

A Greener Chemiluminescence Demonstration

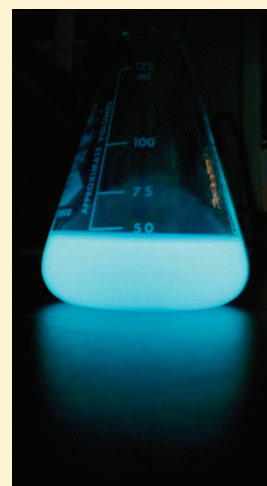
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S Supporting Information

ABSTRACT: Because they are dramatic and intriguing, chemiluminescence demonstrations have been used for decades to stimulate interest in chemistry. One of the most intense chemiluminescent reactions is the oxidation of diaryl oxalate diesters with hydrogen peroxide in the presence of a fluorescer. In typical lecture demonstrations, the commercially available oxalate diesters, bis(2,4,6-trichlorophenyl)oxalate (TCPO) or bis(2,4-nitrophenyl)oxalate (DNPO), are used. These compounds are dissolved in volatile, nonbiodegradable, and toxic organic solvents. The products of the chemiluminescent reaction are carbon dioxide and either 2,4,6-trichlorophenol or 2,4-dinitrophenol, both of which are aquatic and terrestrial toxins. To avoid these toxic pollution sources, we have designed an impressive chemiluminescent reaction employing divanillyl oxalate, 1.0 M NaOH, hydrogen peroxide, a fluorescer (e.g., perylene), and triacetin as solvent. The products of this “greener” chemiluminescent reaction are carbon dioxide and vanillin. Both vanillin and triacetin are biodegradable and possess minimal toxicity. This environmentally friendlier chemiluminescent reaction is visible in a darkened room for as long as 45 minutes.

KEYWORDS: Elementary/Middle School Science, First-Year Undergraduate/General, High School/Introductory Chemistry, Second-Year Undergraduate, Demonstrations, Organic Chemistry, Public Understanding/Outreach, Esters, Fluorescence Spectroscopy, Green Chemistry



Chemiluminescence is light emission from a chemical reaction. Peroxyoxalate chemiluminescence involves the reaction of oxalate diesters with hydrogen peroxide to generate unstable 1,2-dioxetanedione, which decomposes into electronically excited carbon dioxide (Scheme 1). The excited CO_2 transfers energy to a fluorescer or fluorophore, which releases light upon decay to the ground state.^{1,2}

Cyalume “light sticks” utilize this same chemistry for emergency lighting, fishing lures, and entertainment. The commercially available oxalate diesters, bis(2,4,6-trichlorophenyl)oxalate (TCPO) and bis(2,4-nitrophenyl)oxalate (DNPO), are typically used in both lecture demonstrations and laboratory experiments in chemiluminescence.^{3–6} However, the serious environmental toxicities of the products 2,4,6-trichlorophenol⁷ and 2,4-dinitrophenol,⁸ as well as exposure to potentially hazardous organic solvent vapors in an open air setting, have encouraged us to redesign this demonstration along greener lines. In our demonstration, hazardous solvents such as dichloromethane are replaced with triacetin, a low volatility, nontoxic, and biodegradable compound,⁹ and the oxalate diester is divanillyl oxalate **1**,¹⁰ which is readily prepared in one step from the artificial flavoring agent vanillin **2** (Scheme 2). In addition to CO_2 , the product of our chemiluminescent reaction is terrestrially nontoxic vanillin **2**.¹¹

DEMONSTRATION

Overview

This demonstration first requires the preparation of oxalate diester **1** by the instructor (Scheme 2). The reaction of **1** dissolved in triacetin (1,2,3-triacetoxypropane) with alkaline hydrogen peroxide in the presence of various fluorescers produces a

dramatic and colorful light display. Although toxic chemicals must be used to prepare **1**, there are no irritating solvent vapors in the lecture demonstration itself, and both the solvent and reaction products are biodegradable.

Chemicals and Glassware

Oxalyl chloride; vanillin; triethylamine; ethyl acetate; triacetin; perylene [peri-dinaphthalene or other fluorescers such as rubrene, tetracene, or 9,10-bis(phenylethynyl)anthracene]; 30% hydrogen peroxide; 1.0 M NaOH (aq); magnesium sulfate, anhydrous; 100% ethanol; deionized water.

Test tube (18 × 150 mm); 250 mL Erlenmeyer flask; magnetic stir bar; spatula; plastic pipet tips (100–1000 μL); manual pipettor (1000 μL).

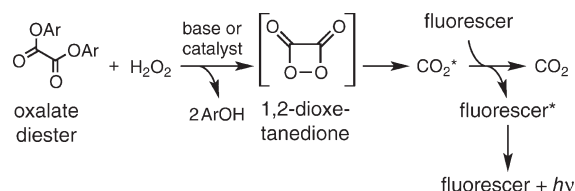
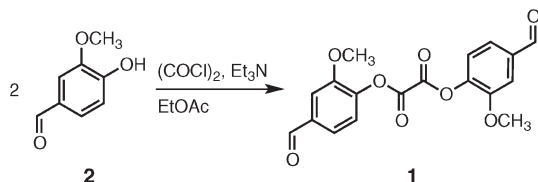
Preparation of Divanillyl Oxalate **1**

In a dry, 250 mL Erlenmeyer flask equipped with a magnetic stir bar, vanillin **2** (3.215 g, 21.13 mmol) is dissolved with stirring in 50 mL of ethyl acetate. Triethylamine (2.242 g, 22.16 mmol) is added and the solution immediately turns yellow. The flask is placed in an ice bath, and oxalyl chloride (1.334 g, 10.51 mmol) is added dropwise by pipet over a 5 min period. The reaction mixture is removed from the ice bath. After an hour, the reaction is quenched with 100 mL of deionized water and extracted with three 50 mL portions of ethyl acetate. The combined ethyl acetate extracts are washed with 150 mL of 1.0 M HCl(aq), then 100 mL of deionized water. The organic phase is dried with anhydrous MgSO_4 , gravity filtered, and rotary evaporated to a

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Scheme 1. The Peroxyoxalate Chemiluminescence Reaction

Scheme 2. Preparation of Divanillyl Oxalate **1** from the Artificial Flavoring Agent Vanillin **2**

light yellow solid. The crude product is recrystallized in 150 mL of 100% ethanol, producing a pale yellow crystalline solid (mp 208–211 °C). The structure and purity of **1** were confirmed by ^1H NMR and ^{13}C NMR spectra (see the Supporting Information) and elemental analysis. The yield was 2.776 g (74%).

Chemiluminescence Procedure

The demonstrator should wear gloves and goggles! After preparation of **1**, 21 mg of **1** is dissolved completely in 3.0 mL of triacetin in an 18 × 150 mm test tube (solution best premade due to slow dissolution of **1**), 6 mg of perylene is added, followed by 1.0 mL of 1.0 M NaOH(aq) by pipettor. Then, 1.0 mL of 30% H_2O_2 is added by pipettor and the room is darkened. The test tube, covered by a gloved finger, is vigorously shaken producing an intense greenish–blue light that lasts for 45 min. The same demonstration has been successfully scaled up in a 250 mL Erlenmeyer flask by increasing the quantities 10-fold and stirring the reaction mixture continuously with a magnetic stir bar. Replacement of triacetin and 30% H_2O_2 with ethyl acetate and 3.0% H_2O_2 increases the “naked eye” chemiluminescence longevity to at least 2.5 h in a darkened room.

HAZARDS

Oxalyl chloride is a lachrymator and can cause eye, lung, and skin damage. Triethylamine is caustic and foul-smelling and can cause eye, lung, and skin damage. The 30% H_2O_2 can cause burns and should be handled with gloves. If the demonstrator uses ethyl acetate instead of triacetin to increase chemiluminescence longevity, please note that ethyl acetate liquid and vapors can cause lung irritation and gastrointestinal disturbance and should be avoided. Wearing gloves, the demonstrator should decant ethyl acetate from a bottle in a fume hood into an Erlenmeyer flask and cover the flask with Parafilm before bringing the flask out of the hood. Perylene should also be handled with gloves because of potential skin irritation. Wear goggles and gloves when handling 1.0 M NaOH(aq) and 1.0 M HCl(aq) because these solutions can cause eye and skin burns. Triacetin and vanillin are both food additives; they do not cause skin irritation or have irritating vapors. Anhydrous magnesium sulfate is also safe to handle.

DISCUSSION

This demonstration successfully provides a dramatic chemiluminescence experience using greener materials. In the future, the development of a synthetic route to **1** that avoids toxic starting materials would make this entire process environmentally benign.

ASSOCIATED CONTENT

Supporting Information

^1H NMR and ^{13}C NMR spectra of divanillyl oxalate. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

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