

Laboratory Experiments on the Electrochemical Remediation of the Environment



Part 7: Microscale Production of Ozone

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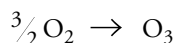
Ozone is a powerful oxidant and disinfectant. It has been used in Europe in drinking water treatment for over a century. Additional uses and advantages as an environmentally clean oxidant and disinfectant in water treatment and in several new processes in chemical and pulp industries have increased its popularity (1–10) (see Tables 1 and 2 in the Supplemental Material^W). Challenges encountered when using ozone include its hazards, cost, short decomposition time, and low solubility (6, 9, 11) (see Table 3 in the Supplemental Material^W).

Ozone Production

The main techniques used for the production of ozone are described below (for more details, see Table 4 in the Supplemental Material^W).

Corona Discharge (Silent Electric Discharge) Process

Air or oxygen is passed through an intense, high voltage (3,700–12,500 V), high-frequency alternating current field (6, 11). The discharge process forms ozone:



with a typical concentration range of 2.5 and 7.5% by weight when produced without mechanical refrigeration, depending on the use of air or oxygen, respectively. This is by far the most common way of producing ozone commercially.

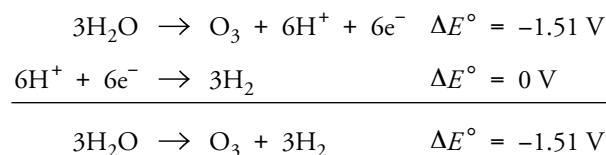
UV Irradiation

Ozone produced by UV-irradiation of air has a concentration in the range of a few thousand parts per million (8). This method is used for the production of small quantities of ozone.

Electrochemical Process

Because of the high capital costs coupled with low ozone concentrations involved in the methods of production just described, the electrochemical route has been sought as an

alternative (2–4, 6, 9, 12–20). (Advantages and challenges in using the electrolytic approach are summarized in Table 5 of the Supplemental Material.^W) PbO₂ grown on Ti or Pt substrates is the material of choice for electrode fabrication owing to the simplicity of preparation and good efficiency. The reactions involved in the electrolytic production of ozone are (6):



Note that dioxygen, $E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$, is also evolved at the anode.

Rationale

In light of these considerations and data, and since ozone destroys (oxidizes) organic materials whether they be rubber products that we do not wish to damage, organic contaminants in drinking water that we do wish to destroy, organic food colors, and so forth, it is clear that it would be important for students to be able to prepare and test ozone in a simple and safe way. Since the use of the traditional techniques (A and B) in a teaching laboratory is limited by equipment cost and safety requirements, we sought the electrochemical route to develop an experiment to produce and test ozone with simple equipment and materials. Here we describe an inexpensive and reliable method that generates microscale quantities of ozone in a steady-flow device so that ozone can be tested or used in a variety of experiments designed by the user. The device can be used to deliver ozone on demand (i.e., unplug the power source and you turn off the ozone; plug it back in and ozone is produced again). It is suitable for students taking general, inorganic, or introductory environmental chemistry laboratories.

Experimental

Fabrication of the Electrochemical Cell

A cell is made with a plastic transfer pipet (thin stem Beral pipet) as the container, 3 M H_2SO_4 as the electrolyte, a graphite rod from a pencil (or mechanical pencil) as the cathode, and a platinum wire as the anode. The power source is a 9-V battery or a suitable dc power source. An ice bath is required to prevent softening of the plastic pipet (it may even melt) owing to the high current passing through the system, and to increase the ozone yield (Figure 1). With this setup, 7–8 mL of gas/min is typically generated. The ozone produced can easily be detected by its odor and by direct contact with a moistened starch–KI indicator paper, which immediately becomes dark. If the reaction is to be done for more than a few minutes, the use of a fume hood is necessary.

Ozone Quantitation

The rate and quantity of ozone produced are analyzed by bubbling it through a solution containing I^- ions. This produces I_3^- ions, which then react with a standardized solution of $\text{S}_2\text{O}_3^{2-}$ to a colorless endpoint (i.e., to remove the color of the blue starch–KI indicator). The preparation of the solutions is given in the Supplemental Material.¹¹

Hazards

Ozone is explosive when concentrated, and its high oxidizing power promotes strong interaction (frequently leading to degradation) with surrounding materials. Its oxidizing action is nonselective. The electrolyte solution (3 M sulfuric acid) is corrosive and should be handled with care. Eye protection must be used. The acid solutions resulting from the experiments for ozone production may be neutralized and discarded down the drain. The rest of the solutions can be discarded according to local regulations.

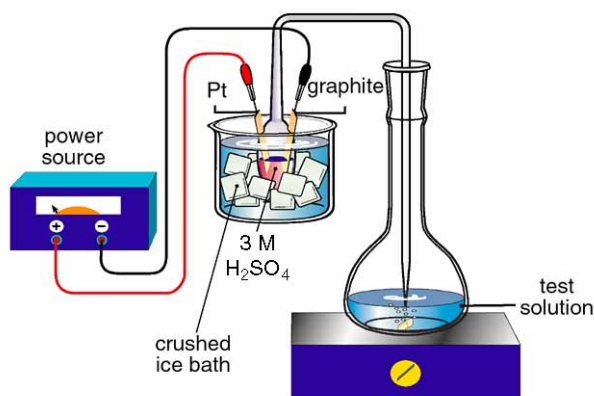


Figure 1. Electrochemical cell schematics and setup.

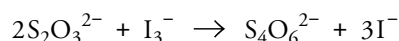
Results and Discussion

Determination of the Rate of Ozone Production

A volumetric flask containing KI, H_2SO_4 , and a few drops of aqueous starch solution is used for ozone collection. A moistened starch–iodide indicator paper placed at the mouth of the flask serves to establish that ozone loss due to diffusion is not occurring. A buret containing $\text{Na}_2\text{S}_2\text{O}_3$ solution is positioned above the mouth of the flask. As the ozone is generated, it bubbles through the KI(aq) to produce KI_3 (aq), which is blue in the presence of starch. The reaction is:



The titration with $\text{Na}_2\text{S}_2\text{O}_3$ solution can be conducted as the ozone is being generated with a new endpoint established as a function of time. The volumes of $\text{Na}_2\text{S}_2\text{O}_3$ solution required to attain the endpoints as a function of time for a typical ozone generator are given in Figure 2. The slope gives the rate of $\text{Na}_2\text{S}_2\text{O}_3$ solution added to be 0.311 mL/min. Given the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution (5.06×10^{-3} M), the rate of $\text{Na}_2\text{S}_2\text{O}_3$ added in terms of moles is 1.57×10^{-6} mol/min. The ionic reaction between KI_3 and $\text{Na}_2\text{S}_2\text{O}_3$ is:



Thus, the rate of KI_3 production is determined to be 7.85×10^{-7} mol/min. Given the reaction between ozone and KI to produce KI_3 (above), the rate of ozone production is determined to be 7.85×10^{-7} mol/min. The rate of all gases produced was determined to be 7.6 mL/min that corresponds to 3.1×10^{-4} mol/min at 300 K and 1 atm. Thus, ozone constitutes approximately 0.25% (or 2500 ppm) of the gases produced.

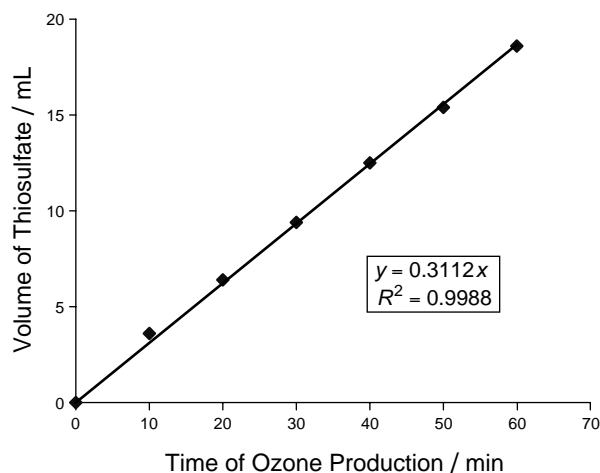


Figure 2. Rate of ozone production.

Reaction between Blue Food Coloring and Ozone

To observe the effect of ozone on some dyes, a solution of blue food coloring can be reacted with ozone. The absorbance is measured at $\lambda_{\max} = 630$ nm with a UV-vis spectrophotometer. The sample is then returned to the flask for continued reaction. Typical results are shown in Figure 3.

Reaction between Green Food Coloring and Ozone

Green food coloring is a mixture of blue and yellow. The yellow color is far less reactive towards ozone than blue, so that solutions of green food coloring turn yellow then colorless. In an experiment analogous to the one described above for blue food coloring, one can monitor the absorbance of green food coloring at its two absorption maxima wavelengths, 630 nm and 427 nm. Typical results are given in Figure 4.

Conclusions

We present a series of experiments for the production and testing of ozone in a laboratory session with simple equipment and materials.

^uSupplemental Material

Five tables describing details of the experiment and instructions for the students are available in this issue of *JCE Online*.

Acknowledgments

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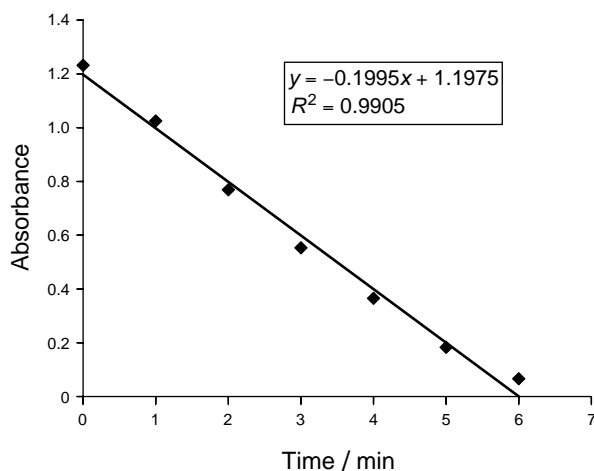


Figure 3. Absorbance decrease of blue food coloring with ozone.

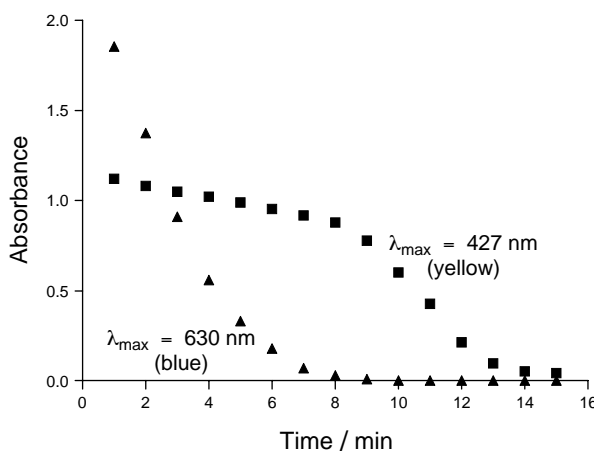


Figure 4. Absorbance decrease of green food coloring with ozone.

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