Oscillating Chemical Reactions

[modified from an article by Earle S. Scott, Rodney Schreiner, Lee R. Sharpe, Bassam Z. Shakhashiri, and Glen E. Dirreen]

Introduction

Oscillating reactions are among the most fascinating of chemical reactions. In one type of reaction, a mixture of chemicals goes through a sequence of color changes, and this sequence repeats periodically. In another, the mixture periodically emits a burst of gas, foaming up. To many, oscillating reactions are engaging examples of "chemical magic." To those having some acquaintance with chemistry, these reactions are a mystery and a challenge. To everyone, they are memorable demonstrations of the wonder of chemistry.

Perhaps what makes oscillating reactions so fascinating to chemists is that they seem to contradict common sense. Experience tells us that, under a given set of conditions, chemical reactions go in only one direction. We rarely find a chemical reaction that appears to reverse itself, much less to do so repeatedly. When we do encounter such a reaction, we may be inclined to draw an analogy to a simple physical oscillator such as a pendulum. A pendulum oscillates from side to side through its equilibrium position, and these oscillations can be attributed to the interconversion between the potential and kinetic energy of the pendulum. Analogous to this physical process, the chemical oscillator may seem to swing through its equilibrium composition. However, this is contrary to the second law of thermodynamics, which asserts that once a chemical system reaches equilibrium, it cannot deviate from that condition spontaneously. Therefore, oscillations in chemical reactions cannot be like the oscillations of a pendulum; chemical reactions cannot oscillate through the equilibrium condition.

A more appropriate physical model for an oscillating chemical reaction would be a grandfather's clock. The hands of the clock pass repeatedly (twice daily) through the same position, but the energy stored in the elevation of the weights decreases continuously as the clock runs. In an oscillating chemical reaction, the concentrations of some components of the reaction mixture pass repeatedly through the same value, but the energy-releasing reaction that drives the oscillations proceeds continuously toward completion. Just as the clock is running down while its hands rotate, the chemical oscillator is running down toward equilibrium as it oscillates. In order to exhibit oscillations, a chemical system must be far from its equilibrium composition.

The oscillations in an oscillating chemical reaction are driven by the decrease in free energy of the mixture. This decrease is what drives *all* chemical reactions, but not all chemical reactions exhibit oscillations. There must be some feature peculiar to oscillating reactions that allows them to display this unusual behavior. This feature occurs in the pathways these reactions take as they approach equilibrium, in other words, in their reaction mechanisms. The pathway that a reaction follows determines how the concentrations of its components change as the reaction proceeds. The more complex the pathway of the reaction is, the more complex the changes in concentration of the components can be.

How do reactions oscillate?

The problem of how oscillating chemical reactions occur has been examined theoretically to establish ways in which oscillations can happen. The reaction mechanisms of all known chemical oscillators have at least three common features. First, while the oscillations occur, the chemical mixture is far from equilibrium, and an energy releasing reaction occurs whose energy drives the oscillating "sideshow." Second, the energy-releasing reaction can follow at least two different pathways, and the reaction periodically switches from one pathway to another. Third, one of these pathways produces a certain intermediate, while another pathway consumes it, and the concentration of this intermediate functions as a "trigger" for the switching from one pathway to the other. When the concentration of the intermediate is low, the reaction follows the producing pathway, leading to a relatively high concentration of the intermediate. When the intermediate's concentration is high, the reaction switches to the consuming pathway, and the concentration of the intermediate decreases. Eventually the reaction reverts to the producing pathway. The reaction repeatedly switches from one pathway to the other.

We will explore these general ingredients of an oscillating reaction using the CKS software later, after performing the experiments on a particularly visually striking oscillating reaction, the Briggs-Rauscher reaction.

Briggs-Rauscher Reaction

Abstract

Three colorless solutions are combined in a large beaker and stirred on a magnetic stirrer. The solution becomes amber, then blue-black, and then colorless again. This sequence of color changes repeats with a period of approximately 15 seconds at 25°C. The period of the oscillation gradually increases, and after several minutes, the blue-black color persists. The electrical potential of the solution oscillates along with its color, and the range of these oscillations is about 60 mV.
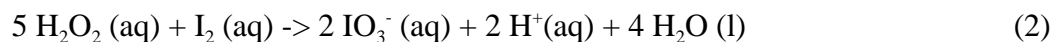
Discussion

The Briggs-Rauscher reaction was developed by Thomas S. Briggs and Warren C. Rauscher of Galileo High School in San Francisco [1]. It is perhaps the most visually impressive of the chemical oscillators. A stirred batch of solution goes through 15 or more cycles of colorless, to amber, to blue-black, before ending as a blue-black mixture with the odor of iodine.

The Briggs-Rauscher (BR) reaction is a hybrid of two other oscillating chemical reactions, the Bray-Liebhafsky (BL) reaction and the Belousov-Zhabotinsky (BZ) reaction. Bray was investigating the dual role of H_2O_2 as an oxidizing agent and a reducing agent when he discovered oscillations in the evolution of oxygen gas from the reaction mixture [2]. He mixed H_2O_2, KIO_3, and H_2SO_4, and in this mixture, hydrogen peroxide reduced iodate to iodine and was oxidized to oxygen gas in the process.

$$5\ H_2O_2\ (aq) + 2\ IO_3^-\ (aq) + 2\ H^+(aq) \to I_2\ (aq) + 5\ O_2(g) + 6\ H_2O\ (l) \qquad (1)$$
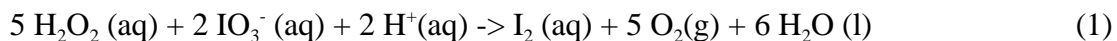
The hydrogen peroxide also oxidizes iodine to iodate.

$$5\ H_2O_2\ (aq) + I_2\ (aq) \to 2\ IO_3^-\ (aq) + 2\ H^+(aq) + 4\ H_2O\ (l) \qquad (2)$$

The net result of these reactions is the iodate catalysis of the disproportionation of hydrogen peroxide.

$$2\ H_2O_2\ (aq) \to O_2\ (g) + 2\ H_2O\ (l) \qquad (3)$$

The discovery of oscillations prompted Liebhafsky to study this reaction before 1933 and after 1969 [3], when he retired from a career as an industrial chemist, but few others paid much attention to this reaction until after the discovery of the BZ reaction. Belousov reported oscillations during the reaction of citric acid with acidic bromate ions and cerium(IV) ions [4]. This oscillatory behavior was exploited by Zhabotinsky, who discovered that oscillations still occurred if certain other organic compounds, such as malonic acid, were substituted for citric acid, and if other one-electron transfer agents, such as Mn(II) ions, were substituted for cerium ions [5-7].

Briggs and Rauscher combined the hydrogen peroxide and iodate of the BL reaction with the malonic acid and manganese ions of the BZ reaction, and discovered the oscillating reaction that bears their name. In the BR oscillating reaction, the evolution of oxygen and carbon dioxide gases

and the concentrations of iodine and iodide ions oscillate. These oscillations are represented in the figure. Iodine is produced rapidly when the concentration of iodide ions is low. As the concentration of iodine in the solution increases, the amber color of the solution intensifies. The production of I^- increases as $[I_2]$ increases, and these ions react with iodine molecules and starch to form a blue-black complex containing the pentaiodide ion (I_5^-) [9]. Most of the O_2 and CO_2 is produced during the formation of I_2. The $[I_2]$ reaches a maximum and begins to fall, although $[I^-]$ rises further and remains high as $[I_2]$ continues to decline until the solution clears. Then the $[I^-]$ suddenly falls and the cycle begins again. This cycle repeats a number of times until the solution ends as a deep blue mixture that liberates iodine vapors.
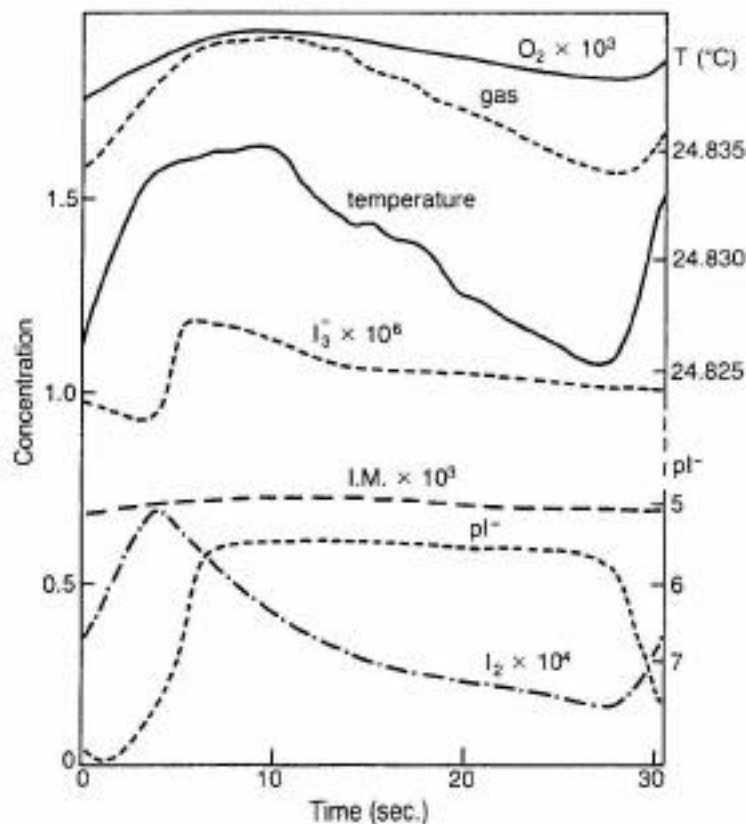

Figure. Variations with time of O_2, I_3^-, iodomalonic acid, and I_2 concentrations (in moles per liter), of pI^-, of gas evolution (in arbitrary units), and of temperature (in Celsius) during one oscillation of a BR reaction (Source: Figure 4 [8]).
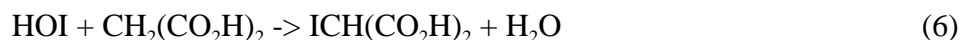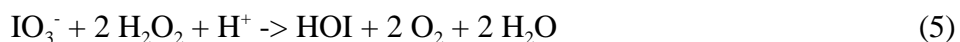
The mechanism of this reaction has been studied by Cooke [10-12], by Furrow and Noyes [13-15], and by De Kepper and Epstein [16]. The results of their investigations led them to similar conclusions about the nature of the mechanism. Much of the proposed mechanism is a direct transfer of the mechanism of the BZ reaction to the iodate-hydrogen peroxide system. The proposed mechanism is only a skeleton of what happens during the reaction. It does not account for the production of CO_2, nor does it identify the ultimate organic products of the reaction; these

factors are still under investigation. However, it does explain the origin of the oscillations in the concentrations of I_2 and I^-.

The transformation that accounts for the oscillations in the BR reaction is represented in equation 4.

$$IO_3^- + 2\ H_2O_2 + CH_2(CO_2H)_2 + H^+ \rightarrow ICH(CO_2H)_2 + 2\ O_2 + 3\ H_2O \qquad (4)$$
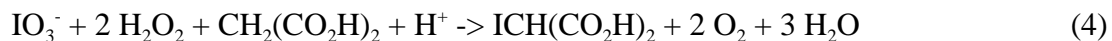
This transformation is accomplished through two component reactions (equations 5 and 6).

$$IO_3^- + 2\ H_2O_2 + H^+ \rightarrow HOI + 2\ O_2 + 2\ H_2O \qquad (5)$$

$$HOI + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H_2O \qquad (6)$$

The first of these two reactions can occur via two different processes, a radical process and a nonradical process. Which of these two processes dominates is determined by the concentration of iodide ions in the solution. When $[I^-]$ is low, the radical process dominates; when $[I^-]$ is high, the nonradical process is the dominant one. The second reaction (equation 6) couples the two processes. This reaction consumes HOI more slowly than that species is produced by the radical process when that process is dominant, but it consumes HOI more rapidly than it is produced by the nonradical process. Any HOI which does not react by equation 6 is reduced to I^- by hydrogen peroxide as one of the component steps of the nonradical process for reaction 5. When HOI is produced rapidly by the radical process, the excess forms the iodide ions, which shut off that radical process and start the slower nonradical process. Equation 6 then consumes the HOI so rapidly that not enough is available to produce the iodide ion necessary to keep the nonradical process going, and the radical process starts again. Each of the processes of equation 5 produces conditions favorable to the other process, and, therefore, the reaction oscillates between these two processes.

The mechanism will be discussed in more detail below.

PROCEDURE

Materials

3 liters distilled water
410 mL 30% hydrogen peroxide, H_2O_2
43 g potassium iodate, KIO_3
4.3 mL concentrated (18M) sulfuric acid, H_2SO_4
16 g malonic acid, $CH_2(CO_2H)_2$
3.4 g manganese(II) sulfate monohydrate, $MnSO_4 \cdot H_2O$
0.3 g soluble starch
20 g sodium thiosulfate, $Na_2S_2O_3$ (See Disposal section for use.)
4 2-liter beakers
gloves, plastic or rubber
hot plate
2 glass stirring rods
100-mL beaker
50-mL beaker
magnetic stirrer, with 2-inch stirring bar
platinum electrode (optional)
double-junction reference electrode[†] (optional)
strip-chart recorder (optional)
2-liter glass cylinder

[†] The reference electrode must not leak chloride ions into the solution, because chloride ions interfere with the mechanism of the oscillating reaction and inhibit the oscillations.

Preparation

The required solutions will be prepared beforehand, according to the following directions:

Solution A-1. Pour 400 mL of distilled water into a 2-liter beaker. Wearing gloves, pour 410 mL of 30% hydrogen peroxide into the beaker of water. Dilute the solution to 1.0 liter with distilled water. This solution is 4.0M in H_2O_2.

Solution A-2. Place 43 g of potassium iodate and approximately 800 mL of distilled water in the second 2-liter beaker. Add 4.3 mL concentrated H_2SO_4 to this mixture. Warm and stir the mixture until the potassium iodate dissolves. Dilute the solution to 1.0 liter with distilled water. This solution is 0.20M in KIO_3 and 0.077M in H_2SO_4.

Solution A-3. Dissolve 16 g of malonic acid and 3.4 g of manganese(II) sulfate monohydrate in approximately 500 mL of distilled water in the third 2-liter beaker. In the 100-mL beaker, heat 50 mL of distilled water to a boil. In the 50-mL beaker, mix 0.3 g of soluble starch with about 5 mL of distilled water and stir the mixture to form a slurry. Pour the slurry into the boiling water and continue heating and stirring the mixture until the starch has dissolved (1-2 minutes). The solution

may be slightly turbid. Pour this starch solution into the solution of malonic acid and manganese(II) sulfate. Dilute the mixture to 1.0 liter with distilled water. This solution is 0.15M in malonic acid and 0.020M in $MnSO_4$.

Set the remaining 2-liter beaker on the magnetic stirrer and place the stirring bar in the beaker.

To record the potential of the solution as the oscillating reaction proceeds, connect the platinum electrode to the positive terminal of the strip-chart recorder and the reference electrode to the negative terminal. Mount the electrodes on the 2-liter beaker so that they will be immersed when the beaker contains 1500 mL of liquid.

SAFETY HAZARDS   --   IMPORTANT!!!

The reaction produces iodine in solution, in suspension, and also as a vapor above the reaction mixture. The vapor or the solid is very irritating to the eyes, skin, and mucous membranes.

Because 30% hydrogen peroxide is a strong oxidizing agent, contact with skin and eyes must be avoided. In case of contact, immediately flush the affected area with water for at least 15 minutes; get immediate medical attention if the eyes are affected. Avoid contact between 30% hydrogen peroxide and combustible materials. Avoid contamination from any source, because any contaminant, including dust, will cause rapid decomposition and the generation of large quantities of oxygen gas. Store 30% hydrogen peroxide in its original, closed container, making sure that the container vent works properly.

Because sulfuric acid is a strong acid and a powerful dehydrating agent, it can cause burns. Spills should be neutralized with an appropriate agent, such as sodium bicarbonate ($NaHCO_3$), and then rinsed clean.

Malonic acid is a strong irritant to skin, eyes, and mucous membranes.

EYE GOGGLES MUST BE WORN AT ALL TIMES. THIS IS SERIOUS.
You may also want to wear latex gloves to protect your hands.

DISPOSAL

The chemicals used in this experiment will be disposed by the TA's afterwards according to the following protocol:

The reaction produces copious amounts of elemental iodine (I_2), which should be reduced to iodide ions before disposal. To do so, carefully add 10 g of sodium thiosulfate to each mixture and stir it until the mixture becomes colorless. Caution! The reaction between iodine and thiosulfate is exothermic, and the mixture may become hot. The cold solution should then be flushed down the drain with water.

MEASUREMENTS

There will be six stations, each monitoring the BR reaction under different conditions: four or five stations will be set up to take measurements at varying temperatures from about 17°C to 28°C, and one or two will be set up with a colorimeter. The data collection will proceed through the PASCO instruments connected to the laptop computers at the station. You should work in groups of about 3 students, and each group will take measurements in rotation at the four different stations (the three temperature conditions and the colorimeter). At each of the fixed temperature stations, you can choose the temperature to be measured (adjusting with ice and the heater), as long as you keep the temperature relatively constant. We suggest hot and cold temperatures within 10 degrees of room temperature.

Answer the questions posed below, recording all expectations, observations, and conclusions in your lab notebook. The answers to the questions may require reading the discussion following this section, as well as observations from the experiments. **Read this section completely before starting experiments.**

At each station, you will initiate the oscillating BR reaction by adding equal quantities of the three solutions at once, and then initiating the data recording by pushing the "REC" button in Science Workshop. Before initiating, you will first need to stabilize the temperature of the water bath, as well as the three solutions by turning the droppers each with their solution with their bulbs in the water bath to bring the solutions to temperature. Be sure that the magnetic stirrer is spinning at a good pace--the reaction needs to be well mixed to maintain a good periodicity in the reaction.

Using the attached light meter (or colorimeter), monitor the oscillations in the electrical potential. The output will be a recorded wave (similar to that seen in the figure above) which will show increases and decreases which also correspond to the changes in color. For each station, you should:

> Pour equal quantities of solution A-1 and solution A-2 into the beaker on the magnetic stirrer. Adjust the stirring rate to produce a large vortex in the mixture. Pour an equal quantity of solution A-3 into the beaker. (This will produce a mixture whose nominal contents are 0.050M malonic acid, 0.0067M Mn^{2+}, 0.067M IO_3^-, 1.3M H_2O_2, and 0.038M H_2SO_4.) The initially colorless solution will become amber almost immediately. Then, it will suddenly turn blue-black. The blue-black will fade to colorless, and the cycle will repeat several times with a period which initially lasts about 15 seconds but gradually lengthens. After a few minutes, the solution will remain blue-black.

> The solutions can be mixed in any order, as long as they are combined quickly.

From the mechanism above, we can anticipate that the entire cycle will involve a fast phase and a slow phase in the color change. Which kinetic steps do these correspond to? How much time does it take in the fast phase? In the slow phase? Does this period of time change as the reaction progresses? Why? Be sure to record the temperature at which you have made your measurements.

After completing the different temperatures, do you notice a trend in the changes (if any) in the time periods for the fast and slow phases of the reaction? What relation might you postulate to fit the temperature dependence of the time periods? How do you think the periods might be related to the rates of the corresponding elementary steps in the reaction? From your fit of the temperature dependence, what parameters of the reaction energetics might you extract? Do these seem reasonable for the elementary reactions they correspond to?

For the colorimeter station, you will be able to get better quantitative measurements of the concentrations. After the reaction has initiated, find the highest transmittance point. After the reaction has nearly died out, identify the lowest transmittance point. These two points will serve as "100%" and "0%" transmittance. While these are not calibrated, we can use relative ratios of this transmittance to determine relative concentrations.

Save all your data to Excel for future analysis. There has been some difficulty saving directly to a floppy disk (A: drive), so you may want to save first to the desktop (C: drive), and then copy your data to the floppy from the desktop.

To try:

In the above protocol, we initiated the reactions by thorough mixing. What do you expect will happen if the three solutions are not thoroughly mixed? Write your expectations into your notebook, and justify your hypothesis. Test your hypothesis out, and record your observations and conclusions, using the following protocol (or similar one of your design):

Pour 500 mL of solution A-1 into the 2-liter glass cylinder. Carefully pour 500 mL of solution A-2 down the inside of the cylinder to minimize the mixing of the two solutions. Carefully pour 500 mL of solution A-3 into the cylinder, again minimizing the mixing of the solutions. Regions of amber will develop in the solution, and these regions will turn blue-black. The blue-black layers will appear to drift through the solution in the cylinder.

Warning About Chloride Ion Contamination

Chloride ion concentrations in excess of 0.07M suppress the oscillations [17]. Therefore, the vessels used for the preparation of the solutions must be clean. If the oscillations in the electrical potential of the solution are to be observed, a reference electrode that does not leak chloride ions must be used. An ordinary standard calomel electrode or silver-silver chloride electrode is not suitable. A double junction version of one of these electrodes is adequate.

Be sure to carefully rinse the cuvettes and droppers with deionized water between uses.

FURTHER DISCUSSION

The detailed explanation requires attention to the individual steps of the two processes. If iodide ions are present in sufficient concentration, the reaction follows the nonradical process of equation 5. The iodide ions react rather slowly with iodate ions, as represented in equation 7.

$$IO_3^- + I^- + 2\ H^+ \rightarrow HIO_2 + HOI \tag{7}$$

The iodous acid (HIO_2) is further reduced to hypoiodous acid (HOI) by the reaction of equation 8.

$$HIO_2 + I^- + H^+ \rightarrow 2\ HOI \tag{8}$$

(These two equations are analogous to those proposed for the BZ reaction with bromate.) The hypoiodous acid is then reduced by hydrogen peroxide, as indicated by equation 9.

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \tag{9}$$

The net transformation as represented in equation 5 is obtained by the stoichiometric addition of (equation 7) + (equation 8) + 2(equation 9).

Because reaction 5 is slower than reaction 6 under these conditions, so much HOI is used up by reaction 6 that reaction 9 cannot replenish the I^- consumed in reactions 7 and 8; the [I^-] keeps diminishing.

Once the iodide ions have been sufficiently depleted, the nonradical process becomes very slow, and the radical process for reaction 5 can take over. This process involves the five steps represented by equations 10 through 14 [16].

$$IO_3^- + HIO_2 + H^+ \rightarrow 2\ IO_2^\bullet + H_2O \tag{10}$$

$$IO_2^\bullet + Mn^{2+} + H_2O \rightarrow HIO_2 + Mn(OH)^{2+} \tag{11}$$

$$Mn(OH)^{2+} + H_2O_2 \rightarrow Mn^{2+} + H_2O + HOO^\bullet \tag{12}$$

$$2\ HOO^\bullet \rightarrow H_2O_2 + O_2 \tag{13}$$

$$2\ HIO_2 \rightarrow IO_3^- + HOI + H^+ \tag{14}$$

These steps, when combined in the stoichiometry of 2(equation 10) + 4(equation 11) + 4(equation 12) + 2(equation 13) + (equation 14), have the overall result given by equation 5. A significant feature of this process is that, taken together, the first two steps (equations 10 and 11) are autocatalytic--they produce 2 HIO_2 for each one consumed. Therefore, the rate of these steps increases as they occur. Because this radical process is autocatalytic, it causes a rapid increase in the concentration of HOI, which is produced by the disproportionation of HIO_2 (equation 14). This process does not rapidly consume all of the iodate in the solution, because the last step is second

order in the catalytic species. Thus, as its concentration increases because of the autocatalytic nature of the early steps, HIO_2 is ever more rapidly consumed in this last step, and the sequence of reactions quickly reaches a steady state. (Equations 10, 11, and 14 are analogous to those for the BZ reaction involving bromate.)

Equations 11 and 12 indicate the function of the manganese catalyst. The manganese is oxidized in reaction 11 and reduced in reaction 12. Its catalytic effect in the reaction is accounted for through its providing the means for reducing IO_2 radicals to HIO_2, thereby completing the autocatalytic cycle of equations 10 and 11.

The hypoiodous acid produced by the radical process reacts with malonic acid by reaction 6. However, the radical process is faster than reaction 6, and the excess HOI reacts with hydrogen peroxide by reaction 9 to create I^-, which shuts off the radical process and returns the system to the slow nonradical process initiated by reaction 7.

The dramatic color effects arise because reaction 6 does not take place in a single step, but by the sequence of reactions 15 and 16.

$$I^- + HOI + H^+ \rightarrow I_2 + H_2O \tag{15}$$
$$I_2 + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H^+ + I^- \tag{16}$$
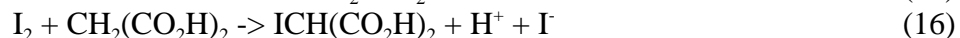
The solution turns amber from the I_2 produced through reaction 15, when the radical process maintains [HOI] greater than $[I^-]$. The excess HOI is converted to I^- through the reaction with H_2O_2 (equation 9). The solution suddenly turns dark blue when $[I^-]$ becomes greater than [HOI], and the I^- can combine with I_2 to form a complex with the starch. With $[I^-]$ high, reaction 5 switches to the slow nonradical process. The color then fades as reaction 6 consumes iodine faster than it is produced. When the system switches back to the rapid radical process, the cycle is repeated.

The above reaction steps constitute a skeleton mechanism for the BR oscillating reaction. Upon initial mixing of the solutions, IO_3^- reacts with H_2O_2 to produce a little HIO_2. The HIO_2 reacts with IO_3^- in the first step of the radical process (equation 10). The autocatalytic radical process follows, rapidly increasing the concentration of HOI. The HOI is reduced to I^- in a reaction with H_2O_2 (equation 9). The large amount of HOI reacts with I^-, producing I_2 (equation 15). The I_2 reacts slowly with malonic acid, but the concentrations of HOI, I_2, and I^- all increase, because reaction 5 is faster than reaction 6. As $[I^-]$ increases, the rate of its reaction with HIO_2 (equation 8) surpasses that of the autocatalytic sequence of reactions 10 and 11. The radical process is then shut off, and the accumulation of reduced iodine is consumed by reaction 6 operating through the sequence of equations 15 and 16. Eventually $[I^-]$ is reduced to such a low value that reactions 10 and 11 become faster than reaction 8, and the radical process takes over again. This oscillating sequence repeats until the malonic acid or IO_3^- is depleted.

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