The influence of pyrocatechol added in pre-oscillatory period on the dynamics of the Bray-Liebhafsky reaction

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Abstract: In the past two decades, chemical oscillators have emerged as a popular tool for the determination of "reactive" analytes due to their great sensitivity toward any kind of external perturbations. They have found application in many fields of applied science enabling relatively easy quantitative and qualitative analyses. In this study influence of pyrocatechol, an important precursor in many organic syntheses, on the pre-oscillatory period of the Bray-Liebhafsky (BL) reaction was examined. The BL reaction was followed by the potentiometric method. In a series of experiments (in a concentration range from 1.5×10^{-5} M to 3×10^{-5} M), pyrocatechol was added 45 minutes after the start of the reaction, causing an immediate appearance of oscillations. For these experimental conditions, the period between the first and second oscillation increases linearly with the added pyrocatechol concentration. The obtained results can be useful for analytical purposes and accordingly, potential determination of unknown pyrocatechol concentration..

Keywords: Bray-Liebhafsky reaction, oscillatory reaction, pyrocatechol, electrochemical measurements, environmental protection

1. Introduction

A chemical system containing only three reactants: hydrogen peroxide, iodate, and sulfuric acid may at first seem very simple, but still the Bray - Liebhavski (BL) reaction is one of the most studied phenomena of nonlinear dynamics [1, 2]. It is an oscillatory reaction, which means that intermediate concentrations oscillate in time, while concentrations of reactants and products change cascadingly. BL represents the catalytic

(in the presence of hydrogen and iodate ions) decomposition of hydrogen peroxide into water and oxygen [1]:

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

However, the very complex mechanism of this chemical reaction abounds in plenty of intermediates, many of which are short-lived and highly reactive [3]. The dynamics of such a system is very specific and, depending on the initial conditions, different dynamic states can be obtained. External perturbators can significantly affect the course of the reaction and their effects can be used to investigate the reaction mechanism, but also in analytical purposes where different ("reactive") analytes are added. Here we investigated the influence of pyrocatechol, a typical phenolic compound that is an important precursor for manufacturing pesticides, flavors, fragrances, and paints. High levels of pyrocatechol in wastewater can be a serious health issue due to its reactivity and toxicity [4]. Pyrocatechol has been already tested in the BL oscillatory system [5, 6], but this is the first time that it has been added in the pre-oscillatory period of the reaction. This can give additional insights into its mechanism of action which can be of particular interest for environmental chemistry.

2. Experimental section

In this study, BL experiments were performed in a well-stirred (σ = 900 rpm) batch reactor and thermostated at (60.0 ± 0.2) °C. The total reaction volume was 55 ml and the initial concentrations of reactants were: $[KIO_3]_0 = 7.35 \times 10^{-2}$ M, $[H_2SO_4]_0 = 4.79 \times 10^{-2}$ M, $[H_2O_2]_0 = 7 \times 10^{-3}$ M. All used chemicals were pro analysis grade, and their solutions were prepared with deionized water (18 MΩ cm). The moment when H_2O_2 was added to the vessel was taken as the beginning of the reaction. Different concentrations of the pyrocatechol were added (100 μl aliquot) into the reaction 45 minutes after the reaction started (see Figure 1.). The reaction was followed by the potentiometric method. The working iodide ion-selective electrode was connected to a double-junction Ag/AgCl reference electrode and potential-time evolution of the BL reaction was followed in time.

3. Results and Discussion

The potential-time curve for the BL reaction without pyrocatechol addition for these experimental conditions is reported in our previous work [5,6]. Here it is important to emphasize that reaction is preceded by the induction period τ_{ind} = 55min, after which six regular oscillations take place. As it can be seen on Figure 1 the pyrocatechol addition in the pre-oscillatory period (45 min after the reaction beginning) caused an instantaneous oscillation thereby shortening the induction period of the reaction. We measured the time between the first and the second oscillation (denoted as $\tau_{1\text{-}2}$) and compared it to the value reported previously for the system without pyrocatechol [5, 6]. For the concentration range from 1.5×10^{-5} M to 3×10^{-5} M parameter $\tau_{1\text{-}2}$ showed linear dependence on pyrocatechol concentration (Figure 2), with the regression equation:

$$\tau_{1-2} = 1.04 \times 10^6 \times C_{Pyrocatechol} + 32.5 \quad (2)$$

where C is the concentration of pyrocatechol in BL system in M.

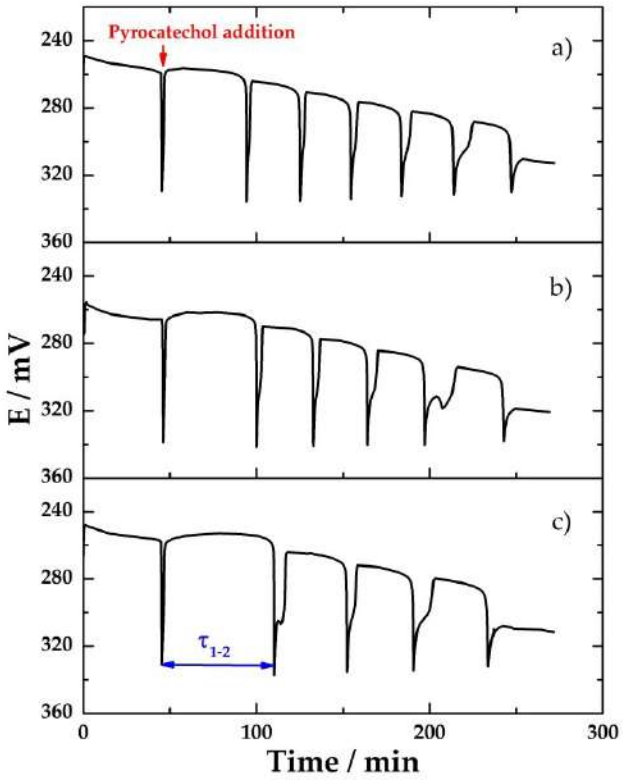

Figure 1. Oscillograms of the BL reaction with different concentrations of pyrocatechol, added 45 minutes after the beginning of the reaction: 3.0×10^{-5} M (a), 9.0×10^{-5} M (b) and 1.2×10^{-4} M (c).

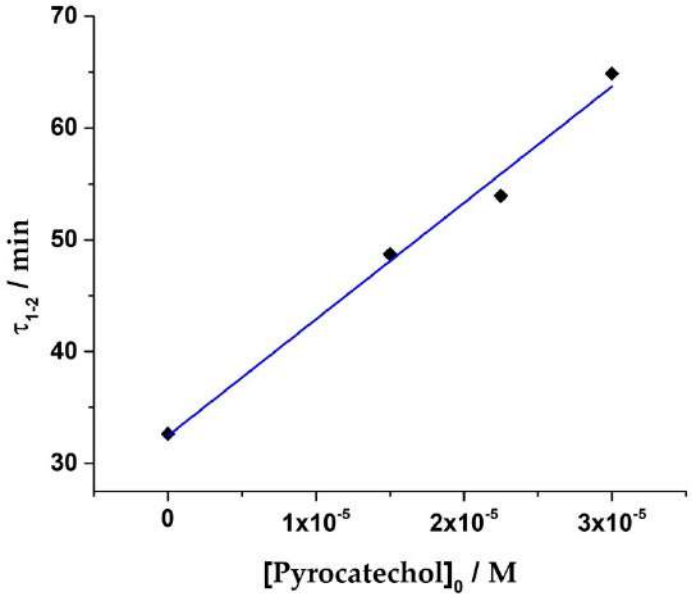

Figure 2. The period between the first and the second oscillations dependence on pyrocatechol concentrations.

Compared to our previous results (where the pyrocatechol was added in and after the oscillatory regime), the slope of the obtained regression equation is slightly lower indicating lower sensitivity of measurement [5,6]. Although different parameters were measured, the experimental conditions and composition of the BL matrix are the same, allowing comparison. Nevertheless, in the specified concentration range, pyrocatechol concentrations can be determined with satisfactory accuracy in the manner presented here.

4. Conclusions

The influence of the pyrocatechol addition in the pre-oscillatory period on the dynamics of the Bray-Liebhafsky (BL) reaction was investigated. Obtained potential-time curves show that pyrocatechol provokes an oscillatory regime immediately. The period between the first and second oscillation, $\tau_{1\text{-}2}$, was chosen as a parameter for comparing the results. In the examined concentration range (1.5×10^{-5} M - 3×10^{-5} M) $\tau_{1\text{-}2}$ linearly increases with the pyrocatechol concentration. This linear dependence can be very useful in future analytical determinations.

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