

## Green chemistry. Sustaining a high-technology civilization\*

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*Abstract:* By learning how to balance natural resource limitations and pollution prevention with economic growth, green chemistry will become the central science of sustainability. The elimination of persistent pollutants is vital for a sustainable civilization. To achieve this, the most important guiding concept is that the elemental composition of technology should be shifted toward the elemental composition of biochemistry. Oxidation chemistry is currently a prolific producer of persistent pollutants. Many arise from the use of chlorine, hypochlorite, or chlorine dioxide in large-scale oxidation processes. Oxidation chemistry can be greened by replacing these with catalyzed alternatives based on Nature's oxidizing agent, hydrogen peroxide. TAML<sup>®</sup> (TetraAmidoMacrocylicLigand) iron catalysts, which were invented at Carnegie Mellon University, are widely patented and are being developed to activate H<sub>2</sub>O<sub>2</sub> for commercial applications. TAML activators are water-soluble, easy to use, function well from neutral to basic pH, are not dominated by nonselective Fenton-like reactivity, are straightforward to synthesize, work effectively in minute concentrations, enable peroxide processes to occur at temperatures well below those of the processes targeted for replacement, and are amenable to modification for capturing novel selectivities. TAML activators are “dial-a-lifetime” catalysts: an activator can be chosen exhibiting a lifetime commensurate with the desired task.

### INTRODUCTION

In this abstract, we will focus on the broader philosophical content of the lecture delivered in New Delhi. The reader can obtain scientific details from the papers referenced and our patents.

The following questions are often raised. Can our civilization change so that individual and collective activities could be carried on into the indefinite future without undermining the welfare of future generations? Could the resulting sustainable civilization be technologically advanced? Science can neither provide all the answers nor know all the problems appropriate to these inquiries. Thus, the feasible ideal is an advanced civilization that does not knowingly compromise the future, what we might call a pro-sustainable civilization. And this is what we should determine to build. For if the goal is such a pro-sustainability, the objection that definitive sustainability is unattainable cannot continue to provide camouflage for resistance to eliminating polluting technologies or for throttling back on the consumption of nonrenewable natural resources. The sustainability predicament is calling us to think, mature, con-

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serve, educate, invent, cooperate, forego, legislate, and regulate our way toward a sustainable future [1]. This will require the profound engagement of original thinkers. Sustainability is now the most important single concept for universities and for other centers of reflection and discovery that can advance its cause.

Because sustainability is significantly determined by how we manipulate matter within the economy, the inventive leadership of chemists is vital to its future [2]. The newly forming field of green or sustainable chemistry is arising to confront the challenge [3]. Green chemists have three great evident fields to develop. First, renewable energy technologies will be the central pillar of a sustainable high-technology civilization. The contribution chemists can make here relates to the development of the economically feasible conversion of solar into chemical energy and the improvement of solar to electrical energy conversion. For example, if the efficiency of solar to electrical energy conversion could be increased by two- to four-fold from the current 10–20%, the sustainability of our civilization would indeed have been augmented greatly. Attaining safe energy sources is so crucial to the future that the chemical community should commit indefinitely a substantial portion of its creative energy to the area. Second, chemical feedstocks must increasingly be obtained from renewable sources to reduce our dependence upon fossilized carbon and to protect the atmosphere. Third, polluting technologies must be replaced by benign alternatives. In this presentation, we will focus on pollution reduction in general and on particular approaches developed by us.

## THE GREENING OF POLLUTING TECHNOLOGIES

Many forces give rise to chemical pollution, but there is an overarching reason why chemical technology pollutes. Most toxicity is elemental in origin. Chemists, when developing new processes, strive principally to attain selective reactions. Diverse reactivity is attained by employment of almost the entire periodic table. In contrast, Nature has to accomplish a huge range of selective processes to run biochemistry. But it does so primarily with just a handful of environmentally common elements. A sweeping reactivity profile is accomplished through a reagent design that is prodigiously more elaborate than the synthetic one. As one result of this strategic difference, our technologies often distribute throughout the environment elements that are toxic because they are used sparingly or not at all in biochemistry. Toxic elements form the first class of persistent pollutants; long-lived radioactive elements are especially dangerous examples. Degradation-resistant molecules form the second class of persistent pollutants. Again, as a result of the strategic difference, persistent molecular pollutants can arise when elements such as chlorine are employed on vast scales in technologies for which there is nothing comparable in Nature. Many examples from the chlorine industry happen also to be potently bioaccumulative [4]. These are the principal reasons why persistent pollutants have come to corrupt every recess of the environment and to pose the greatest chemical threat to the health of all living things.

Consider the organochlorine-persistent organic pollutants (POPs). Polychlorinated dibenzo-dioxins and -furans (PCDDs and PCDFs), called “dioxins” as a class, are perhaps the most deadly known POPs, [4]. They can form in processes such as the bleaching of wood pulp with chlorine-based oxidants, the burning or incineration of chlorine-containing compounds and organic matter, and the recycling of metals. The most toxic dioxin is TCDD, 2,3,7,8-tetrachlorodibenzodioxin, “which elicits a diverse spectrum of biological sex-, strain-, age-, and species-specific effects, including carcinogenicity, immunotoxicity, reproductive or developmental toxicity, hepatotoxicity, neurotoxicity, chloracne, and loss of body weight. These effects vary according to the age, sex, species, and strain of the animals involved” [5]. For example, TCDD was formed as a trace impurity in the production of 2,4,5-T, a once popular herbicide and a component of Agent Orange, a widely used defoliant in the Vietnam War. Exposure to TCDD is implicated in serious health problems among Vietnam veterans and the Vietnamese population [5]. The United Nations Environmental Program (UNEP) International Agreement on POPs lists twelve “priority” pollutant compounds and classes of compounds for global phase-out. All are organochlorines: Aldrin, DDT, Dieldrin, Endrin, Chlordane, Heptachlor, Hexachlorobenzene, Mirex,

Toxaphene, PCBs (polychlorinated biphenyls), PCDDs, and PCDFs [4]. The elimination of persistent pollutants should be green chemistry's number one objective in the pollution reduction area.

A reasonable metaphor for seeing the danger of the persistent pollutant comes from imagining that the chemistry of the ecosphere is like the mail sorter's wall of letter slots in a post office, but with the network of compartments extending virtually to infinity [2]. In this analogy, each compartment represents a separate chemistry so that, for example, thousands of compartments would be associated with a human cell or with stratospheric chemistry. An environmentally mobile persistent pollutant can move from compartment to compartment entering a large number and finding those that it can perturb. Most alterations are probably inconsequential, but others have caused unforeseen catastrophes such as the ozone hole or some of the manifestations of endocrine disruption [4,6]. Most compartments have not been identified. The chemistry of a persistent pollutant in any given compartment usually cannot be foreseen. Considerations such as these should confer reason for copious scientific humility. Because we simply cannot predict ecospherical impacts, we should never forget the precious lessons from our past that persistent pollutants are capable of environmental mayhem and treat them forevermore with extreme caution.

Oxidation chemistry has been a prolific producer of persistent pollutants. Many technologies invented in the last century have relied on the chemistry of elements such as chromium, lead, and mercury that exhibit potent toxicities. But none may have caused more widespread pollution by POPs than chlorine, which in its common natural state as the chloride ion is nontoxic. Chlorine and chlorine-based (hypochlorite, chlorine dioxide) oxidations have been and continue to be practiced on vast scales in pulp bleaching, water disinfection and decontamination, and cleaning [4]. These processes usually produce huge volumes of effluent containing trace and sometimes unmeasurable (but present by implication of well-understood chemistry) quantities of organochlorine POPs. Several factors combine to make highly diluted organochlorine POPs extremely dangerous. First, the effluent streams involved are often vast. For example, a large pulp mill can produce more than 100 M gallons of effluent per day. Second, the POPs end up in natural waterways and often also in the atmosphere from which bioaccumulation may concentrate them in the food chain to the point that serious toxicities become evident. This is how endocrine disrupting chemicals (EDCs) were discovered [4,6]. EDCs may well present a much more serious health threat than carcinogens.

### Catalysts for the greening of oxidation chemistry

Chemists can substantially green oxidation technology by inventing catalysts for the activation of Nature's principal oxidizing agents, oxygen and hydrogen peroxide, and using these to develop new technologies to substitute for chlorine-based processes. To be successful, these new processes must also be more profitable than their chlorine-based targets such that the environmental way can become the most profitable way.

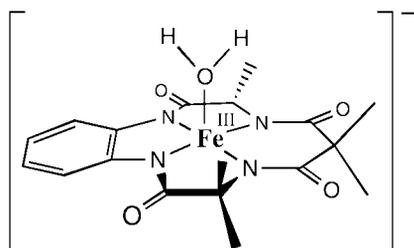
Over the last two decades, we have invented and developed catalysts for activating hydrogen peroxide to give new technologies for numerous fields-of-use [7–12]. They are called TAML activators, and the catalysts have been extensively patented over the last several years. There are two central design features. First, ligand donor groups had to be found which would make the higher oxidation states of metals such as iron ( $\text{Fe}^{\text{IV}}\text{--Fe}^{\text{VIII}}$ ) more accessible. Iron is the element most used in biochemistry to catalyze oxidation processes. Therefore, it is also the least toxic and most important catalytic element for green oxidation technology. To produce useful catalysts, we hypothesized that the electronic structure of the iron had to be reshaped by the ligand set to avoid Fenton chemistry, a catalytic activation of peroxides found for iron salts in water. Fenton chemistry results in the production of highly reactive oxyl radicals that are generally incapable of selective chemistry. We instead needed to produce cytochrome P-450-like metal oxo- or peroxy-reactive intermediates. To allow easier access to oxidized states of iron found in P-450 and to give catalysts with useful lifetimes, the ligand donors had to possess the somewhat mutually conflicting properties of being strongly electron releasing to the metal while also being

resistant to oxidative destruction. The donors also had to be suitable for incorporation into a chelating system to maximize the hydrolytic stability of derivative complexes. Based on leading work of Dale Margerum [13], we have found that secondary organic amides strike a useful balance of the required electronic properties. The *N*-amido donors are also suitable for the production of macrocyclic chelating ligands. By comparison with the chemistry of acyclic tetradentate ligands studied in our program, we can state that macrocycles are critical for achieving for iron the essential resistance to hydrolysis.

Second, the extended body of any chelate system must also be resistant to oxidative degradation. We followed a design loop for 15 years to achieve useful catalysts. The design loop started with the development of a ligand system that we thought would be suitable. A metal complex would then be produced and oxidized until ligand oxidative decay occurred. We would then characterize the ligand degradation products to understand the degradation process. Based on this understanding, we would next produce a modified ligand system in which the sensitive site was replaced with a group thought to be more oxidation resistant and then we would repeat the cycle. While it was clear from the outset that the approach could not be predicted to succeed, our ligand systems did indeed slowly become progressively resistant to oxidative decay, and the approach did lead eventually to remarkably useful catalysts.

#### *TAML activators and their properties*

The prototypical TAML activator is shown in Fig. 1. TAML catalysts activate hydrogen peroxide to give alternatives to polluting chlorine-based technologies, as well as totally new oxidation processes. They are water-soluble, easy to use, and work over a broad pH range. They lead to highly selective chemistry in commercial processes such as pulp bleaching where selectivity is vital. They are straightforward to synthesize in scalable processes and are amenable to modification for capturing novel selectivities. They should be very economical for virtually any application when bulk produced. They are effective in minute concentrations (commonly  $\mu\text{M}$  to nM) and are capable of more than 10 000 turnovers per hour in processes that use virtually all the peroxide for the targeted task; the efficiency is dependent on the conditions employed. Peroxide processes based on TAML activators can work well below the temperatures commonly encountered in chlorine-based counterpart processes, thereby promising significant energy savings. Extensive studies have shown that TAML-activated hydrogen peroxide is useful, for example, in bleaching dye-containing effluent from textile mills, in bleaching the “color” found in the effluent from chlorine dioxide pulp bleaching plants, for inhibiting dye transfer in laundry applications, for destroying organochlorine pollutants such as chlorinated phenols, and for the bleaching of wood pulp itself. TAML activators are the first “dial-a-lifetime” catalysts whereby the catalyst can be chosen such that it will perform the desired task and then destroy itself; “dial-a-lifetime” catalysis is an important green design concept. Currently, the effective lifetime of TAML activators ranges from seconds to several hours. The activators are comprised exclusively of the elements of life, C, H, N, O, Fe (chlorine-substituted macrocyclic ligands are also valuable for academic studies). Demand for TAML activators should range across an array of large oxidation-centered fields leading to economies of scale in production and marketing costs.



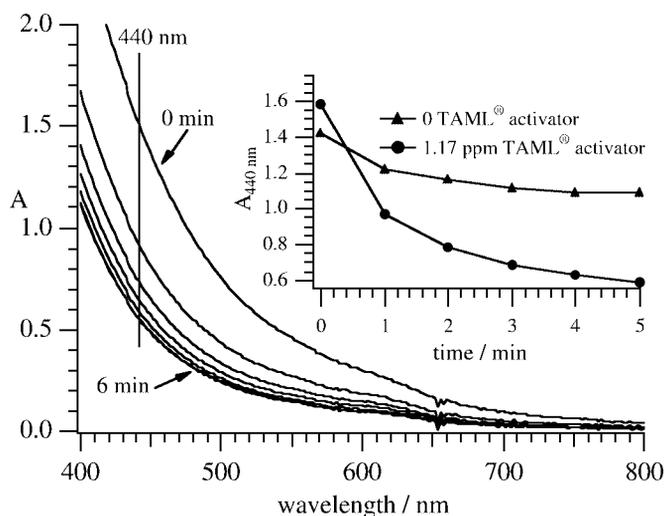
**Fig. 1** A TAML activator.

*TAML-activated H<sub>2</sub>O<sub>2</sub> in the bleaching of effluent from the textile industry*

Through a collaboration with the Office of Technology Assistance of the Massachusetts Executive Office of Environmental Affairs we have begun field trials to determine the ability of TAML-activated peroxide to bleach waste dyestuffs in the effluent streams of textile and paper companies in Massachusetts. While the contents of individual waste streams are confidential, we have been achieving remarkable results, which we can describe in general terms for one candidate company. In the first type of trial, samples of the effluent streams of a textile dyeing plant were collected directly after they had been expelled from the dyeing vats. The samples, which contained complex mixtures of green, orange, and black dyes were treated with TAML-activated peroxide ( $T = 25\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 10$ ,  $2 \times 2.4\text{ }\mu\text{M}$  additions of Fig. 1. TAML activator at  $t = 0$  and  $t = 10$  min.,  $7\text{ mM H}_2\text{O}_2$ , total time = 30 min). The reduction in color was determined by integrating the area under the visible absorption spectrum from 400 to 800 nm before and after treatment and was found to lie in the range of 70 to 80%. In the second type of trial, samples were extracted from a 300 000-gallon aeration basin in which waste streams containing hundreds of components had been collected and forcibly aerated over a period of six months. These black mixtures contained considerable quantities of solid material. Treatment of nonfiltered samples with TAML-activated peroxide ( $T = 35\text{ }^{\circ}\text{C}$ ,  $\text{pH} \approx 10$ , 25 gal. effluent,  $3 \times 1\text{ ppm}$  additions of Fig. 1. TAML activator at  $t = 0$ ,  $t = 13$ , and  $t = 35$  min,  $825\text{ ppm H}_2\text{O}_2 \equiv 78\text{ mL } 35\%$ , total time = 55 min) resulted in both a reduction in the color of the suspended solids and a bleaching to ca. 50% of the color of the soluble dyes in the 400 to 800 nm region of the spectrum.

*TAML-activated H<sub>2</sub>O<sub>2</sub> in the bleaching of color from chlorine dioxide pulp bleach plants*

Because of time constraints, the use of TAML/H<sub>2</sub>O<sub>2</sub> to bleach wood pulp was not discussed in the lecture. However, we highlighted that TAML/H<sub>2</sub>O<sub>2</sub> is able to substantially reduce color in effluent streams from the bleach plants of chlorine dioxide mills. There appears to be no remotely competitive alternative to the remarkable process we have discovered. It has great potential to cost-effectively increase the desirability of water recycling in mills and to allow mill operators to meet the many stringent regional regulations that are developing around the effluent problem of "color". In a matter of minutes at room temperature, TAML/H<sub>2</sub>O<sub>2</sub> can bleach color from 50–90% depending on the nature of the effluent stream. For example, bleaching of color in a D<sub>0</sub> filtrate, the most heavily contaminated with lignin



**Fig. 2** The bleaching of a D<sub>0</sub> filtrate. Conditions: TAML in Fig. 1 = 0.67 mM,  $[\text{H}_2\text{O}_2] = 7.6\text{ mM} \approx 0.20\text{ g}\cdot\text{L}^{-1}$ ,  $T = 23\text{ }^{\circ}\text{C}$ , color change 2439 to 914 pccu, pH adjusted 10.35.

bleaching byproducts, proceeds to 62.5% in 60 min. under the conditions shown in Fig. 2—almost all the bleaching occurs in the first 5 min.

#### *TAML-activated H<sub>2</sub>O<sub>2</sub> in the destruction of chlorinated phenols*

The ability of TAML/H<sub>2</sub>O<sub>2</sub> to destroy chlorinated phenols was described in the lecture.

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