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Acid Rain Demonstration: The Formation of Nitrogen Oxides as a By-Product of High-Temperature Flames in Connection with Internal Combustion Engines

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Many environmental and nonscience chemistry courses and general chemistry texts discuss the problems and chemistry of air pollution. These discussions tend to be abstract, and even science majors have difficulty visualizing the processes. Even though these subjects are mentioned frequently in the news media, there certainly is a lack of comprehension of just how combustion contributes to the air pollution in cities and urban areas. There is one related demonstration on acid rain, and it does not illustrate the formation of nitrogen oxides (*1*). The following demonstration shows the formation of nitrogen oxides resulting from a high-temperature flame.

Procedure

A large (6-liter) Erlenmeyer flask or equivalent vessel is filled with oxygen—preferably in the classroom, to increase the students' awareness. (A 2-liter Erlenmeyer can be used, but the results are less effective.) *Water displacement should not be used.* Nitrogen dioxide reacts with water to form colorless nitric–nitrous acid solution, thus defeating the purpose of the demonstration. Also, the students will not be able to observe the combustion product of water as it condenses on the glass surface and drips out the flask's mouth. The Erlenmeyer is inverted and placed on a ring stand as shown in Figure 1.

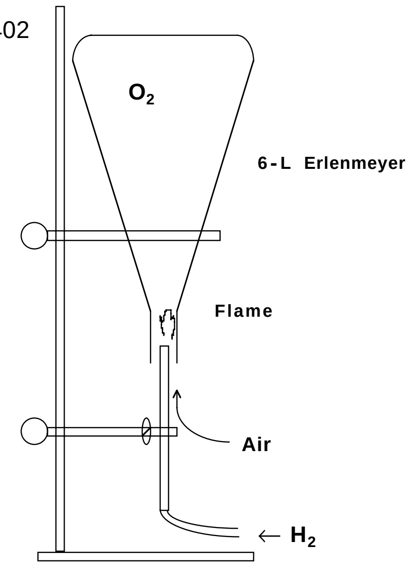

Figure 1. Suggested apparatus setup for demonstrating the formation of water and the side reaction products of nitric oxides.

Be sure the hydrogen delivery tube is flushed out to prevent any air–hydrogen mixture that could explode when one is igniting the hydrogen gas. A good way to ensure that this is done is to "light a hydrogen flame with a hydrogen flame." Place a medium-sized test tube over the outlet of the hydrogen delivery tube. If the delivery tube is filled with hydrogen, then the inverted hydrogen test tube can be lit with a Bunsen burner at a safe distance and the (still inverted) test tube can be returned to the hydrogen delivery tube to light the hydrogen exiting the delivery tube. If the tube has not been completely purged, then the test tube will "pop" and the flame will be out before it can be returned to the hydrogen delivery tube. The hydrogen is ignited at the tip of a glass tube connected to a tank via the usual tubing. The flame height should be adjusted to 2–4 cm. The flame is inserted between 2 and 10 cm into the mouth of the Erlenmeyer flask. There is no danger of a hydrogen–oxygen explosion, since hydrogen is the limiting reagent and merely burns in the oxygen as it would in air. The hydrogen flame is intense and burns at a higher temperature in pure oxygen. Normally hydrogen burns with a nearly colorless flame, but owing to the sodium compounds in the glass, the flame is brilliant orange, approaching the intensity of a sodium vapor lamp owing to the excited state of the sodium ions. The tip of the glass tends to melt and contract to a smaller opening. Also, the flame will many times make an oscillating sound. The pitch can be adjusted or the sound eliminated by raising or lowering the combustion tube. The combustion of hydrogen and oxygen naturally forms water.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l) \qquad (1)$$

As combustion continues, the condensation of the water is very evident even to a large class. The visual presence of water can be enhanced by collecting it on a brown paper towel as it drips from the mouth of the Erlenmeyer flask.

An interesting observation occurs with time: the contents of the flask becomes discolored with a light brown gas, which grows darker as combustion continues. The evidence of the brown gas can be enhanced by placing a white background behind the flask. One can ask the students to identify the product. If they are unable, they can be informed what the product is, or some of the products from the brown gas can be chemically investigated as suggested below. One should ask the students how there could be nitrogen dioxide when initially only oxygen was present in the flask.

Students are usually quick to explain that air is replacing the oxygen that is being burned, and the air is the source of the nitrogen. Even though the actual chemistry is very complicated, the basic reactions are:

$$N_2(g) + O_2(g) \rightarrow 2\,NO(g) \text{ colorless} \qquad (2)$$

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g) \text{ reddish brown} \qquad (3)$$

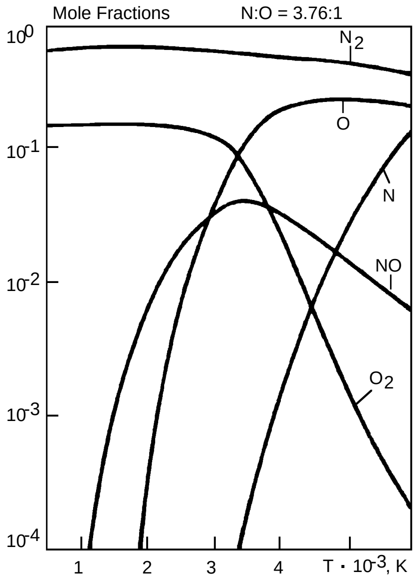

Figure 2. Equilibrium composition of nitrogen–oxygen system as function of temperature (*2*).

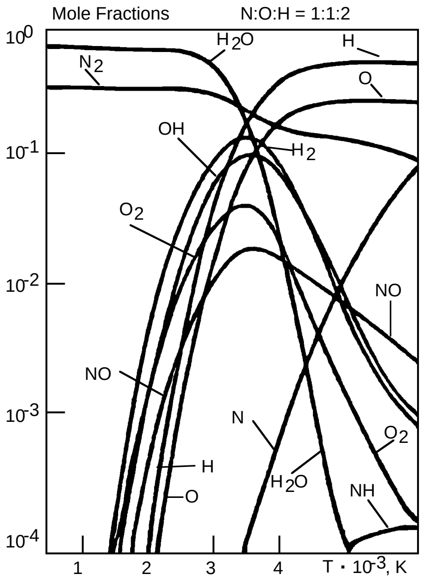

Figure 3. Equilibrium composition of hydrogen–nitrogen–oxygen system as a function of temperature (*1*).

After a short burn the hydrogen flame is removed and turned off. The flask is removed from the stand, and about 500 mL of water is added to the Erlenmeyer flask. The flask is capped and shaken. A brownish aerosol is formed, similar in appearance to the air over a large polluted city. The aerosol will dissolve slowly, usually by the end of a class period if the experiment is performed early in the period.

Two additional steps can be performed to enhance the learning experience. A 50-50 mixture of bromocresol green and thymol blue acid–base indicator (or any other acid–base indicator that will discriminate pH of acid solutions) can be added to a sample of the water used. The indicator will change to orange, suggesting a pH of about 2.[1] One can ask the students what this means. After a short discussion, students usually deduce that the nitrogen dioxide dissolves in the water to form an acid. Actually two acids are formed, nitric and nitrous.

$$2\,NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq) \qquad (4)$$

In addition, the solution's conductivity can be tested. The acidic solution conducts very well.

If one does not have access to hydrogen, natural gas can be substituted. It is not as satisfactory, since 50% of the product is gaseous CO_2, which does not condense. This results in 50% less nitrogen drawn into the flask, with production of less water and nitric oxide.

Safety

Caution: It is suggested that this experiment be performed in or near a hood, since NO_2 is quite toxic. Even though treatment may be administered, there can be residual injury. One should not be exposed to more than 25 ppm during 8 hours; 1/2 to 1 hour's exposure at 100–150 ppm or a few breaths at 200–700 ppm can cause severe pulmonary damage, which may prove fatal in 5–8 hours (*3*).

Disposal

The nitric–nitrous acid solution can be neutralized with excess sodium hydrogen carbonate and flushed down the drain.

Discussion

Nitric oxide (NO) does not begin to form in significant amounts until the temperature is around 1300 °C (*2*). As the temperature is increased, the concentration of the nitric oxide increases until 3100–3400 °C. At higher temperatures, the concentration decreases slightly. The temperature of the hydrogen flame is obviously much hotter than the 1300 °C threshold value. At stoichiometric combustion conditions, the hydrogen flame is around 3000 °C. Most internal combustion engines operate at high temperatures. Figure 2 plots the equilibrium concentrations of nitrogen, oxygen, atomic nitrogen, atomic oxygen, and nitric oxide versus temperature. Figure 3 illustrates conditions closer to those found in the demonstration, since water is present (*3*).

An interesting application of these principles has been applied by an enlightened company called Catalytica, Inc. (*4*). Their philosophy is to not just retrofit processes to eliminate pollution, but to design processes that do not produce pollutants. An example is the combustion of natural gas using a palladium oxide catalyst that holds the combustion temperature near 1300 °C; thus no nitric oxide is formed. If the temperature increases, the palladium oxide dissociates and the combustion process slows. Then the temperature decreases and more oxide is formed, stabilizing the temperature. This technology is being used in the construction of a huge power plant, eliminating the production of nitrogen oxides and with it the need for remedial chemical scrubbers.

Note

1. pH correlation with color for the 50-50 bromocresol green and thymol blue mixture:

Red	1	Orange	2
Yellow	3	Yellow-green	4
Green	5	Greenish blue	6–7
Bluish green	8–9	Blue	10

Literature Cited

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