Incomplete Combustion of Hydrogen. Trapping a Reaction Intermediate.

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Abstract:

The combustion of hydrogen in air is quite complex with at least 28 mechanistic steps and twelve reaction species. Most of the species involved are radicals (having unpaired electrons) in nature. Among the various species generated, a few are stable, including hydrogen peroxide. In a normal hydrogen flame, the hydrogen peroxide goes on to further oxidation resulting in water. In this classroom demonstration, a hydrogen flame is played across the face of an ice cube and the combustion is quenched in an incomplete state. The solution that results contains aqueous hydrogen peroxide that can be tested with two simple chemical tests.

Audience: High school, First-Year Undergraduate / General, Upper-Division Undergraduate

Domain: Demonstrations, Inorganic chemistry

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Introduction.

The combustion of hydrogen is familiar to most students of chemistry:

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(l)$$

Possible mechanisms for this reaction have been studied for over 30 years *(1)*. Reactions that take place in a flame are usually very complicated and varied. For example, a recent article investigating the mechanism of hydrogen combustion proposed two mechanisms that involved twelve chemical species and 34 different reactions *(2)*. Despite the complicated subtleties of these mechanisms, a few simple mechanistic reaction steps are fundamental in understanding hydrogen combustion. A reaction of primary importance is the thermal dissociation of the H_2 bond:

$$H_2(g) \longrightarrow 2\ H\cdot(g) \quad \Delta H = +436\ kJ$$

Reactions such as this are unheard of under normal laboratory temperatures but are important and common at the temperature of a flame. In this case, atomic hydrogen, H•, is formed. Atomic hydrogen, also called the "hydrogen radical" because of its unpaired electron, is extremely reactive towards a variety of species including molecular oxygen:

$$H\cdot(g) + O_2(g) \longrightarrow HO_2\cdot(g)$$

In this prominent reaction, the H· radical produces the $HO_2\cdot$ radical, a high-energy intermediate that is involved in at least five other reactions with species including OH·, H·, ·O·, and another

$HO_2\cdot$, all "normal" components of the gas mixture in a hydrogen/air flame. The reaction between $OH\cdot$ and $HO_2\cdot$ produces water, the final product of hydrogen combustion:

$$OH\cdot(g) + HO_2\cdot(g) \longrightarrow H_2O(g) + O_2(g)$$

The reaction between two $HO_2\cdot$ groups, however, produces hydrogen peroxide:

$$HO_2\cdot(g) + HO_2\cdot(g) \longrightarrow H_2O_2(g) + O_2(g)$$

Hydrogen peroxide is not a normal product of hydrogen combustion, but rather a reaction intermediate that can undergo further high-temperature reactions with either $H\cdot$ or $OH\cdot$:

$$H_2O_2(g) + H\cdot(g) \longrightarrow HO_2\cdot(g) + H_2(g)$$
$$H_2O_2(g) + OH\cdot(g) \longrightarrow HO_2\cdot(g) + H_2O(g)$$

As demonstrated by the second of these reactions, H_2O is ultimately produced as the final product of hydrogen combustion in air. Under certain conditions, $H_2O_2(g)$ can survive as a reaction byproduct.

In addition to these reactions, $H_2O_2(g)$ can undergo O-O bond dissociation to produce $OH\cdot$ radicals:

$$H_2O_2(g) \longrightarrow 2\ OH\cdot(g)$$

As we saw above, $OH\cdot(g)$ is an important species that reacts with $HO_2\cdot(g)$ to produce $H_2O(g)$. For a full discussion of all steps, including several that involve nitrogen from the air, see the article by Brown, Li and Koszykowski *(2)*.

Trapping Hydrogen Peroxide.

In this article we describe a simple experiment that provides evidence for one of the complicated oxidation processes taking place in the flame by "trapping" hydrogen peroxide — the important thermodynamically stable species resulting from the incomplete combustion of hydrogen. In this experiment, we "trap" hydrogen peroxide by playing a hydrogen flame across an ice cube. The combustion process is quenched and hydrogen peroxide dissolves in the ice melt and drips from the bottom of the ice cube. The resulting solution contains approximately 3 x 10^{-4} M $H_2O_2(aq)$ and is suitably concentrated to cause a dramatic color change reaction with both dilute potassium permanganate and starch/iodide solutions.

Apparatus.

The idea for this experiment is quite old. In Partington's 1950 ***Textbook of Inorganic Chemistry***, he describes the formation of small amounts of aqueous hydrogen peroxide by "playing" a hydrogen flame across an ice cube *(3)*. The apparatus we use consists of a glass pipet connected to a one-gallon plastic food storage bag via a 20 cm length of rubber tubing as shown in the Figure.

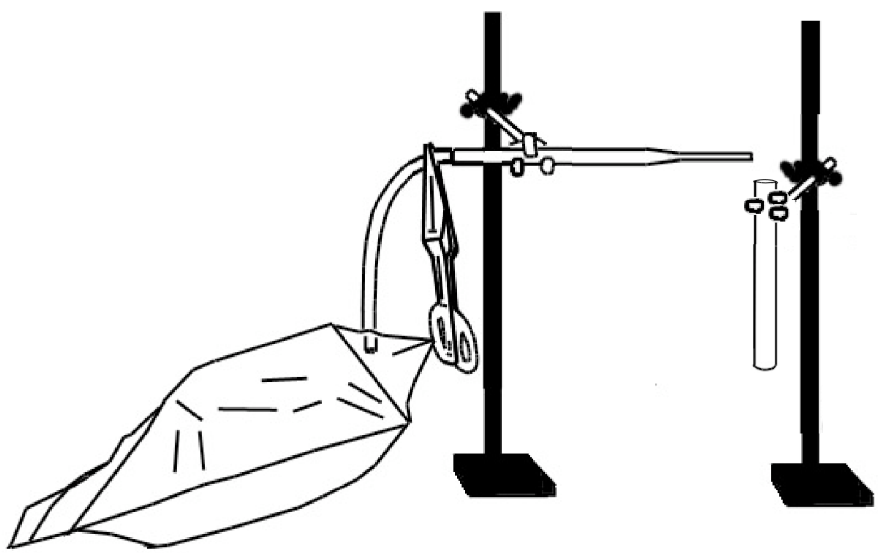

Figure. The apparatus ready for use. The gas bag is simply a plastic food storage bag with a length of tubing poked through a small hole in the bag.

A hemostat stops the flow of hydrogen until one is ready to begin. When it is time for the demonstration, one simply removes the hemostat and ignites the hydrogen issuing from the pipet. The flame is small and often difficult to see, but the heat it produced is easily detected 10 cm away and a piece of paper brought near the flame will ignite. Occasionally, the hydrogen flame will appear yellow due to the sodium in the glass pipet. Using the hemostat, an ice chip is held in front of the flame at close range so that the flame plays across the ice. The test tube is adjusted so that the drippings can be collected. It takes less than one minute to obtain 3 – 5 mL of solution. The flame will often burn a hole through the ice chip. The exact amount of solution collected can be determined by measuring the mass of the test tube before and after collection.

Balloon Option. In place of the plastic food storage bag, one may use a balloon pulled over a 1-hole stopper. A short piece of glass tubing of suitable diameter (8 mm) is inserted into the hole in the stopper; the other end of the glass tubing is inserted into the Latex tubing. The connection between the Latex tubing and glass pipet is the same as described above for the food storage bag. With the balloon option, the hemostat or pinch clamp is used to regulate the flow of hydrogen out of the balloon.

Testing the solution for hydrogen peroxide.

The use of a control is always important. In this case, simply fill a second test tube with a quantity of tap water equal to the amount of drippings collected or collect melt water from another ice cube.

Potassium permanganate test.

To each test tube, add several drops of dilute potassium permanganate solution (approx. 6.3×10^{-4} M $KMnO_4$). This will turn the distilled water pink-purple. In the test tube containing hydrogen peroxide, the permanganate will slowly, over the course of a minute or two, oxidize hydrogen peroxide to O_2(aq), but at this low concentration, bubbles are not noticed. Permanganate is reduced to either Mn^{+2}(aq), which appears colorless due to its low concentration (at higher concentrations, it would be pale pink) or to a yellow-brown color (Mn^{+4}), however, no precipitate of MnO_2 is detected. One may continue to add an equal number of drops of the $KMnO_4$ solution to both solutions until the test tube comprised of drippings starts to persist with a purple color. Color photographs of these results are available in the Supplemental Materials and at our gas chemistry website *(4)*.

Potassium iodide test.

Add 10 drops of a 1.0 M potassium iodide/starch solution to a test tube of collected drippings and to the control solution. The solution with the drippings containing hydrogen peroxide will become faintly blue within a minute and will continue to darken to an intensely deep blue over a period of five minutes. The solution should turn blue indicating the presence of $I_3^-(aq)$ produced by the reaction between KI(aq) and $H_2O_2(aq)$ *(5)*:

$$I^-(aq) + H_2O_2(aq) + H^+(aq) \longrightarrow HOI(aq) + H_2O(l)$$

$$HOI(aq) + 2\,I^-(aq) + H^+(aq) \longrightarrow I_3^-(aq) + H_2O(l)$$

$$2\,I_3^-(aq) + \text{starch} \longrightarrow \text{starch-}I_5^- + I^-(aq)$$

Color photographs of these results are available in the Supplemental Materials and at our gas chemistry website *(4)*.

Materials.

- 1-gallon (4 L) Ziploc (or equivalent) freezer-quality plastic bag
- two hemostats (or screw clamp and a test tube holder, forceps, tweezers, or equivalent)
- Latex tubing, 1/8-inch (3.175 mm) ID, 20 cm length
- two small ring stands with two clamps
- glass Pasteur pipet
- lighter or matches
- test tube, 18 x 150 mm, two
- graduate cylinders, 10 mL and 100 mL or volumetric flasks, 10 mL and 100 mL

Chemicals.

- hydrogen, (CAS Number 1333-74-0)
- potassium permanganate, 0.010 g, (CAS Number 7722-64-7)

- potassium iodide, 1.66 g, (CAS Number 7681-11-0)
- starch, (CAS Number 9005-25-8)
- ice chips

Instructions.

1. Prepare 6.3 x 10^{-4} M $KMnO_4$ solution. Dissolve 0.010 g $KMnO_4$ per 100 mL solution.
2. Prepare starch-iodide solution. Make a slurry of 1 g potato starch in 20 mL distilled water in a small beaker. Heat the slurry with stirring until the color goes from the opaque white to a translucent gel. Remove from heat. Prepare 1.0 M KI solution: dissolve 1.7 g potassium iodide, KI, in 10 mL water. For each demonstration, mix 3 mL KI(aq) with 1 mL starch.
3. Construct the gas bag from a 1-gallon plastic food storage bag by poking a pen or pencil through the middle of the bag. The hole should be smaller in diameter than the Latex tubing. Moisten the 20 cm length of tubing and work it through the hole in the bag. It will form a tight seal. Full details for preparing gas bags can be found in Part 22 of our microscale gas chemistry series in ***Chem13 News*** *(6)* or at our website *(4)*.
4. Obtain hydrogen from a compressed cylinder if available; it is convenient and the purity is good. Connect the Latex tubing directly to the gas regulator. Adjust the pressure to 100 kPa (1 atm, 15 psi) using the gas regulator knob. Use the flow valve to slowly discharge the desired amount of gas into the plastic gas bag. Do not overfill the gas bag. Seal the gas bag shut with the hemostat pinching the tubing as shown in the Figure. Hydrogen can be prepared by a simple method we have described in our aforementioned gas bag article *(6)*. Instructions are also available in our book *(7)* and at our website *(4)*. Gases prepared by this method contain small amounts of air but will not affect the outcome.
5. Assemble the entire apparatus as shown in the Figure.
6. Remove the hemostat and ignite the hydrogen issuing from the pipet. Keep flames away from the gas bag itself! You may need to press gently on the gas bag (or add a small weight on top of the bag) to discharge hydrogen at a suitable rate to sustain a flame.
7. Play the flame against the ice chip and collect 3 – 5 mL drippings in a clean test tube. Extinguish the flame by pinching the tubing with the hemostat.

8. Perform the chemical tests for hydrogen peroxide.

Safety Concerns and Hazards.

Always wear safety glasses! Hydrogen is highly flammable. Do not bring open flames in the vicinity of the gas bag of hydrogen. Do not use hydrogen where sparks are generated.

Supplemental Material

A Quicktime movie of this demonstration is available at *JCE Online* and at http://mattson.creighton.edu/HydrogenPeroxide/Hydrogen_peroxide.html. The movie was produced by Jiro Fujita of Creighton University.

Literature Cited:

1. A literature search produced over ten matches for "hydrogen" + "combustion" + "mechanism". Many were done by the Russians over the last 30+ years. In the following study, kinetic rate constants for several "elementary processes" of hydrogen combustion were determined: Balakhnin, V. P.; Gershenzon, Y. M.; Kondrat'ev, V. N.; Nalbandyan, A. B.; *Dolk. Akad. Nauk SSSR* **1966**, *170(5),* 1117 – 20.
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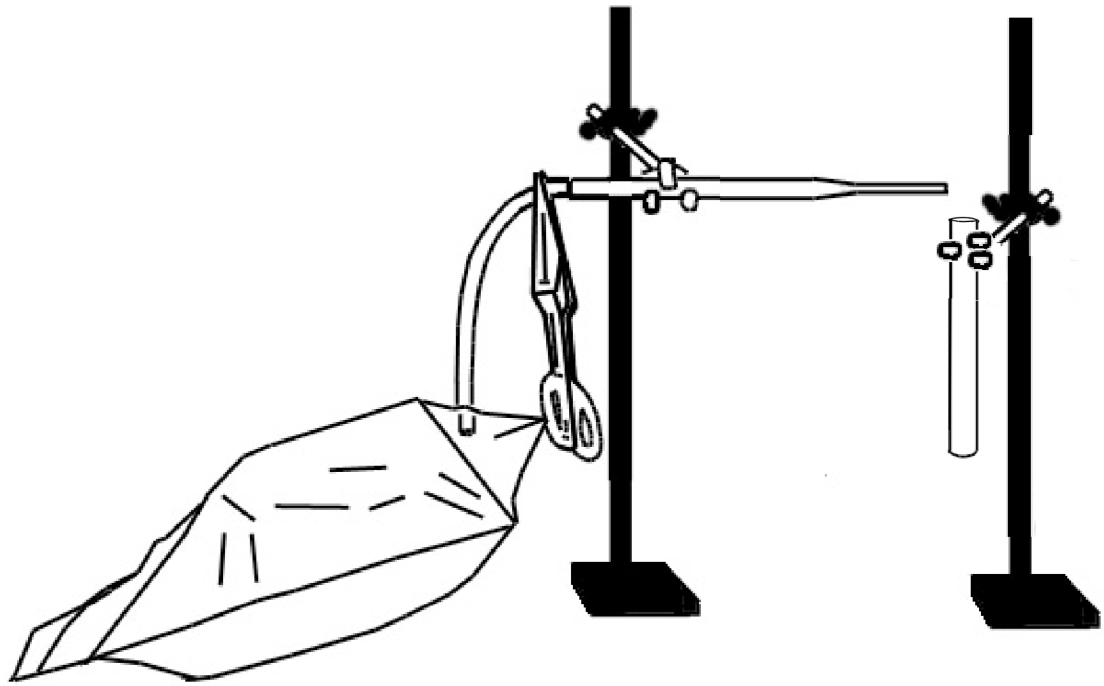

Figure. The apparatus ready for use. The gas bag is simply a plastic food storage bag with a length of tubing poked through a small hole in the bag.