

# TAML Oxidant Activators: A New Approach to the Activation of Hydrogen Peroxide for Environmentally Significant Problems

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## ABSTRACT

In the Institute for Green Oxidation Chemistry, we develop oxidation catalysts with useful lifetimes via an iterative design process in which oxidation-sensitive ligand groups are identified and replaced. The process has led to catalysts with greatly enhanced stability toward oxidative and hydrolytic degradation. The iron catalysts described herein can be comprised exclusively of biochemically common elements. They are efficient and selective peroxide activators for many areas of technology. They are water-soluble and are effective in minute quantities (nanomolar to low micromolar) over a broad pH range. Various green chemistry applications are sketched.

## Introduction

Many scholars believe that our civilization, as it is currently operated, is not sustainable. For example, the late Hans Jonas has argued eloquently that our ethical foundations need to be revised to guide us to build a sustainable future in the technological age.<sup>1</sup> Paul Hawken and the Lovins have proposed numerous ways that technology should be practically adjusted to favor sustainability.<sup>2</sup> A number of authors have highlighted Theo Colborn's revolutionary insight into the dangers of substances that interfere with hormonally controlled biological processes.<sup>3,4</sup> The writings of these authors and other like-minded scholars belong at center stage in the thinking and educational activities of chemistry. While a separate group of scholars think that sustainability concerns are exaggerated, in my opinion, sustainability is the single most important idea for universities for the next century.<sup>5,6</sup>

Terry Collins is the Thomas Lord Professor of Chemistry at Carnegie Mellon University, where he directs the Institute for Green Oxidation Chemistry. He is an Honorary Professor at the University of Auckland, New Zealand. He was born in Auckland on October 12, 1952. He earned his B.Sc. (1974), M.Sc. (1975), and Ph.D. (1978) degrees from the University of Auckland, where his graduate advisor was Warren R. Roper. After postdoctoral work at Stanford University with Jim Collman, he joined the faculty of Caltech in 1980 and the faculty of Carnegie Mellon University in 1987. Among his research awards is the 1998 Presidential Green Chemistry Challenge Award. He has written and lectured widely on the possibilities before chemists to develop vibrant new economies to promote sustainability. His research program is focused on greening oxidation technologies by designing nontoxic catalysts for activating natural oxidants, especially hydrogen peroxide, for nonpolluting oxidations. He is an Associate Editor of the journal *Green Chemistry*. His catalyst design work has overlapped with the design of molecular magnetic compounds.

Certain components of the sustainability quandary are obvious. First, while the unparalleled potency of contemporary science has enabled our technological achievements to tower above those of prior civilizations, the more novel of our difficulties originate from this same power. Second, we have been rapidly consuming the planetary endowment of nonrenewable resources on which so much of our technology depends while simultaneously emitting polluting substances at unprecedented rates. Third, persistent pollutants, especially those that are also bioaccumulative, present serious threats to the health of humans and other occupants of the ecosphere. Fourth, a number of the worst of these agents are substantially or completely of anthropogenic origin. Thus, while science and technology now significantly define our civilization, certain associated characteristics present forbidding downsides. Sustainability oriented scientific research and especially green chemistry can help us to systematically eliminate these downsides.<sup>7</sup>

Before embarking on arguments for technological fixes, I affirm that wealthy countries and particularly the United States need to change their attitudes and policies to favor the more conservative use of natural resources, especially nonrenewable ones, and I acknowledge that avoiding hypocrisy in this area is challenging. But many important sustainability-oriented adaptations of the technology base will not occur without the participation of chemists. In addition to emphasizing conservation, we can and should progress by inventing new ways of manipulating matter within the economy. Chemists are the master manipulators of matter. We have the ability to thoughtfully create new compositions of matter and processes specifically to cope with the technological problems of sustainability.

The central mission of green chemistry is to invent new processes that do not pollute to replace incumbent polluting technologies. Simple principles of common sense that translate into both practical chemistry and practical justice are the basic fabric of green chemistry. They have been expounded by Paul Anastas and John Warner as the "principles of green chemistry".<sup>7</sup> Almost everyone wins from green chemistry. Successful green chemistry will strengthen public confidence in the integrity of the chemical research community while it removes from industry many of the burdens associated with waste disposal and environmental regulatory compliance. It will also lead to a sea of change in chemical education since green chemistry is replete with multidisciplinary challenges that have as their goal the creation of valuable new technologies to promote sustainability. The three biggest chemical sustainability challenges pertain to developing new technologies for (a) solar energy conversion to electrical or chemical energy, (b) pollution elimination, and (c) renewable chemical feedstocks.<sup>5</sup> As one example, it has been claimed that every 20 days, the Earth receives from sunlight the energy equivalent of the entire estimated planetary reserves of oil, coal, and natural gas.<sup>8</sup> Safe energy

is all around us, simply waiting for chemists and other scientists to invent efficient, nonpolluting ways to capture and deploy it.<sup>6</sup> As another example, by moving the elemental balance of technology closer to that of biochemistry, chemists will eliminate much of the pollution attributable to chemical technology<sup>9,10</sup> and avoid spreading elements through the ecosphere that are unfamiliar to biological processes and often toxic as a consequence.

In the historically polluting field of oxidation chemistry, broader use of Nature's major oxidants, oxygen and hydrogen peroxide, could significantly reduce the environmental burden of persistent pollutants, many of which are produced from metal- and chlorine-based oxidation processes.<sup>11</sup> In addition, with the availability of effective catalysts, both oxidants have immense potential in cleanup applications for eliminating toxic and polluting substances and undesirable organisms. I will show here that our Institute is contributing to realizing this potential for hydrogen peroxide. In the tradition of *Accounts of Chemical Research*, I will focus on my group's/Institute's work. In 1994, I published an Account in this journal describing our 1980-initiated ligand design approach aimed at attaining better oxidation catalysts.<sup>12</sup> By 1994, we had learned how to make high oxidation state and strongly oxidizing middle and later transition metal compounds that are stable. The work had culminated at that time in a set of rules for guiding the design of oxidation-resistant ligands suitable for supporting resilient oxidation catalysts.<sup>12</sup>

In the intervening years, we have continued to follow the same ligand design strategy and have succeeded in attaining practical, efficient, and selective catalysts for activating hydrogen peroxide in an ideal manner for greening specific global chemical technologies as well as for cleanup processes. Our catalytic oxidant activators have been trademarked in the USA and Europe as TAML (for tetraamido macrocyclic ligand) activators. TAML activators and their uses are becoming extensively patented in many parts of the world.<sup>13</sup> Recently, Craig Jones has written an excellent monograph on hydrogen peroxide chemistry.<sup>14</sup> Hydrogen peroxide is a key reagent in numerous enzymatic oxidations. With an annual production of more than 1.3 million tonnes, H<sub>2</sub>O<sub>2</sub> is also an important commodity chemical for industrial oxidations. The search for useful peroxide catalysts has involved numerous groups for many decades, and important catalyzed processes have been developed in such fields as fine chemical syntheses, environmental applications, chemical purification, and hydrometallurgy.<sup>14</sup> However, in contrast with biochemical processes, catalysis is still significantly absent from industrial peroxide technologies, especially from the really large-scale processes that are found in pulp and paper manufacture, household laundering, industrial and institutional cleaning, and water disinfection, and much more is possible in environmental cleanup applications. In addition, better peroxide catalysts could contribute to the fields of commodity and specialty chemical syntheses, petroleum refining, and to the decontamination of chemi-

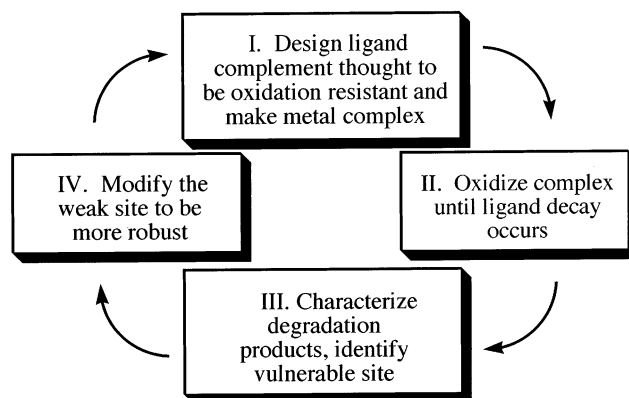


FIGURE 1. Design loop followed for obtaining oxidation-resistant ligands.

cal and biological terrorism and warfare agents, among other fields.

TAML oxidant activators have been designed such that they can be composed entirely of principal biochemical elements, C, H, N, O and Fe, and be devoid of toxic functionalities.<sup>9</sup> This allows one to plan, as much as is possible, to substitute an environmentally deleterious technology with an environmentally safe one. TAML activators are being widely studied by industry in diverse fields-of-use and are currently undergoing industrial scale-up syntheses. Their potential to advance the pollution reduction mission of green chemistry forms the underlying theme of the rest of this Account. Continuing on from the 1994 Account, the design history, nature, properties, and behavior of TAML catalysts and the research aspects of their reduction to practice for selected technologies will be described briefly. I will also sketch various studies that have formed the basis of patent applications or recently published patents where journal manuscripts are currently being prepared.

## The Design of Peroxide-Activating Catalysts

Tetradentate ligands were chosen for development to leave one to two coordination sites on a transition metal ion available for coordination and activation of hydrogen peroxide.<sup>15</sup> To apply catalyzed peroxide for most applications, one must first design the catalyst to avoid the Fenton chemistry that occurs when metal ions such as ferrous or ferric iron interact with peroxides, especially in water.<sup>14</sup> This complicated chemistry is characterized by the liberation of oxygen, noted for example when peroxide is used to disinfect wounds, coupled among other likely reaction channels to the production of hydroxyl radicals. The hydroxyl radical is a potent H-atom abstractor—the O–H bond of water at 119.6 kcal·mol<sup>-1</sup> is much stronger than most C–H bonds. Consequently, most abstractions of H• from carbon by OH• are exothermic. Thus, Fenton chemistry is superb for disinfecting and cauterizing wounds, but it is not selective enough to be useful for most technologies and tends instead to bring about the oxidative decomposition of organic compounds.

For broadly valuable catalysis, one wants instead for a metal ion to produce with peroxide another type of

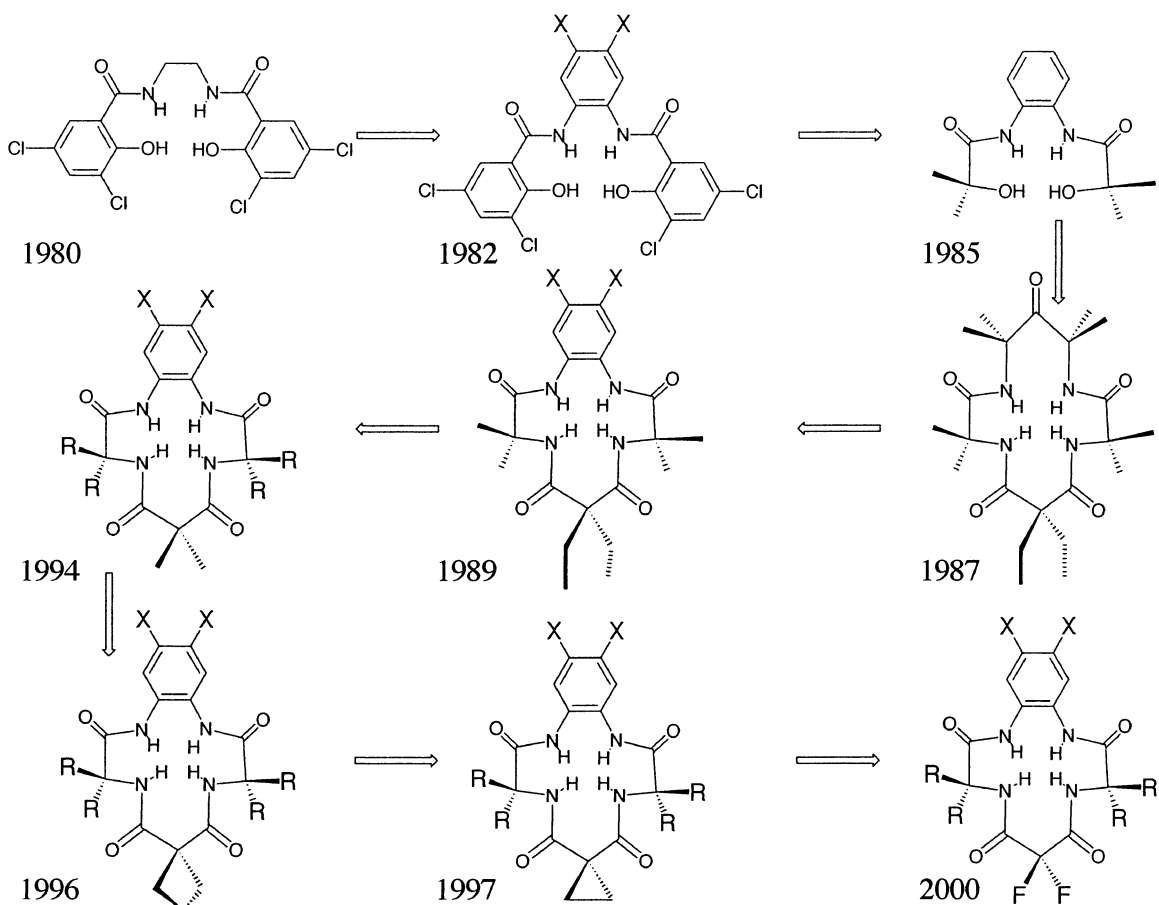
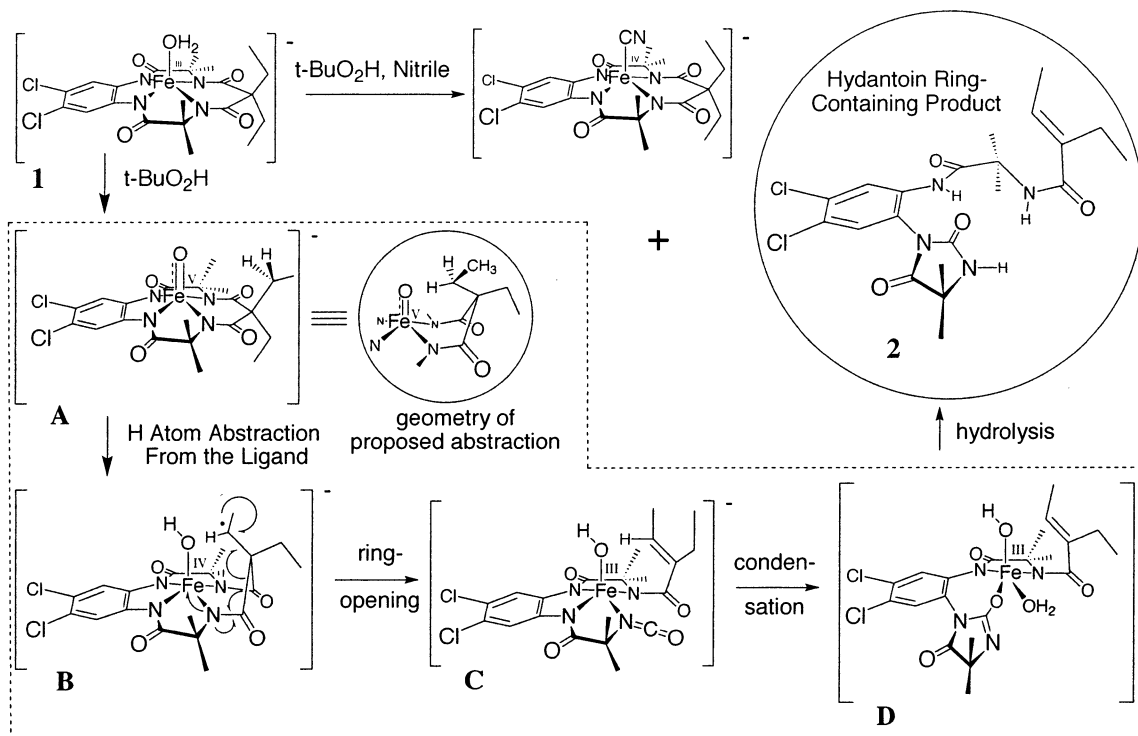


FIGURE 2. Evolution of tetradentate ligand systems that, in general, are progressively more suitable for supporting peroxide-activating catalysts.

reactive intermediate, one that is still very reactive but more selective than the reactive intermediates of Fenton systems. It is broadly recognized that one such possible intermediate is a terminal metal-oxo complex and that others are peroxy and bridging oxo complexes of various types. The terminal oxo complex can arise when a single catalytic metal ion abstracts an oxygen atom from hydrogen peroxide and discards water, making the two-electron-oxidized metal-oxo species. This reactivity channel is found in the iron-based cytochrome P-450 enzymes. It is also found when manganese(III) tetraamido-*N* macrocyclic ligand and related complexes are treated with peroxides; the first stable Mn(V)-monooxo complexes were produced and fully characterized by us.<sup>16,17</sup> These overly stabilized diamagnetic complexes can be activated by incorporation of a switching site in the macrocyclic ligand to which electron-withdrawing cations bind to increase the electrophilicity of the oxo ligand (**9**). This design approach has led thus far to Mn(V)-oxo complexes that are mild oxygen atom transfer agents.<sup>18</sup> To induce a small-molecule catalyst to follow the metal-oxo reactive intermediate reactivity channel over the Fenton channel, we believe that one should bind to the metal ion electron-releasing ligands to favor the formal metal-based two-electron oxidation that coincides with oxo ligand formation. We have focused predominantly on deprotonated secondary amide ligands to provide an appropriate ligand field, since these are comparatively strong *s*-donors, as

originally shown by Dale Margerum, negatively charged, and have proven to be sufficiently oxidation resistant. Iron has become the most important catalytic element for TAML activators. The exact nature of the reactive intermediates in the processes described below is the subject of ongoing investigation. Our working hypothesis is that Fe-TAML activator/peroxide oxidations involve iron-oxo reactive intermediates.<sup>19</sup> High selectivity has been found for a number of the processes described, such as wood pulp bleaching, indicating that a general Fenton-like mechanism is not operating—peroxide treatment of wood pulp requires prior and simultaneous removal of metal ions that promote Fenton chemistry or selectivity is reduced.<sup>20</sup> Moreover, we have found that complexes of macrocyclic tetraamido-*N* ligands, as opposed to acyclic tetradentate amido-*N*-containing ligands, can be made sufficiently resistant to be useful not only to oxidative degradation, but also to hydrolysis.<sup>21</sup> These and other ideas and findings have been blended at various times into an evolutionary process in which our tetradentate ligand systems have advanced to be progressively more resistant to oxidative decay and their complexes to be progressively more stable toward hydrolysis (Figure 2).

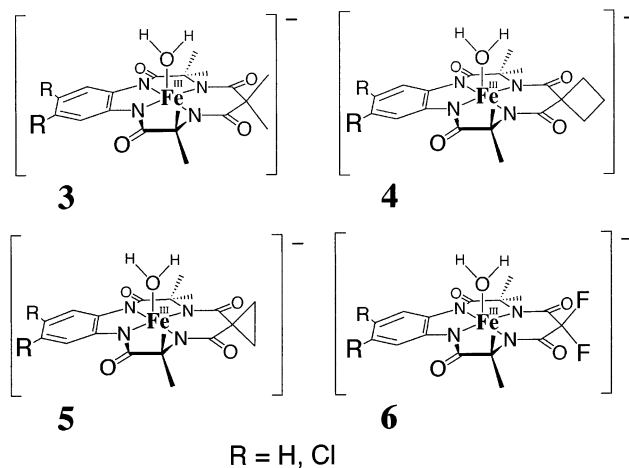
One cycle in the design loop of Figure 1 was followed after it was established that the TAML activator, **1** (Figure 3), catalyzes the oxidation by *tert*-butyl hydroperoxide of nitriles bearing  $\alpha$ -C-H bonds.<sup>19</sup> Both free radical autoxidation and metal-oxo processes are likely to be involved



**FIGURE 3.** One cycle in the design loop in which the methylene C–H bonds of the geminal ethyl groups of **1** were identified as the oxidatively vulnerable site—postulated mechanism enclosed.

in the catalytic nitrile oxidation. In the course of the catalysis, it was found that **1** slowly degrades to produce a hydantoin-containing product, **2**. We postulated that the degradation was initiated via a H-atom abstraction from a methylene position of the geminal ethyl groups by an iron-oxo intermediate, akin to the structurally isolated manganese(V) analogues (Figure 3).<sup>17</sup> Both intermolecular and intramolecular abstractions are possible, but it is reasonable to assume that the intramolecular process will dominate under conditions of low catalyst and high substrate concentrations, as in this case where the substrate is the solvent. If such an abstraction does indeed initiate decomposition, then it is reasonable to assume that the rate of catalyst degradation could depend on the strength of the C–H bond. Approximately  $3\text{ kcal}\cdot\text{mol}^{-1}$  can be added to this bond strength by changing the geminal groups from ethyl to methyl, such that a less stable primary instead of a secondary radical results from the abstraction. Thus, the iterated catalysts, **3** (Figure 4), were prepared and studied.

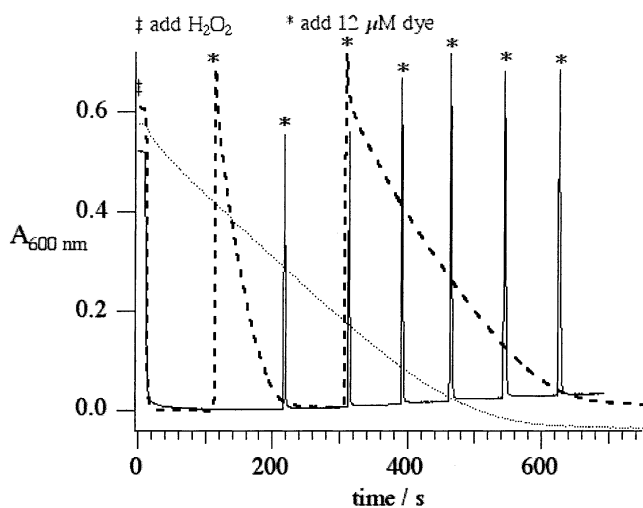
In an experiment developed by Colin Horwitz, the impact on catalyst lifetime of this subtle change was shown to be dramatic (Figure 5), with **3** having a longer lifetime and, consequently, greater utility than **1**.<sup>22</sup> Furthermore, in unpublished work, it was determined that **3** appears to undergo a related degradation. Thus, we have continued to focus on iterating this portion of the ligand to further extend the lifetime and have produced TAML activators **4**, **5**, and **6** (Figure 4). TAML activators **4** and **5** were produced to test the intramolecular abstraction idea (Figure 3, circle). They are longer-lived than **3**, and we will shortly publish the design logic and properties of these



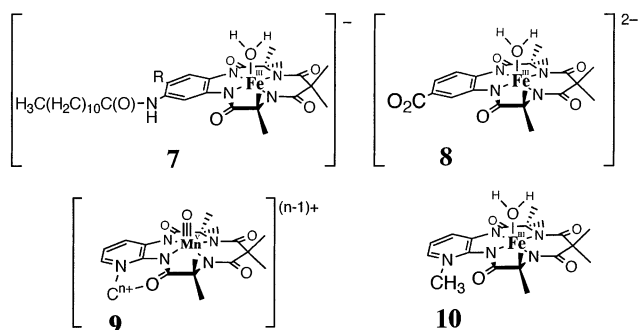
**FIGURE 4.** TAML catalysts iterated to extend catalyst lifetimes.

systems as well as an accurate parametrization of the relative lifetimes of a series of TAML catalysts.

TAML catalysts can be adapted to achieve targeted selectivities. By changing the substituents on the six-membered chelate ring, not only can the effective catalyst lifetime be changed, but also the rate of catalyst hydrolysis can be significantly altered. As with oxidative stability, we have discovered that resistance to hydrolysis can become a controllable feature of ligand design over a broad pH range. We have used substituent effects to alter the hydrolysis rate by more than 11 orders of magnitude,<sup>21</sup> with the practical consequence that TAML activators have been developed that are sufficiently resistant to hydrolysis to have useful lifetimes from pH 1 to pH 13; this catalyst design work will soon be published.



**FIGURE 5.**  $A_{600 \text{ nm}}$  vs time plot of the bleaching of a series of 12  $\mu\text{M}$  aliquots of pinacyanol chloride using (---) 0.0  $\mu\text{M}$  catalyst, single aliquot; (—) 0.43  $\mu\text{M}$  **3**, seven aliquots; (- - -) 0.43  $\mu\text{M}$  **1**, three aliquots. \* denotes addition of a 12  $\mu\text{M}$  aliquot of pinacyanol chloride after the first bleaching reaction, and ‡ denotes addition of 4 mM H<sub>2</sub>O<sub>2</sub>. Reaction conditions: pH 10;  $T = 25^\circ\text{C}$ ; 4 mM H<sub>2</sub>O<sub>2</sub>, 4 ppm Dequest 2066.



**FIGURE 6.** TAML catalysts modified to achieve specific selectivity properties.

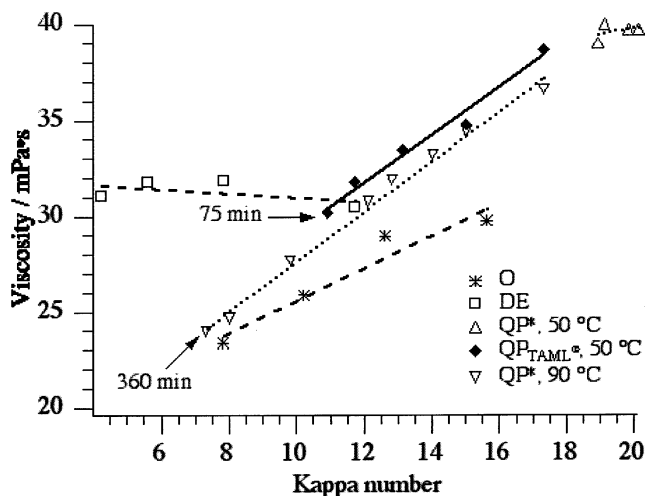
Substituent effects on other reactivity features are also significant. Substitution on the benzene ring of **2** with a hydrophobic tail,  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{NH}-$  (Figure 6), produces **7**, a micelle-forming catalyst in its own right that also forms mixed micelles with dodecyltrimethylammonium bromide (DTAB). Aqueous solutions containing the mixed micelles can dissolve and bleach with hydrogen peroxide a water-insoluble dye that can be shown to dissolve via attraction to the Stern layer of the micelle.<sup>23</sup> Substitution on the benzene ring of **2** with the anionic group,  $\text{CO}_2^-$ , giving **8** (Figure 6), increases the negative charge of the catalyst. This has been shown to introduce a rate disincentive for the catalyst to attack substrates on negatively charged heterogeneous supports. Using charged (**8**, **9**,<sup>18</sup> **10**), hydrophilic, hydrophobic (**7**), or other directing groups on TAML catalysts to partition the reactivity to favor or disfavor attack at various substrates is the idea captured by the term, “hunter TAML catalysts”.<sup>23</sup> This idea can be expressed in many novel ways to guide the development of peroxide-activating catalysts with predetermined selectivity behavior. This work, for which a patent has recently been allowed, will be fully published in the near future.

## Selected Technological Applications of TAML Catalysts

TAML activators have been shown to be efficient and selective peroxide oxidation catalysts. TAML activator/peroxide systems are directly or potentially applicable in diverse fields-of-use including the industries of pulp and paper, water treatment, textiles, cleaning, laundry, petroleum refining, chemical and biological terrorism and warfare (CBTW) agent decontamination, and others.<sup>13</sup> The following properties make them desirable for these applications. Fe-TAML activators are capable of more than 10 000 turnovers per hour in certain applications.<sup>23</sup> They do not waste peroxide rapidly through disproportionation because they generally exhibit weak catalase activity.<sup>24</sup> They are water-soluble, easy to use, and active under both neutral and basic conditions. They generally lead to rapid processes at mild temperatures and under ambient pressure, in which they are effective in nanomolar to micromolar concentrations. In the last section of this Account, I will describe one broad area of utility of TAML activator/peroxide by presenting reactivity features found in decomposing a range of pollutants and contaminants of industrial effluent streams. The utility appears to be broad, and the ease of application attractive—effluent treatment is a major cost factor in most industrial chemistry processes. The following is a selective list of the demonstrated applications of TAML activators.

**Pulp and Paper Applications.** In the pulp and paper industry, Fe-TAML activator/peroxide processes can either eliminate the production of pollutants by substituting for the processes that produce them, or reduce the environmental burden of existing technologies by rapidly destroying product pollutants in effluent streams. Indeed, this industry has a number of historically difficult problems where Fe-TAML activator/peroxide technology can offer attractive solutions while improving operating costs at potentially negligible capital investment and enhancing product quality, environmental performance, and energy efficiency.<sup>10,25–29</sup> In many developed countries, the industry currently uses chlorine dioxide as the principal bleaching agent for making strong white paper that does not yellow on aging. This growth and domination of bleaching by  $\text{ClO}_2$  is a phenomenon of the past decade that has involved a substantial and laudable capital intensive retooling of the industry.

Chlorine bleaching, the principal process employed throughout the 20th century, produces unacceptable quantities of chlorinated pollutants, including polychlorinated dibenzodioxins and dibenzofurans, PCDDs and PCDFs. PCDD/Fs chlorinated in the 2,3,7,8-positions are exceptionally toxic.<sup>30,31</sup> At the most serious levels of concern, several are persistent and bioaccumulative and are potent endocrine disruptors—in vanishingly small quantities, 2,3,7,8-tetrachlorodibenzodioxin and its related toxic congeners have the ability in mammals to interfere with the hormonally controlled processes of reproduction, mating behavior, neurological and immune system function, and other features of development, growth, and



**FIGURE 7.** Selectivity for bleaching of kraft pulp with H<sub>2</sub>O<sub>2</sub> (4%) at 50 °C by **4** ( $R = Cl$ ). Q indicates EDTA pretreatment, and \* indicates treatment in the presence of DTMPA. O is oxygen bleaching. DE is ClO<sub>2</sub> bleaching followed by alkaline extraction. P is peroxide bleaching. P<sub>TAML</sub> is TAML activator/peroxide bleaching. One kappa unit = 0.15% lignin on the pulp by oven dried weight. In all cases, **4** was added in 0.1 mg quantities, and the data were collected 15 min after each addition for a total reaction time of 75 min. DE is ClO<sub>2</sub> treatment followed by alkaline extraction.

function.<sup>11,32</sup> In many developing countries, chlorine is still widely used as the principal bleaching agent because of cost factors, but the persistence, volatility, and ability of PCDD/Fs to concentrate in fatty tissues, and thereby transport around the planet and concentrate up the food chain, means that they are global pollutants regardless of where they are produced.

How can one develop processes for this industry that promote environmental protection while being economically realistic over as much of the international economy as possible? The most likely method for success will lie in the development of a totally chlorine-free (TCF) technology that will be as globally viable as possible based upon the vital industrial drivers of product quality and cost. High-quality white paper is achieved by removing all of the lignin from the lignin–cellulosic composite, wood pulp. TAML catalysts promise to help here. In collaborations with the groups of Professor James Wright of Auckland University and Drs. Robert Allison and Ian Suckling at PAPRO, New Zealand, we have found that TAML catalysts activate H<sub>2</sub>O<sub>2</sub> to rapidly bleach wood pulp at high selectivity from room temperature to 90 °C, providing an exceptionally mild new TCF approach (Figure 7). TAML activator/peroxide is capable of giving a selective TCF process for pulp bleaching when compared with incumbent TCF processes. The selectivity at 50 °C is competitive with chlorine dioxide bleaching (called D bleaching) down to a kappa number of approximately 10 (one kappa unit = 0.15% lignin on the pulp), or about 60–75% delignification for an average kraft pulp if the data obtained on *Pinus radiata* pulp transfer well to other pulps. In wealthier countries, kraft pulp could be delignified, in principle, first with TAML activator/peroxide and finished with chlorine dioxide for a product comparable

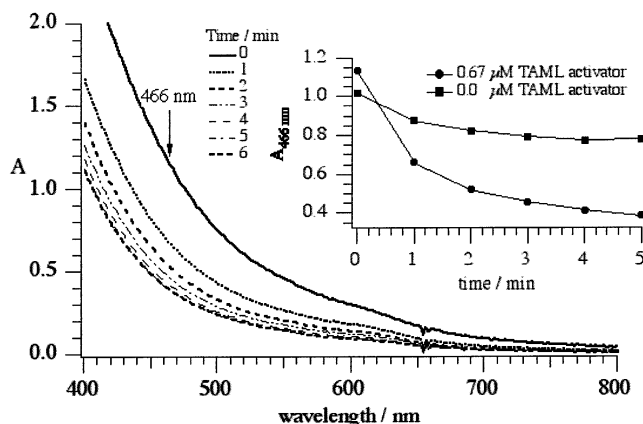
in quality to pure D-bleached pulp. But there is more development to be done for attaining a broadly appealing bleaching technology because TAML activator/peroxide is currently less selective than D bleaching at low kappa numbers. However, with catalyst lifetimes under reasonable control, hunter catalysts with a special affinity for the lignin on the pulp are being developed with the idea that these will deliver selectivity comparable or superior to that of chlorine dioxide across the entire lignin removal process. Such catalysts should also improve the already good efficiency of peroxide usage and enhance further the remarkable rates already achieved for delignification with the prototype catalysts. Thus, our research efforts in this area are focused partly on achieving effective hunter catalysts that might produce stronger bleached pulp than can be gained even from chlorine dioxide bleaching. A cost-effective bleaching system with these advantages could entice more mills around the world to move away from chlorine bleaching.

Other groups have been working to produce alternative TCF pulp bleaching technologies based upon metal catalysts.<sup>33</sup> In my opinion, the polyoxometalate (POM)/oxygen approach being developed and promoted by Ira Weinstock and Craig Hill,<sup>34</sup> a so-called catalyzed process, is seriously flawed and does not represent an environmentally benign approach for developing TCF technologies. The quantities of heavy metals required in the Hill/Weinstock process are simply staggering, such that the approach defies the common conception in the chemical community of what a catalyst actually is.<sup>35</sup> The approach replaces the environmental concerns of organochlorines with the potentially equally or more serious concerns associated with heavy metal ion toxicity.

In collaboration with the groups of Professor Wright (Auckland) and Dr. Trevor Stuthridge (Forest Research NZ), we have found that TAML activator/peroxide bleaches “color” in ClO<sub>2</sub> bleach plant effluents. Chlorinated organics are also significantly reduced in the treatment, and these properties suggest that a viable technology for remediation is already in hand. “Color” is the industrial term for the tea color that stains the effluent streams of pulp mills. It is recalcitrant for the following reason. Chlorine dioxide (and chlorine) removes lignin from pulp primarily as low molecular mass fragments ( $M_w \leq 1000$  Da) with some high molecular mass material ( $M_w > 1000$  Da). The heavier lignin fragments present the environmental problem of color. Aerobic bacterial treatment removes most of the lighter material but is ineffective at breaking down the heavier lignin fragments—probably, the large lignin fragments are simply too big for the bacteria to ingest. Color resides primarily on the high molecular mass material. It very often intensifies in the treatment ponds and reactors of the industry. Color is both an aesthetic and an ecological problem. It alters light penetration into rivers and lakes, thereby disturbing the ecological system. TAML activator/peroxide presents a technology that is remarkable in being environmentally safe, effective, nontoxic, and remarkably trivial to apply for this application. Color can be reduced typically by 50%

**Table 1. Mass Balance on First Pass Treatments of TCP and PCP with Fe-TAML-Activated H<sub>2</sub>O<sub>2</sub> (9 min)**

	TCP			PCP		
	(mM)	% C	% Cl	(mM)	% C	% Cl
CO + CO <sub>2</sub>		35 ± 5			45 ± 3	
Cl <sup>-</sup>			83 ± 2			87 ± 4
oxalic acid	1.71 ± 0.04	11		3.4 ± 0.2	23 ± 1	
formic acid	1.53 ± 0.14	5				
chloromaleic acid	1.17 ± 0.02	16	8			
dichloromaleic acid				1.27 ± 0.03	17 ± 1	10
malonic acid	0.74	7.5				
hydroxymalonic acid	0.45	6.5				
chloromalonic acid	0.65	4.5	3	0.6	6	2
chlorinated aromatics	0.07	2	1			
total		87.5 ± 5%	95 ± 2%		91 ± 5%	99 ± 4%

**FIGURE 8.** Bleaching of a D<sub>0</sub> filtrate following the first ClO<sub>2</sub> bleaching step. Conditions: **3** (R = H) = 0.67 mM, [H<sub>2</sub>O<sub>2</sub>] = 7.6 mM ≈ 0.20 g·L<sup>-1</sup>, T = 23 °C, color change 2439 to 914 pccu, pH adjusted 10.35.

on introduction of a TAML activator into the effluent stream in low micromolar concentrations with small quantities of H<sub>2</sub>O<sub>2</sub> (Figure 8). The process proceeds rapidly at room temperature. Effluent streams tend to be hot as they exit the mill.

In this environmental application, it is significant that the prototype TAML activator that works so well here is comprised exclusively of biochemically common elements and groups that are similar in constitution to proteins. Toxic elements, such as most of the heavy metals, are the prototypical persistent pollutants<sup>5</sup> and should be strongly avoided in remediation processes such as this, where vast effluent streams empty directly into natural water systems. TAML catalysts have known lifetimes and should not be persistent. The treated effluent streams have been studied for toxicity following full treatment; by luminescent bacterial assays, TAML activator/peroxide treatment does not increase the low toxicity commonly found for the fully treated effluent.

**Other Water Treatment Applications.** The textile industry has a large problem with colored effluent streams. Approximately 80 dyes form the global industry's palette for the coloring of commercial fabrics. TAML activator/peroxide can readily bleach most of these dyes. For most dyes, the process proceeds rapidly at room temperature. Some dyes require heating. In a collaboration with Paul Richard and his colleagues from the Office of Technology Assistance, a component of the Executive Office of Environmental Affairs of the State of Massachusetts, we have

been showing that the effluent streams of a number of test companies in that state can be rapidly bleached. With most dyes, color removal is complete and bleaching is achieved with very small quantities of TAML activator and peroxide—it is important that treated effluent be examined for toxicity, and this remains to be studied.

A broad scientific search has been underway for almost two decades to find a facile, inexpensive, environmentally safe method for degrading chlorophenols into harmless products. Over the past six decades, chlorophenols have found wide use in pesticides, disinfectants, wood preservatives, personal care formulations, and many other products.<sup>36</sup> They are significant components of the effluent streams of pulp bleaching with elemental chlorine. However, growing knowledge of the toxicities and environmental fates of specific chlorophenols has caused governments to regulate these compounds; five chlorophenols are listed by the U.S. Environmental Protection Agency (EPA) as priority pollutants, including 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP).<sup>37</sup> It has been proposed that anthropogenic PCP, once used in large amounts as a wood preservative, could be responsible for a substantial fraction of the global environmental burden of polychlorinated dioxins.<sup>38</sup> In a collaboration with Drs. Dieter Lenoir and Karl-Werner Schramm of the Institut für Ökologische Chemie of the GSF (Forschungszentrum für Umwelt und Gesundheit) in München, we have studied the use of TAML activator/peroxide to decompose chlorinated phenols.

We have extensively investigated the decomposition of 2,4,6-TCP and PCP since these compounds, for good reasons, have been used by Bernard Meunier<sup>39,40</sup> and others<sup>24</sup> to test technologies for chlorophenol destruction. In minutes, in water, under ambient conditions of temperature and pressure, PCP and TCP are completely destroyed at catalyst:substrate ratios of 1:715 and 1:2000, respectively.<sup>24</sup> The fate of 90% of the carbon and >95% of the chlorine has been determined in each case (Table 1). Neither dioxins nor any other toxic compounds are detectable products. The catalysts have also been demonstrated to have low toxicity by a luminescent bacterial assay (LUMISTox), suggesting that an environmentally safe process will result, subject to favorable full ecotoxicological and toxicological examinations.

With current concerns regarding the proliferation of environmental toxins, an eminently practical, inexpensive

green process for cleaning up pollutants in a variety of situations from natural water bodies to entrapped waste streams prior to treatment or release is greatly needed; this is especially true for chlorinated pollutants.

The U.S. EPA has recently mandated that the sulfur content of diesel and gasoline should be greatly reduced, 500 to 15 ppm and 300 to 30 ppm, respectively.<sup>41,42</sup> The most difficult to remove sulfur in petroleum raw materials resides in dibenzothiophenes. The most challenging of these to desulfurize are alkylated in positions that sterically protect the sulfur atoms, e.g., 4,6-dimethyldibenzothiophene. It has been estimated that the petroleum refining industry will need to spend ca. \$8 billion over the next few years to meet the new EPA standards, especially if attractive alternatives to hydrocracking are not developed.<sup>42</sup> Thus, various researchers are investigating alternatives. Many are focused on oxidation approaches to convert thiophenes to sulfoxides or sulfones since these can be more easily separated from the petroleum base products.<sup>43–45</sup>

Catalytic activation of H<sub>2</sub>O<sub>2</sub> is a popular approach under study for these oxidations.<sup>46,47</sup> But there are many challenges associated with emerging systems, such as expectations of large capital requirements, the use of stoichiometric amounts of catalysts, poor catalyst stabilities, the need for more than one catalyst for aliphatic and aromatic sulfur compounds, and low selectivity during oxidation leading to undesirable polymers and coke. In a collaboration with Dr. Anthony Cugini and colleagues at the National Energy Technology Laboratory in Pittsburgh, we have learned that TAML activator/H<sub>2</sub>O<sub>2</sub> rapidly and selectively oxidizes alkyl sulfides, thiophenes, benzothiophenes, and dibenzothiophenes to the corresponding sulfones. The processes are characterized by quantitative yields within minutes at 60 °C and atmospheric pressure.<sup>23</sup> This suggests that TAML activators may offer a facile, markedly inexpensive oxidation technology for desulfurization of petroleum- and coal-based mixtures.

## Conclusion

Chemistry has an important role to play in achieving a sustainable civilization on Earth. Chemical sustainability problems are determined largely by economy–ecosphere material flows. Chemical education and research has paid too little attention to these flows, with the result that a plethora of chemical problems that must be solved to achieve a sustainable civilization are being addressed either by just a handful of researchers or not at all. One can be optimistic that this situation, which is improving year by year, will get much better, because green chemistry is primarily about inventing technologies that not only improve the quality of life and promote sustainability, but also create substantial wealth in the conventional economic sense. TAML oxidant activators are broadly significant inventions that can impact many fields of use, some of which have been sketched above. They offer an arena for the chemist to discover and develop much needed oxidation processes, to study the mechanisms of

the chemical reactions involved, and to continue the fascinating process of oxidation catalyst design and its interplay with the reactivity behavior of the catalysts in different areas of technology.

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