BLEACHING WITH GREEN OXIDATION CHEMISTRY

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Introduction

Whether you're washing the dirt off your face, cleaning grease from your hands or removing the stain on your shirt, chemistry is at work, helping you to remove unwanted dirt, grease and stain molecules. Keeping clean is often about removing color. In essence, stains are color where you don't want it. Stain 'removal' is usually decolorizing, or bleaching, not complete removal of the stain molecules.

Most likely when you hear the word 'bleach,' you think of Clorox® laundry and household bleach (1). The active ingredient in bleach, the chemical sodium hypochlorite, keeps your T-shirts white and your bathtub sparkling. If you've ever spilled Clorox® on something colored, you know it can also turn your favorite red sweater, white. Alternative "non-chlorine" bleaches are also available. They contain hydrogen peroxide instead of sodium hypochlorite. The chemical hydrogen peroxide is also the bleaching agent in many hair dyes. Alone, peroxide gives the "peroxide blonde" color, but most permanent dyes use peroxide as well, either to remove natural dye in the hair or to activate the new dye (2).

Dilute hydrogen peroxide (3%) is also commonly found in medicine cabinets. It is used as an antiseptic for minor cuts and scrapes, and is also a good way to remove bloodstains from clothing. The bubbling that occurs when the peroxide encounters blood is due to its decomposition into oxygen gas and water (Eqn. 1).

$$H_2O_2 \rightarrow \tfrac{1}{2}\, O_2 + H_2O \qquad \text{(Eqn. 1)}$$

During this process, hydrogen peroxide oxidizes the colored compounds in the blood.

Oxidation

Oxidation is most generally defined as losing electrons, and reduction is gaining electrons. The two processes occur together, so one compound is reduced in the process of oxidizing another compound. Another definition of oxidation is the gain of oxygen atoms (Eqn. 2) or the loss of hydrogen atoms. Reduction is then the loss of oxygen atoms or the gain of hydrogen atoms (Eqn. 3).

Oxidation of Carbon:	$C + O_2 \rightarrow CO_2$	(Eqn. 2)
Reduction of Nitrogen:	$N_2 + 3H_2 \rightarrow 2\, NH_3$	(Eqn. 3)

The color of compounds is a physical property caused by the chemical structure of the molecules. When an oxidizing agent removes electrons, or oxidizes, a molecule, the chemical structure of the molecule is changed and the physical property of color is altered. The decomposition of hydrogen peroxide involves the formation of free radicals. These reactive intermediates oxidize other molecules by removing electrons or hydrogen atoms from them.

Peroxide Activator Catalysts

The research conducted by Terry Collins' group at the Institute for Green Oxidation Chemistry at Carnegie Mellon University (3) provides a fitting example of green chemistry, in keeping with this year's theme for National Chemistry Week, "Chemistry Keeps Us Clean." Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous materials. The principles of benign design, selective catalysis, energy efficiency, and pollution prevention are all incorporated into the design of this greener bleaching agent.

Professor Collins has developed tetraamido macrocyclic ligands (TAML®) that, coordinated with a transition metal, effectively catalyze hydrogen peroxide oxidation (4). An example of a TAML® oxidant activator is shown in Figure 1.

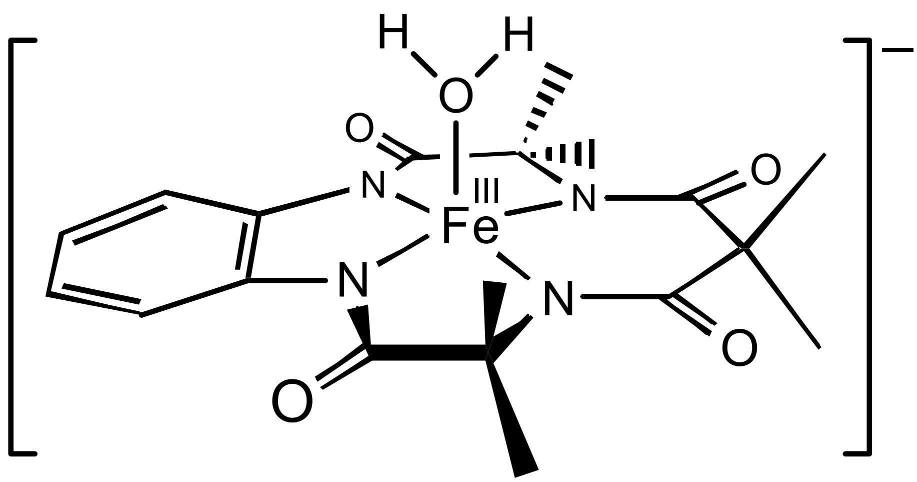


Figure 1: Structural example of a TAML® oxidant activator

His work received the Presidential Green Chemistry Challenge Award in 1999 (5). The TAML® oxidant activators offer an environmentally friendly alternative for chlorine-based bleaching processes. Made from natural biochemical elements, they are highly selective catalysts that reduce energy costs and not only prevent pollution, but are also useful in pollution remediation.

Motivation

In addition to common use as a household cleaner and hair dye, oxidative bleaching is also used in the pulp and paper, textile and laundry industries. Hydrogen peroxide (H_2O_2) is a greener alternative to chlorine (Cl_2), chlorine dioxide (ClO_2) and sodium hypochlorite (NaOCl) that are traditionally used for bleaching color from substances. In chlorine containing bleaches, oxidation often involves addition of chlorine atoms (rather than oxygen atoms) to the colored compound. For certain applications, the addition of chlorine leads to the formation of hazardous byproducts, such as dioxins, shown in Figure 2 (6).

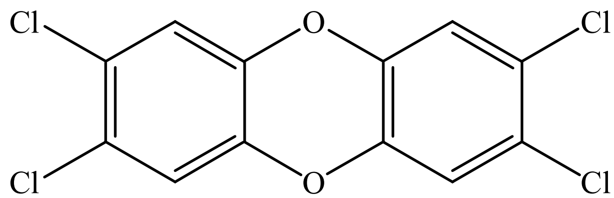


Figure 2: Structure of 2,3,6,7-tetrachlorodibenzo-4-dioxin

But hydrogen peroxide does not contain any chlorine atoms; it oxidizes by either adding oxygen or removing hydrogen atoms. Therefore, the oxidized compound cannot contain organo-chlorine type pollutants, and the problem of hazardous pollution is prevented at the source.

Challenges for Peroxide Bleaching

The challenge of replacing traditional bleaching agents with hydrogen peroxide is twofold. First, the peroxide oxidation process can be unselective. Since molecules exposed to hydrogen peroxide might encounter free radicals, their destruction rather than the desired oxidation may result. Second, successful bleaching with H_2O_2 requires higher temperatures and pressures and longer reaction time. This means higher costs for energy, equipment and labor for the process. The TAML® oxidant activators were designed to meet both of these challenges.

To avoid uncontrolled destruction of molecules, the catalysts were designed to favor a different intermediate in the oxidation process. The catalysts form activated peroxides that are still very reactive, but much more selective than the free radicals formed during the normal decomposition of hydrogen peroxide.

By its nature, catalysis lowers the energy requirement for a reaction. Using the TAML® catalysts lowers temperature and time requirements for the bleaching process. For the pulp and paper industry, this adds up to huge energy savings. The TAML® oxidant activators have been skillfully developed over the past 20 years to optimize the oxidation of compounds by hydrogen peroxide.

Applications of TAML® Oxidant Activators

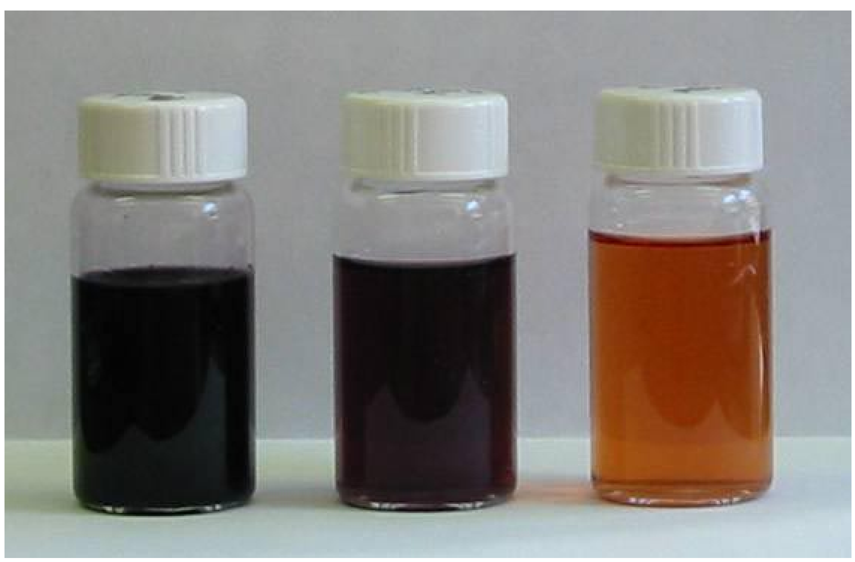
The cleaning applications of TAML® activators include bleaching the lignin in wood pulp (7), decolorizing the effluent from the pulp and paper and textile industries (8), and destroying free dye molecules in clothes laundering (9). Other practical applications in related areas are under investigation.

Lignin is a complex array of molecules that holds the cellulose in wood together. It is also responsible for the brown color of paper, like that used for paper grocery sacks. In order to get bright white paper, the lignin must be removed. The paper industry traditionally used chlorine for this purpose. In the past 10 years, most of the industry has moved to chlorine dioxide, which minimizes the formation of dioxins that result from chlorine treatment. Bleaching with TAML® activators and hydrogen peroxide offers another advance in the greening of the process, by completely eliminating the formation of dioxin waste.

Lignin is also responsible for the dark color associated with the effluent from paper mills. While the effluent from chlorine dioxide based delignification processes does not pose a high toxicity hazard, it is an aesthetic and environmental problem. TAML® activated peroxide treatment of the effluent removes most of the color, as shown by the photograph in Figure 3 (10).

Figure 3: 70% color reduction of paper mill effluent achieved using the TAML® activator and hydrogen peroxide.

TAML® activators have also been used with hydrogen peroxide to successfully decolorize the dyes in the effluent from textile mills. The photograph in Figure 4 (11) shows the significant removal of color achieved by the catalyzed oxidation.



A B C

Figure 4: Starting dye bath solution in dyeing jig (A), sample of dye bath solution after >90% of the dyestuffs have been transferred to the fabric (B), and the decolorized solution after using TAML® activator and hydrogen peroxide (C).

Very recently the TAML® technology has been applied to laundry. One of the challenges faced in reducing laundry water usage is the problem of dye transfer. The highly selective activator uses the peroxide present in some detergents to hunt and destroy free dye molecules, while leaving those dyes bound to fabric alone. You can wash your favorite red sweater with your bright white T-shirts and have both come out looking as good as new.

The catalysts developed by Professor Terry Collins and his colleagues at Carnegie Mellon University provide a superior example of the application of green chemistry to several practical cleaning and industrial processes. The principles of designing safer chemicals, using selective catalysis, improving energy efficiency, and preventing hazardous waste were applied in developing this greener chemical bleaching product.

References

(1) For more information about the science of Clorox® bleaching visit their Web Site: http://www.clorox.com/science/
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(9) Collins , T. J. "TAML® Oxidant Activators."
(10) Horwitz, Colin. Personal Communication, 17 September 2002.
(11) Ibid.