Fantastic Four-Color Oscillator

Introduction

You won't believe your eyes as you watch this amazing oscillating reaction! This four-color oscillator will get your students' undivided attention as they observe a solution flash from green to blue to purple to red. And that's not all—this four-color cycle will repeat itself for well over an hour!

Concepts

- Oscillating reactions
- Chemical equilibrium
- Oxidation–reduction reactions
- Kinetics/catalysts
- Reaction mechanisms

Materials

1,10-phenanthroline, $C_{12}H_8N_2 \cdot H_2O$, 0.23 g
Cerium(IV) ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, 2.7 g
Iron(II) sulfate, $FeSO_4 \cdot 7H_2O$, 0.12 g
Malonic acid, $CH_2(CO_2H)_2$, 8 g
Potassium bromate, $KBrO_3$, 9.5 g
Potassium bromide, KBr, 1.8 g
Sulfuric acid solution, H_2SO_4, 3.0 M, 225 mL
Distilled or deionized water, approximately 1 L
Beaker, 1-L
Erlenmeyer flasks, 250-mL, 3
Graduated cylinder, 50-mL
Magnetic stirring bar
Magnetic stirring plate
Spatula

Safety Precautions

A small amount of elemental bromine gas is released from the reactions in this demonstration; adequate ventilation is necessary. Potassium bromate is a strong oxidizing agent and poses a fire risk in contact with organic material; it is a strong irritant and moderately toxic. Malonic acid is a strong irritant, slightly toxic, and corrosive to eyes, skin, and respiratory tract. Potassium bromide is slightly toxic by ingestion and a severe body tissue irritant. Cerium(IV) ammonium nitrate is a strong oxidizer and a skin irritant. Iron(II) sulfate is slightly toxic by ingestion and 1,10-phenanthroline is highly toxic by ingestion. Sulfuric acid solution is corrosive to eyes, skin, mucous membrane, and other body tissue. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.

Preparation

Solution A (0.23 M $KBrO_3$) — In a 250-mL Erlenmeyer flask, dissolve 9.5 grams of potassium bromate in 250 mL of distilled or deionized water. Label this solution as "Solution A."

Solution B (0.31 M $CH_2(CO_2H)_2$ and 0.059 M KBr) — In a second 250-mL Erlenmeyer flask, dissolve 8 grams of malonic acid and 1.8 grams of potassium bromide in 250 mL of distilled or deionized water. Label this solution as "Solution B."

Solution C (0.019 M $Ce(NH_4)_2(NO_3)_6$ and 2.7 M H_2SO_4) — In a third 250-mL Erlenmeyer flask, dissolve 2.7 grams of cerium(IV) ammonium nitrate in 25 mL of distilled or deionized water and add 225 mL of 3.0 M sulfuric acid. Label this solution as "Solution C."

Solution D (0.50% ferroin solution) — To prepare 50 mL of stock solution, dissolve 0.12 grams of iron(II) sulfate in 50 mL of distilled or deionized water. In the resulting solution, dissolve 0.23 grams of 1,10-phenanthroline. Label this solution as "Solution D."

Procedure

1. Place a 1-L beaker on the magnetic stirring plate and place the magnetic stirring bar in the beaker.
2. Pour all of Solution A and Solution B into the 1-L beaker.

3. Adjust the stirrer to produce a vortex in the solution. The solution may become amber, and will turn colorless after about one minute.
4. Once the solution is colorless, add all of Solution C and only 15 mL of Solution D. (Note: The solution composition is now 0.077 M BrO_3^-, 0.10 M malonic acid, 0.020 M Br^-, 0.0063 M Ce^{4+}, 0.90 M H_2SO_4, and 0.17 mM ferroin.)
5. Keep stirring the green cloudy mixture and it will become a green solution. Over a period of about a minute, the color of the solution will change from green to blue, then to violet, and finally to red-brown.
6. The color of the solution will suddenly return to green, and the cycle will repeat itself more than 20 times, lasting over an hour.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. The reaction mixture should be neutralized with sodium carbonate and flushed down the drain with excess water according to Flinn Suggested Disposal Method #24a.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Evidence, models, and explanation
Content Standards: Grades 9–12
Content Standard B: Physical Science, structure and properties of matter, chemical reactions

Tips

- Solutions A–D may be prepared in advance, stoppered, and labeled until needed for the presentation. Solution shelf life is good. The demonstration can easily be scaled up or down to suit your needs.
- The discussion and explanation of this oscillating reaction can be quite complicated for beginning chemistry or general science students. However, it is not necessary to fully understand the reaction mechanism in order to appreciate the spectacular chemistry that occurs in this demonstration. Thus, this demonstration can be performed at any level of science with the explanation suited to the level of the class. A complete discussion is included in this handout; however, further information can be found by reviewing the original reference (see References section).

Discussion

This oscillating reaction demonstrates the classic Belousov-Zhabotinsky (BZ) reaction which is a cerium-catalyzed bromate–malonic acid reaction.

The overall reaction occurring in this demonstration is the cerium-catalyzed oxidation of malonic acid by bromate ions in dilute sulfuric acid. The bromate ions are reduced to bromide ions, while the malonic acid is oxidized to carbon dioxide and water. The overall reaction can be represented by Equation 1:

$$3CH_2(CO_2H)_2 + 4BrO_3^- \rightarrow 4Br^- + 9CO_2 + 6H_2O \qquad \textit{Equation 1}$$

In order to gain some understanding and appreciation for how this overall reaction can produce the amazing, repetitive color changes observed in the demonstration, it is necessary to look at the reaction mechanism or, in other words, how the reactants are transformed into products.

The mechanism involves two different competing processes—Process A involves ions and two-electron transfers; Process B involves radicals and one-electron transfers. The dominant process at any particular time is dependent on the bromide ion concentration. Process A (see Equation 2a) occurs when the bromide ion concentration rises above a certain critical level, while Process B (see Equation 3a) is dominant when the bromide ion concentration falls below a certain critical level. Oscillations occur because Process A consumes bromide ions, leading to conditions which favor Process B. Process B (indirectly) produces bromide ions, which leads to conditions which favor Process A.

Process A

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad \textit{Equation 2a}$$

Bromate ions are reduced by bromide ions through a series of oxygen transfers (two-electron reductions) as shown in Equation 2a. This reaction occurs when Solutions A and B are mixed. The amber color which may develop is caused by the production of elemental bromine. This color soon disappears as the bromine reacts with malonic acid as shown in Equation 2b.

$$Br_2 + CH_2(CO_2H)_2 \rightarrow BrCH(CO_2H)_2 + Br^- + H^+ \qquad \textit{Equation 2b}$$

Process A results in an overall decline in the bromide ion concentration and, once the necessary intermediates are generated and most of the bromide ions are consumed, the rate becomes negligible and Process B takes over.

Process B

$$2BrO_3^- + 12H^+ + 10Ce^{3+} \rightarrow Br_2 + 10Ce^{4+} + 6H_2O \qquad \textit{Equation 3a}$$

Bromate ions are reduced by cerium(III) ions to produce bromine through a simple redox reaction as shown in Equation 3a. Process B produces Ce(IV) ions and Br_2. Both of these species react at least in part to oxidize the malonic acid (see Equation 2b) and the bromomalonic acid (see Equation 3b) to form additional bromide ions. As the concentration of bromide ions increases, the rate of Equation 2a increases until eventually Process A once again dominates.

$$BrCH(CO_2H)_2 + 4Ce^{4+} + 2H_2O \rightarrow Br^- + 4Ce^{3+} + HCO_2H + 2CO_2 + 5H^+$$

Equation 3b

As the reaction oscillates between Process A and Process B, triggered by changes in the bromide ion concentration, concentrations of other species in solution oscillate as well—these concentration changes will explain the color changes observed. While Process A occurs, the cerium ions are in their reduced state, Ce(III). During Process B, some cerium ions are oxidized to Ce(IV) and thus the ratio of Ce(III) to Ce(IV) oscillates as well.

The indicator used in this demonstration is ferroin, which is tris(1,10-phenanthroline) ferrous sulfate. As the concentration of Ce(IV) increases, the Ce(IV) oxidizes the iron in ferroin from Fe(II) to Fe(III). The Fe(II) complex is red while the Fe(III) complex is blue; thus the color of the solution changes as the iron is oxidized. As the concentration of Ce(III) increases, the Fe(III) is reduced back to Fe(II) and the color of the solution changes accordingly.

The color changes in this demonstration, however, are more complex than simple red-blue oscillations from the ferroin. There are also changes in color due to the cerium ions in solution—Ce(III) is colorless while Ce(IV) is yellow. A simplified equation to help explain the color changes is shown below, Equation 4:

$$\underset{\textbf{yellow}}{\mathrm{Ce(IV)}} + \underset{\textbf{red}}{\mathrm{Fe(II)}} \rightleftarrows \underset{\textbf{blue}}{\mathrm{Fe(III)}} + \underset{\textbf{colorless}}{\mathrm{Ce(III)}} \qquad \textit{Equation 4}$$

A possible explanation for the appearance of the oscillating colors in solution is provided; however, a more complete understanding of the color changes might be gained by reviewing the original references.

Green = The yellow Ce(IV) is oxidizing Fe(II) to blue Fe(III); a small amount of Fe(II) has been oxidized to the blue Fe(III) complex; thus, the mixture of yellow and blue forms a green solution.

Blue = All Ce(IV) is reduced to colorless Ce(III); all Fe(II) is oxidized to the blue Fe(III) complex; thus, the solution is blue.

Violet = The colorless Ce(III) is reducing the blue Fe(III) complex to the red Fe(II); the mixture of blue and red appears violet.

Red = All of the blue Fe(III) is reduced to the red Fe(II) complex; colorless Ce(III) is present; the solution appears red.

References

Shakhashiri, B. Z. Chemical Demonstrations: A Handbook for Teachers of Chemistry; University of Wisconsin Press: Madison; 1985; Vol. 2, pp 257–261.

Materials for the *Fantastic Four-Color Oscillator* are available from Flinn Scientific, Inc.

Catalog No.	Description
P0136	Potassium Bromate, 100 g
M0091	Malonic Acid, 25 g
P0137	Potassium Bromide, 100 g
C0287	Cerium(IV) Ammonium Nitrate, 25 g
S0143	Sulfuric Acid, 18 M, 473 mL
F0016	Iron(II) Sulfate, 500 g
P0155	1,10-phenanthroline, 5 g

The above demonstration was developed by Flinn Scientific, Inc. into a demonstration kit. Each kit contains enough chemicals to perform the experiment at least seven times. Excite, energize, and bring back the "magic" of chemistry using Flinn Chemical Demonstration Kits.

Catalog No.	Description
AP4833	Fantastic Four-Color Oscillator—Chemical Demonstration Kit

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.