Book of Proceedings

The Ninth International Congress
of the Serbian Society of Mechanics
July 5-7, 2023, Vrnjačka Banja, Serbia

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Year of publication
2023

ISBN-978-86-909973-9-8

L-TYROSINE INFLUENCE ON THE REACTION KINETICS OF IODATE-HYDROGEN PEROXIDE OSCILLATORY REACTION

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Abstract

The impact of L-tyrosine amino acid on the kinetics of the BL oscillatory reaction was investigated under closed reactor conditions. The study was focused on examining the sensitivity of the BL reaction matrix to tyrosine perturbations. A high sensitivity of the BL matrix to very low tyrosine concentrations was observed.

Keywords: L-tyrosine, Bray-Liebhafsky reaction, oscillatory reactions.

1. Introduction

The Bray-Liebhafsky (BL) reaction is the oldest known oscillating reaction that represents the catalytic decomposition of hydrogen peroxide into oxygen and water, in the presence of iodate (IO_3^-) and hydrogen ions (H^+). [1] It is represented by chemical reaction:

$$2H_2O_2 \xrightarrow{H^+, IO_3^-} 2H_2O + O_2 \tag{1}$$

Although the BL reaction was discovered more than a century ago and appears to be simple because it involves only three reactants, it has a very complex and unexplored mechanism that may include a series of stable and unstable intermediate species, including radical ones: $IO_2^\bullet$, $HOO^\bullet$, $HO^\bullet$, and $I^\bullet$.

The Bray–Liebhafsky oscillatory reaction proved to be useful in determining the activity of various analytes under closed and open reactor conditions due to its extreme sensitivity to external stimuli (perturbations). In this study, the impact of L-tyrosine on the BL reaction kinetics under closed reactor conditions was investigated. The amino acid L-tyrosine (4-hydroxyphenylalanine, C9H11NO3) is a precursor for the synthesis of the catecholamines dopamine (DA) and norepinephrine (NE). Under stressful conditions, DA and NE levels drop, which can compromise cognitive function. By increasing catecholamine levels in the brain, L-tyrosine supplementation may be able to reduce the cognitive decline caused by acute stress. Also, it is a precursor for biosynthesis of thyroid hormones through the iodination process. To explain tyrosine activity, numerical simulations were performed using the proposed model of the BL oscillatory reaction.

The response of the BL matrix to a low concentration of tyrosine single pulse perturbations (about 1×10^{-6} M) was investigated both numerically and experimentally. [2]

2. Experimental part

All experiments were carried out in a closed well-stirred reactor (with stirring rate, σ = 900 rpm) and thermostated at T = 54.0 ºC. The reaction volume was 38.8 ml. The initial concentrations of the reactants were: $[KIO_3]_0 = 1.40 \times 10^{-1}$ mol dm^{-3}, $[H_2SO_4]_0 = 4.23 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2]_0 = 2.84 \times 10^{-3}$ mol dm^{-3}. All stock reactants solutions were pro analysis grade and prepared in deionised water. The substances were added to the reaction vessel in the following order: KIO_3, H_2SO_4 and when the temperature and potential were stabilised, H_2O_2 was added. The moment when H_2O_2 was added to the vessel was taken as the beginning of the reaction. Forty minutes after the addition of H_2O_2, 200 µl of commercial L-tyrosine of different concentrations was added. The time evolution of the BL reaction was followed by the platinum electrode as a working electrode and a double junction Ag/AgCl electrode as a reference electrode.

3. Numerical simulation

Numerical simulations were performed in MATLAB, using the ODE15s solver routine based on the Gear algorithm for the integration of stiff differential equations. The proposed model of the BL reaction [3] was used with the original rate constants recalculated to the temperature used in the experiment. The concentrations of all reactants were identical to the experimental values.

4. Conclusions

The impact of l-tyrosine on the kinetics of the BL reaction under closed reactor conditions was investigated because of its importance in the synthesis of the catecholamines dopamine (DA) and norepinephrine (NE). The impact of L-tyrosine was analysed under closed reactor conditions and by numerical simulations. The results show a great potential for the BL matrix in the analysis of L-tyrosine. Numerical simulations indicate several possible pathways of influence.

Acknowledgement: We are grateful to the financial support from Ministry of Science, Technological Development and Innovation of Republic of Serbia (Grant Numbers 172015 and 45001, and Contract numbers 451-03-47/2023-01/200026 and 451-03-47/2023-01/200146. This research was supported by Science Fund of Republic of Serbia #Grant Number. 7743504, NES.

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