



ON THE Mn(II) AND Ce(III) ROLE ON THE I₂ PRODUCTION IN THE SYSTEM { IO₃⁻, H₂O₂, H⁺ }

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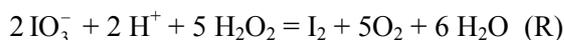
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The Mn(II) and Ce(III) ions role on the iodine production in the systems: { I⁻, IO₃⁻, H⁺ }, and { IO₃⁻, H₂O₂, H⁺ } with reference to the { IO₃⁻, Meⁿ⁺, H₂O₂, MA, H⁺ } was investigated. We proved experimentally the formation of the metal-iodate complex ions, [MnIO₃]⁺, [CeIO₃]²⁺, that represent the key intermediates in the hydrogen peroxide decomposition reaction with iodine production.

INTRODUCTION

The hydrogen peroxide decomposition in water and oxygen was proved¹ to take place with an appreciable rate in the presence of the Fe(II), Fe(III), complex combinations like Mn(dipyridyl)₂ or complex ions like [MnHCO₃]⁺.

Cooke proved experimentally that the iodine formation rate increases considerably in the presence of Mn(II) and Ce(III) ions in the reduction reaction:²⁻⁹



It was proved experimentally^{10,11} that no Mn(II) but the [MnIO₃]⁺ complex ions catalyse the reduction reaction (R). In the present work we prove experimentally that indeed the [MnIO₃]⁺ and also [CeIO₃]²⁺, which were put in evidence using the spectral methods and cyclic voltammetry, catalyse this reaction. In order to study the influences of the complex ions on the iodine formation we followed spectrally the iodine formation in time in two different systems, { I⁻, IO₃⁻, H⁺ } (the Dushman reaction), and { IO₃⁻, H₂O₂, H⁺ } (named BL system).

EXPERIMENTAL

Chemicals: The all chemicals used were provided by Merck Comp.

1. The Dushman Reaction

The kinetics of the Dushman reaction were performed using a Shimadzu UV-Viz Spectrophotometer at $\lambda = 469 \text{ nm}$.

The following concentrations were used:

- [KIO₃] = 4.33 x 10⁻⁴ M;
[KI] = 2.166 x 10⁻³ M;
[HClO₄] = 2.6 x 10⁻³ M (fig.1, curve 1)
- [KIO₃] = 4.33 x 10⁻⁴ M;
[KI] = 2.166 x 10⁻³ M;
[HClO₄] = 2.6 x 10⁻³ M;
[Ce³⁺] = 2x10⁻⁵ M from Ce(NO₃)₃ x 6 H₂O (fig. 1, curve 2)
- [KIO₃] = 4.33 x 10⁻⁴ M; [KI] = 2.166 x 10⁻³ M;
[HClO₄] = 2.6 x 10⁻³ M; [Mn²⁺] = 10⁻³ M from MnSO₄ x H₂O; (fig. 1, curve 3)
- [KIO₃] = 4.33 x 10⁻⁴ M; [KI] = 2.166 x 10⁻³ M;
[HClO₄] = 2.6 x 10⁻³ M; [Mn²⁺] = 10⁻³ M;
[Ce³⁺] = 2x10⁻⁵ M (fig.1, curve 4)

2. The cyclic voltammetry

The cyclic voltammograms were performed using a PGZ 301 potentiostat produced by Radiometer France. The software was Voltmaster 4. The working electrode used in the cyclic voltammetry experiments was a platinum disc (1 cm²), a platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode.

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The scanning rate was

50mV s⁻¹. The following mixtures were prepared:

- a. [KIO₃] = 3 x 8 x 10⁻³ M;
[HClO₄] = 0.053 M (fig.2, curve 1)
- b. [KIO₃] = 3 x 8 x 10⁻³ M;
[Mn(II)] = 8 x 10⁻³ M from MnSO₄.H₂O;
[Ce(III)] = 8 x 10⁻⁵ M from
Ce(NO₃)₃ x 6H₂O; [HClO₄] = 0.053 M (fig.2, curve 2)
- c. [Mn(II)] = 8 x 10⁻³ M;
[Ce(III)] = 8 x 10⁻⁵ M; [HClO₄] = 0.053 M (fig. 3)
- d. [KIO₃] = 8 x 10⁻³ M;
b. [HClO₄] = 0.053 M (fig.4, curve 1)
- e. [KIO₃] = 8 x 10⁻³ M;
[Mn(II)] = 8 x 10⁻³ M; [HClO₄] = 0.053 M (fig.4, curve 2)
- f. [Mn(II)] = 8 x 10⁻³ M; [HClO₄] = 0.053 M; (fig. 5)

3. The iodine formation in the system { IO₃⁻, H₂O₂, H⁺ } (BL) in the Mn(II), Ce(III) and Mn(II)+Ce(III) presence was followed spectrally using a Shimadzu UV-Viz Spectrophotometer at λ = 460 nm.

The following solutions were prepared:

- a. [KIO₃] = 4.4 x 10⁻² M;
[HClO₄] = 5.8 x 10⁻³ M;
[H₂O₂] = 1.2 M; (curve 1, fig.4)
- b. [KIO₃] = 4.4 x 10⁻² M;
[Mn(II)] = 8 x 10⁻³ M;
[HClO₄] = 5.8 x 10⁻³ M; [H₂O₂] = 1.2 M; (curve 2, fig.4)
- c. [KIO₃] = 4.4 x 10⁻² M;
[Ce(III)] = 4 x 10⁻⁵ M;
[HClO₄] = 5.8 x 10⁻³ M; [H₂O₂] = 1.2 M; (curve 3, fig.4)
- d. [KIO₃] = 4.4 x 10⁻² M;
[Ce(III)] = 4 x 10⁻⁵ M; [Mn(II)] = 8 x 10⁻³ M;
[HClO₄] = 5.8 x 10⁻³ M; [H₂O₂] = 1.2 M; (curve 4, fig.4)

4. BR measurements

Oscillations in the system { IO₃⁻, Meⁿ⁺, H₂O₂, MA, H⁺ } (noted BR), with Meⁿ⁺ = Mn(II) or Ce(III), MA = malonic

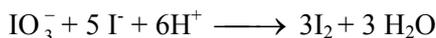
acid, were followed potentiometrically by recording the potential of a platinum electrode. The electrode was connected to a multimeter (WTW, model pH 540 GLP, Weilheim i. OB, Germany) controlled by an IBM-compatible PC. The accuracy of the multimeter was ± 1 mV. The data acquisition program Multi Achat II (WTW, Weilheim i. OB, Germany) was used. The multimeter was equipped with a temperature sensor with an accuracy of ± 0.1°C. All solutions and reaction mixtures were maintained at constant temperature (25.0 °C) using a thermostating system (accuracy ± 0.1 °C).

The mixture containing the solutions with the concentrations: [Mn(II)] = 4.8 x 10⁻⁴ M, [NaIO₃] = 0.067 M; [MA] = 0.05 M; [H₂O₂] = 1.2 M; [HClO₄] = 0.053 M did not presented an oscillating regime because of the low concentration of Mn(II).

The mixture containing the solutions with the concentrations: [Mn(II)] = 4.0 x 10⁻⁴ M, [Ce(III)] = 8 x 10⁻⁵ M, so the concentration of the metal ions being equal to that of Mn(II) in the measurement with Mn(II) ions only as catalyst, 4.8 x 10⁻⁴ M, [NaIO₃] = 0.067 M; [MA] = 0.05 M; [H₂O₂] = 1.2 M; [HClO₄] = 0.053 M presented an oscillating regime with a long time duration (4000 s). (fig.7)

RESULTS AND DISCUSSION

a. The Dushman reaction is:



and the iodine formation in time is presented in the fig. 1, curve1.

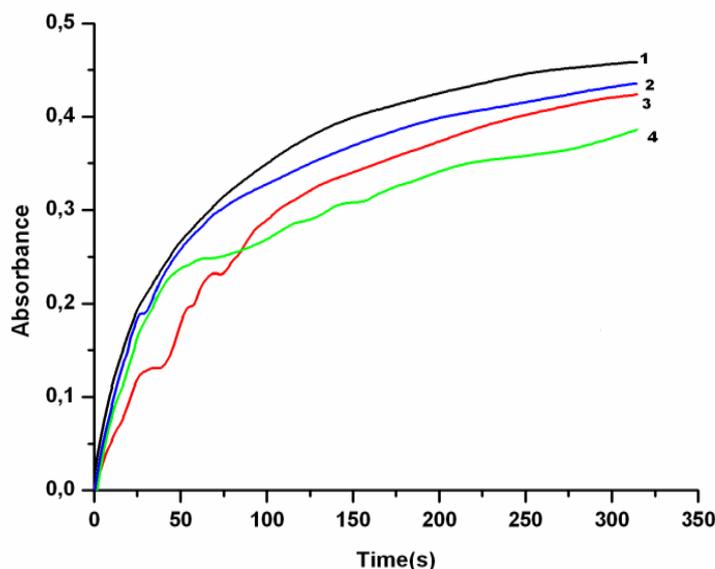


Fig. 1 – The Dushman reaction (curve 1); the Dushman reaction in the Ce(III) presence (curve 2); the Dushman reaction in the Mn(II) presence (curve 3); the Dushman reaction in the Mn(II) and Ce(III) presence (curve 4).

It can be observed that adding a concentration of $[Ce^{3+}] = 2 \times 10^{-5}$ M to the mixture corresponding to the Dushman reaction, the value of the absorbance is diminished from 0.454 to 0.430 (curve 2, fig. 1) and the concentration of $[Mn^{2+}] = 10^{-3}$ M diminished the value of the absorbance to 0.420 (curve2, fig.1). Adding a concentration of the

metal ions of $[Mn^{2+}] = 10^{-3}$ M and $[Ce^{3+}] = 2 \times 10^{-5}$ M the value of the absorbance is diminished from 0.454 to 0.385 (fig. 1, curve 4).

b. The following cyclic voltammograms were recorded:

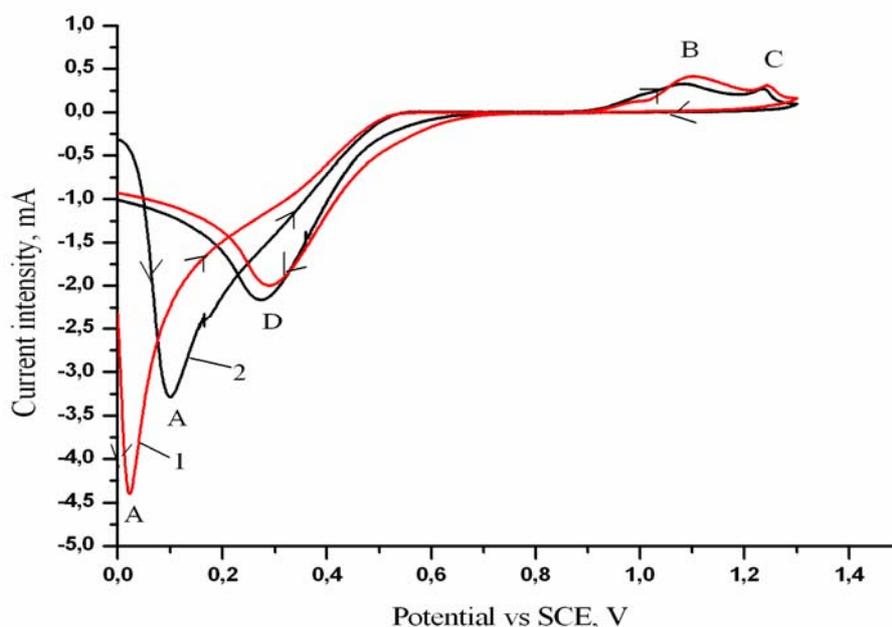


Fig. 2 – The cyclic voltammograms of the iodate (curve 1) and iodate in the Mn(II) and Ce(III) presence (curve2).

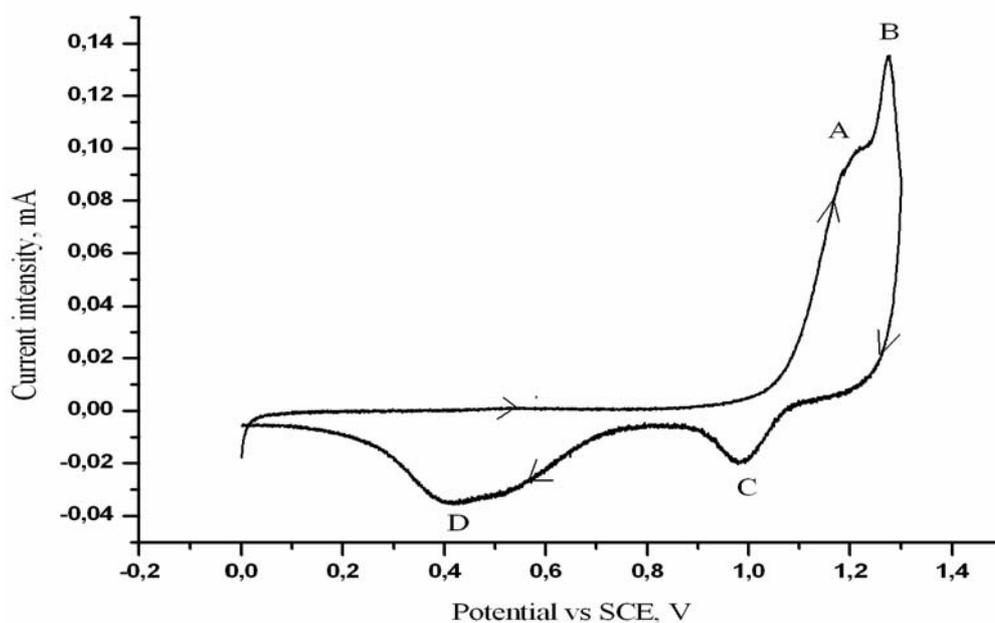


Fig. 3 – The cyclic voltammogram of Mn(II) and Ce(III).

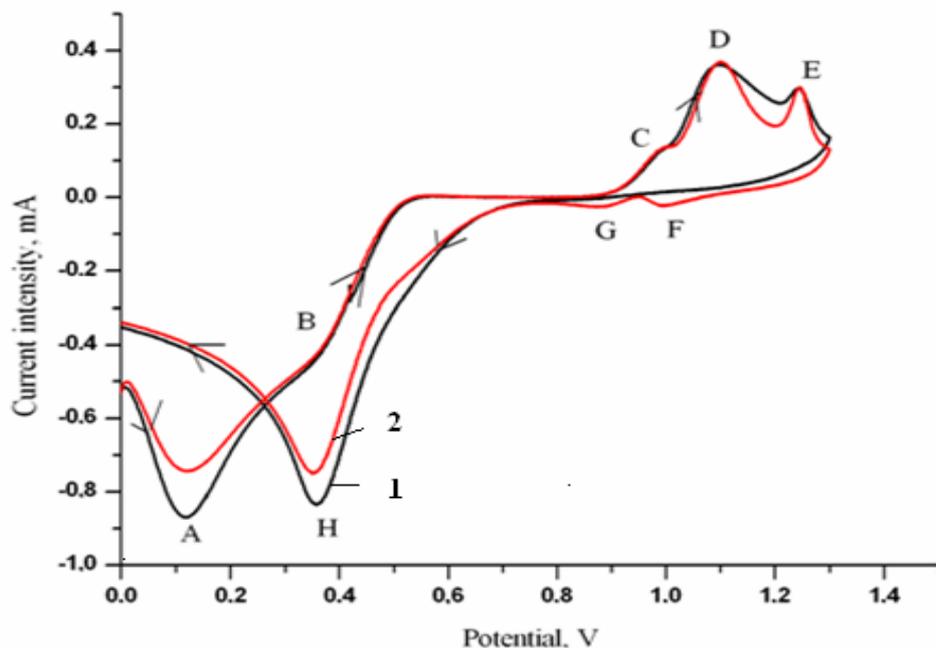


Fig. 4 – The cyclic voltammograms: iodate (curve 1) and iodate in the Mn(II) presence (curve 2).

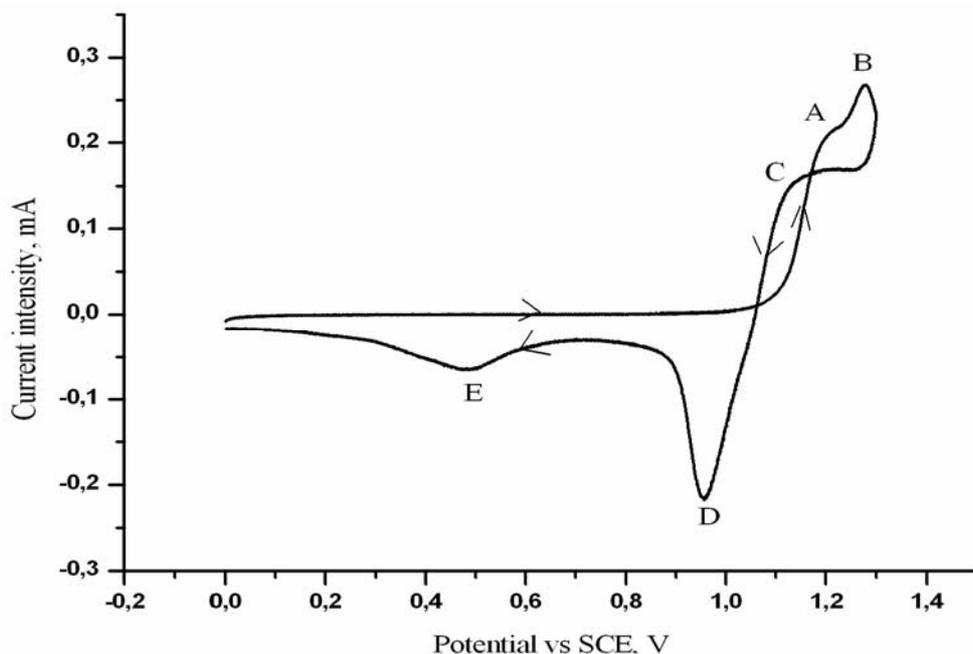


Fig. 5 – The cyclic voltammogram of Mn(II).

Comparing the cyclic voltammograms of iodate and iodate in the metal ions presence, it can be observed that the reduction peak D, from fig. 5 became the reduction peak F in the cyclic voltammogram – fig. 4 and also the peaks corresponding to the iodate are diminished in the presence of Mn(II) ions (the curves 2 in the fig. 4).

In the Mn(II) and Ce(III) presence, the reduction peak A of the iodate from fig. 2, curve 2, is removed and also the current intensity is reduced.

c. The study of the iodine formation in time in the BL system is presented in the fig. 6.

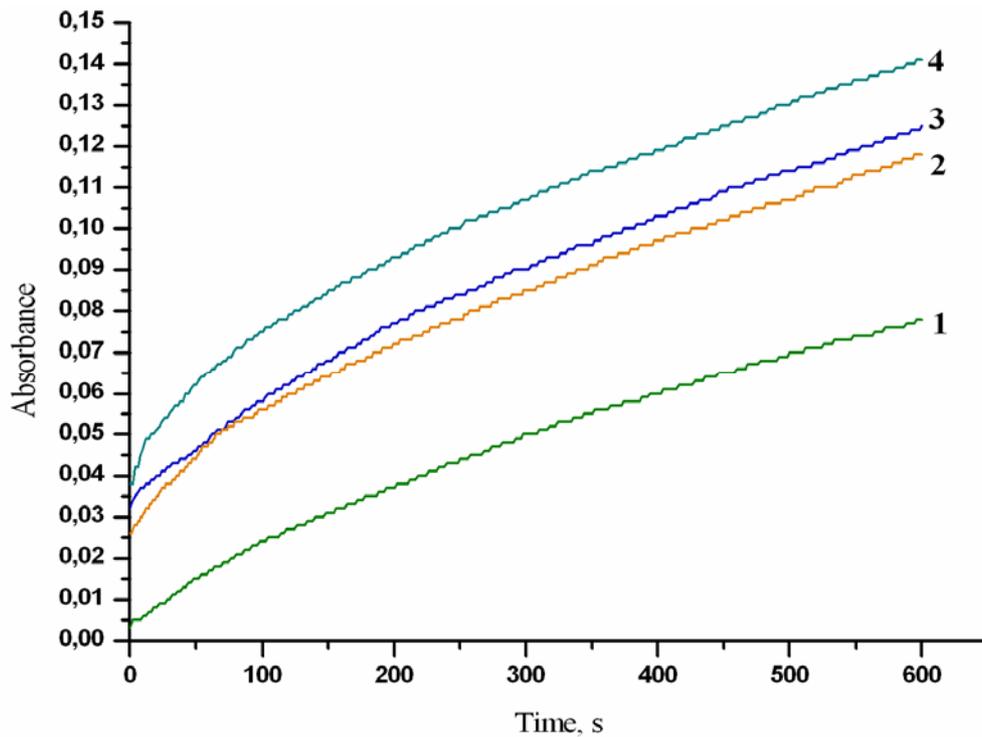


Fig. 6 – The iodine formation vs time: the BL system (curve 1); the system BL + Mn(II) (curve 2); the system BL + Ce(III) (curve 3); the system BL + Mn(II) + Ce(III) (curve 4).

It can be observed that a concentration of 4×10^{-5} M [Ce(III)] is more efficient in the iodine formation than 8×10^{-3} M [Mn(II)].

d. The BR measurements prove that a mixture of [Mn(II)] = 4.0×10^{-4} M and [Ce(III)] = 8×10^{-5} M is

more efficient in the oscillating regime appearance than the same concentration of Mn(II). (fig.7). So, a concentration of 8×10^{-5} M Ce(III) is much more efficient in the autocatalysis appearance than the same concentration of Mn(II).

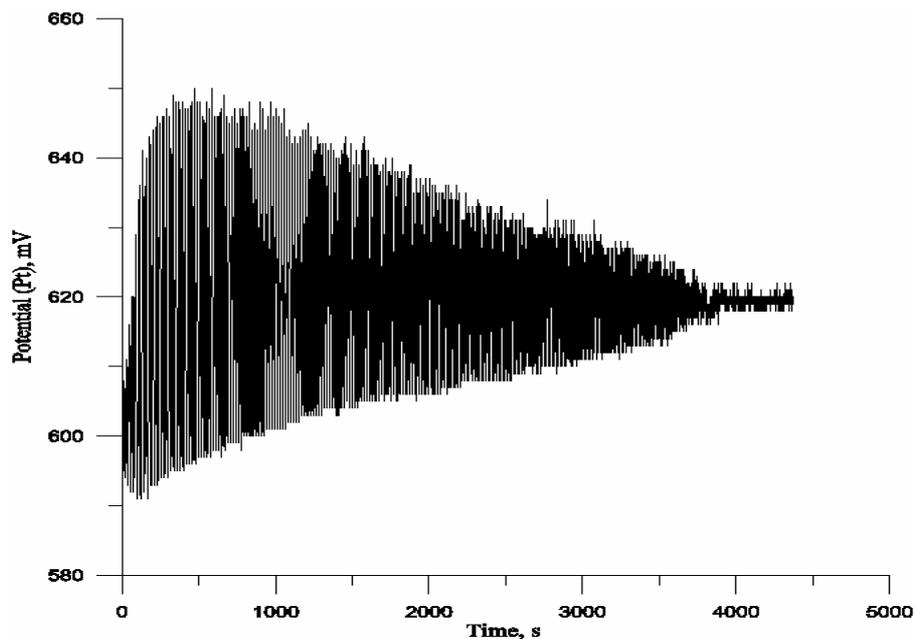
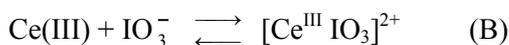
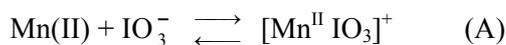


Fig. 7 – The autonomous oscillator recorded in the mixture: [Mn(II)] = 4.0×10^{-4} M, [Ce(III)] = 8×10^{-5} M, [NaIO₃] = 0.067 M; [MA] = 0.05 M; [H₂O₂] = 1.2 M; [HClO₄] = 0.05 M.

The formation of the complex ions that was proved experimentally (fig. 1, fig. 2, fig. 3 and 4) is due to the equilibrium:



Knowing the extinction coefficient of I_3^- at 469 nm, $\epsilon = 720 \text{ cm/M}$, we calculated the maximum concentrations of I_3^- at equilibrium state, for the cases given by the curves 1, 2 and 3, fig. 1, namely:

$$[\text{I}_3^-]_{1(\text{eq})} = (0.454/720) = 6.3 \times 10^{-4} \text{ M},$$

$$[\text{I}_3^-]_{2(\text{eq})} = (0.430/720) = 5.972 \cdot 10^{-4} \text{ M} \text{ and respectively}$$

$$[\text{I}_3^-]_{3(\text{eq})} = (0.420/720) = 5.83 \times 10^{-4} \text{ M. (} l=1 \text{cm).}$$

The equations (A), (B) were used to calculate the iodate concentrations which reacted in the absence of Mn(II) and Ce(III) (the curve 1, fig. 1) and in the presence of Ce(III) and Mn(II) (the curves 2 and 3, fig. 1):

$$[\text{IO}_3^-]_{1(\text{reacted})} = 2.1 \times 10^{-4} \text{ M}, \quad [\text{IO}_3^-]_{2(\text{reacted})} = 1.99 \cdot 10^{-4} \text{ M} \text{ in the presence of Ce(III) and in the}$$

$$[\text{Mn}^{2+}]_{\text{eq}} = [\text{Mn}^{2+}]_{\text{initial}} - [\text{Mn}^{2+}]_{\text{complex}} = 1 \times 10^{-3} \text{ M} - 1.6 \times 10^{-5} \text{ M} = 9.84 \times 10^{-4} \text{ M}$$

The iodate concentration at equilibrium in presence of Ce^{3+} is given by the expression:

$$[\text{IO}_3^-]_{\text{eq}} = [\text{IO}_3^-]_{\text{initial}} - \{[\text{IO}_3^-]_{2(\text{reacted})} + [\text{IO}_3^-]_{\text{complexed}}\} = 4.33 \times 10^{-4} - (1.99 \times 10^{-4} + 1.1 \times 10^{-5}) = 2.23 \times 10^{-4} \text{ M}$$

It is possible to calculate:

$$\frac{Mn^{2+}_{\text{initial}}}{IO_{3\text{ initial}}} = \frac{1 \cdot 10^{-3}}{4.33 \cdot 10^{-4}} = 2.31 \quad (1)$$

$$\frac{Mn^{2+}_{\text{initial}}}{IO_{3\text{ complexed}}} = \frac{1 \cdot 10^{-3}}{1.6 \cdot 10^{-5}} = 62.5 \quad (2)$$

According to the last ratio it follows that for 62.5 Mn(II) ions there is only one IO_3^- ion to form the $[\text{MnIO}_3]^+$ complex ion. For Ce(III) the calculations are:

$$K_{(\text{Mn})} = \frac{MnIO_3_{\text{eq}}}{Mn^{2+}_{\text{eq}} IO_{3\text{ eq}}} = \frac{1.6 \cdot 10^{-5}}{9.84 \cdot 10^{-4} \cdot 2.23 \cdot 10^{-4}} = 72.91 \quad (5)$$

respectively,

$$K_{(\text{Ce})} = \frac{CeIO_3^2_{\text{eq}}}{Ce^{3+}_{\text{eq}} IO_{3\text{ eq}}} = \frac{1.1 \cdot 10^{-5}}{9.0 \cdot 10^{-6} \cdot 2.23 \cdot 10^{-4}} = 5480.80 \quad (6)$$

presence of Mn(II), $[\text{IO}_3^-]_{3(\text{reacted})} = 1.94 \times 10^{-4} \text{ M}$, respectively. The difference, $[\text{IO}_3^-]_{1(\text{reacted})} - [\text{IO}_3^-]_{2(\text{reacted})} = 1.1 \times 10^{-5} \text{ M}$ represents the iodate amount that participated to the $[\text{CeIO}_3]^{2+}$ complex ion formation and the difference $[\text{IO}_3^-]_{1(\text{reacted})} - [\text{IO}_3^-]_{3(\text{reacted})} = 1.6 \times 10^{-5} \text{ M}$ represents the iodate amount that participated to the $[\text{MnIO}_3]^+$ complex ion formation. The concentration of $[\text{CeIO}_3]^{2+}$ complex ion is equal to the concentration of the IO_3^- complexed, $[\text{CeIO}_3]^{2+} = [\text{IO}_3^-]_{\text{complexed}} = 1.1 \times 10^{-5} \text{ M}$. The Ce^{3+} concentration at equilibrium state is: $[\text{Ce}^{3+}]_{\text{eq}} = [\text{Ce}^{3+}]_{\text{initial}} - [\text{Ce}^{3+}]_{\text{complex}} = 2 \times 10^{-5} \text{ M} - 1.1 \times 10^{-5} \text{ M} = 9.0 \times 10^{-6} \text{ M}$. The concentration of $[\text{MnIO}_3]^+$ complex ion is equal to the concentration of the IO_3^- complexed, $[\text{MnIO}_3]^+ = [\text{IO}_3^-]_{\text{complexed}} = 1.6 \times 10^{-5} \text{ M}$. The Mn^{2+} concentration at equilibrium state is:

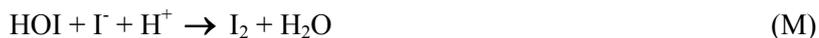
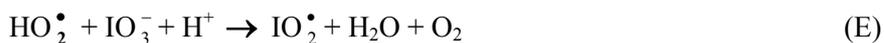
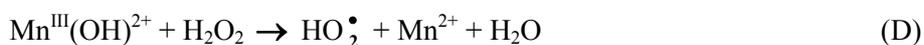
From the values of the ratios (2) and (4) it results that the $[\text{CeIO}_3]^{2+}$ complex ion formation takes place in solution with a much higher probability than the $[\text{MnIO}_3]^+$ formation. From the values of the equilibrium constants it results that the stability of the $[\text{CeIO}_3]^{2+}$ complex ion is much higher than the stability of the $[\text{MnIO}_3]^+$ ion complex. Consequently, for the equal concentrations of Mn(II) and Ce(III) ions the

concentration of $[\text{CeIO}_3]^{2+}$ complex ion is $(62,5/1,81) = 34,53$ times larger than the concentration of $[\text{MnIO}_3]^+$ complex ion. This concentration of $[\text{CeIO}_3]^{2+}$ complex ion determines the system to oscillate. This analysis leads to a very important conclusion:

Neither Mn(II) nor Ce(III) ions react with H_2O_2 , but $[\text{Mn}^{\text{II}}\text{IO}_3]^+$ and $[\text{Ce}^{\text{III}}\text{IO}_3]^{2+}$ complex ions react with H_2O_2 according to the reactions:



The $\text{Mn}^{\text{III}}(\text{OH})^{2+}$, $\text{Ce}^{\text{IV}}(\text{OH})^{3+}$ and HO^\bullet species start the iodine formation reactions.



Indeed, Cooke demonstrated that IO_2^\bullet represents the key- intermediary in the I_2 formation mechanism.^{12,13}

We propose the reactions (A), (B), (C), (D). The reactions (E) – (M) were proposed by Furrow and Noyes.¹⁴⁻¹⁷

HO_2^\bullet radical plays an important role in the IO_2^\bullet radical appearance, according to the reaction (E).

CONCLUSIONS

In this work we proved experimentally, using the kinetic study of the Dushman reaction and the

cyclic voltammetry, the formation of the $[\text{Mn}^{\text{II}}\text{IO}_3]^+$ and $[\text{Ce}^{\text{III}}\text{IO}_3]^{2+}$ complex ions. The formation rate of I_2 in the BL system is directly connected with the $[\text{MnIO}_3]^+$ and $[\text{CeIO}_3]^{2+}$ complex ions concentration in the system that was proved using a spectral method. We calculated that the formation constant of $[\text{CeIO}_3]^{2+}$ is much larger than that of $[\text{MnIO}_3]^+$.

The $[\text{MnIO}_3]^+$ and $[\text{CeIO}_3]^{2+}$ complex ions are the key intermediate initiating the mechanism of the decomposition of H_2O_2 with the iodine production. We demonstrated using BR measurements that the oscillating regime appearance is also connected with the level of concentrations of the $[\text{MnIO}_3]^+$ and $[\text{CeIO}_3]^{2+}$ complex ions in the system. Much lower

concentrations of the later are able to generate oscillations.

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REFERENCES

1. A. A. Sycev and V. G. Isak, "Koordinacionnie soedimenia marganta katalize", Ed. Stiinta, Kisinev, 1990, p. 84.
2. W. C. Bray, *J. Am. Chem. Soc.*, **1921**, *43*, 1262.
3. W. C. Bray and H. A. Liebafsky, *J. Am. Chem. Soc.*, **1931**, *53*, 38.
4. G. Schmitz, *J. Chim. Phys.*, **1987**, *84*, 957.
5. G. Schmitz, *Phys. Chem. Chem. Phys.*, **1999**, *1*, 4605.
6. G. Schmitz, *Phys. Chem. Chem. Phys.*, **2001**, *3*, 4741.
7. H. A. Liebafsky, *J. Am. Chem. Soc.*, **1932**, *54*, 1792.
8. H. A. Liebafsky, *J. Am. Chem. Soc.*, **1932**, *54*, 3499.
9. D. O. Cooke, *Reac. Kin. and Cat. Lett.*, **1976**, *4*, 329.
10. M. Bourceanu, A. Bîrzu and G. Bourceanu, *Rev. Roum. Chim.* **2003**, *48*, 527.
11. M. Bourceanu, A. Bîrzu and G. Bourceanu, *Rev. Roum. Chim.*, **2003**, *48*, 535.
12. D. O. Cooke, *Int. J. Chem. Kinet.*, **1980**, *12*, 683.
13. D. O. Cooke, *Int. J. Chem. Kinet.*, **1980**, *12*, 671.
14. S. D. Furrow and R. M. Noyes, *J. Am. Chem. Soc.*, **1982**, *104*, 32.
15. S. D. Furrow and R. M. Noyes, *J. Am. Chem. Soc.*, **1982**, *104*, 42.
16. R. M. Noyes and S. D. Furrow, *J. Am. Chem. Soc.*, **1982**, *104*, 45.
17. S. D. Furrow, *J. Phys. Chem.*, **1982**, *86*, 3089.