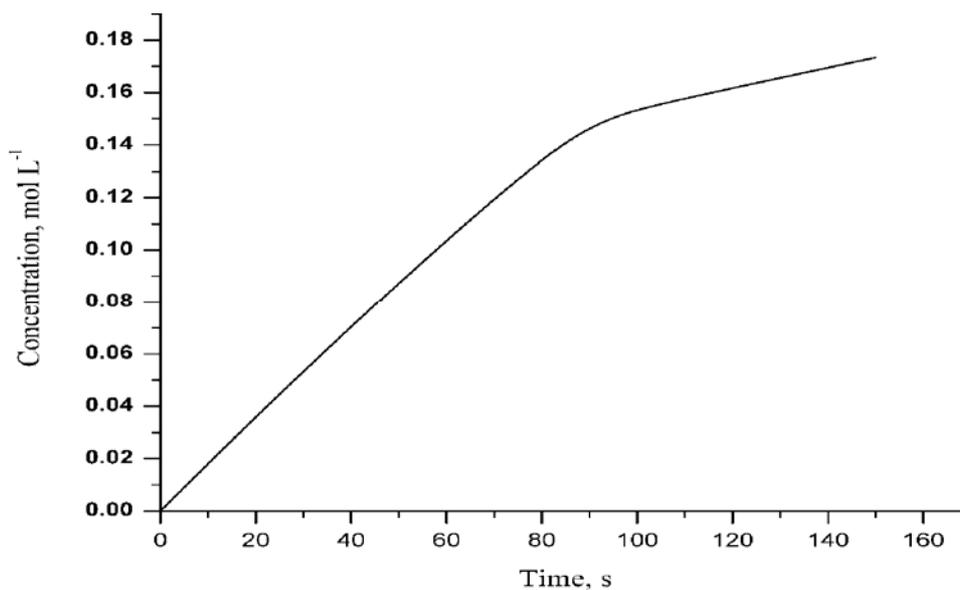


Fig. 4 – The temporal evolution of the iodine concentration with $[\text{H}_2\text{O}_2] = 1.2 \text{ M}$; $[\text{Mn}^{2+}] = 8 \times 10^{-3} \text{ M}$ and: $[\text{IO}_3^-] = 4.4 \times 10^{-2} \text{ M}$ (curve 1), $[\text{IO}_3^-] = 2 \times 4.4 \times 10^{-2} \text{ M}$ (curve 2), $[\text{IO}_3^-] = 0.5 \times 4.4 \times 10^{-2} \text{ M}$ (curve 3).

So, the model proposed by us is in total agreement with the experimental data of Cooke.

From the temporal evolution of the H_2O_2 disappearance (Fig. 5) and the O_2 appearance (Fig. 6) it could be observed that exists a slope change which corresponds exactly to the total disappearance time of IO_3^- or of the full production of I_2 , in our case, $t = 84.6 \text{ s}$. After this point, as we will prove further, the H_2O_2 decrease concentration and the O_2 increase concentration will follow another path.

Fig. 5 – The H₂O₂ evolution in time.Fig. 6 – The O₂ evolution in time.

The inflexion point is determined through the extrapolation of the linear portions. This point allowed us to determine the number of H₂O₂ moles which were consumed and the number of O₂ moles which appeared in the 84.6 s interval time. From the both representations we have found $n_{\text{H}_2\text{O}_2} = 0.1833$ mol respectively, $n_{\text{O}_2} = 0.1465$.

The stoichiometric coefficients could be calculated knowing the number of H₂O₂ moles which were consumed and the number of O₂ moles which appeared, from the global reaction (R_{5red}) in two ways:

a) From the reaction rate equation (2) that is unique, $v = 2.600 \cdot 10^{-4}$, we obtained the stoichiometric coefficient of H₂O₂, respectively of O₂:

$$v = \frac{1}{v_{\text{H}_2\text{O}_2}} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{v_{\text{H}_2\text{O}_2}} \frac{0.1833}{84.61} = \frac{2.166 \cdot 10^{-3}}{v_{\text{H}_2\text{O}_2}} = 2.600 \cdot 10^{-4} \Rightarrow v_{\text{H}_2\text{O}_2} = 8.3300$$

$$v = \frac{1}{v_{O_2}} \frac{\Delta[O_2]}{\Delta t} = \frac{1}{v_{O_2}} \frac{0.1465}{84.61} = \frac{1.7314 \cdot 10^{-3}}{v_{O_2}} = 2.600 \cdot 10^{-4} \Rightarrow v_{O_2} = 6.6592$$

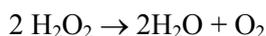
b) From the IO_3^- initial concentration using the reduction global equation (R_{red}).

If 0.044 mol IO_3^- reacts with 0.1833 mol H_2O_2 , then 2 mol IO_3^- reacts with $v_{H_2O_2} = 8.3318$ mol H_2O_2 .

We obtained in the same way for O_2 , $v_{O_2} = 6.6591$ mol. These values are in agreement with the coefficients $v_{H_2O_2}$ and v_{O_2} obtained from the unique expression of the reaction rate (2).

So, from 1.2 mol H_2O_2 , 0.1833 mol H_2O_2 react according to the global reaction (R_{red}) until the whole iodate amount will be consumed.

The difference, 1.2 mol $H_2O_2 - 0.1833$ mol $H_2O_2 = 1.0167$ mol H_2O_2 participates to the reactions R_1, R_2, R_3 and R_{13} . These reactions take place due to the Mn(II) which is renewable continuously, until the whole H_2O_2 amount is consumed. $R_g = R_1 + R_2 + R_3 + R_{13} \Rightarrow$



According to this reaction, it results that 1.0167 mol H_2O_2 decomposes due to this 4 reactions where do not participate the species with iodine. So, for 1.0167 mol H_2O_2 corresponds 0.5083 mol O_2 .

Indeed, if we consider only the reactions R_1, R_2, R_3 , and R_{13} , taking as initial condition $[H_2O_2] = 1.016$ from numerical integration we obtained the temporal evolution from Fig. 7.

It can be observed from Fig. 7 that $[O_2]_{final} = 0.5084$ mol.

The total number of O_2 mol = $0.1465 + 0.5083 = 0.6548$ mol.

Using the numerical integration for the all 13 reaction set on a time interval 10 000 s, the total number of moles is 0.6549 (Fig. 8).

The values of the rate constants are given in the Table 1.

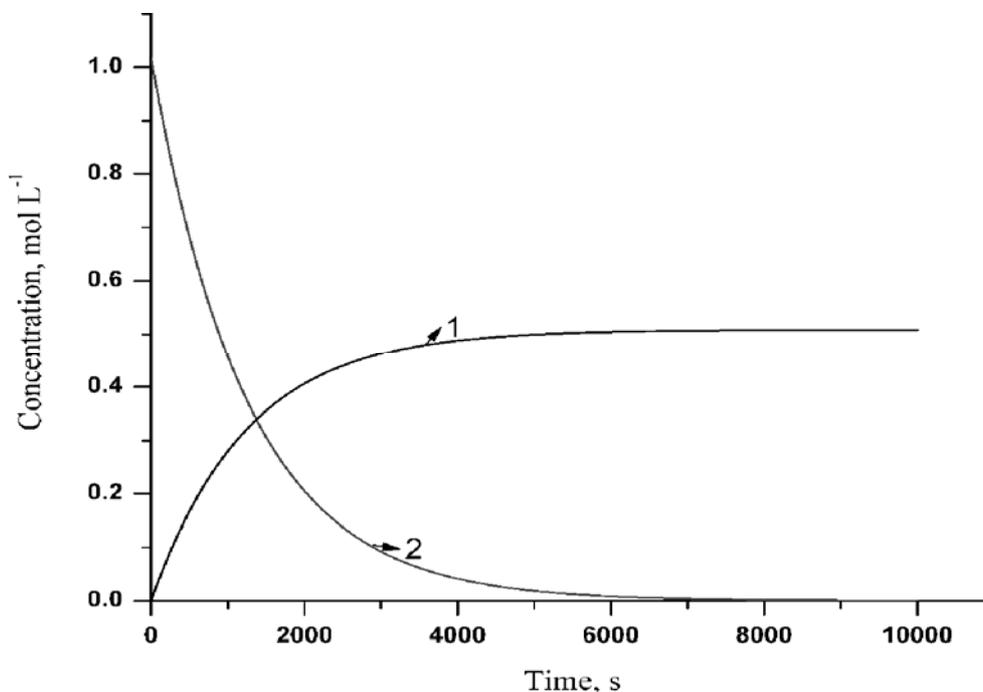


Fig. 7 – The H_2O_2 evolution in time (curve 2) and the O_2 evolution in time (curve1).

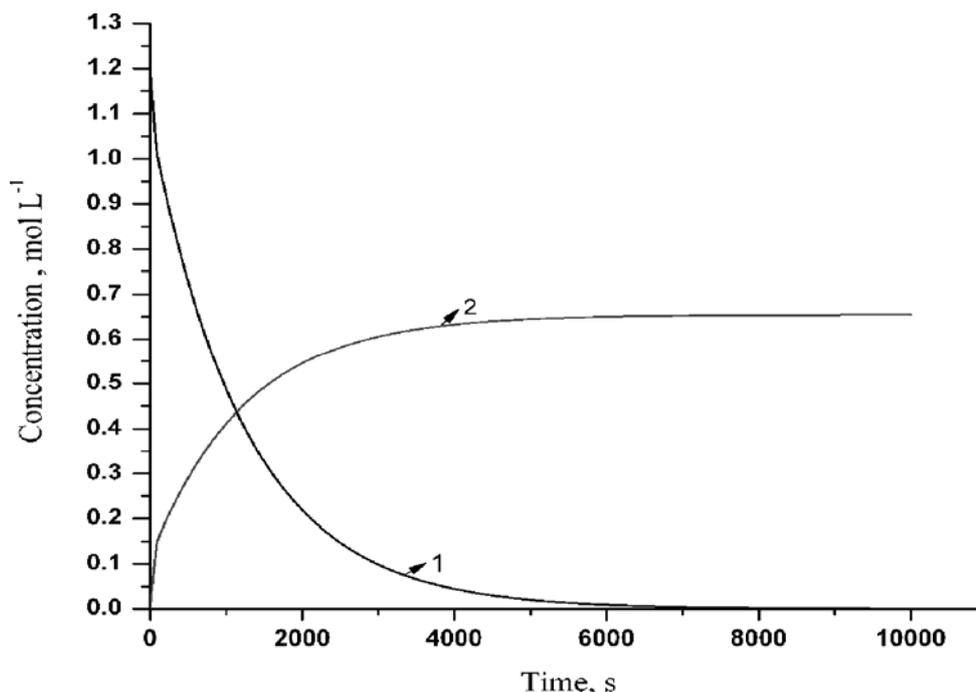


Fig. 8 – The H₂O₂ (curve 1) and O₂ (curve 2) evolution in time.

Table 1

The rate constants used for the integration of reaction set 1

Reaction	Rate constants used in this work and literature	
(R ₁)	this work (new)	
(R ₂)	$1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	1, 27
(R ₃)	$3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	22, 27, 28
(R ₄)	$3.5 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$	28
(R ₅)	$3.06 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$	23
(R ₆)	$2.3 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$	28
(R ₇)	$180.18 \text{ M}^{-2} \text{ s}^{-1}$	22, 27, 29
(R ₈)	$6.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	27-29
(R ₉)	$2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	26
(R ₁₀)	$1.4 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$	22, 27-29
(R ₁₁)	$1.43 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	28
(R ₁₂)	$3.1 \times 10^{12} \text{ M}^{-2} \text{ s}^{-1}$	22, 27-29

CONCLUSIONS

It was proposed and discussed a mechanistic model of iodine formation in the Bray-Liebhafsky Reaction taking into consideration the hydrogen peroxide decomposition in the $[\text{Mn}^{\text{II}}\text{IO}_3]^+$ complex ion presence as initiation reaction.

We discussed our results in terms of the proposed model that proved good agreement with Cooke's experimental results.

The reactive species $\text{Mn}^{\text{III}}(\text{OH})^{2+}$ and HO^\bullet that appear in the reactions (B₄), (B₅), (B₆) și (R₁), are responsible by the considerable increase of the I₂ amount in the Mn(II) presence.

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