

THE MINOR INFLUENCE OF CALCIUM DOPED PHOSPHATE TUNGSTEN BRONZE ON THE BRIGGS-RAUSCHER REACTION DYNAMICS

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Abstract: The Briggs-Rauscher (BR) oscillatory reaction is the oxidation of malonic acid in the presence of hydrogen peroxide and iodate in the acidic environment, which is catalyzed by ions of manganese. This reaction is very sensitive to the presence of additives. In this paper, the BR reaction has been used to investigate the phosphate tungsten bronze as well as calcium doped tungsten bronze, obtained by thermal treatment. The addition (0.01-0.08 g) of phosphate tungsten bronze and calcium doped phosphate tungsten bronze has a different effect on the dynamics of the Briggs-Rauscher reaction. In the case of the addition of phosphate tungsten bronze in the Briggs-Rauscher reaction, the linear dependence of the length of the oscillatory period on the mass of the added bronze was obtained, while in the case of addition of calcium doped phosphate tungsten bronze, the oscillatory period does not significantly change with an increase of added mass. The mechanism of calcium doped and undoped phosphate tungsten bronze action in BR reaction is probably adsorptive, and it will be the subject of future work.

Keywords: oscillatory reactions, Briggs-Rauscher reaction, phosphate tungsten bronze, calcium doped phosphate tungsten bronze, thermal treatment.

1. INTRODUCTION

The oscillatory chemical reactions are complex dynamic systems, in which the concentrations of reactants and products, by the oscillatory change of intermediate concentration, cascadingly vary, reflecting on that way the periodical changes

in speed of their evanescence, i.e. the speed of their formation [1]. Briggs-Rauscher (BR) reaction is one of the most attractive chemical oscillating reactions, in which the oxidation of malonic acid ($\text{CH}_2(\text{COOH})_2$, in the presence of hydrogen peroxide (H_2O_2) and potassium iodate (KIO_3), is catalyzed by manganese ions (Mn^{2+}) in acidic medium [2,3]:



In a closed reactor, with continuous mixing, at room temperature and for the particular concentrations of the reactants, with the addition of starch as an indicator, BR reaction solution will change the color from dark blue, through a colorless, pale yellow to yellow. This color change cycle will be shifted until the concentrations of reactive species move in „phase space” to the non-oscillatory region and oscillatory reaction ends.

Briggs-Rauscher reaction is the subject of intensive testing for many years, both in order to find its complex mechanism, as well as for the analytical

application. It is known that this reaction is sensitive to many organic molecules (for example, antioxidants), which by the addition in the BR system, influence on the change in the dynamic state of the system by disrupting the oscillatory evolution of the system, i.e. oscillations. It has been shown that the concentration of appended additive is in linear correlation with the time required for the oscillations of the system to be extinguished. Hence, this reaction is often used for quantitative purposes, for measuring antioxidant activity [5]. This is a very important practical aspect of BR reaction, where the changes in the

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dynamics of the oscillatory system are used for chemical analysis. The possibility of potential application of BR reaction for investigation of insoluble phosphate tungsten and calcium doped phosphate tungsten bronzes is the basic idea of this work.

Bronzes are obtained by thermal treatment of heteropoly acids (polyoxometallates) [6-8]. Pauling gave the first three-dimensional structural formula of heteropoly acid with well-defined positions of the atoms and their coordination [9]. Keggin has first discovered the crystallographic structure of 12-tungstophosphoric acid [10] by using the X-ray diffraction and its basic structural unit represents Keggin's anion [11-14]. Keggin's anion has coordinate structure and consists of central tetrahedron XO_4 ($X = P, Si, As, B, Al$ etc.), encircled with 12 slightly deformed octahedra MO_6 ($M = W, Mo, V, Ta$ or Nb) bonded via common oxygen atoms. Twelve atoms M are on twelve cube's borders in which center is atom X [10]. Bronzes, in which the arrangement of the tetrahedra PO_4 and the octahedra WO_6 is such to form pentagonal or hexagonal channels [15] are obtained by „destroying” of Keggin's anion by thermal treatment. Bronzes obtained by

thermal treatment are insufficiently investigated bronzes and there is a little knowledge about their chemical behavior.

In this paper, a sensitive oscillatory reaction is used in order to test and compare phosphate tungsten and calcium doped phosphate tungsten bronze. This is a completely new approach to material testing, whereby the changes in oscillatory dynamics, in the presence of various bronzes, are followed and compared, in order to obtain information about the properties of the materials themselves. Recently, we examined the influence of lithium doped phosphate tungsten bronze and phosphate tungsten bronze [16], and this paper represents a continuation of the study and examines the effect of calcium doped phosphate tungsten bronze on the dynamics of the BR oscillatory reaction.

2. EXPERIMENTAL

All experiments are performed in a stationary, well-mixing and the isothermal reactor (reaction volume 25.0 ± 0.1 ml) (Figure 1.).

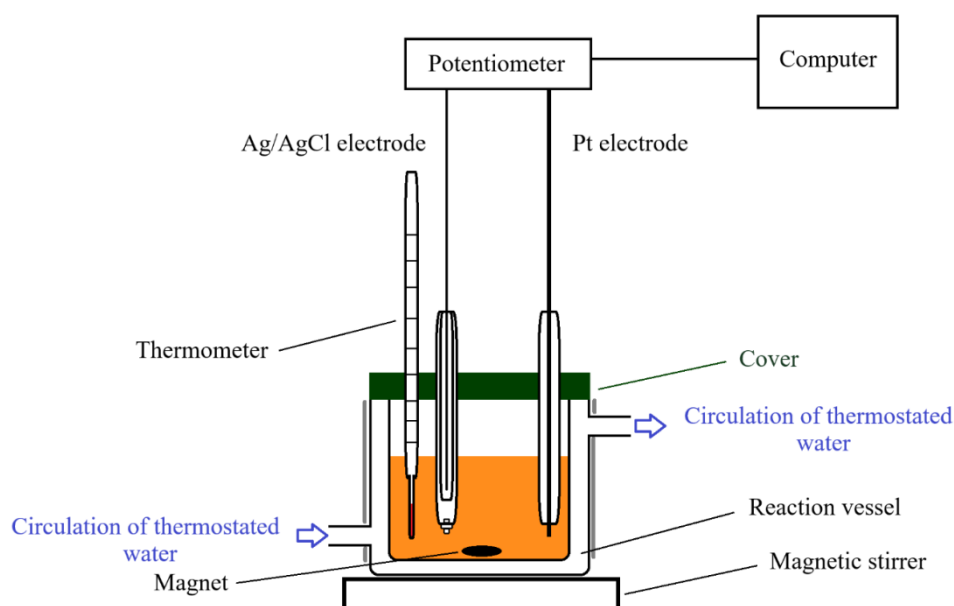


Figure 1. Schematic representation of the closed reactor was used to study the Briggs-Rauscher reaction

A glass cell (METHROM EA 876-20) was used as a reaction vessel, with a double thermostating walls and a cover that closes the reaction vessel (reactor). There are five holes on the cover and three of them are used for the reference electrode, working electrode and thermometer. In each series of experiments, the electrodes and thermometer are being put in the cell at the same place. The cell cover allows maintaining constant reactor

geometry, i.e. electrodes and thermometer, as well as the consistency of the reaction volume.

During the experiment, the temperature of the reaction vessel was regulated and maintained (37 °C) using the following thermostat (Julabo, ED, Germany), recovery value ± 0.1 °C.

For adjustment and maintenance, the constant rate of mixing the reaction solution was used as a magnetic mixer (Ingenieurbüro, M. Zipperer GmbH, Cat-

ECM5, Staufen, Denmark). In all experiments, the rate of mixing the reaction solution is constant (900 rpm).

The evolution time of Briggs-Rauscher reaction system has been followed by a potentiometric method using pH activator EH4 (manufacturer-Measuring instrument Miljkovic Budimir et al. o.d. p.o.), which is directly linked to the computer that automatically registers the difference in the potential of the working electrode and the potential of the reference electrode. As a working electrode, Pt electrode (METHROM AG. Serial No. 6.0301.100) was used, while reference electrode was Ag/AgCl electrode (METHROM AG. Serial No. 6.0726.100) with an electrolytic bridge, stuffed with KCl/K₂SO₄ solutions.

All of the used chemicals are p.a. grade (CH₂(COOH)₂ – Acrös Organics, MnSO₄ Fluka, while HClO₄, KIO₃, H₂O₂ – Merck) and are used for preparing solutions without further purification. Deionized water (specific resistance 18 MΩ·cm⁻¹), used for preparing solutions, is prepared by Millipore system for water (Mili-Q, Bedford, MA, USA). In all experiments, the reactants are being put into reaction cell in next following steps: 7 ml CH₂(COOH)₂, 5 ml MnSO₄, 5 ml HClO₄, 5 ml KIO₃. After achievement of desired temperature (37.0 °C) and stabilization of potential of working electrode, appropriated masses of phosphate tungsten bronze (0.0109 g ± 0.0001 g; 0.0202 g ± 0.0001 g; 0.0212 g ± 0.0001 g; 0.0308 g ± 0.0001 g; 0.0504 g ± 0.0001 g; 0.0722 g ± 0.0001 g), respectively, and calcium doped phosphate tungsten bronze (0.0138 g ± 0.0001g; 0.0179 g ± 0.0001g; 0.0268 g ± 0.0001 g; 0.0308 g ± 0.0001g; 0.0558 g ± 0.0001 g; 0.0737 g ± 0.0001 g; 0.0956 g ± 0.0001 g; 0.1110 g ± 0.0001 g), respectively, have being added into the reaction system. After the addition into the reaction system, bronze is being a mixture for 3 minutes (900 rpm) and afterward 3 ml H₂O₂ is added. The moment of the addition of H₂O₂ into the reaction cell has been taken as the beginning of BR reaction.

The initial concentrations of the reactants in the system were: [CH₂(COOH)₂]₀ = 0.0789 mol dm⁻³, [MnSO₄]₀ = 0.00752 mol dm⁻³, [HClO₄]₀ = 0.03 mol dm⁻³, [KIO₃]₀ = 0.0752 mol dm⁻³ and [H₂O₂]₀ = 1.269 mol dm⁻³.

The phosphate tungsten bronze and calcium doped phosphate tungsten bronze are obtained by thermal treatment of 12-tungstophosphoric heteropoly acid and calcium salt of 12-tungstophosphoric heteropoly acid. The defervescence speed is constant (10 °C per minute) to the temperatures at which Keggin's anion is transformed. Above the temperature of „destroying” Keggin's anion, samples are held in a furnace for 10 minutes.

The synthesis of 12-tungstophosphoric heteropoly acid (H₃PW₁₂O₄₀ · 29H₂O) is done by the procedure described in detail in reference [17]. Calcium salt of 12-tungstophosphoric heteropoly acid (CaHPW₁₂O₄₀ · 6H₂O) is prepared by ion exchange of H⁺ ion from heteropoly acid with calcium ion.

3. RESULTS AND DISCUSSION

Figure 2 presents oscillograms (or time evolutions) of BR reaction without the addition of phosphate tungsten bronze (a), as well as in the presence of different masses of phosphate tungsten bronze: (b) 0.0109 g; (c) 0.0504 g; (d) 0.0722 g.

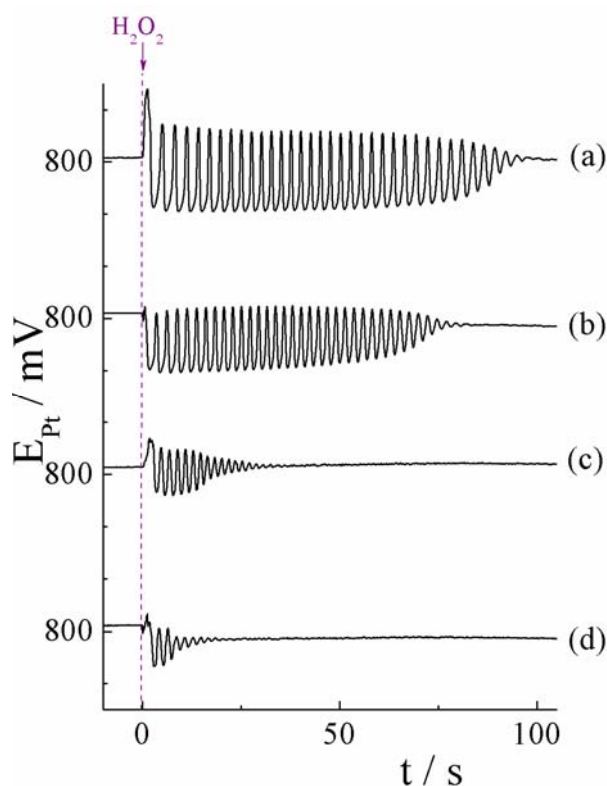


Figure 2. BR oscillograms obtained by platinum electrode without the addition of phosphate tungsten bronze (a) as well as in the presence of different masses the tungsten bronze phosphate: (b) 0.0109 g; (c) 0.0504 g and (d) 0.0722 g

From Figure 3., it can be underlined that the dependence of oscillatory period length from added mass of phosphate tungsten bronze is linear. Whereas, obtained dependence follows the saturation kinetics because the addition of 0,07 g of phosphate tungsten bronze comes into saturation [16]. Obtained linear dependence till the mass of added phosphate tungsten bronze of 0,05 g can be used as a calibration diagram [16].

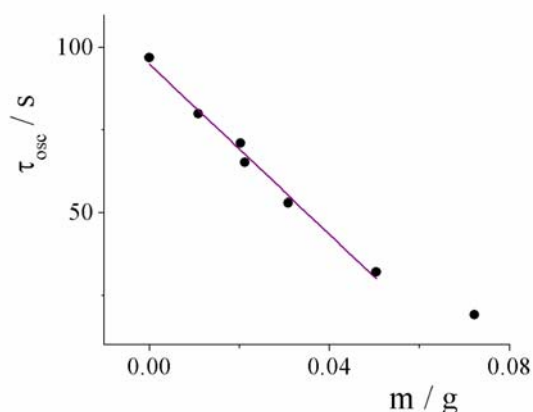


Figure 3. The dependence of oscillation time of the BR system from the mass of added phosphate tungsten bronze

Figure 4 presents oscillograms (or time evolutions) of BR reaction without the addition of calcium doped phosphate tungsten bronze (a), as well as in the presence of different masses of calcium doped phosphate tungsten bronze: (b) 0.0138 g; (c) 0.0268 g; (d) 0.0956 g.

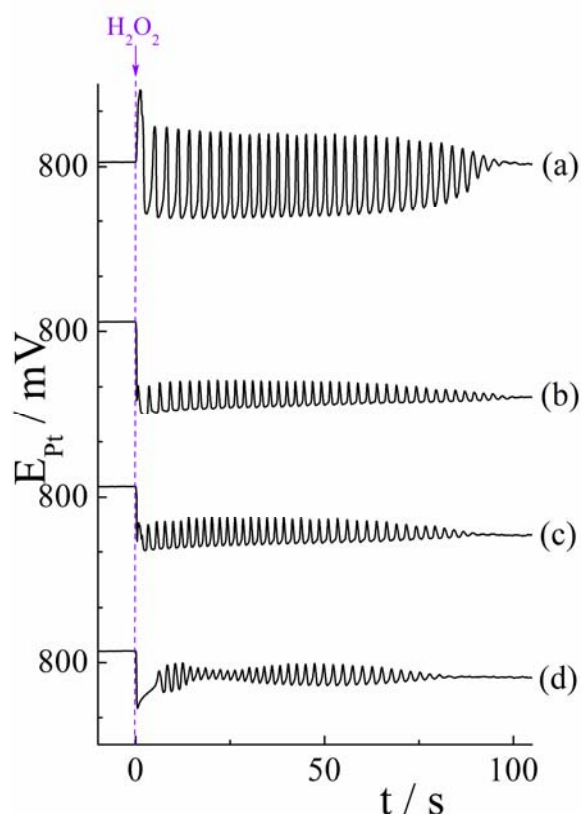


Figure 4. BR oscillograms obtained by platinum electrode without the addition of calcium phosphate doped tungsten bronze (a) as well as in the presence of different masses calcium phosphate doped tungsten bronze (b) 0.0138 g; (c) 0.0268 g and (d) 0.0956 g

From Figure 4, it can be seen that increase in the mass of calcium doped phosphate tungsten bron-

ze doesn't lead to significant decrease in oscillation time of BR reaction, but it leads to significant decrease in oscillation amplitude. As well as in the case of phosphate tungsten bronze, a decrease in oscillation amplitude can be assigned to increase in inhomogeneity of the system, by the addition of insoluble calcium doped phosphate tungsten bronze. The addition of insoluble bronzes and increase in inhomogeneity (existence of solid and liquid phase in reaction) is being reflected on the development of oscillations in the reaction system, i.e. the oscillation amplitude is amortized (Figure 2. and 4.).

The dependence of oscillation time (τ_{osc}) from the mass of added calcium doped phosphate tungsten bronze in BR system is represented in Figure 5. As it can be seen from Figure 5., the addition of different masses of calcium doped phosphate tungsten bronze does not considerably effect on basic BR oscillogram length, obtained without the addition of bronzes. The addition of different masses of calcium doped phosphate tungsten bronze leads to scattering of the oscillatory period length around the basic BR oscillogram, which cannot be used for calibration curve and quantitative determination of the unknown mass of calcium doped phosphate tungsten bronze (Figure 5.).

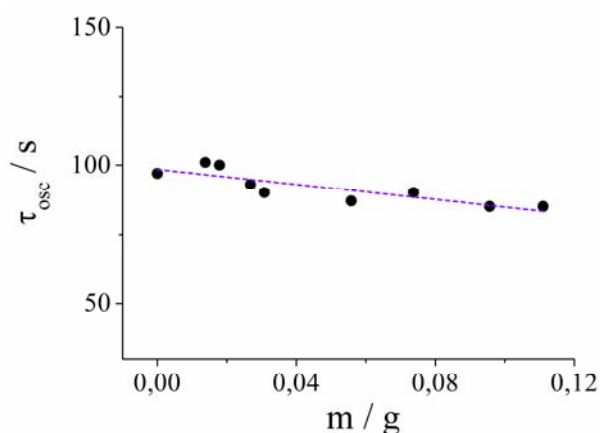


Figure 5. The dependence of oscillation time of the BR system from the mass of added calcium doped phosphate tungsten bronze

Comparing graphics obtained, it can be concluded that the dependence of BR oscillation time from the added mass of calcium doped phosphate tungsten bronze (Figure 5.) is significantly different from the dependence of BR oscillation time from the mass of phosphate tungsten bronze added (Figure 3.). Namely, the addition of calcium doped phosphate tungsten bronze slightly influences the oscillatory period length and it cannot be used for determination of the unknown mass of the bronze. Furthermore, obtained behavior indicates a different mechanism of action of phosphate tungsten bronze and calcium doped phosphate tungsten bronze on the oscillatory

Briggs-Rauscher reaction. With respect to attendance of metals and the possibility of a huge number of their oxidation states, bronzes have expressed oxide-reduction properties. The Briggs-Rauscher reaction is an oscillatory reaction in which the oxidation and reduction branches are alternately dominated, hence, the attendance of the bronzes can influence the oscillatory dynamics. However, with respect to the low solubility of the bronzes in aqueous solutions [18], the mechanism of action of bronzes is probably adsorptive. Namely, phosphate tungsten bronzes are well-known adsorbers of hydrogen peroxide [19], which is one of the most important BR reaction species, responsible for the oscillation of the system. Obtained behavior can be assigned to different adsorption of hydrogen peroxide on phosphate tungsten and calcium doped phosphate tungsten bronze. The results obtained can indicate the presence of a major number of activation centers for binding hydrogen peroxide on phosphate tungsten bronze with regard to the doped bronze of the same kind. Further research will be done in order to determine adsorption isotherms and to measure the specific surface for these two materials.

4. CONCLUSION

In this work, the Briggs-Rauscher oscillatory reaction is used for the examination of phosphate tungsten bronze and calcium doped phosphate tungsten bronze. The addition of 0.01 g – 0.11 g of phosphate tungsten bronze and calcium doped phosphate tungsten bronze has a different influence on the Briggs-Rauscher reaction dynamics. In the case of the addition of phosphate tungsten bronze in the Briggs-Rauscher reaction, it is obtained the linear dependence of oscillatory period length from the mass of added bronze. Obtained linear dependence can be used as a calibration curve for determination of the unknown mass of phosphate tungsten bronze. In the case of the addition of calcium-doped phosphate tungsten bronze, there were no significant deviations from the basic BR oscillogram. The results obtained indicate the different mechanism of action of these two bronzes in the oscillatory reaction. Because the phosphate tungsten bronzes are potentially good adsorbers of hydrogen peroxide, resulting behavior can be attributed to different adsorption of hydrogen peroxide on phosphate tungsten and calcium doped phosphate tungsten bronze. The phosphate tungsten bronze proved to be a much better adsorber of hydrogen peroxide than calcium doped phosphate tungsten bronze. The used Briggs-

Rauscher oscillatory reaction is an innovative method for testing different properties of bronzes.

5. ACKNOWLEDGEMENT

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МАЛИ УТИЦАЈ КАЛЦИЈУМОМ ДОПИРАНЕ ФОСФАТ ВОЛФРАМОВЕ БРОНЗЕ НА ДИНАМИКУ БРИГС–РАУШЕР РЕАКЦИЈЕ

Сажетак: Бригс–Раушер (БР) осцилаторна реакција је реакција оксидације малонске киселине у присуству водоник-пероксида и јодата у киселој средини, која је катализована јонима мангана. Ова реакција је веома осетљива на присуство адитива. У овом раду, БР реакција је коришћена за испитивање фосфат волфрамове бронзе, као и калицијумом допиране фосфат волфрамове бронзе, које су добијене термичким третманом. Додатак (0,01–0,11 g) фосфат волфрамове бронзе и калицијумом допиране фосфат волфрамове бронзе има различит утицај на динамику Бригс–Раушер реакције. У случају додатка фосфат волфрамове бронзе у Бригс–Раушер реакцију, добијена је линеарна зависност дужине осцилаторног периода од масе додате бронзе, док у случају додатка калицијумом допиране фосфат волфрамове бронзе, осцилаторни период се не мења значајно са повећањем масе додате бронзе. Механизам деловања калицијумом допиране и недопиране фосфат волфрамове бронзе на БР реакцију је вероватно адсорпциони процес и биће предмет будућих истраживања.

Кључне ријечи: осцилаторне реакције, Бригс–Раушер реакција, фосфат волфрамове бронза, калицијумом допирана фосфат волфрамове бронза, термички третман.

