

Oxone/ Fe^{2+} Degradation of Food Dyes: Demonstration of Catalyst-Like Behavior and Kinetic Separation of Color

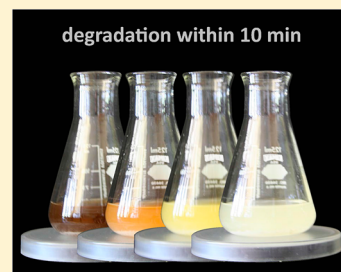
Ruth E. Nalliah*

Department of Chemistry, Huntington University, 2303 College Ave., Huntington, Indiana 46750, United States

S Supporting Information

ABSTRACT: A demonstration of the degradation of food coloring dyes by oxidation via the Fenton reaction can be substituted with a simpler demonstration using the oxidant oxone with iron(II) ions as an activator. The addition of small amounts of solid oxone and iron(II) sulfate to solutions containing mixtures of food coloring results in successive degradation of food dyes within minutes, also showing a kinetic separation of color. Because food dyes of different colors degrade at different rates, successive changes in color during degradation can be observed for various dye mixtures. Catalyst-like behavior is also demonstrated; in the absence of a transition metal such as iron to activate the oxone, negligible color degradation is observed within the time frame of the demonstration. The demonstration presents an opportunity to introduce topics such as structural characteristics of organic chromophores, the catalyst-like behavior of a transition metal, the practical importance of chemical kinetics, and challenges involved in finding eco-friendly methods of efficiently oxidizing pollutants, including not only waste dyes but also personal care products and excreted pharmaceuticals.

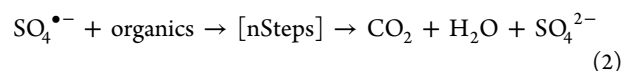
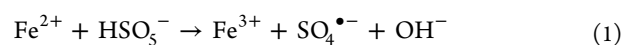
KEYWORDS: General Public, High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Analogies/Transfer, Catalysis, Dyes/Pigments, Free Radicals, Green Chemistry, Kinetics



Environmental awareness needs to be raised regarding the worldwide problem of unmetabolized drugs, personal care products, dyes, and a host of other products released into the waterways, remnants of which persist over time and remain in drinking water below therapeutic doses.^{1,2} Chemists continue to research economical, safe, and effective ways to degrade these substances at the point sources, without producing more toxic byproducts. Numerous means of degradation have been proposed, including the highly effective Fenton reaction involving hydrogen peroxide and iron(II) sulfate, first reported in 1894.³ A demonstration of food coloring degradation by the Fenton reaction has been published in this *Journal*.⁴ More recently, oxone (potassium peroxydisulfate, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), which has found many uses as an oxidizing agent in chemical reactions⁵ as well as in commercial swimming pool formulations, denture cleansers, laundry bleach, and other industrial applications,⁶ has been investigated along with transition metal activators for use in the degradation of pharmaceuticals and personal care products released in wastewaters.⁷ Oxone, although an irritant, has been described in the literature as an eco-friendly reagent that forms harmless potassium salts as byproducts.^{6,8} Practical advantages of oxone include availability in solid form, relative stability as a solid compared to other types of oxidizing agents, and the ability to function as an oxidizer without additional reagents for pH control.^{7,9} The oxone demonstration described here has the advantage of being performed by adding solids directly, with no weighing and minimal solution preparation.

The classic explanation for the degradation of organic compounds via oxone in the presence of a transition metal is

that oxidation occurs by the formation of several types of highly oxidative sulfate radical intermediates in solution,¹⁰ with a key step being the generation of the $\text{SO}_4^{\bullet-}$ radical in the presence of transition metals such as iron(II) (eqs 1 and 2)¹¹



Oxone alone has been shown to degrade crystal violet without an added metal,¹² however, with most degradation studies, a transition metal is added to speed up the oxidation process and has been described as having catalyst-like behavior.^{10,11} The behavior of the iron(II) is considered to be only catalyst-like because of iron speciation and precipitation; a species functioning completely as a catalyst would be fully regenerated during the reaction, and therefore, less of it would be required.¹⁰ Although the cobalt(II) ion has been shown to activate oxone more effectively than iron(II),⁷ the less toxic iron(II) ion accelerates degradation reactions of the food coloring dyes sufficiently fast that color changes occur within a few minutes, providing a time frame that is highly suitable for demonstrations.

Commercially available food coloring solutions provide readily available, easily disposable solutions of dyes that provide a vivid, visual indication of chromophore degradation. Because the dyes FD&C Blue 1, Red 40, and Yellow 5 found in common food coloring formulas degrade at different rates in

this reaction, kinetic separation of color can be observed using various dye mixtures, and a class can also be asked to predict the color changes for a mixture of three dyes during oxidation, based on observations with several other mixtures.

MATERIALS

The following items are needed:

- Solid oxone (CAS Number 70693-62-8, available from Sigma-Aldrich)
- Solid iron(II) sulfate (the anhydrous form is recommended and is available from VWR; the heptahydrate produces an undesirable orange color with oxone)
- Food coloring set containing FD&C dyes Blue 1, Red 40, and Yellow 5 (food dyes containing Red 3 are not recommended); or concentrated aqueous solutions of each of the above pure dyes, in droppers (CAS Numbers 3844-45-9, 25956-17-6, and 1934-21-0, respectively, available from Sigma-Aldrich)
- Deionized or distilled water
- Four Erlenmeyer flasks, 125 mL
- Two spatulas
- Two magnetic stirrers and four stir bars (recommended)

PROCEDURE

A few drops of green food coloring are added to deionized water (approximately 100 mL) in an Erlenmeyer flask (125 mL). Alternately, pure, concentrated aqueous solutions of Blue 1 and Yellow 5 can be added dropwise to give a visible green color. The solution is mixed and half of the solution is poured into another Erlenmeyer flask (125 mL) to make two identical solutions. Preferably, a stir bar is added to each flask and magnetic stirring is begun with each solution. A pea-sized portion of solid iron(II) sulfate is added to the solution in the second flask, which will turn cloudy. Then a pea-sized portion of solid oxone is added to each flask simultaneously (or nearly simultaneously) and the color is observed. The generation of sulfate radicals facilitated by the iron(II) ions in the second flask degrades the Blue 1 dye within the first several minutes, causing the solution to turn yellow, whereas the solution in the flask without the iron remains green. The yellow color begins to disappear after several more minutes, leaving the solution in the second flask a faint off-white (or nearly colorless with a white residue if the solution is left for a more extended time).

The oxidation can be repeated using a drop of red food coloring (or Red 40 solution) and a drop of blue food coloring (or Blue 1 solution). When both iron(II) sulfate and oxone are added to the purple solution, the Blue 1 dye degrades leaving the Red 40 dye; in turn, the remaining red color disappears more quickly than the remaining yellow color did in the previous green mixture. Students can then be asked to predict the color change sequence of a brown mixture formed by mixing the red, blue, and yellow dyes and can observe that the solution turns from brown to orange to yellow as the Blue 1 degrades first, followed by the Red 40 and then the Yellow 5.

The time scale of degradation can be controlled by the conditions. Faster degradation, which may be more convenient during class, is obtained using aqueous stock solutions of pure dyes than with the commercial household food coloring solutions used here, resulting in nearly complete loss of color within 6 min for the former, compared to a range of approximately 6–15 min for the latter. The Kroger brand food coloring solutions used in this experiment contained

propylene glycol, which may have been the cause of the decreased degradation rates, because it has been shown that alcohols with an alpha-hydrogen react with sulfate radicals.¹⁰ On the other hand, the commercial food coloring mixtures sometimes yield a more pronounced sequence of color changes due to the slower reactions, especially if a mixture of red and yellow is observed. In addition, if solutions are not stirred continuously, degradation rates slow significantly; if desired, a trial may be done without automatic stirring if the instructor wishes to demonstrate the effect of stirring on the rate. Tested variations on the demonstration are in the Supporting Information.

HAZARDS

Splash goggles should be worn. Because oxone is a significant skin irritant (corrosive), gloves are recommended for students working with the solid substance. The conditions of this demonstration do not necessitate the use of a fume hood. Final solutions are acidic (pH 2) and should be neutralized with about a teaspoon of baking soda prior to disposal. Because solutions contain iron at approximately 1000 ppm, local regulations may require dilution prior to disposal. If the reaction is deemed suitable for home-use with online chemistry laboratory kits, appropriate warnings should be given about the reaction of oxone with halides to produce halogen gas.

DISCUSSION

The demonstration allows an opportunity to display the chemical structures of the food dyes (Supporting Information) in order to show similarities among chromophore structures and discuss how the destruction of a chromophore, typically the conjugated parts of a dye molecule, results in loss of color. The rapid changes in color in the flask with added iron(II), compared to the mixture without iron(II), allows students to observe dramatically increased reaction rates caused by a catalyst-like substance, as well as rate differences caused by structural differences in the dye molecules. A reaction involving a mixture of colors can be set up during a portion of a class and other topics discussed as the reaction changes colors. The demonstration has been used to introduce the concept of chemical kinetics in a first-year undergraduate chemistry course, as well as to discuss applications of reaction rates in the kinetics portion of an upper-division undergraduate physical chemistry course. Students enjoyed participating in the predictive aspect of the demonstration, as well as discussing potential research applications described below.

A key purpose of the demonstration was to stimulate student thinking about the environmental research challenges of attempting to degrade excreted drugs at the point source. Students were reminded that because the human metabolism of pharmaceuticals is rarely 100% efficient, many types of excreted pharmaceuticals ranging from birth control pills to psychoactive drugs, as well as their metabolic byproducts, are currently being released into the environment at low but pervasive levels that can eventually result in tap water contamination.^{1,2} Because the reaction involving oxone and iron(II) has been shown to degrade pharmaceuticals and personal care products,⁷ students could be asked to think about the challenges involved in developing a product such as an automatic toilet bowl cleaner containing a solid oxidant mixture such as oxone and an iron(II) salt, which could be installed in homes and hospital rooms of individuals taking large quantities of prescription

drugs. To what extent could excreted pharmaceuticals be oxidized during or after a single toilet flush, and how could that be investigated? What might be some additional environmental, municipal, or septic tank problems caused by the resulting acidity of solution, the added iron, and reactions of other substances with various oxidation byproducts of the oxone reactions? What further research would need to be undertaken before this type of product should be recommended for release to the population? On the other hand, what advantages and disadvantages would be involved with routinely using oxone reactions in advanced oxidation technologies (AOT) at the water treatment plant?

■ ASSOCIATED CONTENT

📄 Supporting Information

Structures of the food color dyes FD&C Blue 1, Red 40, and Yellow 5 for use in presentations; a figure showing timed photographs of the demonstration; and results from other variations of the demonstration, including additional dyes that have been tested. This material is available via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rnalliah@huntington.edu.

Notes

The authors declare no competing financial interest.

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