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The Splendor of One Chemical Reaction

Abstract

Mix three colorless solutions into a 2L beaker and sit them on a magnetic stirring device. Suddenly the colorless solution turns amber, then blue-black, then back to colorless. The colors continue to oscillate in a steady interval; gradually the intervals shorten until after about 5 minutes, the blue-black color remains.

Materials

3 Liters of distilled water	410 mL 30% Hydrogen peroxide, H_2O_2
43 g, potassium iodate KIO_3	4.3 mL 18M sulfuric acid H ₂ SO ₄
16 g malonic acid, CH ₂ (CO ₂ H) ₂	3.4 g manganese(II) sulfate monohydrate
0.3 g soluble starch	20 g sodium thiosulfate, Na ₂ S ₂ O ₃
4-2 L beakers	disposable gloves
Hot plate	glass stirring rods
Beakers, 100 mL & 50 mL	magnetic stirrer, 2" stirring bar

Safety

The reaction produces iodine in solution and vapor. The vapor begins to escape when the reaction stops oscillating. The vapor can be extremely irritating to eyes, skin, mucous membranes and lungs. Have a large 20-gallon bucket with lid on hand and set the reaction beaker into the bucket. Put the lid on the bucket and place it under a laboratory fume hood ASAP and begin the quenching process described under disposal. 30% hydrogen peroxide is a strong oxidizing agent, which can cause serious burns. Any affected areas should be washed for 15-20 minutes with plenty of water before getting emergency attention. If the hydrogen peroxide comes into contact with other chemicals it could result in a very exothermic explosive reaction. Hydrogen peroxide should be kept in a safe place within the lab. Sulfuric acid is a strong acid and can cause burns. The vapors should not be inhaled to avoid serious lung damage. Spills should be neutralized with a weak base such as sodium bicarbonate. Malonic acid is a strong eye, skin and respiratory irritant. Take great care in working with all of these chemicals by preparing your solutions in a vented fume hood wearing the appropriate gloves and safety goggles.

Procedure

Prepare the three colorless solutions A, B and C.

<u>Solution A</u>

Add 400 mL of distilled water to one of the 2000 mL beakers and carefully pour in 410 mL of 30% H₂O₂. Add distilled water up to the 1 Liter mark. Place the solution into a 1 L storage container labeled Solution A.

<u>Solution B</u>

Take a second 2000 mL beaker and add 43 g of $KIO_3 + 800$ mL of distilled water. Place on a magnetic stir apparatus and add a magnetic stir bar. Warm the beaker using low heat while stirring and add in 4.3 mL of concentrated sulfuric acid. Dilute the solution to 1 Liter with distilled water and continue to stir until all the KIO_3 is dissolved. When the reaction solution is cool, pour into a 1 L storage container labeled Solution B.

Solution C

Take a third 2000 mL beaker and dissolve 16 g of malonic acid and 3.4 g of manganese (II) sulfate monohydrate in 500 mL of distilled water. While this beaker is stirring on a magnetic stir plate, heat 50 mL of distilled water to a boil in a separate 100 mL beaker. In another 50 mL beaker, mix 0.3 g of starch with about 5.0 mL of water into a paste (slurry). Pour the slurry into the 100 mL beaker of boiling water and heat for a couple minutes until the starch dissolves. Pour this solution into the Solution C reaction beaker and dilute to 1 Liter with distilled water. When the solution is cool pour into a 1 L storage container labeled Solution C.

The solutions can be prepared a couple weeks in advance. Make sure they are stored in a well ventilated and temperature controlled storage room.

Presentation: Place a 2000 mL beaker on a magnetic stir apparatus and place inside of it a 2" magnetic stir bar. Start it stirring before you pour anything into the beaker. Start out by pouring in 500 mL of the colorless Solution A, then add 500 mL of the colorless Solution B, finally pour in 500 mL of the colorless Solution C.

Discussion

At first the colorless solution becomes an amber color, then suddenly it changes to a blue-black, the blue-black then fades to colorless and the solution begins to oscillate

changing colors for about 5 minutes. The oscillations initially come about every 15 seconds almost allowing you to approximate time from the reaction. However, gradually the oscillation frequency increases until the limiting reagent runs out. Two high school teachers, Thomas Briggs and Warren Rauscher from Galileo High School in San Francisco California, developed the Briggs Rauscher reaction. They published their paper in the Journal of Chemical Education in 1973. It took about a decade for some of the top chemists in the country to sort out the complex maze of equations involved.

A simplified overall scheme is shown below:

$$IO_{3}^{-} + 2 H_2O_2 + CH_2(CO_2H)_2 + H^+ ---- > ICH(CO_2H)_2 + 2 O_2 + 3 H_2O$$
 Equation 1

$$IO_{3} + 2H_2O_2 + H^+ ----> HIO + 2O_2 + 2H_2O$$
 Equation 2

$$HIO + CH_2(CO_2H)_2 ----> ICH(CO_2H)_2 + H_2O$$
 Equation 3

$$I^{-} + HIO + H^{+} -----> I_{2} + H_{2}O$$
 Equation 4
 $I_{2} + CH_{2}(CO_{2}H)_{2} ----> ICH(CO_{2}H)_{2} + H^{+} + I^{-}$ Equation 5

Equation 1 shows an over simplified mechanism for the reaction. Here we have the reactants coming together producing iodomalonic acid.

In Equations 2 & 3, we have oversimplified the entire reaction by summarizing it in two equations. In the first equation, we produce hypoiodous acid, which can form via a radical pathway or a non-radical pathway. The hypoiodous acid from both of the pathways reacts in the second equation to produce the iodomalonic acid. There are probably another 10 or more equations behind these two equations. Summarizing: The hypoiodous acid can be produced via either a radical or nonradical pathway. If it is produced via a radical mechanism more hypoiodous acid is produced than can be used up in Equation 3. The excess hypoiodous acid runs down and starts reacting as depicted in Equations 4 & 5. This is where the color comes in. When the I- is the principle ion present (Equation 5), the solution is clear. Then as the hypoiodous acid reacts with the iodide ion (Equation 4), the iodine starts to increase. When both the iodide and iodine are present, they combine to form a pentaiodide ion complex, which seeks out the starch in the solution and inserts itself into the helical structure of the amylose portion of the starch molecule. This results in a blue-black color, as the iodine concentration increases from the reaction of hypoiodous acid and iodide. Eventually the iodide disappears and there is iodine,

which gives the amber color. The reaction continues to oscillate between the colors until the iodate or malonic acid is used up.

Disposal

The reaction produces large amounts of elemental iodine (I_2) , which needs to be reduced to iodide ions for disposal. Use sodium thiosulfate by simply sprinkling it onto the beaker containing the Briggs solution and this will cause the solution to foam up. The reaction between the iodine and thiosulfate is very exothermic the beaker becomes hot. Continue sprinkling until the foaming dies down. Eventually the reaction stops and the solution becomes colorless. The cold neutralized solution can then be disposed of following all local and state regulations for disposal.

References

T. S. Briggs and W. C. Rauscher, *J. Chem. Educ*. 50: 496 (**1973**).

Shakhashiri, B. Z. *Chemical Demonstration: A Handbook for Teachers of Chemistry*; The University of Wisconsin: Madison, **1985**; Vol. 2, p. 248-256.

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