Solvent Variations of the Briggs-Rauscher Reaction

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Abstract: The Briggs-Rauscher (BR) oscillatory reaction is one of the more interesting and colorful oscillatory reactions. It has surpassed the demonstration realm, as it has found use as a method to assess antioxidant capacity. However, this application as an antioxidant assay is limited to water-soluble samples. In the constant search for different, novel applications, we report the effects of various sample solvents on the behavior of the BR reaction. Our investigation looked at how changes in the solvent used to dissolve samples altered the time intervals of BR reaction's oscillations. The solvents used were ethanol, isopropanol, 1-propanol, acetone, and acetonitrile. Addition of ethanol had no effect on the BR oscillations. Isopropanol, 1-propanol, and acetone shorten the oscillation time. A test using acetonitrile discarded solvent polarity effects. Our results suggest that solvents that accelerate the enol pathway rate affect the oscillations of the BR reaction. Finally, samples can be safely dissolved in ethanol and used in the BR reaction.

Keywords: *oscillatory reaction, Briggs-Rauscher reaction, solvent variation, and enol pathway.*

Introduction

The Briggs-Rauscher (BR) reaction is an oscillating reaction that changes between two cycles back and forth until it reaches equilibrium. The two cycles the reaction oscillates between correspond to a radical state and a non-radical state. The main reaction is:

$$IO_3^- + 2\ H_2O_2 + CH_2(CO_2H)_2 + H^+ \rightarrow ICH(CO_2H)_2 + 2\ O_2 + 3\ H_2O \quad \text{(Eq 1)}$$

This main reaction can be broken down into two component reactions. The first component reaction;

$$IO_3^- + 2\ H_2O_2 + H^+ \rightarrow HOI + 2\ O_2 + 2\ H_2O \quad \text{(Eq 2)}$$

can occur via a radical or a non-radical process. When $[I^-]$ is low, the radical process dominates; when $[I^-]$ is high, the non-radical process dominates. The BR reaction is mostly used as demonstration.[1] Recently, Cervellati reported its use as a method to assess antioxidant capacity.[2] Application as an antioxidant assay is limited to water-soluble samples. In this short communication we report the effects of various sample solvents on the behavior of the BR reaction. Our results describe how changes in the solvent used to dissolve samples altered the time intervals of BR reaction's oscillations.

Methods and Results

A typical preparation of the Briggs Rauscher reaction was utilized.[3] When all stock solutions were prepared the solvents were tested as follows. Take 5mL of the sodium iodate solution, 5mL of starch solution, and 10mL hydrogen peroxide. Once a stir bar has been placed in a 100mL beaker, start to mix the sodium iodate solution and starch solution in the beaker over a stirring plate. Then add the peroxide; the solution turns amber yellow then dark blue. Start the timer when the first dark blue color appears until the next dark blue appears. This is the oscillation time (usually 13-18 seconds). This is also the control time for each trial. Repeat the step above and when the second deep blue color appears, add 1mL of solvent solution. Measuring the time from the second blue to the third blue appearance determines any solvent effects.

The solvents investigated were water, ethanol, 1-propanol, isopropanol, acetone, and acetonitrile. Addition of water and ethanol had no effect on the oscillation time (Figure 1, left). Acetone, 1-propanol, and isopropanol shortened the oscillation time (Figure 1, right). Acetonitrile had no effect on the BR oscillation time.

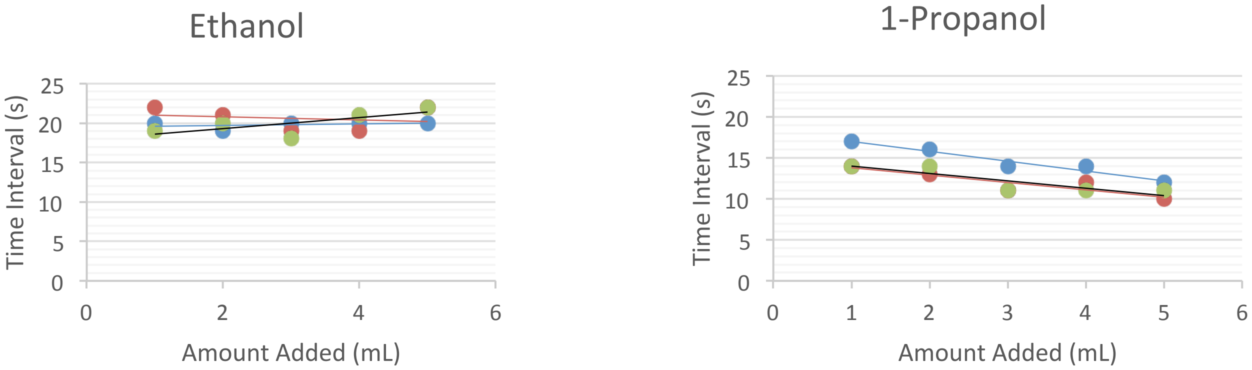

Fig. 1: (Left) Effect of ethanol on the oscillation time of the BR reaction. (Right) Effect of 1-propanol on the oscillation time of the BR reaction.

Results can be understood analyzing the second component reaction:

$$HOI + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H_2O \qquad \text{(Eq 3)}$$

The dramatic change from amber to dark blue occurs as the iodide ion slowly is being produced and is less than the HOI, and the excess HOI reacted with hydrogen peroxide allows for a conversion to the iodide ion, creating the dark blue change. This is where the enol reaction mechanism takes place.

$$I^- + HOI + H^+ \rightarrow I_2 + H_2O \qquad \text{(Eq 4)}$$

$$I_2 + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + I^- + H^+ \qquad \text{(Eq 5)}$$

Leopold *et al*. suggested an intramolecular mechanism, featuring a six-member cyclic transition state, is postulated to account for the results on the enolization of malonic acid (Eq 5).[4] We hypothesize that sample solvents that disrupt the postulated mechanism will affect the BR oscillations. In the case of 1-propanol and isopropanol, longer and branched alcohols disrupt the proposed mechanism. Two suggested disruption pathways: De-stabilization of proposed six-member ring, and alcohol reaction with iodide. Acetone can readily undergo enol reaction mechanism pathway, which has the effect of adding more malonic acid. Finally, polarity can be discarded as a factor since acetonitrile did not disrupt the BR oscillations.

Conclusions

Addition of ethanol had no effect on the BR oscillations. Acetone, isopropanol, and 1-propanol shorten the oscillation time. A test using acetonitrile discarded solvent polarity effects. Our results suggest that solvents that disrupt the enol pathway affect the oscillations of the BR reaction. Finally, samples can be safely dissolved in ethanol and used in the BR reaction.

Conflicts of Interest

The authors declare no conflict of interest.

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