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THE INFLUENCE OF LIPOIC ACID ON BRIGGS-RAUSCHER OSCILLATING REACTION

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ABSTRACT. Active Briggs-Rauscher mixture is developing through two competing paths: a radical and a non-radical one. Antioxidant added to the mixture reacts with free radicals involved in the radical path and inhibits the oscillations. Addition of lipoic acid (the antioxidant we used) to Briggs-Rauscher mixture causes the immediate cessation of oscillations. After some time the oscillations reappears. The inhibition time depends on the concentration of the lipoic acid.

INTRODUCTION

Briggs-Rauscher (BR) oscillatory reaction represents the oxidation of malonic acid by hydrogen peroxide and iodate with manganese (II) ions as a catalyst, in acidic medium.

Cook [1] started the investigations regarding to the mechanism of BR and was followed by Noyes and Furrow. They studied BR mixture in batch conditions and proposed a skeleton mechanism [2, 3, 4]. A similar mechanism was proposed by De Kepper and Epstein [5] but they were taking into account several phenomena that appear in open conditions (continuous-flow stirred tank reactor, CSTR). Fujieda and Ogata [6], Happel and Sellers [7] reported a mechanistic study of this oscillatory reaction, too.

According to their proposal the global reaction (R1), consisted in the oxidation and iodination of malonic acid or its derivative, represents the sum of two steps (R2), (R3).

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

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

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

Reaction (R2) takes place in two different ways.

At high iodide-ion concentration the mechanism will obey a non-radical path:

$$IO_3^-+I^-+2H^+\rightarrow HIO_2+HOI \quad (R4)$$

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

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

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

If the iodide-ion concentration is smaller than a critical value, the reaction (R2) will follow the radical path:

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

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

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

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

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

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

When iodide-ion concentration increases above the critical value, the radical way changes into the non-radical one. The skeleton of the mechanism was presented above in order to explain the oscillations in the concentration of the main intermediates: iodine, iodide-ion, oxyiodine species like HOI, HIO_2, IO_2 and hydroperoxyl radical HOO.

The existence of the radical path makes BR suitable to react with antioxidants. Franz [8] reported for the first time such an experience, followed by Cervellati and Furrow [9, 10, 11]. Antioxidants that were added to an active BR mixture caused the immediate cessation of oscillations. After some time the oscillatory behavior is regenerated. The inhibition time depends linearly on the concentration of the antioxidant. Cervellati and Furrow assumed that the antioxidant added to BR mixture subtracts HOO· radicals and stops the oscillatory regime.

This inhibitory effect on the active BR of the free-radical scavengers indicates a possibility to develop an analytical procedure for monitoring their antioxidant activity.

The aim of the present paper is to report the antioxidant activity of lipoic acid (1,2-dithiolane-pentanoic acid) via inhibition effect on active BR mixture.

RESULTS AND DISCUSSION

In biological systems the antioxidant capacity of lipoic acid occurs through different mechanisms such as metal chelation, activated oxygen species scavenging, recycling of other antioxidants or repair of damaged molecules induced by oxidative stress [12].

The addition of lipoic acid solution to the active BR mixture causes the immediate cessation of the oscillations. After some time the oscillatory behavior was regenerated.

This behavior is presented in Figure 1. It is to be mentioned that frequency and amplitude of oscillations was the same before and after the break.

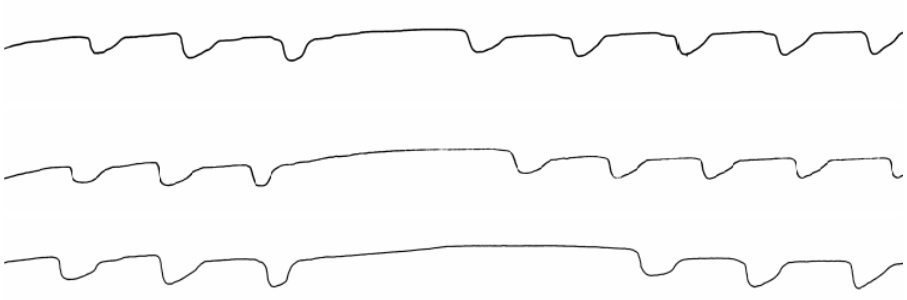

Figure 1. *Inhibitory effect of the lipoic acid solutions: a) $0.31\cdot10^{-3}$ M, b) $0.63\cdot10^{-3}$ M, c) $1.25\cdot10^{-3}$ M*

The inhibition time (the time elapsed between the cessation and the regeneration of the oscillatory regime) depends linearly on the concentration of the lipoic acid. The dependence of the inhibition time vs. concentration of lipoic acid is presented in Figure 2.

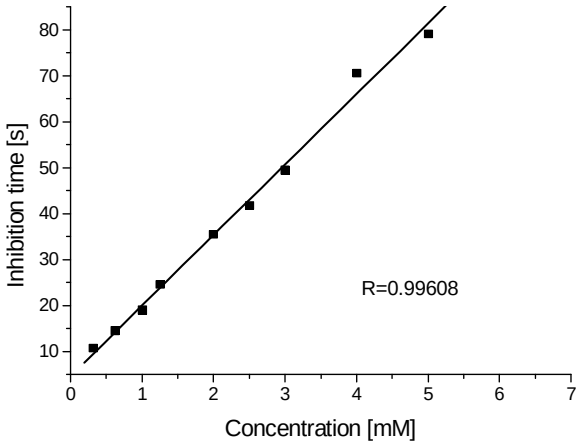

Figure 2. *Graph of the inhibition time vs. concentration of lipoic acid*

This linear relationship between the inhibition time and the concentration of the lipoic acid indicates the possibility to develop an analytical method for monitoring the activity of antioxidant. This method is simple, rapid and reproducible. At low lipoic acid concentrations (below 0.3 mM) the inhibition time is comparable with the oscillation period, for this reason the linear correlation between the inhibition time and the concentration is not observable.

EXPERIMENTAL

Briggs-Rauscher mixture was prepared in a double-walled glass reactor. Experiments were carried out in thermostated conditions, VEB-MLW type thermostat was used. The temperature of the mixture was controlled by a circulating water bath. A magnetic stirrer ensured uniform mixing. In order to follow the time course of redox potential a platinum electrod and a double-junction saturated calomel electrode were used. Time course of redox potential was monitored with a "Metrohm E 478" recorder. Inhibition time was determined with a stopper-watch.

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.) and lipoic acid (Merck p.a.) were used without further purification. Stock solutions were made. The first solution was obtained by mixing the sulfuric acid and the sodium iodate. The acid's concentration was kept 0.2 M and the iodate's concentration was 0.16 M. 0.1 M malonic acid and 0.026 M manganese (II) sulfate composed the second solution. The third solution was the hydrogen peroxide, its concentration was 2.64 M. These solutions were mixed in such a way that $[H^+]$=0.05 M; [malonic acid]=0.025 M; [Mn(II)]=0.0065 M $[H_2O_2]$=1.32 M and $[IO_3^-]$=0.04 M concentrations were ensured.

Lipoic acid was dissolved in water-ethanol mixture (4:1) and a stock solution was made. Its concentration was $5 \cdot 10^{-3}$ M.

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