ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2011, *56*(8), 803-809

THE EFFECT OF THE Ce(III)-IODATE INTERACTIONS IN THE BRIGGS-RAUSCHER OSCILLATING REACTION

Rodica NIȚOI*

Faculty of Chemistry, “Al.I. Cuza” University of Iaşi, Bd.Carol I no.11, Iaşi, 700506, Roumania

Received August 23, 2010

The role of Ce(III)-Iodate interactions in the Briggs-Rauscher system was investigated. It was proven experimentally that the species in the form of $[Ce^{III}(IO_3)_n]^{3-n}$ and $Ce(IO_3)_3$ are involved catalytically in the reaction mechanism of the Bray-Liebhafsky and Briggs-Rauscher reactions. Some mechanistic interpretations are presented.

INTRODUCTION

The Briggs-Rauscher oscillating reaction (noted BR), which takes place in the system {IO_3^-, H_2O_2, organic substrate, Mn(II) or Ce(III), H^+},[1] is of interest in the study of non-linear dynamics applied to physics and biology, meteorology and economics.[2] As it is known, many complex natural phenomena are governed by simple dynamic laws. Chemical oscillating reactions are no exception, because they exhibit complex behavior often based on relatively simple dynamic rules and interactions, which determine the values of the relevant kinetic constants and transport coefficients, result from short range interactions (valence forces, hydrogen bonds, Van der Waals forces).[3]

The prior studies of the mechanism of the Bray-Liebhafsky oscillating reaction (BL), taking place in the system {IO_3^-, H_2O_2, H^+} that is a subsystem of the BR system have shown that the hydrogen peroxide decomposition is catalyzed by iodate ions in an acidic medium:[4]

$$2\,IO_3^- + 2\,H^+ + 5\,H_2O_2 = I_2 + 5O_2 + 6\,H_2O \qquad (R)$$

Mechanistic studies of iodine intermediates in iodate-hydrogen peroxide oscillators have been carried out.[5]

Cooke proved experimentally that Mn(II) added to a BL system increased considerably the I_2 production rate,[6] and that Ce(III) can replace Mn(II) in the BR Reaction.[7]

It was also shown[8] that the kinetics of the reaction (R) are closely related to the kinetics of the Dushman reaction:[9]

$$IO_3^- + 5\,I^- + 6H^+ \longrightarrow 3I_2 + 3\,H_2O \qquad (D)$$

In the present work, on the basis of our studies,[10,11,12] we intend to prove experimentally – using cyclic voltammetry and a spectral method – that the species in the form of $[Ce^{III}(IO_3)_n]^{3-n}$ catalyze the decomposition of hydrogen peroxide in BL system, and that $Ce(IO_3)_3$ is directly involved in the oscillating regime appearance in the BR system. The optimal concentrations of the reactants, which determine an oscillating regime appearance in the presence of the $Ce(IO_3)_3$ precipitate, were also found.[12]

The study of the effect of interactions of metal-iodate ions on the hydrogen peroxide decomposition in the Bray-Liebhafsky reaction and on the mechanism of the Briggs-Rauscher reaction, representing a different way to tackle this topic, is of great importance as it supplies new information concerning the mechanistic interpretation for these chemical oscillators as well for the general theories of dynamic behavior.[12]

---

* Corresponding author: rodicanitoi@yahoo.com

RESULTS AND DISCUSSION

Cyclic voltammograms were obtained for the investigated systems:

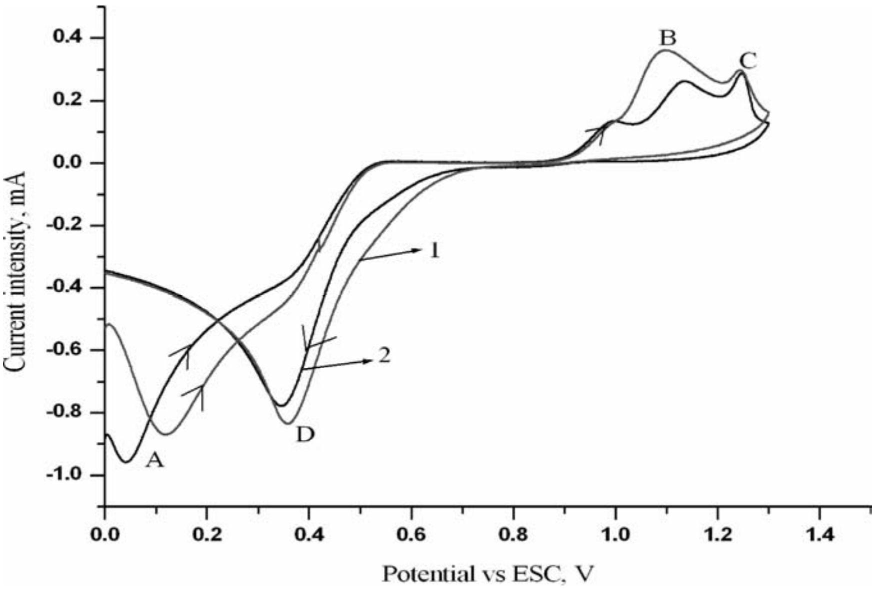

Fig. 1 – The cyclic voltammogram of: [KIO_3] = 8 x 10^{-3} M; [$HClO_4$] = 0.053 M (curve 1); [KIO_3] = 8 x 10^{-3} M; [Ce(III)]= 8 x 10^{-5} M; [$HClO_4$] = 0.053 M (curve 2).

Comparing these cyclic voltammograms of iodate (curve 1, Fig.1) and iodate in the Ce(III) presence (curve 2, Fig.1), it can be observed that the oxidation peaks B and C, due to oxidation of products resulted from the initial reduction process of iodate (peak A), are reduced in the Ce(III) presence. This fact is due to the reduction of iodate amount that is involved in the equilibrium process:

$$\mathrm{Ce(III)} + n\mathrm{IO}_3^- \rightleftarrows [\mathrm{Ce^{III}}(\mathrm{IO}_3)_n]^{3-n} \qquad (1)$$

The study of the iodine formation in the Dushman reaction (D) (curve 1, Fig. 2) has shown that the presence of the Ce(III) and Mn(II) ions affects the iodine amount formation in time.

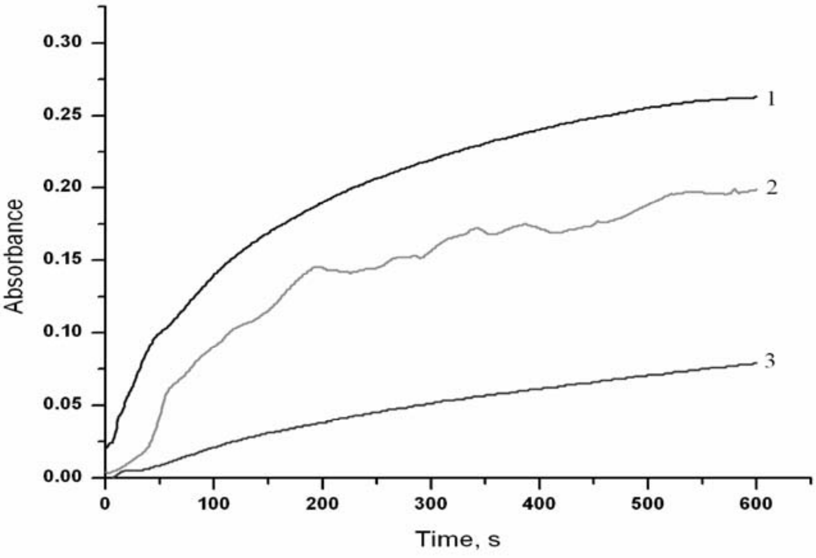

Fig. 2 – The iodine formation versus time for: [KIO_3] = 2.165 x 10^{-4} M; [KI] = 1.083 x 10^{-3} M; [$HClO_4$] = 1.3 x 10^{-3} M; Dushman Reaction (curve1); with [Ce(III)]= 1 x 10^{-3} M (curve 2); with [Mn(II)]= 8 x 10^{-3} M (curve 3).

It can be observed that the value of absorbance decreased from 0.263 to 0.079 in the presence of a concentration of [Mn(II)] = 8 x 10^{-3} M (curve 3, Fig.2) and to 0.199 in the presence of a concentration of [Ce(III)]= 1 x 10^{-3} M (curve 2, Fig.2). Ce(III) has a stronger effect on the iodate anions. This is due to the fact that a part of the iodate anions are involved in the equilibrium (1) and (2):

$$\mathrm{Mn(II)} + n\mathrm{IO}_3^- \rightleftarrows [\mathrm{Mn}^{\mathrm{II}}(\mathrm{IO}_3)_n]^{2-n} \qquad (2)$$

So, the interactions metal–iodate ions cannot be neglected in the mechanistic studies of the Briggs-Rauscher reaction.

The kinetics of iodine formation in BL system showed differences of iodine amount formation in different systems.

As it can be observed (Fig. 3), the iodine formation in the system {IO_3^-, H_2O_2, H^+} (BL), in the presence of Ce(IV), Ce(III) and Mn(II) in time, had shown that a concentration of 2 x 10^{-5} M of Ce(IV) (curve 4, Fig. 3) had almost the same catalytic efficiency on the iodine production in the BL system as a concentration of 4 x 10^{-5} M of Ce(III) (curve 3, Fig.3) and as 8 x 10^{-3} M of Mn(II) (curve 2, Fig. 3). This fact could demonstrate that the metal–iodate ions interactions are important in the catalytic decomposition of H_2O_2 [10,11]. Ce(III) being a stronger electropositive ion comparatively to Mn(II), a bigger number of iodate anions are involved in the equilibrium (2), the interactions are stronger, and a higher amount of iodine forms in the BL reaction (R).

The BR potentiometric measurements proved that the induction time of BR oscillators containing Ce(III) is depending directly by the concentration of $Ce(IO_3)_3$ that is present from the start in the system, thus: the system with [Ce(III)] = 5 x 10^{-3} M showed an induction time of 80 s, [Ce(III)] = 3 x 10^{-3} M – 100 s; [Ce(III)] = 1.5 x 10^{-3} M – 150 s; [Ce(III)] = 7.5 x 10^{-4} M – 400 s.

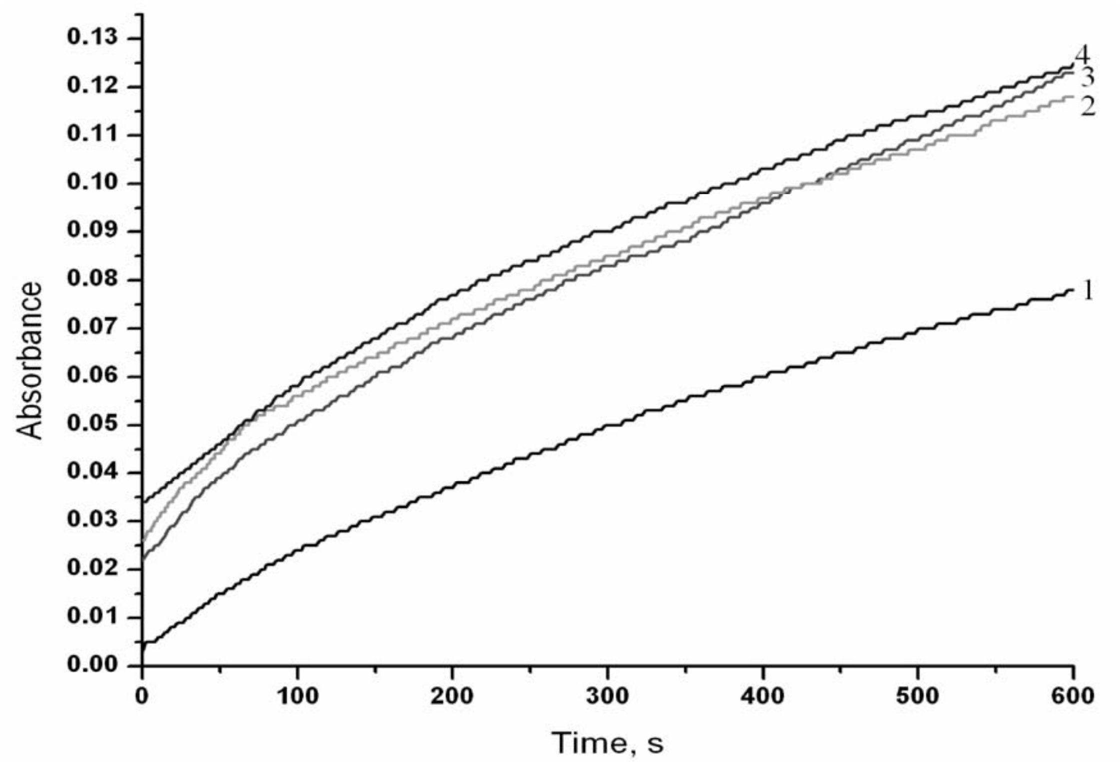

Fig. 3 – The iodine formation versus time in: [KIO_3] = 4.4 x 10^{-2} M; [$HClO_4$] = 5.8 x 10^{-3} M; [H_2O_2] = 1.2 M- BL system (curve 1); with [Mn(II)] = 8 x 10^{-3} M (curve 2); with [Ce(III)]= 4 x 10^{-5} M (curve 3); with [Ce(IV)] = 2 x 10^{-5} M (curve 4).

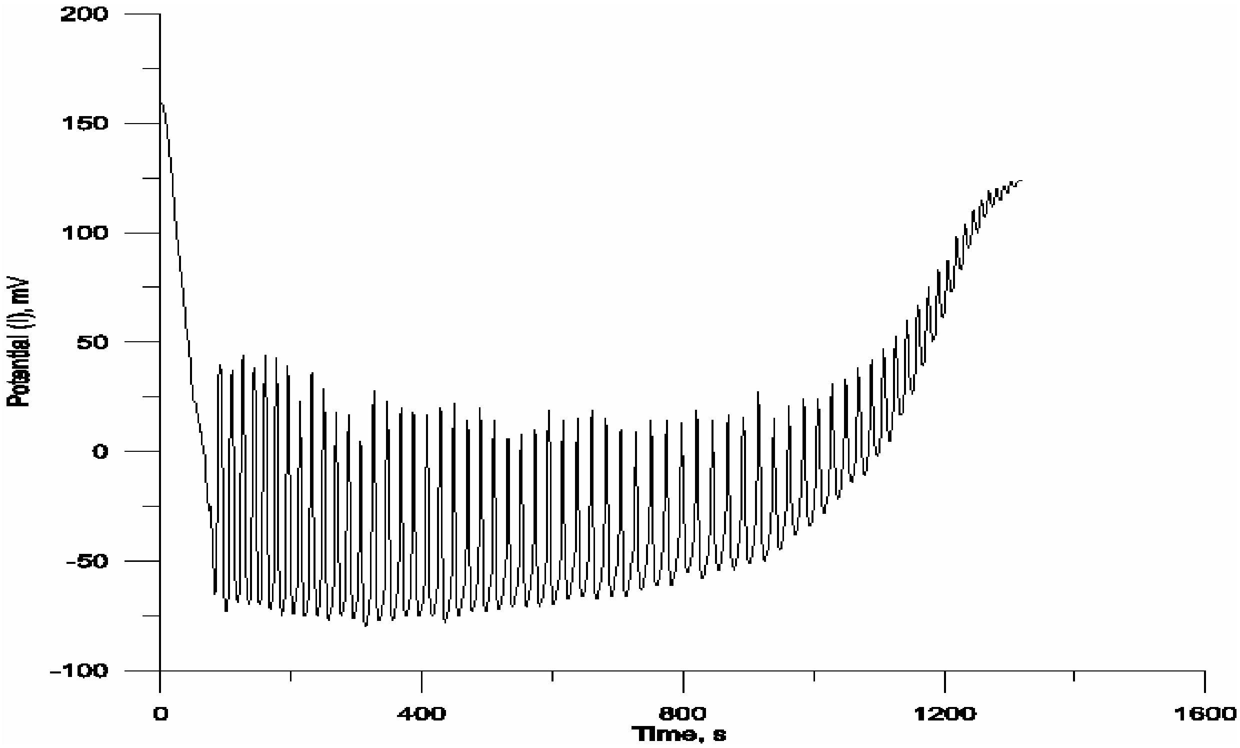

Fig. 4 (A) – BR oscillator with: [Ce(III)] = 5 x 10^{-3} M; [$NaIO_3$] = 0.02 M; [MA] = 0.05 M; [H_2O_2] = 1.2 M; [H_2SO_4] = 0.05 M.

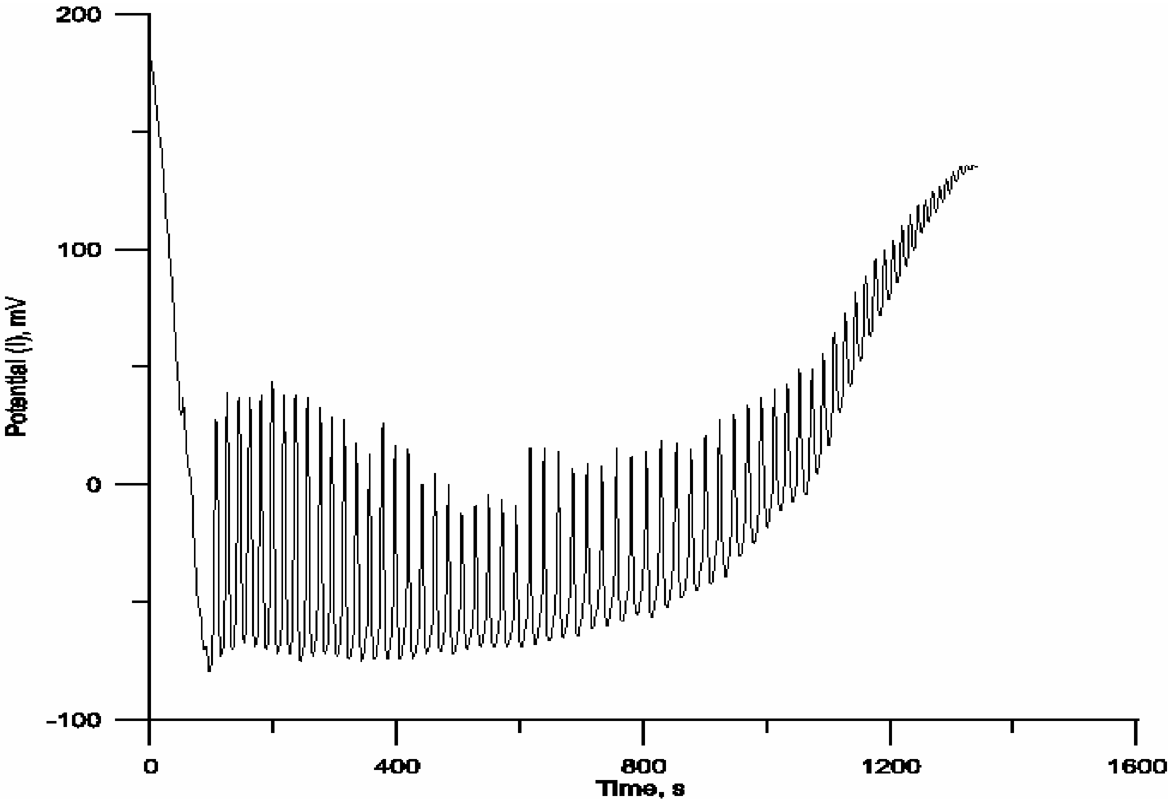

Fig. 4 (B) – BR oscillator with: [Ce(III)] = 3 x 10^{-3} M; [$NaIO_3$] = 0.02 M; [MA] = 0.05 M; [H_2O_2] = 1.2 M; [H_2SO_4] = 0.05 M.

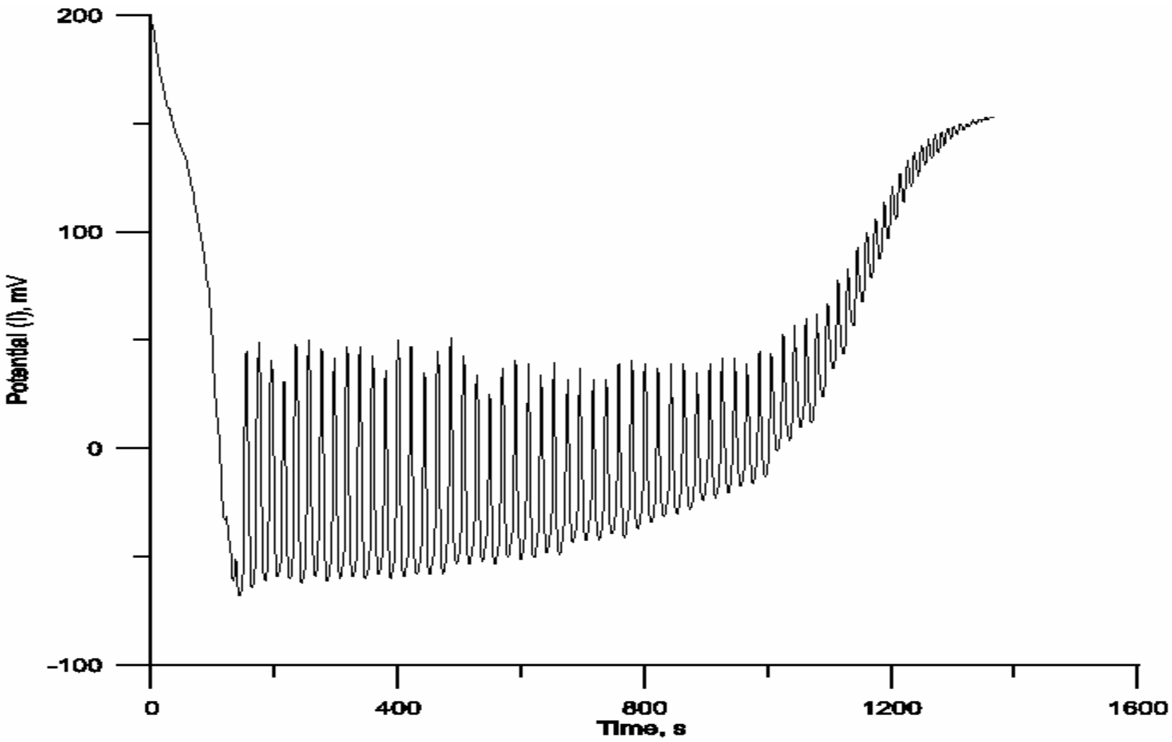

Fig. 4 (C) – BR oscillator with [Ce(III)] = 1.5 x 10^{-3} M; [$NaIO_3$] = 0.02 M; [MA] = 0.05 M; [H_2O_2] = 1.2 M; [H_2SO_4] = 0.05 M.

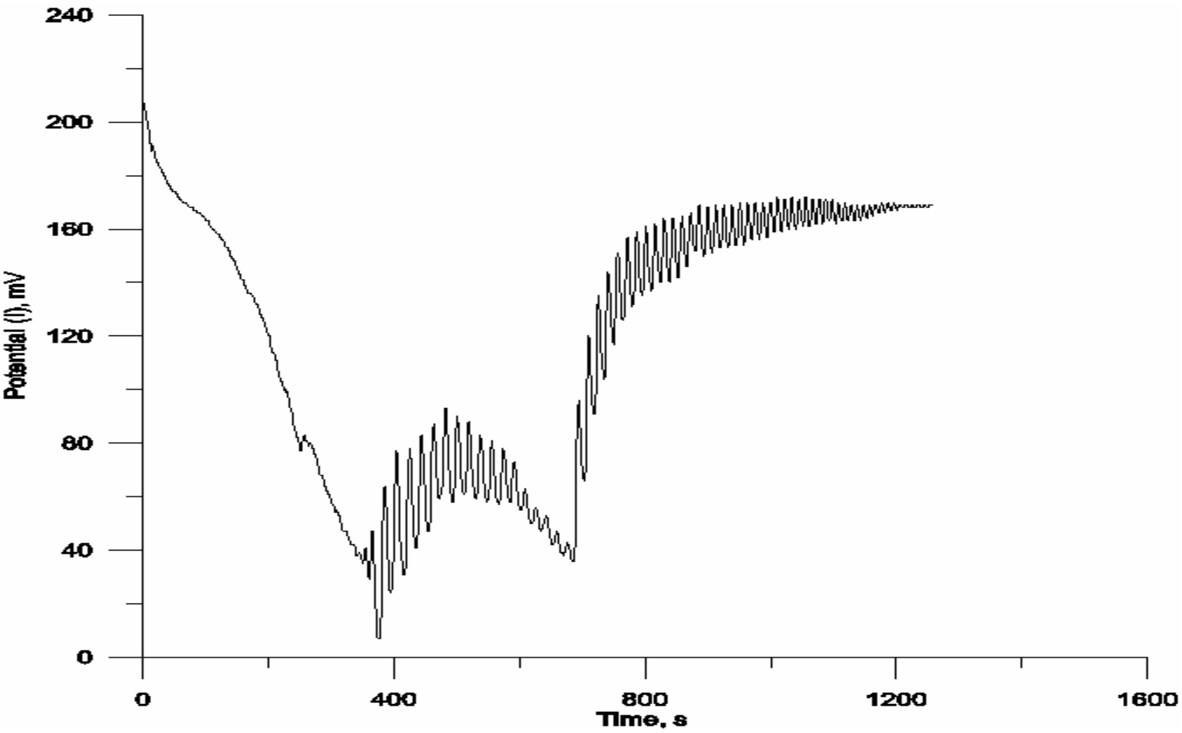

Fig. 4 (D) – BR oscillator with [Ce(III)] = 7.5 x 10^{-4} M; [$NaIO_3$] = 0.02 M; [MA] = 0.05 M; [H_2O_2] = 1.2 M; [H_2SO_4] = 0.05 M.

The reaction starts in a heterogeneous system, with a white color that is specific to $Ce(IO_3)_3$ precipitate, color which disappears after the first seconds of the magnetic stirring. During the oscillating regime, the white color does not appear anymore, but after 1200 s, at the end of the oscillating regime, a white precipitate appears. It is interesting that even in the case of a lower concentration of Ce(III) = 7.5 x 10^{-4} M (D, Fig.4), the end of the oscillating regime is after 1200 s, the same for all systems (A-C, Fig.4). The BR oscillator D has shown the excitability phenomenon: the oscillations are quenching and then reappear again.

The experimental observations can be resumed as it follows:

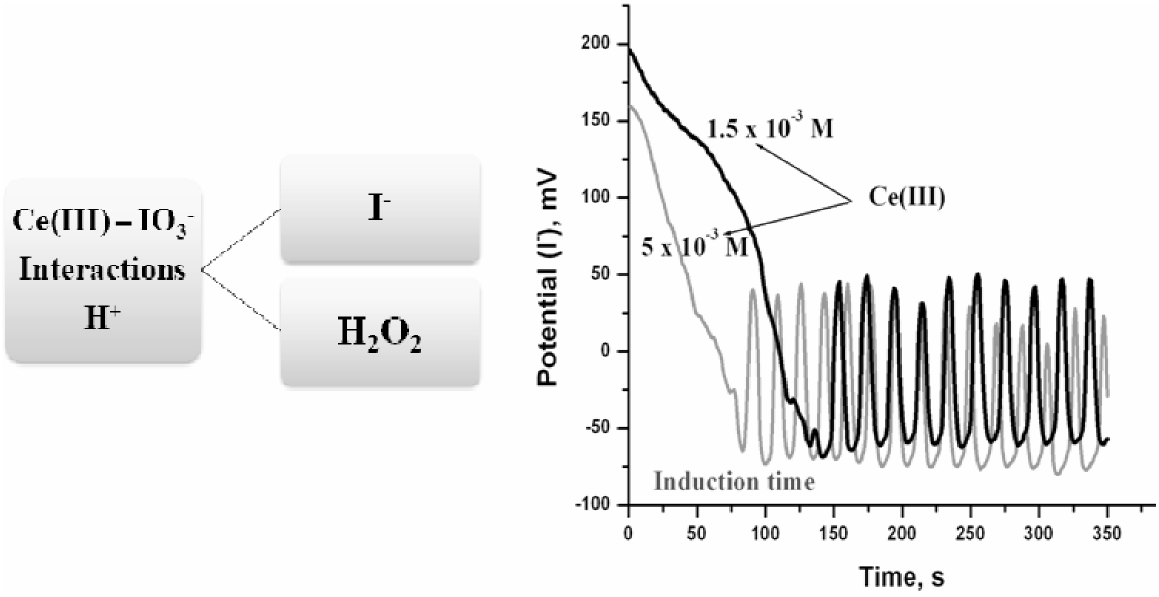

Fig. 5 – The role of the Ce(III)-IO_3^- interactions, proven experimentally in the Dushman and BL systems, on the induction time of BR oscillator with Ce(III).

The following observations concerning the analysis of the systems (I){ IO_3^-, Ce(III)}, (J) { IO_3^-, H_2O_2, Ce(III), H^+}, (K) { IO_3^-, Ce(III), H^+}, (L) { IO_3^-, Ce(III), MA, H^+}, (M) { IO_3^-, Ce(III),H_2O_2, MA, H^+}, have shown that in the system (I), the white color appeared due to the $Ce(IO_3)_3$ precipitate formation, while the white color, due to the $Ce(IO_3)_3$ in system (J), turned in yellow in the H_2O_2 presence, due to the $Ce(IO_3)_4$ formation. This fact suggested that $Ce(IO_3)_3$ decomposes H_2O_2. In the systems (K) and (L) the white color due to the $Ce(IO_3)_3$ precipitate did not disappear even under a long time magnetic stirring, while in the system (M) the white color disappeared in the H_2O_2 presence after the first seconds of magnetic stirring.

It could be observed from the BR measurements that at low Ce(III) concentrations, or low $Ce(IO_3)_3$ concentrations, the induction time increased.

It is possible that the reaction in this case is between $Ce(IO_3)_3$ and H_2O_2 as follows:

$$Ce(IO_3)_3 + H_2O_2 -> [Ce(OH)]^{3+} + HO^{\bullet} + 3\ IO_3^-$$

$[Ce(OH)]^{3+}$ and $HO^{\bullet}$ species would react further as $[Mn(OH)]^{2+}$ and $HO^{\bullet}$ species do in the BR catalyzed system with the formation of $HO_2^{\bullet}$ and $IO_2^{\bullet}$ radicals.

Indeed, Cooke, Furrow and Noyes proposed a model using $IO_2^{\bullet}$ as the key- intermediary in the I_2 formation mechanism.[13]

EXPERIMENTAL

Chemicals: Ce (III) from $Ce(NO_3)_3$ x 6 H_2O, Ce (IV) from $Ce(SO_4)_2$ x $4H_2O$, Mn(II) from $MnSO_4$. H_2O, IO_3^- from KIO_3 or $NaIO_3$, $HClO_4$, I^- from KI, H_2O_2.

All chemicals used were provided by Merck Comp. The concentration of hydrogen peroxide was determined initially by titrating with $KMnO_4$.

The calculations of the final concentrations of the solutions took into account the values of molar solubility of $Ce(IO_3)_3$ and $Ce(IO_3)_4$. For $Ce(IO_3)_3$, $K_{ps} = 3.2 \times 10^{-10}$ (25 °C), the molar solubility is $[Ce(IO_3)_3] = 1.84 \times 10^{-3}$ M. For $Ce(IO_3)_4$, $K_{ps} = 4.8 \times 10^{-17}$ (25 °C), the molar solubility is $[Ce(IO_3)_4] = 1.8 \times 10^{-4}$ M.

The cyclic voltammograms were performed using a PGZ 301 potentiostat produced by Radiometer France. The software was Voltamaster 4. The working electrode used in the cyclic voltammetry experiments was a platinum disc (1 cm^2), a platinum wire was used as the counter electrode, and a saturated calomel electrod (SCE) was used as the reference electrode. The scaning rate was 50mV s^{-1}. The next mixtures were prepared:

$[KIO_3] = 8 \times 10^{-3}$ M; $[HClO_4] = 0.053$ M (Fig. 1, curve 1)

[KIO$_3$] = 8 x 10^{-3} M; [Ce(III)]= 8 x 10^{-5} M; [HClO$_4$] = 0.053 M (Fig.1, curve 2)

The iodine formation in the system $\{I^-, IO_3^-, H^+\}$ (Dushman reaction), (Fig. 2), in the Mn(II) and Ce(III) presence, was followed spectrally by using a Shimadzu UV-Viz Spectrophotometer at λ = 469 nm. The following concentrations were used:

[KIO$_3$] = 2.165 x 10^{-4} M; [KI] = 1.083 x 10^{-3} M; [HClO$_4$] = 1.3 x 10^{-3} M; (curve 1, Fig. 2) ; [KIO$_3$] = 2.165 x 10^{-4} M; [KI] = 1.083 x 10^{-3} M; [HClO$_4$] = 1.3 x 10^{-3} M, [Ce(III)]= 1 x 10^{-3} M- (curve 2, Fig.2).

[KIO$_3$] = 2.165 x 10^{-4} M; [KI] = 1.083 x 10^{-3} M; [HClO$_4$] = 1.3 x 10^{-3} M; [Mn(II)]= 8 x 10^{-3} M (curve 3, Fig.2)

The iodine formation in the system $\{IO_3^-, H_2O_2, H^+\}$ (BL) in the Mn(II), Ce(III), Ce(IV) presence was followed spectrally by using a Shimadzu UV-Viz Spectrophotometer at λ = 460 nm (Fig.3).

The following concentrations were used:

[KIO$_3$] = 4.4 x 10^{-2} M; [HClO$_4$] = 5.8 x 10^{-3} M; [H$_2$O$_2$] = 1.2 M; (curve 1, Fig.3)

[KIO$_3$] = 4.4 x 10^{-2} M; [Mn(II)] = 8 x 10^{-3} M; [HClO$_4$] = 5.8 x 10^{-3} M; [H$_2$O$_2$] = 1.2 M; (curve 2, Fig. 3)

[KIO$_3$] = 4.4 x 10^{-2} M; [Ce(III)] = 4 x 10^{-5} M; [HClO$_4$] = 5.8 x 10^{-3} M; [H$_2$O$_2$] = 1.2 M; (curve 3, Fig. 3).

[KIO$_3$] = 4.4 x 10^{-2} M; [Ce(IV)] = 2 x 10^{-5} M; [HClO$_4$] = 5.8 x 10^{-3} M; [H$_2$O$_2$] = 1.2 M; (curve 4, Fig. 3).

The BR potentiometric measurements in the system $\{IO_3^-, H_2O_2, Ce(III), MA, H^+\}$ (MA = malonic acid) were carried out using an Orion iodide selective electrode with a double junction (Fig. 4 A-D), under magnetic stirring. 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 mixture were maintained at constant temperature (23.0 °C) using a thermostat system (accuracy ± 0.1 °C).

The following systems were analyzed:

[Ce(III)] = 5 x 10^{-3} M; [NaIO$_3$] = 0.02 M; [MA] = 0.05 M; [H$_2$O$_2$] = 1.2 M; [H$_2$SO$_4$] = 0.05 M – Fig. 4 (A)

[Ce(III)] = 3 x 10^{-3} M; [NaIO$_3$] = 0.02 M; [MA] = 0.05 M; [H$_2$O$_2$] = 1.2 M; [H$_2$SO$_4$] = 0.05 M – Fig. 4 (B).

[Ce(III)] = 1.5 x 10^{-3} M; [NaIO$_3$] = 0.02 M; [MA] = 0.05 M; [H$_2$O$_2$] = 1.2 M; [H$_2$SO$_4$] = 0.05 M – Fig. 4 (C).

[Ce(III)] = 7.5 x 10^{-4} M; [NaIO$_3$] = 0.02 M; [MA] = 0.05 M; [H$_2$O$_2$] = 1.2 M; [H$_2$SO$_4$] = 0.05 M – Fig. 4 (D). The Ce(III) concentrations used in the BR measurements are precipitation concentrations of Ce(IO$_3$)$_3$.

Finally, the following systems were analyzed under magnetic stirring: (I) $\{IO_3^-, Ce(III)\}$, (J) $\{IO_3^-, H_2O_2, Ce(III), H^+\}$, (K) $\{IO_3^-, Ce(III), H^+\}$, (L) $\{IO_3^-, Ce(III), MA, H^+\}$, (M) $\{IO_3^-, Ce(III), H_2O_2, MA, H^+\}$, with the concentrations of the solutions:

[Ce(NO$_3$)$_3$. 6 H$_2$O] = 5 x 10^{-3} M

[NaIO$_3$] = 0.02 M

[MA] = 0.05 M

[H$_2$SO$_4$] = 0.05 M

[H$_2$O$_2$] = 1.2 M

CONCLUSIONS

There is a synergistic action of the iodate and Ce(III) ions, which act as species in the form of $[Ce^{III}(IO_3)_n]^{3-n}$, on the H$_2$O$_2$ decomposition, that was demonstrated on the basis of spectrophotometric measurements of the iodine formation in the absence or presence of Ce(III) ions in Dushman and Bray-Liebhafsky reactions, and as Ce(IO$_3$)$_3$ in the BR reaction, proven experimentally using the potentiometric measurements.

REFERENCES

1. T. S. Briggs, W. C. Rauscher, *J.Chem.Educ.*, **1973**, *50,* 496.
2. R.J. Field**,** M Burger**,** (Ed.), "Oscillations and Travelling Waves in Chemical Systems". Ed. John Wiley, New York, 1998, p. 441.
3. I. Prigogine, "Time, Structures and Fluctuations", Nobel Lecture,8 december, 1977. http://nobelprize.org/nobel_prizes/chemistry/laureates/1977/prigogine-lecture.pdf
4. W. C. Bray and H. A. Liebhafsky, *J. Am. Chem. Soc.*, **1931**, *53,* 38.
5. Furrow, S, *J. Phys.Chem*., **1987**, *91*, 2129.
6. D. O. Cooke, *Int. J. Chem. Kinet*., **1980**, *12,* 671.
7. D. O. Cooke, *Reac. Kin and Cat. Lett*, **1976**, *4,* 329.
8. G. Schmitz, *Phys. Chem. Chem. Phys*., **1999**, *1*, 4605.
9. S. Dushman, *J. Phys. Chem*., **1904**, *8,* 453.
10. R. Niţoi, G. Bourceanu, Gh. Nemţoi, *Rev. Roum. Chim.,* **2010**, *55*, 269.
11. R. Niţoi, G. Bourceanu, *Rev. Roum. Chim.,***2011**, *56*, 47.
12. R. Niţoi, "Contributions to the mechanism of the Briggs-Rauscher Oscillating Reaction. Experiment and modeling", PhD thesis, "Al.I. Cuza" Univ. of Iaşi, Roumania, Nov, 2009.
13. S. D. Furrow and R. M. Noyes, *J. AM. Chem. Soc*., **1982**, *104,* 38.