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INFLUENCE OF IODATE ION CONCENTRATION ON OSCILLATIONS IN THE BRIGGS-RAUSCHER REACTION

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ABSTRACT*.* The Briggs-Rauscher oscillating reaction was studied in a batch mode. Mixtures were prepared in such a way that reactant concentrations were at the limit of that concentration interval in which oscillations happen. Iodate-ion concentration was varied and its influence on the oscillations was investigated. Time course of redox potential and iodide-ion concentration were recorded. At low iodate-ion concentration oscillating break was founded.

Introduction

A chemical reaction is oscillatory if two or more intermediate's concentration have extreme values. Briggs-Rauscher (BR) is an oscillatory reaction and is representing the oxidation of malonic acid by hydrogen peroxide and iodate with manganese (II) ion as a catalyst, in acidic medium. The formation velocity of oxygen and carbon dioxide as well as iodine and iodide-ion concentration presents oscillation in this system.

Several scientists investigated the mechanism of BR, namely Cook [1], Furrow and Noyes [2, 4], De Kepper and Epstein [7], Fujieda and Ogata [8] and others [3, 5, 6]. According to their proposal, the global reaction is symbolized with the following equation:

$$IO^-_3+2H_2O_2+CH_2(COOH)_2+H^+\rightarrow ICH(COOH)_2+2O_2+3H_2O \qquad (R1)$$

This represents the sum of the following two steps:

$$IO^-_3+2H_2O_2+H^+\rightarrow HOI+2O_2+2H_2O \qquad (R2)$$

$$HOI+CH_2(COOH)_2\rightarrow ICH(COOH)_2+H_2O \qquad (R3)$$

Reaction (R2) takes place in two different ways. The way in which the system developes is a function of iodide-ion concentration. If the iodide-ion concentration is high, the mechanism will obey the following non-radical steps:

$$IO^-_3+I^-+2H^+\rightarrow HIO_2+HOI \qquad (R4)$$

$$HIO_2+I^-+H^+\rightarrow 2HOI \qquad (R5)$$

$$HOI+H_2O_2\rightarrow I^-+O_2+H^++H_2O \qquad (R6)$$

$$(R2)=(R4)+(R5)+2(R6)$$

If the iodide-ion concentration is smaller than the critical value, the reaction (R_2) will follow the radical path:

$$IO^-_3+HIO_2+H^+\rightarrow 2IO_2\bullet+H_2O \qquad (R7)$$

$$IO_2\bullet+Mn^{2+}+H_2O\rightarrow HIO_2+Mn(OH)^{2+} \qquad (R8)$$

$$Mn(OH)^{2+}+H_2O_2\rightarrow Mn^{2+}+H_2O+HOO\bullet \qquad (R9)$$

$$2HOO\bullet\rightarrow H_2O_2+O_2 \qquad (R10)$$

$$2HIO_2\rightarrow IO^-_3+HOI+H^+ \qquad (R11)$$

$$(R2)=2(R7)+4(R8)+4(R9)+2(R10)+(R11)$$

In BR reaction the non-radical way will change into the radical one if the iodide-ion concentration decreases bellow the critical value. The reaction oscillates between these two processes. The mechanism presented above is only a skeleton of what happens during the reaction. It explains the origin of oscillations in the concentration of iodine and iodide-ion, but not elucidates the path of carbon dioxide's formation, nor identifies the final organic product. That is why BR is still under research.

In most of the cases BR was investigated in continuous-flow stirred tank reactor (CSTR). Nevertheless in some papers batch mode experiments are related.

The system exhibits oscillatory behavior only if the initial concentrations of the reactants fit in a concentration interval. These intervals for the different reactants are: $[H_2O_2]$=0.3-3.5 M, $[IO_3^-]=2*10^{-2}-1*10^{-1}$ M, $[H^+]=5*10^{-2}-2*10^{-1}$ M, $[Mn(II)]=3*10^{-3}-3*10^{-2}$ M, [malonic acid]$=2*10^{-2}-1*10^{-1}$ M [9].

The aim of the present paper is to notice about the system's behavior in case in which the initial mixture is a non-classical one and the iodate-ion concentration is smaller than the inferior limit.

Experimental

Batch experiments were carried out in a 40 ml double walled, water-jacketed cylindrical-shaped glass reactor. Its temperature was controlled by a circulating water bath (VEB-MLW type thermostat). A magnetic stirrer was used to ensure uniform mixing. Time course of redox potential and iodide-ion concentration was followed. Platinum electrode and double-junction saturated calomel electrode was used. Iodide-ion concentration was determined by using an ion selective electrode EMIS-I^-. The time course of the redox potential was monitored with a “Metrohm E 478" recorder, or stored on a PC. Data acquisition was accomplished with a PCI-6023E board (National Instruments) and the Digix program was used.

The reactants sodium iodate (Chemapol, c.p.), manganese (II) sulfate (Reactivul, c.p.), hydrogen peroxide (Merck p.a.), sulfuric acid (Riedel De Haen, p.a.), malonic acid (Reachim, p.a.), potassium iodide (Reactivul, p.a.), potassium nitrate (Reactivul, p.a.) were used without further purification. Parent solutions were made. The first solution was obtained by mixing the sulfuric acid and the sodium iodate. The acid's concentration was kept 0.1 M and the iodate's concentration was varied. 0.2 M malonic acid and $2.6*10^{-2}$ M manganese (II) sulfate composed the second solution. The third solution was the hydrogen peroxide. These solutions were mixed in such a way that $[H^+]=2.5*10^{-2}$ M; [malonic acid]$=5*10^{-2}$ M; $[Mn(II)]=6.5*10^{-3}$ M $[H_2O_2]=2.2*10^{-1}$ M and variable iodate concentrations were ensured.

Results and Discussion

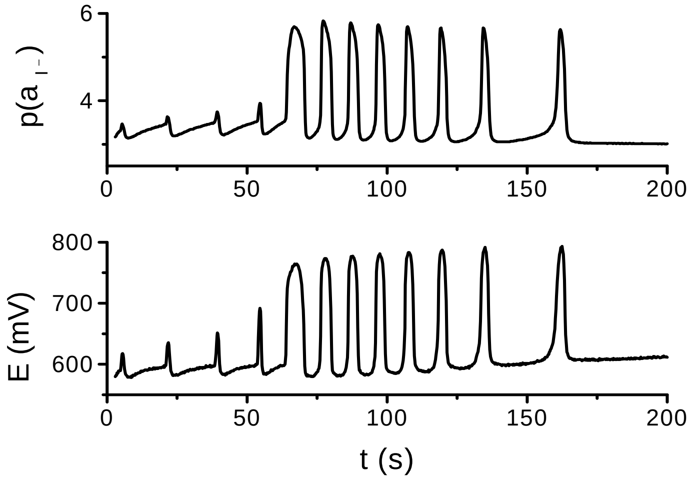

Figure 1. Time course of iodide-ion activity and redox potential for iodate-ion initial concentration $[IO^-_3]=8,5*10^{-2}$ M

BR was investigated in closed reactor. It is to be mentioned that batch experiments can be used only for a few oscillating reactions, but BR is one of them.

As it was revealed above, non-classical initial mixtures were prepared with variable iodate-ion concentration.

These initial concentrations for the iodate-ion had different values between: $8.5*10^{-2}$-$1,25*10^{-2}$ M. It has been distinguished three different behaviors of the system.

At high iodate-ion concentration the reaction started with a few, large period and small amplitude oscillation. These were followed by the classical oscillations, with smaller period and larger amplitude. The above-described behavior is represented in Figure 1. The oscillations had classical shape when iodate-ion's concentration value was included in 2,5*10^{-2}-6,5*10^{-2} M interval. Such an oscillation is represented in Figure 2. In this case the system contained 6*10^{-2} M iodate-ion.

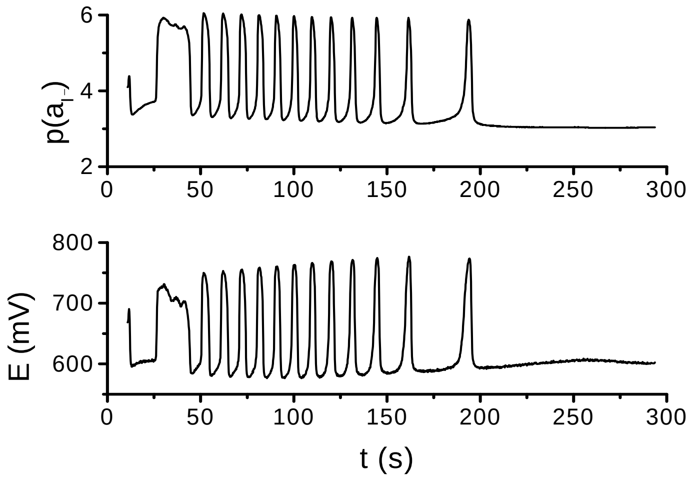

Figure 2. Time course of iodide-ion activity and redox potential for iodate-ion initial concentration $[IO^-_3]$=6*10^{-2}M

With decreasing iodate-ion concentration the increases of amplitude and decreases of period was observed.

At low iodate-ion concentration the system acted in a peculiar way. The cessation of the oscillatory regime and subsequent regeneration of oscillations followed the starting few normal oscillations. This behavior is presented in Figure 3.

The shapes of the oscillations before and after the break are quite different. This can be caused by the different parametrical condition of the oscillation before and after the break.

Oscillation break was described referred to Belousov-Zhabothinsky reaction. In the case of BR was also described an oscillation break, but this was caused by an antioxidant added to the system which scavenged the free radicals [10, 11, 12].

We can conclude that even the non-classical initial mixture exhibits so called normal oscillations. The low iodate-ion concentration causes an oscillating break. The appearance of the break can be explained with the low rate of one of the steps trough which the reaction is developing. It can be caused by the too low concentration of one intermediate species, like the iodide-ion.

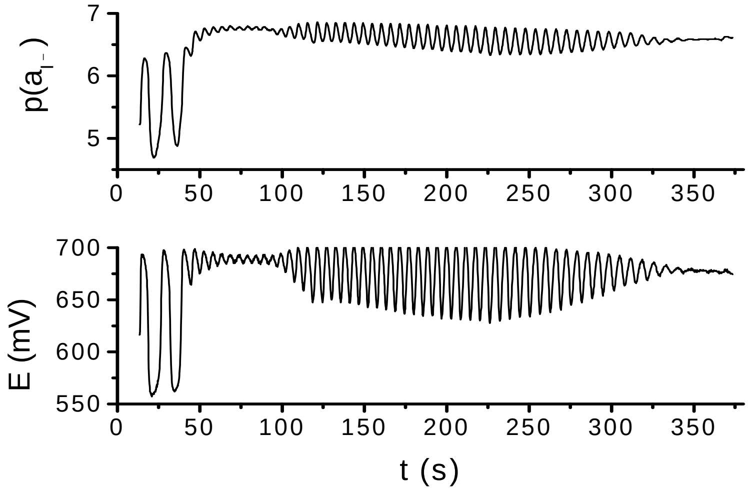

Figure 3. Time course of iodide-ion activity and redox potential for iodate-ion initial concentration $[IO^-_3]=1,38*10^{-2}$ M

The following step will be the modeling of the described oscillation. The comparison of the computational behavior and the real one will elucidate some issues of this nonlinear phenomenon.

REFERENCES

1. D. O. Cooke, *J. Chem. Soc., Chem. Commun.,* 1984, p. 314
2. S. D. Furrow, R. M. Noyes, *J.Am.Chem. Soc.* 1982, **104**, p. 38, p.42
3. V. Vukojevic, P. Graae Sorensen, F. Hynne, *J. Phys. Chem.,* 1996, **100**, p. 17175
4. S. D. Furrow, *J. Phys. Chem.,* 1989, **93**, p. 2817
5. V. K. Vanag, M. V. Alfimov, *J. Phys. Chem.,* 1993, **97**, p. 1884
6. J. Happel, P. H. Sellers, *J. Phys. Chem.,* 1991, **95**, p. 7740
7. P. De Kepper, I. R. Epstein, *J. Am. Chem. Soc.,* 1982, **104** p. 49
8. S. Fujieda, H. Ogata, *Talanta***,** 1996, p. 1989
9. Gy. Bazsa, *Nemlineáris dinamika és exotikus kinetikai jelenségek kémiai rendszerekben*, Debrecen, 1992, p.210.

10. R. Cervelatti, N. Crespi-Perellino, S. Furrow, A. Minghetti, *Helv. Chim. Acta.* 2000, **83**, p. 3179
11. R. Cervellatti, K. Höner, S. Furrow, C. Neddens, S. Costa, *Helv. Chim. Acta,* 2001, **84**, p. 3533
12. K. Höner, R. Cervellati, C. Neddens *Eur. Food Res.Technol.*, 2002, **214.** p. 356