Application Note

Academia

Kinetics of an Oscillating Reaction using Temperature-Controlled UV-Vis Spectroscopy

Characterizing the Briggs-Rauscher reaction at four temperatures simultaneously using an Agilent Cary 3500 UV-Vis

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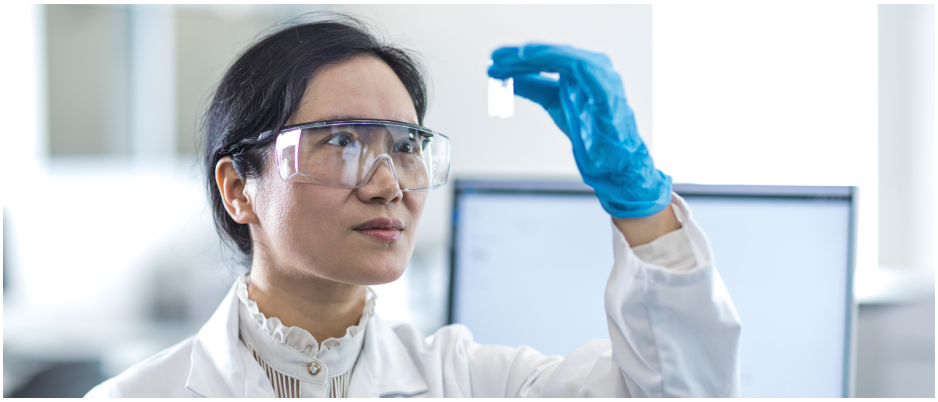

Abstract

The Briggs-Rauscher reaction involves colored intermediates, with kinetics influenced by temperature. Tracking these color changes is achievable using temperature-controlled UV-Vis spectroscopy. However, the experiment requires efficient temperature control, cuvette stirring, and rapid acquisition speed due to the millisecond timescale of the color changes.

In this work, an Agilent Cary 3500 UV-Vis spectrophotometer was used to investigate this reaction at four different temperatures simultaneously. The system's fast data collection and accurate temperature control enabled efficient characterization of complex reaction kinetics.

Introduction

The Briggs-Rauscher reaction is one of the most captivating demonstrations that a chemist can perform.[1] It is an oscillating reaction that cycles through multiple color changes for several minutes, providing a visual example of how chemicals transform in real time (see Figure 1). The reaction involves several chemicals, as described in the sample preparation section of the note. When the reagents are mixed, the clear and translucent solution gradually turns amber before undergoing a striking color change to dark blue. The blue color then gradually fades back to the colorless state. This cycle continues for several minutes until all reagents are consumed.

Briggs-Rauscher reaction

The overall Briggs-Rauscher reaction is described by Equation 1. The reaction is catalyzed by manganese (Mn) and generates oxygen gas (O_2). Some O_2 bubbles can be seen in the pictures presented in Figure 1. However, numerous intermediate reactions take place during the overall oscillation process. To better understand the process, researchers have identified and published many detailed descriptions of the reaction mechanisms.[2]

$$IO_3^- + 2H_2O_2 + CH_2(CO_2H)_2 + H^+ \xrightarrow{Mn^{II}} ICH(CO_2H)_2 + 2O_2 + 3H_2O$$

Equation 1.

There are a few key steps in the Briggs-Rauscher reaction that can be summarized by Equations 2 and 3.

$$IO_3^- + 2H_2O_2 \xrightarrow{H_2SO_4} HIO + 2O_2 + 2H_2O$$

Equation 2.

$$2HIO + 2H_2O_2 \rightarrow 2I^- + 2O_2 + 2H^+ + 2H_2O$$

Equation 3.

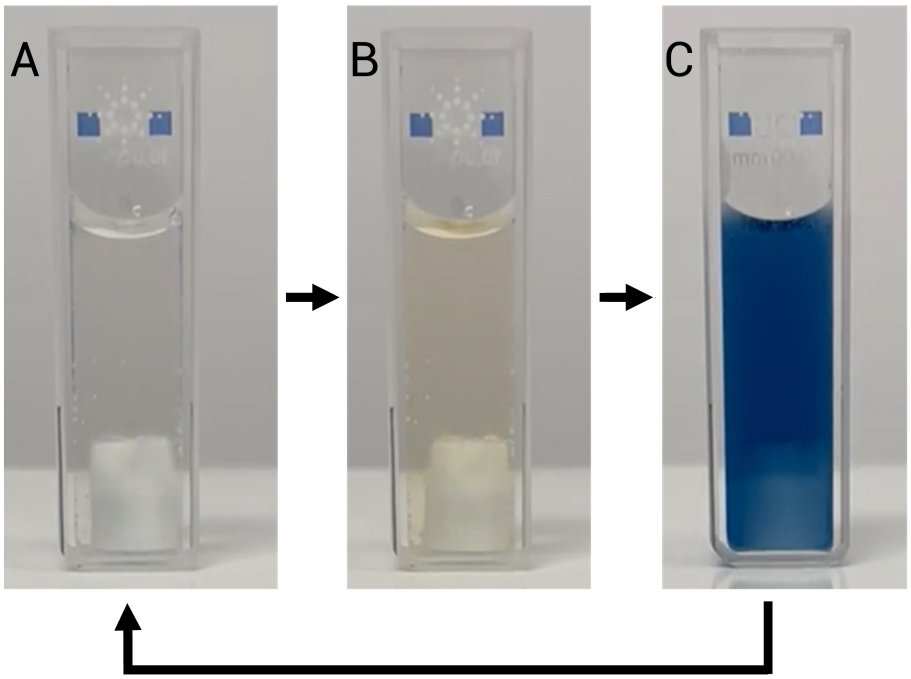

Figure 1. Color changes in the Briggs-Rauscher reaction. (A) Upon the addition of the reactants, the solution is initially clear and translucent. (B) The solution gradually turns to amber, and then dark blue (C), before the color fades to clear (A). These oscillations continue for several minutes before stabilizing.

The intermediate reaction presented in Equation 2 can proceed through two different pathways: a radical and a non-radical process. Both processes proceed at very different speeds, involve different intermediate reactions, and are ultimately responsible for the clocking mechanism of the Briggs-Rauscher reaction.[3,4]

The radical pathway is fast, in that it produces much more HIO than can be consumed by the reaction described in Equation 3. The excess HIO that is produced by the fast radical process eventually leads to the formation of I_2, giving the amber color to the solution, and I_3^-, as shown in Equations 4 and 5. The interaction of the I_3^- with starch, which acts as an indicator in this reaction, leads to the characteristic dark blue color of the solution.

$$I^- + HIO + H^+ \rightleftharpoons I_2 + H_2O \text{ (Amber)}$$

Equation 4.

$$I^- + I_2 \rightleftharpoons I_3^- \xrightleftharpoons{\text{Starch}} \text{Blue complex}$$

Equation 5.

The I^- buildup generated by the radical process allows the slow, non-radical process to start and eventually dominate. The non-radical pathway slowly produces HIO, which is readily consumed by malonic acid, as represented by Equation 6.

$$HIO + CH_2(CO_2H)_2 \xrightarrow{H_2SO_4} ICH(CO_2H)_2 + H_2O$$

Equation 6.

This reaction depletes the solution of all available HIO, which quenches the radical process that needs it to proceed. The reduction of HIO also stops the production of I^-, causing the non-radical process to eventually cease. The excess I_2 in solution then reacts with malonic acid, causing the color to fade, while the radical process resumes, leading to the oscillation.

The Briggs-Rauscher reaction involves colored intermediates, and the kinetics of the intermediate reactions follow thermodynamic fundamentals,

therefore the reactions will be impacted by temperature.[5] Therefore, tracking the rate at which these color changes occur should be achievable by temperature-controlled UV-Vis spectroscopy. However, carrying out this experiment poses a challenge for a UV-Vis instrument. Efficient temperature control and cuvette stirring are required. Also, acquisition speed is important, as the color changes typically occur within a few milliseconds. Lastly, the characteristic dark blue color of the starch-iodide complex likely absorbs visible light.

In this application note, the Agilent Cary 3500 UV-Vis system fitted with the Agilent Multicell Peltier sampling module was used to investigate the well-known Briggs-Rauscher oscillating reaction. The reaction was carried out at four different temperatures, at the same time, using the unique multizone feature of the Multicell that can accommodate up to eight cuvettes. The instrument uses a xenon (Xe) flash lamp with an acquisition speed of 4 ms per reading. This capability allows for the collection of 250 data points per second, enabling comprehensive studies of rapid chemical reaction kinetics.

This multizone functionality allows the temperature of four sample and reference pairs of cuvettes to be set independently from one another during the simultaneous data acquisition of the solutions in the eight cuvettes.

The kinetic parameters obtained at each temperature were used to build an Arrhenius plot (logarithm of a reaction rate constant plotted against the reciprocal of the temperature). The results show how the Cary 3500 UV-Vis Multizone can conduct multiple experiments in parallel, enabling the efficient and effective characterization of reaction kinetics of complex systems.

Experimental

Sample preparation

Three solutions, referred to as Solution A, Solution B, and Solution C, were used to generate the Briggs-Rauscher reaction.[4] Each solution was prepared at a total volume of 250 mL.

- Solution A was prepared by dissolving 10.75 g of potassium iodate (KIO_3) in high purity de-ionized (DI) water, adding 1.125 mL of sulfuric acid (H_2SO_4), and making up to 250 mL using DI water. To ensure that all solid reactants were dissolved, Solution A was placed in an ultrasonic bath for 10 minutes.
- Solution B was prepared by combining 3.9 g of malonic acid ($CH_2(CO_2H)_2$) and 0.85 g of manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) in approximately 100 mL DI water. About 1 g of soluble starch was dissolved in approximately 100 mL boiling water, cooled down to room temperature, and filtered. Both solutions (malonic acid and starch) were combined and made up to 250 mL using DI water.
- Solution C was prepared by combining 100 mL of 30% hydrogen peroxide (H_2O_2) with 150 mL of DI water.

The Briggs-Rauscher reaction was initiated by combining equal volumes (0.75 mL in this study) of solutions A, B, and C.

Instrumentation

The Cary 3500 UV-Vis spectrophotometer is a fully interchangeable modular system that comprises a common UV-Vis engine and interchangeable sampling modules. The instrument uses a xenon (Xe) flash lamp that pulses at 250 Hz as a source and a double, out-of-plane Littrow monochromator (Xe flash lamp is covered by a 10-year warranty).

The spectral bandwidth (SBW) of the monochromator can be varied from 0.1 to 4.0 nm. Optic fiber technology is used to deliver the source signal directly to all cuvettes simultaneously.

For this study, the Cary 3500 UV-Vis was equipped with a Multicell Peltier sampling module that can accommodate eight cuvettes (Figure 2). Each sample was equipped with its own UV-Vis detector, stirrer, and temperature probe. Also, as the source was brought to each cell using optic fiber technology, the signal reached each cuvette simultaneously. The Multicell Peltier sampling module uses an air-cooled Peltier temperature control system that can attain and hold a set temperature between 0 and 110 °C. The system is also capable of temperature ramping at rates ranging from 0.1 to 40 °C/min. Using the multizone feature of the Multicell Peltier, the temperature in each zone can be set independently and monitored with a temperature probe.

In this experiment, the temperatures of zones 1, 2, 3, and 4 were set to 5.0, 10.0, 20.0, and 30.0 °C, respectively. Four pairs of optically matched 10 mm quartz cuvettes, one per zone, avoided the need for zeroing/baselining before starting the measurements. All four sample cells were fitted with a temperature probe to closely monitor, measure, and control the temperature of each zone based on the actual temperature reading of the sample cuvette. All eight cuvettes were fitted with a star-shaped stir bar.

The Multicell Peltier sampling module for the Cary 3500 UV-Vis is equipped with a purge line to prevent condensation on the cuvette outer walls while carrying out experiments at temperatures below the dewpoint of the room temperature. Since some experiments are likely to occur under this threshold temperature, nitrogen (N_2) was used as a purge gas at a flow rate of 10 L/min.

UV-Vis spectra of each of Solutions A, B, and C, and the mixture of Solutions A and B were collected at different temperatures to assess any potential chromophores contained in these solutions (results not shown). Water was used as a reference for these tests. Only H_2O_2 made a significant contribution in the spectral range of interest (290.0 to 950.0 nm). Since the addition of H_2O_2 readily initiates the Briggs-Rauscher reaction, a mixture of solution A and B was chosen as a reference for all subsequent UV-Vis measurements.

For each kinetic experiment, 0.75 mL of Solution A and 0.75 mL of Solution B were added to the sample cuvette. Once the temperature set point had been reached, the solutions were stirred for five minutes to ensure thermal equilibrium within the cuvette.

To establish a baseline measurement, data collection was started before adding Solution C. Once 0.75 mL of Solution C had been pipetted into each sample, cuvette data were collected in the different temperature zones in turn. First, data were collected after 10 s from the 5.0 °C temperature zone, finishing with the 30.0 °C temperature zone at 30 s from the start of data collection.

Scanning kinetic measurements were carried out over a large wavelength range (290.0 to 950.0 nm) to identify the characteristic chromophores associated with each step (amber, blue) of the oscillation. Instrument acquisition parameters are listed in Table 1.

The reaction kinetics at different temperatures were performed using the acquisition parameters listed in Table 2. All measurements were carried out in triplicate.

Figure 2. The Agilent Cary 3500 UV-Vis spectrophotometer with Multicell Peltier sampling module can be used for up to four temperature experiments across eight cuvette positions simultaneously.

Table 1. Agilent Cary 3500 UV-Vis acquisition parameters for the scan kinetics experiment.

Parameter	Setting
Wavelength Range	290.0 to 950.0 nm
Data Interval	4.00 nm
Spectral Bandwidth	4.0 nm
Signal Averaging Time	0.004 s
Stir Speed	800.0 rpm
Temperature	5.0 °C
Time	20.0 min
Scan Rate	60,000 nm/min

Table 2. Agilent Cary 3500 UV-Vis acquisition parameters for the kinetic experiments at different temperatures.

Parameter	Setting			
Zone	Zone 1	Zone 2	Zone 3	Zone 4
Temperature	5.0 °C	10.0 °C	20.0 °C	30.0 °C
Wavelength	610.0 nm			
Spectral Bandwidth	4.0 nm			
Signal Averaging Time	0.004 s			
Stir Speed	800.0 rpm			
Time	5.0 min			
Temperature Control	Probe			

Results and discussion

Scanning kinetics data

Scanning kinetics data were collected at low temperatures to capture spectral features for each colored reaction intermediate. The wavelength range included the visible spectral range (400 to 700 nm) since the color of the intermediates in the Briggs-Rauscher reaction can be seen by the human eye, as shown in Figure 1. The time resolution was set to a scan rate of 60,000 nm/min, generating a UV-Vis spectrum every 1.65 seconds. Selected spectra from the first oscillation measured at 5 °C are displayed in Figure 3.

A mix of Solution A and B was used as the reference (dark green trace). Compared to the reference, features associated with the addition of Solution C (H_2O_2) to Solutions A and B can readily be seen. The intense absorption measured at 300 nm is associated with the edge of the H_2O_2 absorption band in the UV range, as confirmed from the preliminary tests carried out on the individual components (see Experimental section). The absence of absorption bands in the 400 to 700 nm range for the spectra acquired up to 13.20 s suggests that the solution is colorless at this stage (Figure 1A).

In the scans (1 to 13 s), a peak centered at 460 nm slowly rises. Since this solution absorbs blue light radiation between 400 and 500 nm, this spectrum is likely associated with the amber (complementary color) state resulting from the I_2 buildup in the solution (Figure 1B). This conclusion was also drawn from a previous publication focusing on the Briggs-Rauscher reaction mechanism.[6]

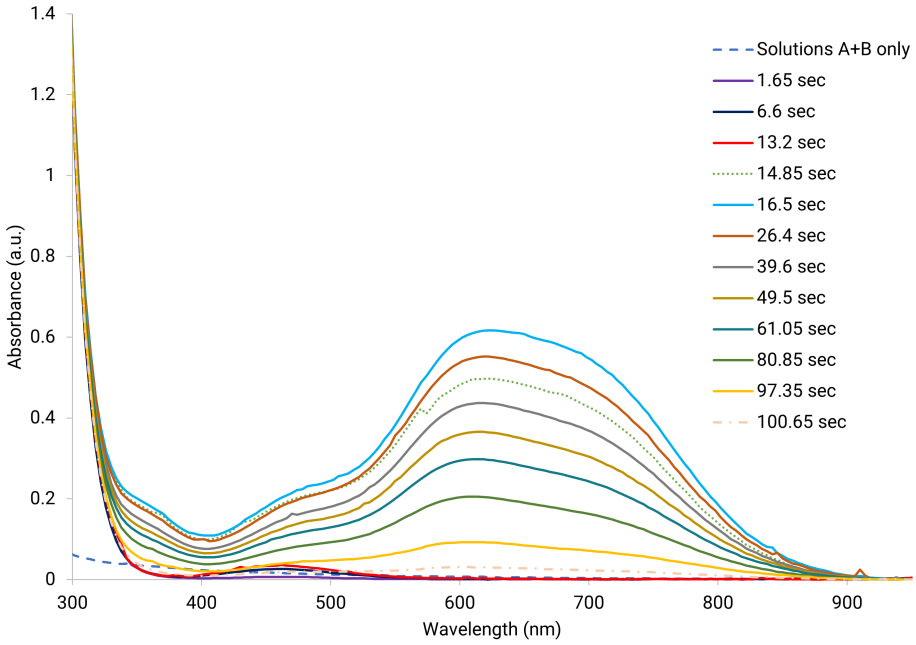

Figure 3. UV-Vis spectrum collected during the first oscillation of the Briggs-Rauscher reaction at 5.0 °C. All spectra were offset-corrected for visualization purposes.

The spectrum acquired a transient state, i.e., while the solution is turning from amber to dark blue. A broad and intense absorbance band, peaking at 610 nm, is clearly evident.

This band is likely associated with the starch-I_3 complex (Figure 1C). Few intermediate spectra could be collected during that transition, suggesting that the color transition takes place at a much faster rate than the scan kinetic time resolution of 1.65 s/scan. Unresolved peaks around 350 and 375 nm can be seen on all subsequent spectra associated with the dark blue iodide-starch complex. Previous work suggests that these chromophores are associated with the mono-iodomalonic acid intermediate ($ICH(CO_2H)_2$) in Equation 1.

The maximum absorbance is readily reached around the 16 s mark, before it slowly decreases over time until a near-colorless solution with no spectral features is obtained again.

From these results, the 610 nm wavelength was selected for further investigation of the impact of temperature on the color switches off the Briggs-Rauscher reaction. The selection was based on sensitivity (most intense) and selectivity (little to no overlap) criteria.

Experiments carried out at different temperatures showed that the maximum absorbance value of 610 nm was constant over the 5 to 30 °C range (data not shown).

Kinetic experiments at different temperatures

Data for all four reactions of the sample/reference pairs that were conducted at different temperatures (5, 10, 20, and 30 °C) were acquired simultaneously. The first two minutes of each kinetic curve, recorded at 610 nm, are shown in Figure 4. This kind of experiment is only possible because each Xe flash lamp UV-Vis source of the Cary 3500 UV-Vis system reaches all eight cuvettes simultaneously using fiber optics and collects up to 250 data points per second.

The oscillation kinetic curves recorded at the different temperatures all shared a similar pattern as highlighted in Figure 4A. A few seconds after the addition of Solution C, the absorbance at 610 nm rapidly rises from almost 0 to 1.5 absorbance units (a.u.). This transition occurs over a time lapse of approximately 1.4 s for the experiment carried out at 5.0 °C and as fast as approximately 0.65 s for the experiment carried out at 30.0 °C (Figure 4D).

The speed of the dark blue color transition is significantly faster than the time-resolution of the scan kinetic experiments previously discussed in Figure 3. The fast-transition time likely explains why few intermediate UV-Vis spectra, spanning over a few hundreds of nanometers, could be collected during the sharp color transition. The speed of color transition also emphasizes the need for instrumentation with a high temporal resolution (precise time measurements) to effectively study and understand the dynamics of the reaction.

The absorbance then slowly decreases (early decay), in a near-linear fashion, for a few seconds. Past a certain point, the slope becomes steeper (late decay) suggesting that the kinetic is entering a different regime. Figure 4 shows that the slope associated with the early and late decay becomes steeper as the temperature increases. It is not possible to assign a specific intermediate reaction to the amplitude of the absorption band at 610 nm, but it could be speculated from prior knowledge that the early decay corresponds to the non-radical process, while the late decay corresponds to the collapse of the starch-iodide complex.[7]

As the reaction proceeds, O_2 is rapidly produced (see Equation 1), leading to abundant bubble formation. When a bubble passes in front of the light source, a sharp absorption spike occurs with 0.004 s signal averaging time, as shown in Figures 4B, 4C, and 4D.

Increasing the signal averaging time to 0.1, 0.5, or 1 s diminishes the occurrence of O_2 bubble spikes in the spectra and enhances the signal-to-noise ratio (S/N), as illustrated in Figure 5.

Bubble formation emphasizes the need for efficient stirring throughout the measurements to clear gas bubbles from the optical path.

The periodic nature of the Briggs-Rauscher reaction can readily be seen in Figure 4. The oscillation period was defined as the time between two subsequent color transitions, as shown in Figure 4C. The oscillation period for each temperature was measured, and the results are shown in Table 3. The results show that the first oscillation period for each temperature was longer than the subsequent ones. Although this difference could be partly attributed to the temperature equilibration following the addition of Solution C, previous work on the subject has also reported similar observations.[6,8]

Following the second oscillation, the periodicity of the reaction stabilizes for a few minutes until the oscillation period time starts to increase at a slow rate. The mean oscillation period value

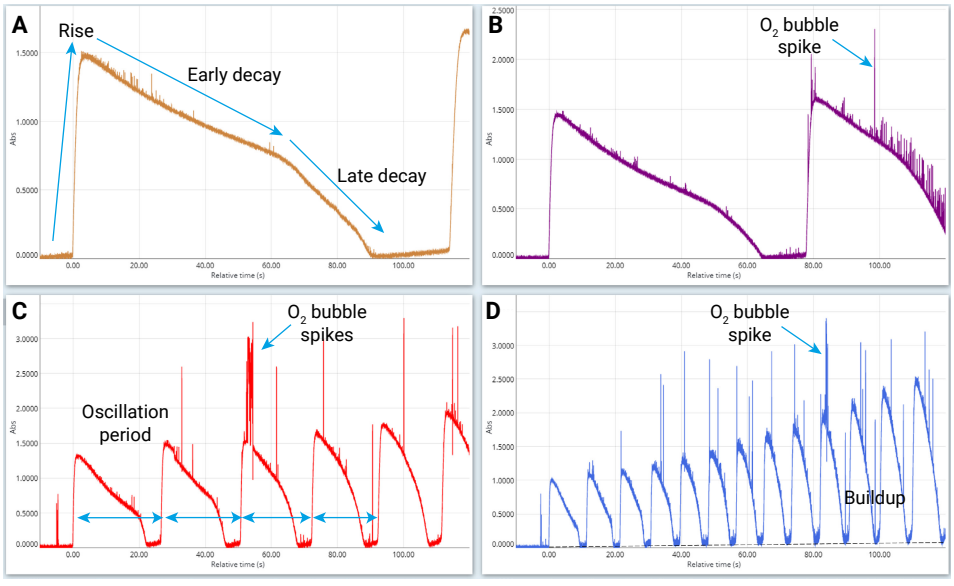

Figure 4. Kinetic curves acquired at 610 nm measured at 5 °C (A), 10 °C (B), 20 °C (C), and 30 °C (D) by the Agilent Cary 3500 UV-Vis. For easier comparison, all curves were offset relative to their first oscillation.

was calculated over the steady-state regime (oscillations 3 to 6). The reported oscillation period values in Table 3 correspond to the mean value from three replicate measurements carried out at each temperature. The associated uncertainty values correspond to the standard deviation within the measured values.

The maximum absorbance measured at 610 nm gradually increased as the oscillations occurred, as seen in Figure 4D. This oscillating process can proceed for an indeterminate amount of time depending on solution temperature, but it is known to usually last between 5 to 10 minutes. The reaction is terminated when the H_2O_2 reduces all malonic acid in solution.

The conclusion of the Briggs-Rauscher reaction is signaled when the clear-transition stage becomes less prominent (dark blue only transitioning to light blue) with each oscillation. Finally, the solution remains a deep blue color. This buildup (attenuation of the color contrast in between oscillations) is represented by the black dashed line in Figure 4D, where the absorbance reading remains above 0 a.u.

The impact of temperature (T) on the rate of a chemical reaction is often described by the Arrhenius equation (Equation 7). In the equation, the reaction rate constant (k) is a function of the activation energy (E_a), the perfect gas constant (R), and a pre-exponential factor (A).

$$k = A/e^{-E_a/RT}$$

Equation 7.

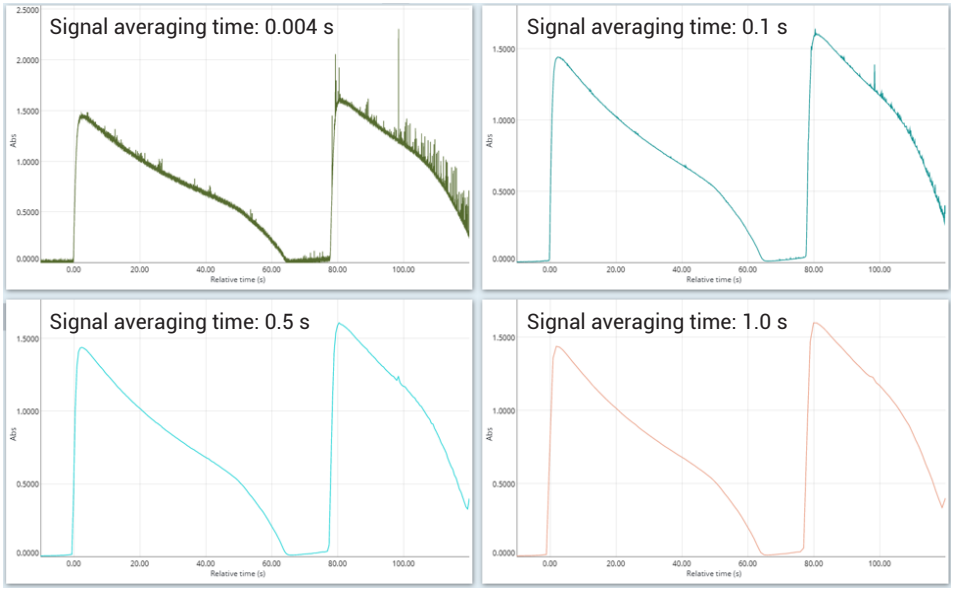

Figure 5. Effect of signal averaging time (0.004, 0.1, 0.5, and 1 s) on the occurrence of O_2 bubble spikes at 10.0 °C.

Table 3. Oscillation period of the Briggs-Rauscher reaction at different temperatures, n = 3.

Temperature (°C)	Oscillation Time Period (s)		
	First Oscillation	Second Oscillation	Oscillations 3 to 6
5.0	121 ± 10	83 ± 3	69 ± 3
10.0	68 ± 3	56 ± 11	47.6 ± 0.4
20.0	27 ± 1	24 ± 1	20 ± 1
30.0	11 ± 2	10 ± 1	8.8 ± 0.6*

* The oscillation period was found to be steady up to the 12th oscillation.

To evaluate if the current work followed basic thermodynamic concepts, an Arrhenius plot was generated using the oscillation frequency (k = 1/oscillation period) as the rate constant. The results are shown in Figure 6.

The oscillation period associated with the steady-state regime (oscillations 3 to 6), as reported in Table 3, was used to calculate k in the Arrhenius plot. The uncertainty bars in Figure 6 are the standard deviation values associated with the mean oscillation period for each temperature, expressed on a natural logarithmic scale.

Although the Briggs-Rauscher oscillating reaction contains over 20 intermediate reactions, the overall process has an Arrhenius-like behavior. The slope of the linear regression was used to calculate the E_a, which was found to be 58 kJ/mol for the overall reaction. This value is in good agreement with previous studies on this oscillating reaction.[8]

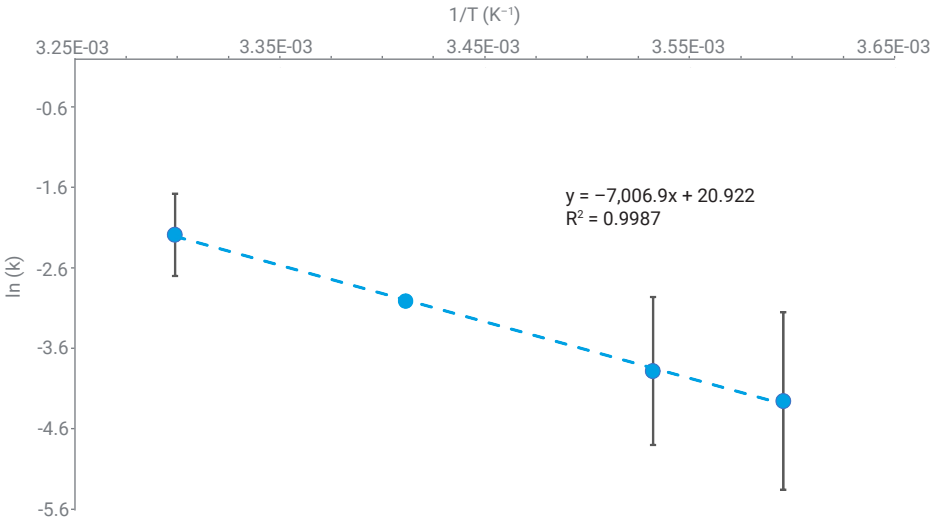

Figure 6. Arrhenius plot generated from the oscillation reaction carried out at different temperatures using the Agilent Cary 3500 UV-Vis spectrophotometer.

Conclusion

An in-depth investigation of the kinetics of the Briggs-Rauscher oscillation reaction was carried out at four different temperatures simultaneously using the Agilent Cary 3500 UV-Vis spectrophotometer with Multicell Peltier sampling module. The unique multizone feature of the Peltier temperature controlled Multicell facilitated the multizone experiments of four pairs of cuvettes. Each pair of cuvettes contained the reagents and reference solutions.

The scan kinetic experiments identified chromophores associated with different intermediates in the reaction, enabling the selection of the most suitable wavelength (610 nm) for single point kinetic measurements of the oscillating reaction. The kinetic measurement results at four temperatures (5, 10, 20, and 30 °C) showed that the oscillating cycle shortened with increasing temperature. To better understand the effect of each temperature on the Briggs-Rauscher oscillation, the data were used to build an Arrhenius plot. The plot was then used to calculate the activation energy, resulting in a calculated value of 58 kJ/mol for the overall reaction. The Cary 3500 UV-Vis spectrophotometer with Multicell Peltier sampling module saves time, while producing valuable data that contribute to a more comprehensive understanding of complex reactions.

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Further information

- Cary 3500 Multicell UV-Vis Spectrophotometer
- Cary 3500 Compact UV-Vis Spectrophotometer
- Cary UV Workstation software
- Data Integrity Options for GMP Facilities for the Agilent Cary 3500 UV-Vis Spectrophotometer Series
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