



PHYSICAL CHEMISTRY 2018

14th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

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Volume I

September 24-28, 2018
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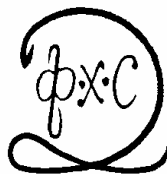
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and

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GALLIC ACID EFFECT ON THE BRIGGS-RAUSCHER REACTION DYNAMICS

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ABSTRACT

The effect of different concentration of gallic acid (GA) on the oscillatory behavior of the Briggs-Rauscher (BR) reaction is reported. In this work, the sample was injected before the start of oscillations. The main effect is the appearance of an induction time that increases with the concentration of GA added. Other parameters as a number of oscillations and oscillatory period are affected. These latter linearly depend on the concentration and can be used for quantitative GA analytical assay in a GA concentration range 3.00×10^{-5} M – 4.00×10^{-4} M. The perturbation is very different from that previously reported, in which samples of phenolics were added to an active BR mixture, indicating that the mechanism of perturbation largely depends on the injection point.

INTRODUCTION

It is well known that the Briggs-Rauscher (BR) system (Malonic acid, KIO_3 , H_2O_2 , Mn^{2+} , H^+) is a hybrid of two more famous oscillating reactions, the Bray-Liebhafsky (BL) and the Belousov-Zhabotinsky (BZ) reactions [1]. The BR oscillating reaction has been used as a test to measure the relative antioxidant activity of free-radicals scavengers, particularly phenolic compounds [2,3]. In this work, the effects of different concentration of gallic acid on the BR system were investigated. The gallic acid (3,4,5-Trihydroxybenzoic acid, GA) is a well-known antioxidant as well as a free radical scavenger. The GA is present in a variety of plants and fruits. Studies on gallic acid and its derivatives have reported their potential in the treatment of oxidative cell stress that accompany several diseases as diabetes, ischemic heart attack, ulcer and other ailments [4].

EXPERIMENTAL

The experiments were carried out in a closed well-stirred (with stirring rate, $\sigma = 900$ rpm) and thermostated (at $T = (37.0 \pm 0.2)$ °C) batch reactor. Initial concentrations of the reactants were: $[\text{C}_3\text{H}_4\text{O}_4]_0 = 0.0789$ M, $[\text{MnSO}_4]_0 = 0.0075$ M, $[\text{HClO}_4]_0 = 0.0300$ M, $[\text{KIO}_3]_0 = 0.0752$ M and $[\text{H}_2\text{O}_2]_0 = 1.2690$ M. A 100 μl aliquot of GA of different concentration was added, yielding an initial concentration of $[\text{GA}]_0 = 3.17 \times 10^{-5}$ M, 5.07×10^{-5} M, 6.34×10^{-5} M, 1.90×10^{-4} M, 3.17×10^{-4} M, 3.81×10^{-4} M, 4.00×10^{-4} M, 4.12×10^{-4} M, 4.44×10^{-4} M and 6.34×10^{-4} M ($\text{M} = \text{mol}/\text{dm}^3$). All chemicals were of analytical grade and used without further purification. Solutions of GA were prepared in methanol whereas all other reactants were dissolved in deionized water. The total volume of the reaction mixture in all experiments was 25 ml. The reactants were added to the reaction vessel in the following order: 7 ml $\text{C}_3\text{H}_4\text{O}_4$, 5 ml MnSO_4 , 5 ml HClO_4 , 5 ml KIO_3 , and when the temperature and potential were stabilized 100 μl of GA was added. Three minutes after addition of GA, 3 ml H_2O_2 was added to the reaction vessel. The instant of H_2O_2 addition was taken as the beginning time of the reaction. The time evolution of the BR reaction was followed potentiometrically. A PC-Multilab EH4 16-bit analog-to-digital converter electrochemistry analyzer was directly connected to the reactor through a Pt working electrode and a double junction Ag/AgCl reference electrode and used to record changes in the Pt-electrode potential.

RESULTS AND DISCUSSION

Traces of potential changes *vs* time are reported in Fig. 1. As can be seen GA concentration from 3.17×10^{-5} M to 6.34×10^{-4} M has a strong influence on the BR oscillatory reaction dynamics: for increasing GA concentration the induction period increases as well. Addition of GA also changes other important parameters of the oscillation train, such as the number and period of oscillations (Figures 1 and 2).

As can be seen from Fig. 2 (a), the induction period is a nonlinear function of GA concentration. On the contrary, in a range of GA concentration from 3.17×10^{-5} M to $4.00 \cdot 10^{-4}$ M, the period of oscillations (Fig. 2 (b)) and the number of oscillations (Fig. 2 (c)) show a clear linearity. Therefore, on the basis of this dependence, the BR reaction can be used for analytical purposes. The concentration of GA above 4.44×10^{-4} M totally quenched the oscillatory behavior (Fig. 1 (e)).

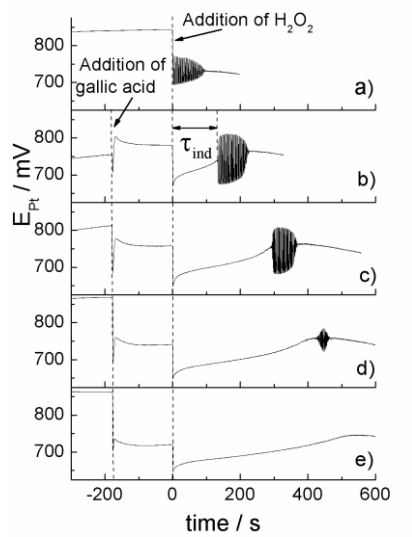


Figure 1. Recording of the Pt-electrode potential versus time for Briggs-Rauscher reaction mixture without GA (a) and with following initial concentrations $[GA]_0 = 5.07 \times 10^{-5}$ M (b), 1.90×10^{-5} M (c), 4.12×10^{-4} M (d), 6.34×10^{-4} M (e).

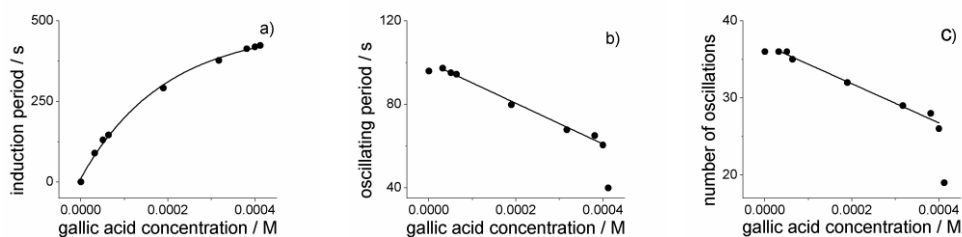


Figure 2. Induction period (a), oscillations period (b) and the number of oscillations (c) as a function of GA concentration.

Recently, we investigated caffeic acid (3,4-Dihydroxy-*trans*-cinnamic acid, CA) under the same experimental conditions [5]. The perturbation was similar to that reported here but the CA concentrations that give the same effects were one order of magnitude smaller than those of GA, at $[CA]_0 > 2 \times 10^{-5}$ M the oscillations were completely quenched. So, it seems that CA (two phenolic OH) is a better antioxidant than GA (three phenolic OH). However, Wright et al. [6] reached the conclusion that the number of phenolic OH groups is largely irrelevant and that it is the strategic placing of such groups that determines the antioxidant activity. They also proposed empirical additivity rules to evaluate the contribution of some groups in a different position to the bond dissociation enthalpy (ΔBDE) of a given OH. Following these rules, we found that the most active OH group for both compound is that in the *p*- position with respect to the acidic group with estimated ΔBDE of -13.9 kcal/mol and -11.6 kcal/mol, for CA and GA respectively. These

estimates are in agreement with the experimental results presented here, showing that CA is a better radical scavenger than GA.

In the previously implemented test [2], operating at 25 °C, the addition of antioxidant sample is made after the second or third oscillation. The effect was an immediate quenching of oscillations that resumed after a period called inhibition time. Inhibition time linearly depended on the concentration of the antioxidant added and was used to evaluate the antioxidant activity. The same authors also studied, besides the subtraction of HOO• radicals, the possible parallel reaction of phenolics with reagents and intermediates. They concluded that the main action of the phenolic compounds during inhibition time is quenching of the radicals [3]. The point of addition clearly affects the dynamics of the perturbed BR reaction by phenols. A study of the differences, from the experimental and mechanistic point of view will be the object of further investigation.

CONCLUSION

Addition of GA before starting the oscillatory evolution in the Briggs-Rauscher oscillating system leads to an induction period that increases with the concentration of GA. Interestingly, this perturbation is very different from that previously studied adding phenolics to an active BR oscillation system. This difference provides the opportunity to deeply investigate the mechanism of a system governed by non-linear dynamics.

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