Chemical Oscillations and Waves in the Physical Chemistry Lab

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The study of oscillating chemical dynamics is an exciting, active area of research that has also been the subject of numerous articles in *this Journal* (*1–15*). Most often, these works have focused on the excellent demonstration value of oscillating reactions and chemical waves but not on actually using them as part of the teaching laboratory. Therefore, we prepared a three-experiment module based on the most widely studied oscillating system, the Belousov–Zhabotinskii (BZ) reaction.

The BZ reaction consists of the acidic bromate oxidation of an organic substrate, catalyzed by a transition metal ion. Oscillations in the $[M^{n+1}]/[M^n]$ ratio can be observed with a platinum electrode, and color changes are visible and can be enhanced using ferroin as an indicator or catalyst. Oscillations also occur in the concentration of bromide ion. Such temporal self-organization can be observed in both batch and flow reactors.

When oscillating reactions were first reported, many believed that the oscillations were an artifact of heterogeneous phenomena, such as bubble formation (*16*, *17*), or were due to the influence of dust particles (*18*). Some argued that such spontaneous temporal self-organization (periodic changes in concentration of reactants and products) violated the second law of thermodynamics (*1*, *19*, *20*). In a spontaneous process, Gibbs Free Energy monotonically (without any local maxima) decreases. Figure 1 shows permissible and invalid temporal evolutions of free energy.

Ilya Prigogine and coworkers realized that a system could organize (decrease its entropy) as long as the net entropy change in the universe was positive (*21–23*). Thus, the concentrations of the intermediates in a reaction can increase and decrease with time (this is not monotonic behavior) while the free energy monotonically decreases. In other words, the decrease in entropy caused by the periodic concentration changes is more than compensated by an entropy increase from other processes. In our body, the spontaneous formation of proteins occurs even though the ΔG of peptide bond formation is positive. Protein synthesis occurs because it is coupled to other reactions whose ΔG is negative, yielding a net decrease in free energy (*24*).

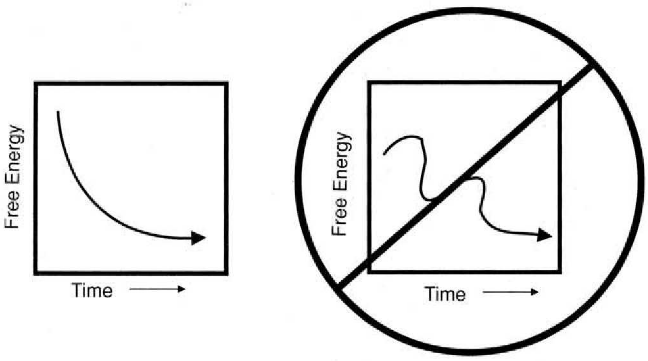

Figure 1. The allowed evolution of free energy in a closed system is shown. The free energy must decrease monotonically, and the reactants must continuously decrease while the products increase. However, the concentrations of the intermediates can oscillate as the system relaxes toward equilibrium.

Under certain conditions the BZ system is not oscillatory, but is instead excitable: It will remain in a quasi-steady state until perturbed. The perturbation will cause the system to undergo one oscillation before returning to its initial state. With such a mixture, it is possible to observe traveling waves of reaction as an autocatalytic reaction couples with diffusion. From an initial homogeneous system, target patterns of waves can arise. These appear strikingly similar to patterns observed in aggregating slime molds (*25*) and in the electrical waves in fibrillating hearts (*26*).

The Experiments

Students worked in three groups, each group doing one of the three labs each week. Devoting so much time to one system helped students become more familiar with the chemistry involved. Also, studying different aspects of such a complicated reaction was a good introduction to the reductive research approach. The students learned not only the phenomenology of self-organization but also basic kinetics.

The three experiments were designed for

- Studying the behavior of the homogeneous system
- Determining the kinetics of the bromination of malonic acid and methylmalonic acid
- Studying the behavior of the unstirred system, including the observation of traveling fronts, target patterns, and spiral waves, and determining the rate constant for an autocatalytic reaction

Oscillations in the Homogeneous Belousov–Zhabotinskii Reaction

The BZ reaction consists of an organic substrate (usually malonic acid), a catalyst, bromate ions, and an aqueous medium. The BZ reaction is driven by the acidic bromate oxidation of the substrate. A complicated mechanism has been proposed explaining the course of this reaction and how oscillation occurs (*27–29*). We do not provide a detailed explanation of the reaction mechanism but refer to excellent descriptions that have appeared in *this Journal* (*4*) and elsewhere (*30*).

Two major features are important concerning these experiments. The bromide ion plays the role of a control variable, switching the system between competing pathways. If a bromide selective electrode is available, the large variations in the Br^- concentrations can be measured.

The oxidation state of the catalyst (cerium) varies between +3 and +4. The most easily measured variable of this reaction is the platinum electrode potential that is a function of the Ce(IV)/Ce(III) concentrations. The change in the [Ce(IV)]/[Ce(III)] can be calculated from the recorded amplitude. Rearranging the Nernst equation, we obtain

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$$\Delta[\mathrm{Ce(IV)/Ce(III)}] = 10^{\Delta E/59\ \mathrm{mV}} \quad \text{at } 25\ ^\circ\mathrm{C} \qquad (1)$$

The goals of the experiment are

- to observe spontaneous temporal self-organization
- to observe and measure the induction period and determine how it is affected by the organic substrate used
- to understand the use of electrodes and the physical chemistry behind their operation
- to understand what a redox indicator is, and to determine if ferroin acts purely as an indicator or affects the reaction dynamics
- to determine the effect of Cl^- and oxygen

Experimental

The electrical potential of the reaction mixture is measured with a platinum electrode and a Hg/Hg_2SO_4 reference (Rainin). It is generally believed that a standard calomel reference electrode cannot be used due to the Cl^- contamination, but Rosenthal recently reported the successful use of one in a BZ reaction (*14*). We found no substantial difference in results if the calomel reference in a pH electrode was used. (The reference signal from the pH meter was used as the reference for the platinum electrode.) The output is recorded on a single-channel strip chart recorder, with the platinum electrode attached to the positive terminal, and the reference to the negative.

The recipe has been obtained from Shakhashiri (*30*). Prepare the following solutions in de-ionized water using volumetric glassware.

Solution A: 3.4 g $NaBrO_3$ dissolved in enough water to make a 100-mL solution.

$[NaBrO_3]$ = 0.23 M (solution A1)
50 mL of solution A1 diluted to 100 mL (solution A2)
50 mL of solution A2 diluted to 100 mL (solution A3)

Solution B: 3.2 g of malonic acid and 0.70 g of KBr dissolved in enough water to make a 100-mL solution; [MA] = 0.31 M; [KBr] = 0.059 M.

Solution C: 0.14 g cerium(IV) ammonium nitrate dissolved in enough 2.7 M sulfuric acid to prepare 100 mL; $[Ce(NH_4)_2(NO_3)_6]$ = 0.019 M.

Solution D: 3.6 g of methylmalonic acid (Aldrich) instead of malonic acid in solution B and 0.70 KBr in 100 mL of water.

Procedure

Now add 15 mL each of solutions A1 and B to a 100-mL beaker equipped with a stir bar. A brown color will appear due to the production of bromine, which disappears as it reacts with the malonic acid. When the solution clears, add 15 mL of solution C. Then position the electrodes immediately so that the induction period may be accurately observed and measured. Stir at a low rate to prevent the inhibition of the oscillations.

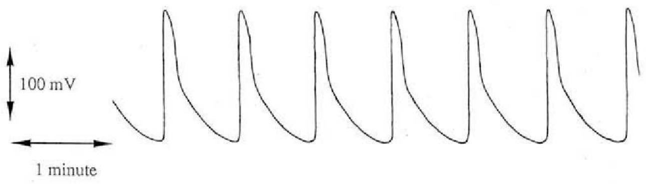

Figure 2. A typical strip chart recorder trace showing the platinum electrode potential as a function of time in a homogeneous Belousov–Zhabotinskii reaction with malonic acid as the substrate. $[KBr]_0 = 1.97 \times 10^{-2}$ M; $[\text{malonic acid}]_0 = 0.10$ M; $[Ce(NH_4)_2(NO_3)_6]_0 = 6.33 \times 10^{-3}$ M; $[NaBrO_3]_0 = 7.67 \times 10^{-2}$ M

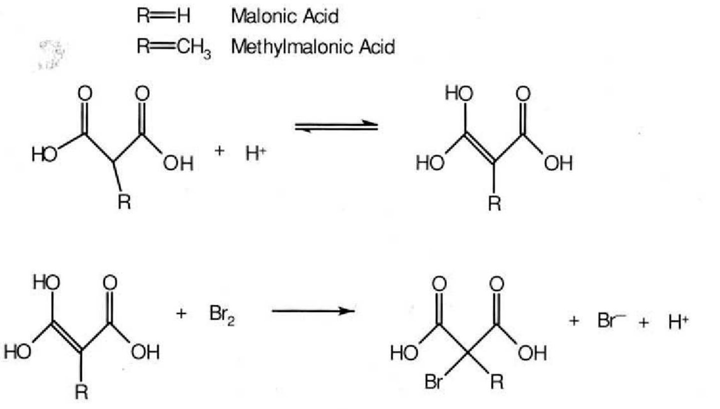

Figure 3. The bromination of malonic (methylmalonic) acid occurs via the enol form.

The recorder may be set at any desired speed (typically about 1 cm/min). The voltage scale is usually set at 250 or 500 mV. Note the time the oscillations commence, the induction period. Also record the period of the oscillations and the amplitude (number of millivolts during one oscillation).

Questions

Students are asked to consider these questions and carry out the following procedures.

(1) After several periods of oscillations, add 2 mL of a 25 mM ferroin solution (Fisher). Ferroin (tris(1,10-phenanthroline)iron(II) sulfate) is a redox indicator. As the [Ce(IV)] increases, it can oxidize the iron in ferroin from iron(II) to iron(III). The iron(II) complex is red, and the iron(III) is blue. Consequently, the color changes as the potential changes. What effect does the ferroin have on the period and amplitude of the oscillations? Is it really acting just as an indicator?

(2) Test the effect of Cl^- by adding a small grain of NaCl. What happens? How long does it take the system to recover (if at all)? Add a pinch. What happens?

(3) Test the effects of oxygen on the system by turning the stirrer to a high speed. Turn it up full speed. Are the oscillations affected?

(4) Field, Körös, and Noyes (*29*) have proposed a mechanism in which radicals play important roles ($BrO_2^\bullet$, $MA^\bullet$). Add a drop of acrylonitrile to an oscillating reaction and explain the relevance of the white precipitate (*31*).

(5) Observe oscillations for a half-hour. Note changes in the period as a function of time. What is the relevance of this change to the second law of thermodynamics?

(6) Prepare a fresh reaction mixture using solution A2. Does it oscillate? If it does, what is the period? Try again with solution A3.

(7) Finally, set up an experiment with methylmalonic acid (solution D) and solution A1, and leave it running for several hours. If you know from other experimental data that the rate of enolization (Fig. 3) affects both the induction period and the period of oscillation, what can you conclude about the rate of methylmalonic acid enolization as compared to malonic acid?

Typical Results

The amplitudes of solutions A1, A2, and A3 were approximately the same. (See Figure 2 for a sample strip chart trace.) The periods of oscillation became increasingly longer with decreased bromate ion concentration. This is consistent with a mechanism in which BrO_3^- plays a role in rate-limiting steps (*4, 29*). However, the period did not change significantly during the 30–40 min spent on each run.

Upon addition of ferroin to the BZ system, we observed that it was not merely acting as a redox indicator. It was acting as an indicator by color changes (Fe(II) is red and Fe(III) is blue), but it also affected the reaction. Both the amplitude and the period were cut approximately in half. Because the Fe(II) (ferroin) is available to reduce the Ce(IV) back to Ce(III), the oscillations may occur faster. Ferroin itself can also catalyze the BZ reaction.

Sodium chloride was added to the reaction mixture to determine how it affects the BZ system. When a grain of salt was added, the amplitude and period were slightly decreased. They decreased further with additional Cl^- ions until the reaction was terminated. The added chloride ions are oxidized to chlorous acid ($HClO_2$), which can then reduce the Ce(IV) back to Ce(III), suppressing oscillations. Oscillations return when the chlorous acid is completely oxidized to ClO_3^- (*32*).

The effects of oxygen were observed by increasing the stirring rate until vortexing occurred, entraining oxygen into the system (*33, 34*). The oscillations cease because the oxygen molecules can react with malonyl radicals present in the reaction via an autocatalytic process that increases the radical concentration. The malonyl radicals react with bromomalonic acid, liberating Br^-. The net effect of oxygen is to increase the bromide concentration beyond the range allowable for oscillations (*35*). When the stirring rate was reduced, the oscillations resumed.

The presence of radicals in the solution was determined by addition of a water-soluble monomer: acrylonitrile. Upon addition of large amounts of acrylonitrile, our oscillations ceased completely, and a white precipitate (insoluble polymer) formed. Polymerization was initiated by the free radicals present in the BZ system.

Finally, a reaction mixture was prepared to determine the effect of the organic substrate; methylmalonic acid was substituted for malonic acid. The methyl group had a large effect, slowing down the periods of oscillation by a factor of 9 and increasing the induction period by a factor of 13. (See the explanation below.)

Determining the Mechanism of Malonic Acid Bromination

An important reaction in the BZ system is the bromination of malonic acid (Fig. 3). Malonic acid enolizes in acidic medium to form the enol (*36, 37*). An equilibrium is reached between these two species, and the acid form is favored. The enol form reacts with the bromine to give bromomalonic acid. In a two-step reaction, the rate of the overall process is controlled by the rate of the slowest step.

We can write differential equations for each step.

Enolization

$$\frac{d[MA]}{dt} = -k_{enol}[MA][H^+] \qquad (2)$$

This process is first-order with respect to the malonic acid concentration.

Bromination

$$\frac{d[Br_2]}{dt} = k_{Br}[enol][Br_2] \qquad (3)$$

The Rate-Determining Step

To simplify matters, the reaction was run under pseudo-first-order conditions using an excess of malonic acid with respect to the bromine. If we observe the concentration of bromine as a function of time, we would expect one of two possible scenarios.

The Bromination

If the reaction is controlled by the rate of bromination, as soon as the bromine reacts with the enol, more enol will form. Because there is an excess of the malonic acid, the concentration of the enol will remain at a constant level, determined by the equilibrium constant for the enolization, during the course of the experiment.

Thus, the rate law for the disappearance of the bromine will be

$$\frac{d[Br_2]}{dt} = -k'_{Br}[Br_2]$$

$$k'_{Br} = k_{Br}[enol] \qquad (4)$$

In this case an exponential decay of the bromine concentration will be observed.

The Enolization

If the enolization is the rate-determining step, then as the enol is formed, bromine will react with it. Because malonic acid is in excess, the rate of enol production will be constant. Therefore, the rate of bromine disappearance will be constant—a zeroth-order reaction.

$$\frac{d[Br_2]}{dt} = -k'_{enol}$$

$$k'_{enol} = k_{enol}[MA]_0[H^+] \qquad (5)$$

In this case a plot of the bromine concentration versus time will yield a straight line whose slope equals $k_{enol}[MA]_0[H^+]$.

If the rate-determining step is the enolization, then changing the structure of the acid should affect the rate. From the experiment on homogeneous oscillations, we know that the methylmalonic acid system behaves very differently from the malonic acid system.

The Transition State

The rate of a reaction is determined by the difference in free energy between the reactants and the transition state. The transition state for enolization requires that the alpha carbon change from sp^3 to sp^2, which means it has more electron density. The presence of a methyl group may change the energy of the transition state, thus affecting the reaction rate.

The goals of the experiment are

- to determine the rate-limiting step and the rate law describing it
- to observe the effect of a methyl group on this limiting step

Experimental

The following solutions are prepared in advance (*38*).

Solution A: 50 mL of 0.6 M $NaBrO_3$/0.6 M H_2SO_4

Solution B: 40 mL of 0.48 M malonic acid

Solution C: 10 mL of 0.48 M methylmalonic acid

Solution D: 0.97 M NaBr (1 g/10 mL)

The change in the concentration of bromine is measured colorimetrically using the HRM setup for the Apple II (*39*), although any spectrophotometer could be used.

Procedure

The malonic acid/sulfuric acid/bromate solution is placed in the cuvette. A sodium bromide solution is added. The bromide ion is oxidized to bromine in situ. The absorbance as a function of time is recorded. Correlation to the $[Br_2]$ is obtained from a calibration curve of absorbance versus known [Br_2]. Alternately, the initial absorbance reading in each run can be used to provide a conversion between absorbance and [Br_2] by calculating the initial bromine concentration from the balanced reaction for the oxidation of Br^-.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (6)$$

To determine a calibration curve for [Br_2] versus absorbance, take 5.0 mL of solution D, and dilute to 10 mL (solution D1). Repeat the dilution with solution D1 (solution D2), and again with solution D2 (solution D3), giving four solutions of bromide.

Place 5 mL of solution A in a Spectronics 20 cuvette into which a micro stir bar has been placed. Add 1 mL of a bromide solution D. Stopper. Record the absorbance. Repeat with fresh bromate and each of the remaining bromide solutions. Calculate the concentration of bromine in each case from the reaction for the oxidation of bromide, and prepare a calibration curve. Set up the computer to run for approximately 5 min.

Questions

Students are asked to carry out the following procedures and consider the following questions.

(1.) Place 4 mL of solution A (bromate) into the cuvette. Place 4 mL of solution B (malonic acid) into the same cuvette. Place the cuvette into the spectrophotometer (the foam block with the HRM setup), and add 0.8 mL of solution D (bromide). Stopper quickly and begin recording data.
(2.) Repeat with 1.6 mL of solution D.
(3.) Repeat with 3.2 mL of solution B, 0.8 mL of water (to keep the concentrations of other species constant), and 0.8 mL of solution D.
(4.) Repeat with 2.4 mL of solution B, 1.6 mL of water, and 0.8 mL of solution D.
(5.) Calculate the concentration of each species and record.
(6.) Print out the absorbance versus time plot. Is it a straight line? If so, fit a line to it, and record the formula for the line. The slope is the important quantitative result. If it is exponential, take the natural logarithm of the absorbance data, and then fit a line.
(7.) Repeat step no. 1 using solution C, the methylmalonic acid. Again, determine the type of curve, and fit a line to the appropriately transformed data.
(8.) Determine the rate-limiting step of the reaction and the kinetics of that step.
(9.) Determine the value of k_{enol} by plotting k'_{enol} versus the initial concentration of malonic acid.

Typical Results

The data obtained clearly verified that the rate-determining step of the reaction was the enolization. The absorbance versus time plot was a straight line, so it was immediately apparent that a zeroth-order reaction was occurring (Fig. 4).

The slope of the calibration curve, $\Delta[Br_2]/\Delta A$, was multiplied by the slope of the slope of the absorbance versus time graph to provide k'. The rate constant of enolization k_{enol} was found using the following equation.

$$k_{enol} = k'/([MA][H^+])$$

Our average value for k_{enol} of malonic acid was $(1.25 \pm 0.18) \times 10^{-2}$ $(M \cdot s)^{-1}$. The rate constant of enolization for methylmalonic acid was found to be 3.8×10^{-3} $(M \cdot s)^{-1}$.

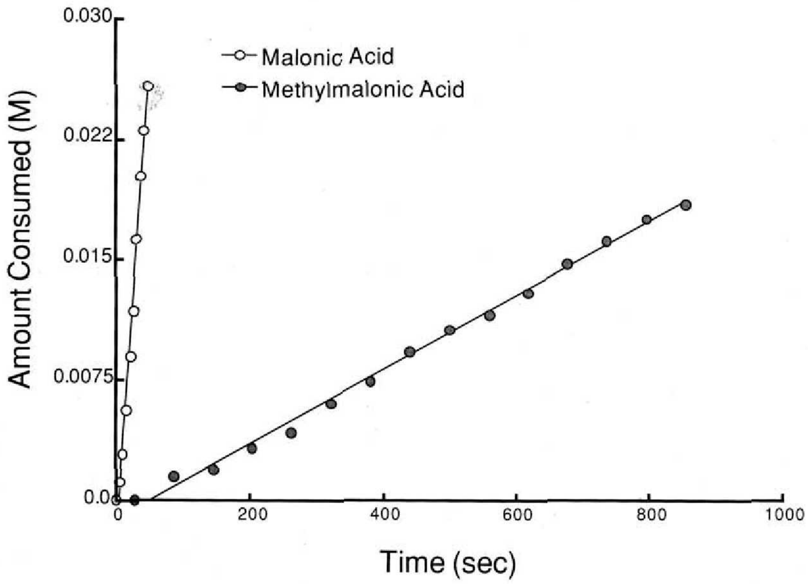

Figure 4. The amount of malonic (methylmalonic) acid consumed during enolization and bromination, as determined from the disappearance of bromine. The curves are straight lines, indicating that the rate-limiting step is the the enolization of malonic or methylmalonic acid. The methylmalonic acid enolizes about 18 times slower. Measurements were made using the HRM colorimeter experiment for the Apple IIE. $[NaBrO_3/H_2SO_4]_0 = 0.25$ M, [malonic acid]$_0$ = [methylmalonic acid]$_0$ = 0.20 M, $[NaBr]_0 = 0.162$ M

In sample 2, we kept the malonic acid concentration essentially constant and added excess NaBr to the mixture. An increase in concentration of bromine from 0.053 M to 0.097 M decreased the rate by about 15%. If bromination had been the rate-determining step, this addition of more bromine would have increased the reaction rate significantly. The slight decrease in rate is due to the slight decrease in [MA] (0.218M to 0.200M).

The methylmalonic acid solution demonstrated the effect of a methyl group on the enolization rate. Sample 5 contained an equal amount of methylmalonic acid in place of malonic acid. Changing the organic substrate produced a distinct decrease in the reaction rate from 8.4×10^4 M/s to 2.3×10^5 M/s. The increase in the period of oscillation in the BZ reaction with methylmalonic acid as the substrate is caused by the slower enolization rate.

The literature values for k_{enol}(MA) and k_{enol}(MMA) are 1.066×10^{-3} $(M \cdot s)^{-1}$ and 5.7×10^{-5} $(M \cdot s)^{-1}$ (*36, 37*). These values were obtained using a 1 M solution of H_2SO_4, so we are unable to compare our answers with the literature values directly. However, the ratio of rate constants for malonic acid and methylmalonic acid should be equal to our ratio. Our ratio turned out to be about 32, whereas the literature value ratio is about 19. The major source of uncertainty was the instability of our colorimeter during the long time required for the methylmalonic acid reaction.

Unstirred BZ System: Measuring Rate Constants with a Ruler

If an autocatalytic reaction is left unstirred, extremely interesting behavior can be observed. Diffusion, instead of causing concentration gradients to disappear, can couple to the autocatalytic reactions to produce reactions that propagate through the medium.

Exothermic reactions can be autocatalytic if sufficient heat is produced to accelerate the rate of reaction via the Arrhenius temperature dependence. When allowed to proceed in unstirred reactors, chemical reaction fronts may develop. A simple example is a burning cigarette (*12*).

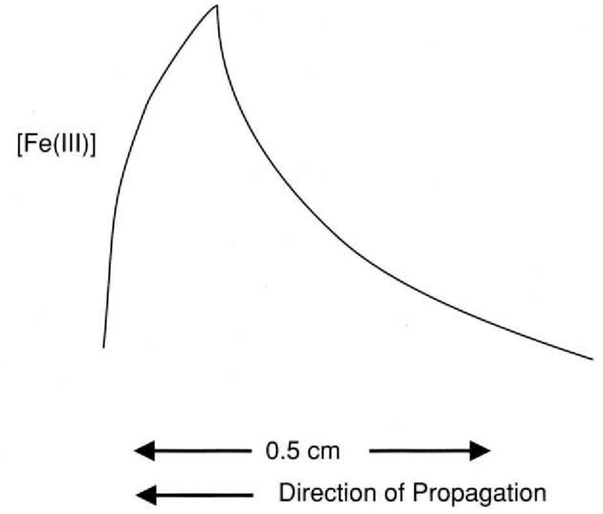

Figure 5. A schematic diagram of an oxidizing front in the ferroin-catalyzed bromate oxidation of malonic acid. The very sharp gradient in the oxidized catalyst is caused by the autocatalytic reaction of $HBrO_2$. The gradual reduction in the trailing edge of the front occurs as the system relaxes back to a state similar to its condition before the front propagated. This is analogous to grass growing back after a brush fire.

Excitability

An excitable system is one that is quiescent until sufficiently perturbed. Then it proceeds through a range of states until returning to its initial quiescent state. Nerve and heart cells are examples of excitable systems (*26*).

In an excitable system the behavior is more interesting than the simple case of a traveling front because after the reaction passes through a point, the reactants are regenerated. (Some other material slowly reacts to replenish the needed species.) Consider a grass fire. After the fire passes, the grass can regrow, and then another fire can spread. How frequently fires pass through a specific region depends on how fast the grass grows. So if you looked from a satellite over a long period, you could observe fire "waves" spreading, for example, through a prairie. The slower the grass grows, the wider the distance between the rings of fire.

Waves in the BZ system propagate as rings of oxidation called "trigger waves" that form "target patterns." Initially, a solution is homogeneous. Then a small excess of $HBrO_2$ is formed. It is not clear if this occurs due to a spontaneous concentration fluctuation or via a heterogeneous reaction (perhaps on a dust particle). The excess $HBrO_2$ catalyzes more of its own production. As the increasing concentration of $HBrO_2$ diffuses into neighboring regions, $HBrO_2$ production is stimulated there as well. A front of reaction propagates out from the initial perturbation and can be followed by the oxidation of the ferroin catalyst (Fig. 5).

If the target pattern is disturbed, it is possible to observe spiral waves that look like pinwheels (*40–44*). Similar behavior has been observed in heart muscle and may be related to the onset of fibrillation during a heart attack (*26*).

In this experiment we would like to determine the rate constant of an important autocatalytic reaction in the BZ reaction.

$$\frac{d[HBrO_2]}{dt} = k[H^+][BrO_3^-][HBrO_2] \tag{7}$$

However, measuring it directly is difficult because we cannot run an experiment in a beaker in which we mix bromate and $HBrO_2$ in acid solution. ($HBrO_2$ is not a stable species.) In the BZ system, the formation of $HBrO_2$ is accompanied by the oxidation of the metal ion that we observe as a propagating color change.

Tyson proposed the following expression for the wave velocity in terms of the $HBrO_2$ diffusion coefficient and the autocatalytic reaction (*45*).

$$\text{velocity} = 2(kD[H^+][BrO_3])^{1/2} \tag{8}$$

where D is the diffusion coefficient of $HBrO_2$ (2×10^{-5} cm^2/s).

The goals of this experiment are

- to test this model by determining the sensitivity of front velocity to concentration of ferroin, $[BrO_3^-]_0$, and $[H^+]_0$
- to use this data to calculate a value for k
- to observe the phenomenology of waves and spirals

Experimental

The following solutions are prepared in advance (same solutions as used for the enolization experiment).

Solution A:	100 mL of 0.6 M $NaBrO_3$/0.6 M H_2SO_4
Solution B:	40 mL of 0.48 M malonic acid
Solution C:	25 mM ferroin (Fisher)
Solution D:	0.97 M NaBr (1g/10 mL)

Students prepare the following additional solutions.

- Take 40 mL of solution A, and dilute to 50 mL (solution A1); 0.48 M $NaBrO_3$/0.48 M H_2SO_4.
- Take 20 mL of solution A2, and dilute to 25 mL (solution A2); 0.38 M $NaBrO_3$/0.38 M H_2SO_4.
- Take 10 mL of solution A, and dilute to 20 mL (solution A3); 0.3 M $NaBrO_3$/0.3 M H_2SO_4.

Procedure

The following procedure is presented by Epstein (*38*). Into a small Erlenmeyer flask, introduce 7 mL of solution A, 3.5 mL solution B, and 1 mL of solution D. Stopper and allow to stir on a magnetic stirrer. The brown color is due to bromine, which forms from the oxidation of bromide by bromate. The bromine slowly disappears as it reacts with the malonic acid to form bromomalonic acid (see experiment 2). When the solution has cleared, add 0.5 mL of the 25 mM ferroin solution and stir.

The reaction may oscillate between red and blue, but ignore this. Use a pipet to transfer sufficient solution to a clean petri dish. Cover the dish and wait.

Questions

Students are asked to consider these questions and carry out the following procedures.

(1) You will notice small rings of blue forming in the red solution. Notice how rapidly the blue color spreads. Calculate how long a molecule would take to diffuse just 1 cm ($D = 10^{-5}$ cm^2/s, distance = $\alpha(Dt)^{1/2}$). Clearly, simple diffusion cannot account for the speed of color propagation.

(2) You will see bubbles form. What are they? Recent work indicates that they are not CO_2, but CO (*46*). If too many form to see the waves clearly, swirl the dish around. New waves will form.

(3) What happens when two waves collide? How is this different from water waves?

(4) What happens when a wave encounters a barrier? Does it reflect?

(5) To make a spiral, slowly move a pipet tip through the center of a target pattern. In which direction does the spiral rotate?

(6) Repeat the above experiment. Use graph paper to measure the change in the radial distance from the center of a target pattern as a function of time. The slope of the line

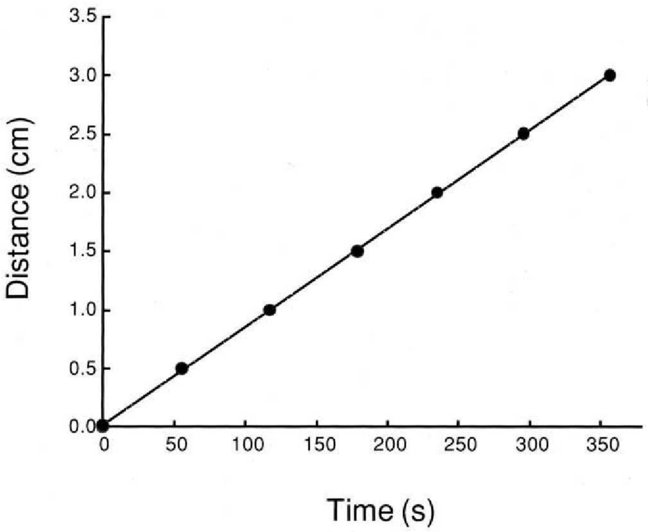

Figure 6. The velocity of the ferroin-catalyzed bromate oxidation waves as a function of the acidic bromate concentration. The slope, 4.1 $cm^2\ min^{-2}\ M^{-2}$, equals $4kD$, following eq 11. Using $2 \times 10^{-5}\ cm^2/s$ as the diffusion coefficient for $HBrO_2$, we get a rate constant of 14 $M^{-2}s^{-1}$.

drawn through this data will provide the wave speed. Also measure the wavelength (the distance between fronts).

(7) Does the velocity remain constant with time? If not, why?

(8) Repeat these measurements for the following solutions.

  (a) Use 0.2 mL of ferroin instead of 0.5 mL with solution A. Is there any effect?

  (b) Using 1.0 mL of ferroin and the same volumes of other reagents, make velocity and wavelength measurements for solutions A1, A2, A3.

(9) Plot the velocity as a function of the square root of the product of $[H^+]$ and $[BrO_3^-]$. Fit a line. Using the slope and the diffusion coefficient of $HBrO_2$, calculate the rate constant of the autocatalysis reaction. Compare it to the reported value of 20 $M^{-2}s^{-1}$.

(10.) Does the velocity depend on the ferroin concentration?

Typical Results

As the concentration of BrO_3^- and sulfuric acid decreased, the wave velocity decreased. A plot of

$$\text{velocity}^2 \text{ vs. } [H^+][BrO_3^-]$$

was also constructed to solve for k from eq 8 because the slope is $4kD$. The slope of this graph was 4.1 $cm^2\ min^{-2}\ M^{-2}$ (Fig. 6). A rate constant of 14 $M^{-2}\ s^{-1}$ was calculated using a diffusion coefficient for $HBrO_2$ of $2 \times 10^{-5}\ cm^2/s$ (*45*). The percentage deviation from the literature value of 20 $M^{-2}\ s^{-1}$ is 30%, based on the experiments of Field and Noyes (*28*) and Showalter (*47*).

For each concentration of bromate ion/acid, several velocity measurements were recorded. Data collected from the same samples do not indicate substantial change of the velocity with time. Keeping $[BrO_3^-][H_2SO_4]$ constant, ferroin concentration was increased from 0.5 mL to 2 mL. The average velocity of the waves was decreased from 0.65 cm/min to 0.64 cm/min when the ferroin concentration was increased. With a standard deviation of ±0.03 cm/min, this is not a significant decrease. Equation 8 predicts that the front velocity should be independent of the ferroin concentration.

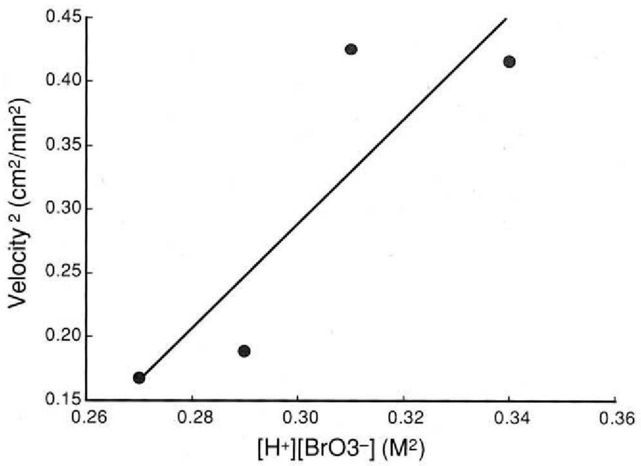

Figure 7. The velocity of the ferroin catalyzed bromate oxidation waves, as a function of the acidic bromate concentration. The slope, 4.1 $cm^2min^{-2}M^{-2}$,equals 4kD, following eqn. (11). Using 2×10^{-5} cm^2/s as the diffusion coefficient for $HBrO_2$ yields a rate constant of 14 $M^{-2}s^{-1}$.

Several qualitative observations of the unstirred BZ system were made. The chemical waves of the reaction mixture did not behave like water waves. When one of the blue waves ran into a wall, no reflection was observed. The wave simply terminated. This observation is in agreement with the grass/fire analogy. If a fire encountered a barrier that it could not penetrate, it would eventually die out, not reflect back to where it had already burned. Also, when two waves collided, there was no interference. Again, the waves annihilated one another. A 0.3 M $[BrO_3^-][H_2SO_4]$ solution was perturbed using a small pipet, creating two counter-rotating spirals.

Wavelengths and distances between fronts were also measured for each solution. The lower the concentration of reactants available, the farther apart the waves should propagate, and the longer the wavelength should be. The wavelengths were expected to increase with decreased bromate ion/acid concentration because less bromous acid would be formed. Our wavelength data were inconclusive because no trend was observed.

In order to achieve accurate results from this experiment, convection must be eliminated. An open container allows evaporation, causing temperature gradients and convection. Even if the there is no air/solution interface, concentration and temperature gradients are generated by waves, which can cause convection (*12*, *48–52*). To eliminate convection, the reaction must be carried out in a gel (*53*). However, reducing the thickness of the solution layer would substantially reduce convection. Such thin layers are difficult to create because the solution will not wet the petri dish. Field and Winfree have suggested using a surfactant (*54*).

Conclusion

Advances in nonlinear dynamics and nonequilibrium thermodynamics can be successfully incorporated into the physical chemistry lab by studying three aspects of the Belousov–Zhabotinskii reaction. Students can directly observe the phenomena of temporal and spatial self-organization. Moreover, they can apply the reductive approach to learn about a complicated system by studying its components.

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