Data mining from oscillatory reactions perturbed by Usnic acid

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Abstract: The influence of Usnic acid was investigated in two iodate based oscillatory reactions: Bray Liebhafsky and Briggs-Raucher with the aim of possible application in determining the reactivity of this acid in complex reaction systems. Obtained results show that Usnic acid added in similar concentration has different influence on these two oscillatory systems.

Keywords: Bray Liebhafsky, Briggs-Raucher, oscillatory reaction, Usnic acid

1. Introduction

Since their discovery, oscillatory reactions have become intriguing kinetic systems for studying their complex mechanisms involving a large number of intermediate species. Additionally, the Bray-Liebhafsky (BL) [1] and the Briggs-Rauscher (BR) [2] oscillatory reaction have proven to be highly sensitive to the concentration of added analytes due to their nonlinearity resulting in various dynamic states. Specifically, if an analyte reacts with reactants or intermediate species of an oscillatory reaction, under given experimental conditions, there will be a change in the amplitude, number and frequency of oscillations, the total duration of the oscillatory regime, and may even lead to complete suppression of oscillatory behavior. This study aims to explore and compare how sensitive the BL and BR reactions are to the addition of Usnic acid, seeking to identify which system responds more significantly to this particular phenolic compound.

Usnic acid is a naturally occurring dibenzofuran derivative and belongs to the class of lipoid phenolic compounds. It is one of the most studied secondary metabolites of lichens. Usnic acid is primarily known for its antimicrobial, antifungal, anti-inflammatory, and antitumor properties.

2. Experimental

The Usnic acid used in this research was isolated from the lichen Cladonia foliacea (Huds.) Willd. collected from Balkan Mountains in Serbia. The lichen was macerated using an acetone solvent and filtered to obtain an acetone extract. The extract was separated using column chromatography and eluted gradient with n-hexane and ethyl acetate solvents. After that, the fraction containing Usnic acid was evaporated and recrystallized in ethanol–chloroform solvent system to give bright yellow needles that were characterized using a ^{1}H-NMR spectrometer. The purity of the isolated Usnic acid was determined by HPLC–UV and amounted to 98.9%.

Usnic acid was tested in two oscillatory reactions: the BL and BR reactions, both of which are based on iodates. All experiments were conducted in a closed reactor equipped with an efficient mixer (σ = 900 rpm). The temporal evolution of the system was monitored potentiometrically, utilizing a platinum (Pt) electrode as the measuring electrode and a silver/silver chloride (Ag/AgCl) electrode as the reference. All solutions were prepared using deionized water, except for the Usnic acid solution, which was prepared in ethanol.

The experimental conditions for testing the BL reaction were as follows: temperature (T) = 62.0 °C, initial concentration of potassium iodate ($[KIO_3]_0$) = 7.35×10^{-2} M, initial concentration of sulfuric acid ($[H_2SO_4]_0$) = 6.13×10^{-2} M, and initial concentration of hydrogen peroxide ($[H_2O_2]_0$) = 5.10×10^{-3} M. Different concentrations of Usnic acid were introduced to the BL reaction mixture 10 minutes after the addition of hydrogen peroxide, during the induction period.

The experimental conditions for testing the BR reaction were as follows: temperature (T) = 36.7 °C, concentration of malonic acid = 7.89×10^{-2} M, concentration of manganese(II) sulfate ($MnSO_4$) = 7.52×10^{-3} M, concentration of perchloric acid ($HClO_4$) = 3.0×10^{-2} M, concentration of potassium iodate (KIO_3) = 7.52×10^{-2} M, and concentration of hydrogen peroxide (H_2O_2) = 1.176 M. Different concentrations of Usnic acid were added to the BR reaction mixture three minutes prior to the addition of hydrogen peroxide, thereby initiating the BR reaction.

3. Results and dissection

Response of the BL and BR systems to the addition of different concentrations of Usnic acid is presented in Figure 1. Figures 1. (a1) and (b1) show BL and BR oscillograms without the addition of Usnic acid, respectively. When Usnic acid is added to the BL system in the pre-oscillatory period (a2, a3), there is an extension of the pre-oscillatory period, and therefore an extension of the length of the oscillogram. Also, there is

immediate increase of electrode potential at the moment when Usnic acid is added. However, the amplitude of the oscillations does not change significantly with the addition of Usnic acid to the BL reaction system, nor does the number of oscillations. Figures 1. (b2) and (b3) show BR oscillograms with the addition of different concentrations of Usnic acid added 3 minutes before the initiation of the BR reaction. Obtained experimental results show that Usnic acid has a weak effect on the BR reaction, which is reflected only in the change of the oscillation amplitudes. Also, we can notice that Usnic acid does not affect the characteristic periods of the BR reaction, such as the oscillatory period, the length of the oscillogram, and the number of oscillations. For the tested concentrations of Usnic acid, it can be concluded that Usnic acid has a greater influence on the BL reaction than on BR and that the BL reaction proved to be more sensitive to the presence of Usnic acid.

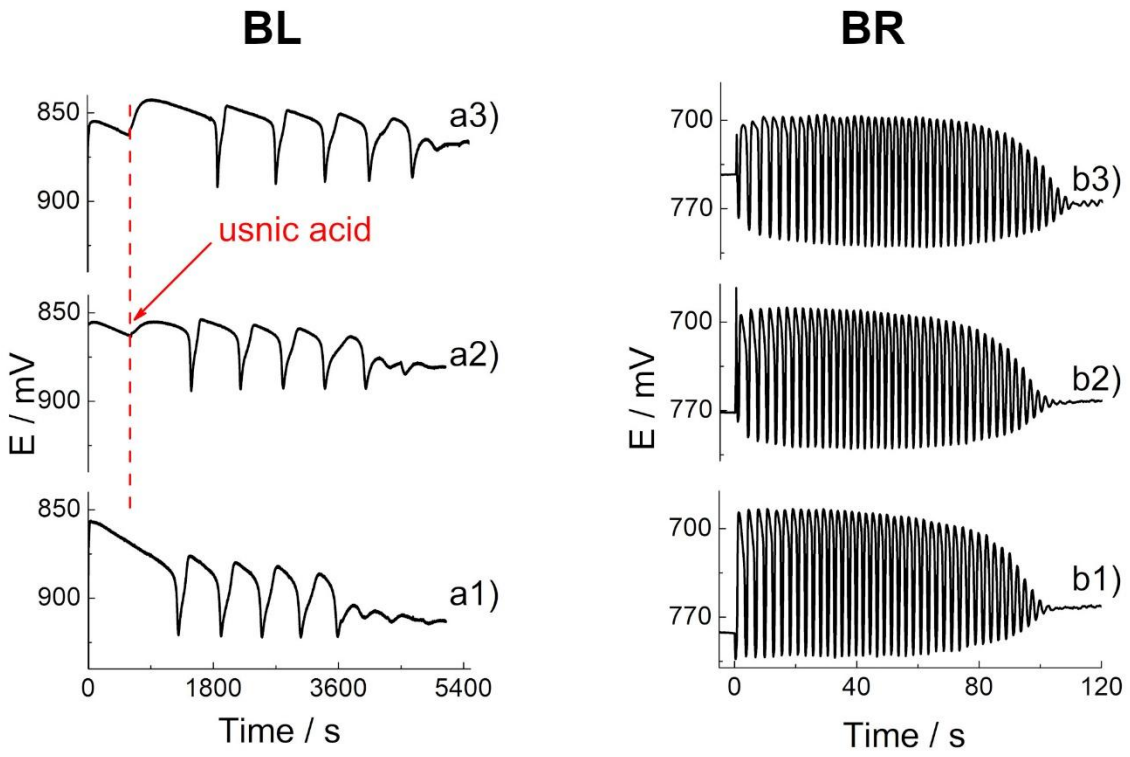

Figure 1. BL and BR oscillograms without the addition of analyte (a1 and b1) and with the addition of various concentrations of Usnic acid during the pre-oscillatory period in BL reaction (a2) 3.69×10^{-6} M and (a3) 7.38×10^{-6} M and 3 minutes before the addition of hydrogen peroxide in BR reaction (b2) 4.12×10^{-6} M and (b3) 1.23×10^{-5} M.

4. Conclusions

Effect of Usnic acid on two iodate-based oscillatory reactions, BL and BR, was monitored by the potentiometric method. Obtained results show that the addition of similar concentrations of Usnic acid has different influence on these two systems. The Usnic acid addition did not make a characteristic response of the BR system, but the addition

of usnic acid in BL prolonged the length of the pre-oscillatory period. For the tested Usnic acid concentrations, we can conclude that the BL reaction proved to be significantly more sensitive than the BR reaction.

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