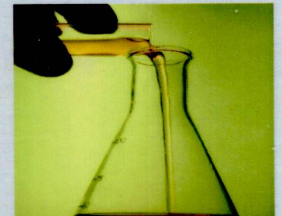
Jeffrey T. Pearlman
Editor

Green Chemistry Research Trends

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GREEN CHEMISTRY RESEARCH TRENDS

PREFACE

Green chemistry, also called sustainable chemistry, is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances. Whereas environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, green chemistry seeks to reduce and prevent pollution at its source. In 1990 the Pollution Prevention Act was passed in the United States. This act helped create a modus operandi for dealing with pollution in an original and innovative way. It aims to avoid problems before they happen.

As a chemical philosophy, green chemistry derives from organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and even physical chemistry. However, the philosophy of green chemistry tends to focus on industrial applications. Click chemistry is often cited as a style of chemical synthesis that is consistent with the goals of green chemistry. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice. It is distinct from environmental chemistry which focuses on chemical phenomena in the environment.

This new book presents significant research advances in this new field.

Expert Commentary - The attention being given to climate change issues by the media, industry leaders, political figures, and the general public has significantly increased during the past several years. Addressing climate change in a meaningful way during the next decades has wide-ranging implications for the global energy system. Green Chemistry can make important contributions to Greenhouse Gas emissions reduction, mitigation strategies, and the sustainable generation, storage, and utilization of carbon-constrained energy resources. At the same time, the increase in awareness and concern about these issues provides some unique opportunities for enhancing the acceptance of Green Chemistry as a component of increasingly popular "Green" business strategies and life styles. A Policy Statement on "Global Climate Change" recently adopted by the American Chemical Society provides strong arguments and specific recommendations for moving in this direction. Since the chemical enterprise, the energy market, and the climate system are all global in scale, it is essential to develop such strategies in concert with international partners.

Short Communication A - The formation of carbon-carbon and carbon-heteroatom bonds are important steps in organic synthesis, and our ability to prepare new organic molecules is inextricably linked to the discovery of new methods that achieve this objective. Palladium salts have emerged as particularly exciting catalysts. Most of the widely used examples of palladium catalysis consist of nonoxidative methods, especially cross-coupling reactions.

Oxidation reactions tend to be more challenging because they require the use of an external oxidant and because the conditions are incompatible with air-sensitive phosphine ligands, which have been critical to the success of nonoxidative coupling reactions. As a result, palladium-catalyzed oxidation reactions have received less attention than their nonoxidative counterparts. However, they are expected to lead to mild, general, and selective methodologies able to make the already known or new chemical transformations environmentally sustainable through the direct transformation of C-H bonds. In addition, they have the potential to fundamentally change retrosynthetic approaches to complex molecules synthesis. The present commentary focuses on the recent progress in palladium oxidative reactions that involve the direct functionalization of C-H bonds, which could compete with the well-known Pd(0)-catalyzed methodologies. Since this field is currently in its infancy, the article will point out some challenges that still remain.

Short Communication B - Three-dimensional scaffolds of biodegradable poly(lactic acid) (PLA)/organically modified silica (o-SiO_2) with high porosities and homogeneously interconnected pore network were successfully fabricated using melt-molding/particulate-leaching method. The morphology of PLA/o-SiO_2 scaffolds showed highly porous and open-cellular pore structure with pore size in the range between 150~250 μm and interior porosity larger than 80%. The compressive strength of PLA/o-SiO_2 composite scaffold was increased from 28.1 MPa for neat PLA scaffold to 35.5 MPa for PLA/o-SiO_2 composite scaffold. From the biodegradable test, the weight loss of scaffolds increases with increasing time. Therefore, the presence of SiO_2 in PLA/o-SiO_2 composite scaffold can accelerate the degradation rate of scaffolds.

Chapter 1 - This chapter presents a complete picture of current knowledge on microwave-assisted separations of food and natural products. It provides the necessary theoretical background and some details about extraction by microwaves, the technique, the mechanism, some applications, and environmental impacts. Microwave-assisted separation is a research topic which affects several fields of modern chemistry. All the reported applications have shown that microwave-assisted separation is an alternative to conventional techniques for food and natural products. The main benefits are decreases in extraction times, the amount of energy and solvents used, and CO_2 emissions.

Chapter 2 - The origin and fundamentals of green analytical chemistry have been discussed from the literature published about clean analytical, environmentally friendly or green methods. Special attention has been paid to the strategies and tools to greener both, the sample pretreatment and the analytical methods. Based on the principles of toxic reagents replacement, miniaturization and automatization, it is possible to reduce drastically the reagents consumption and the amount of wastes generated. So, nowadays analysts have additional criteria than basic ones to select the most appropriate methodology to do analytical determinations in an accurate, precise, sensitive and selective way but also in a sustainable way, avoiding the side effects of the use of analytical chemistry.

Chapter 3 - Transition-metal catalyzed [2 + 2 + 2] cyclotrimerization of alkynes is one of the most powerful synthetic tools presently available to construct aromatic arene rings. After the pioneering work of Reppe in 1948, a wide variety of metal complexes have been developed for this atom economical transformation, the catalytic reactions being usually performed in organic media. Nevertheless, in order to fulfil the Green Chemistry´s principles, the scenario has started to change and remarkable efforts have recently been made in the search of active catalysts able to promote alkyne-cyclotrimerizations in the so-called "green solvents". The high flammability, volatility and toxicity of conventional organic solvents have stimulated the search for environmentally benign substitutes. Among them, water, ionic liquids and supercritical fluids are promising alternatives. The aim of this contribution is to highlight the developments achieved in the field of metal-catalyzed [2 + 2 + 2] alkyne cyclotrimerizations employing these green solvents. Related [2 + 2 + 2] co-cyclization reactions of alkynes with unsaturated organic substrates (nitriles, carbon dioxide, etc.) will also be discussed.

Chapter 4 - Ionic Liquids or, to name them more appropriately, ambient-temperature Ionic Liquids (ILs) are a relatively new class of solvents that enjoyed an explosive growth of applications, both synthetic (organic and inorganic synthesis) and non-synthetic ones (electrochemical and analytical applications as well as material processing and process machinery). [1].

Chapter 5 - This article is an attempt to look through the development at the Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences of ecologically favorable and economically benefited clean chemical processes for metallocomplexe catalysis (olefins dimerisation and dienes polymerization) in order to find out their significant commercial status for future commercialization of "green chemistry" processes.

Chapter 6 - On the basis of the twelve principles of Green Chemistry [1], important effort of current research is directed at changing stoichiometric with catalytic reactions, toxic reactants with sustainable ones, and volatile flammable solvents with alternative ones, devoid of these problems. Oxidation reactions of organic compounds are among the most useful chemical transformations for which such effort is in progress. Particularly important is the attempt to replace classical oxidants with dioxygen [2] or hydrogen peroxides,[3] that are economical and sustainable oxidizing reagents. However, they need to be activated, for example by metals. In this respect, transition metal peroxides, either as such or formed in situ [4] play a crucial role.

Chapter 7 - Free radical benzylic bromination is one of the most important reactions for the functionalization of alkyl aromatic compounds leading to benzyl bromides, which are important chemicals and starting compounds for further transformation. This classical Wohl-Ziegler bromination utilizing N-bromosuccinimide (NBS) in carbon tetrachloride is now considered unsuitable due to the high environmental burden of this reaction. This chapter presents new developments in the field of free radical benzylic bromination that transforms the classical Wohl-Ziegler bromination into a more environmentally friendly alternative. It first looks at research on the substitution of chlorinated solvents with more environmentally benign ones, like water, ionic liquids, non-chlorinated organic solvents and the use of solventless reactions. Next, research into the substitution of NBS with molecular bromine as the basic halogenating reagent without the use of solvent or in aqueous media is discussed. Finally, this chapter reviews current research into how the use of molecular bromine can be avoided altogether and instead, generated *"in situ"* by oxidative halogenation with hydrogen peroxide, by electrochemical oxidation or from a bromate/bromide couple prepared from a bromine precursor in a commercial method of preparation.

Chapter 8 - In this chapter the effects of environmentally friendly additives on formation and growth of sparingly soluble salts are presented in a concise way. Specifically, the influence of a biodegradable, environmentally friendly polysaccharide-based polycarboxylate, carboxymethyl inulin (CMI), on the crystal growth kinetics of calcium oxalate has been studied. The spontaneous crystallization method was used to delineate the crystallization kinetics of calcium oxalate (CaC_2O_4, CaOx). The results demonstrate that the retardation in crystal growth is controlled by the carboxylation degree of the CMI and its concentration. These studies also show that CMI additives direct calcium oxalate crystallization from calcium oxalate monohydrate (COM) to calcium oxalate dihydrate (COD). Colloidal silica is known to be a substantial problem in silica-laden process waters. Although silica "technically" is not a salt, it is often categorized with them, as it brings about the same problems as mineral scale deposits (reduced heat transfer, etc.). We also report a strategy to retard silicic acid condensation in supersaturated aqueous solutions by using non-toxic, "green", zwitter-ionic phosphonomethylayed chitosan (PCH). An overview of the use of green additives in water treatment is also presented.

CONTENTS

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Expert Commentary

GREEN CHEMISTRY, CLIMATE, AND ENERGY

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ABSTRACT

The attention being given to climate change issues by the media, industry leaders, political figures, and the general public has significantly increased during the past several years. Addressing climate change in a meaningful way during the next decades has wide-ranging implications for the global energy system. Green Chemistry can make important contributions to Greenhouse Gas emissions reduction, mitigation strategies, and the sustainable generation, storage, and utilization of carbon-constrained energy resources. At the same time, the increase in awareness and concern about these issues provides some unique opportunities for enhancing the acceptance of Green Chemistry as a component of increasingly popular "Green" business strategies and life styles. A Policy Statement on "Global Climate Change" recently adopted by the American Chemical Society provides strong arguments and specific recommendations for moving in this direction. Since the chemical enterprise, the energy market, and the climate system are all global in scale, it is essential to develop such strategies in concert with international partners.

During the middle of the Eighteenth Century, Colonial America experienced a religious revival known as the "Great Awakening" [1, 2]. This manifested itself in the form of spontaneous, community based religious activities which represented a reaction against the "Established", i.e. Anglican church practices imported from (and perhaps imposed by) the English colonial masters. Many commentators suggest that this revival was a direct precursor of the American Revolution and the War for Independence, as in the following:

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> "The increase of dissent from the established churches during this period ... and the democratization of the religious experience was an impulse that fed the fervour that resulted in the American Revolution." [3]

Subsequent "Awakenings" during the early Nineteenth Century resulted in agitation for the abolition of slavery in both the United States and England. Even though the institution of slavery had been regarded as essential to the economies of both of these countries, the abolitionist movements ultimately succeeded in their goals.

In our own time, another type of "Great Awakening" may be taking place. In this case, the American public seems to be finally waking up to the fact that our use of energy resources, particularly fossil fuel resources, is inherently unsustainable, poses a threat to both our economy and our security, and is one of the principal drivers of global climate change [4]. If climate change is to be addressed in a meaningful and effective way, emissions of anthropogenic greenhouse gases – in particular, carbon dioxide from fossil fuel combustion – will have to be stabilized in the near term, and substantially reduced afterwards. Indeed, a reduction in carbon emissions by 70 to 80 per cent from 1990 levels ("Factor Four" [5], [6]) will be required to maintain atmospheric CO_2 concentration at or below 550 ppm_v, which is widely accepted as the upper limit for "avoiding dangerous climate change" [7].

To achieve this goal, major changes will be required in the way that we produce and use the energy required to maintain the global economic system. Carbon-emitting fossil fuels (coal, oil, and natural gas), which currently provide ~ 85% of our energy supply, will have to be replaced by carbon-neutral sources such as solar, wind, geothermal, and other renewable sources [8]. Given the scale of the global energy system, and the long lead times required to bring about significant changes in such a system, it is also essential that the efficiency with which energy is used be greatly increased as well.

Green Chemistry can provide important contributions to meeting the climate and energy challenges. In fact, several of the "Twelve Principles of Green Chemistry" [9] directly address some of these issues:

> "Energy requirements [for chemical processes] ... should be minimized" and
> "Raw material or feedstock should be renewable rather than depleting."

More broadly, the basic green chemistry strategies of source reduction, efficient use of resources, and minimizing waste emissions are essential tools for transforming the global energy system. A recent NRC Report [10] identified eight "Grand Challenges" for addressing sustainability in the chemical industry. Four of these are especially relevant to climate, energy, and feedstock issues:

- Derive chemical products from biomass sources, rather than continue dependence on petroleum and natural gas as raw materials
- Develop future alternative energy derived from renewable sources such as biomass, wind, solar thermal, and photovoltaic technologies.
- Reduce the energy intensity of chemical processing
- Develop technology and strategies for separation, sequestration, and utilization of carbon dioxide resulting from fossil fuel combustion

Recognizing the important role that chemistry has to play in climate and energy issues, the American Chemical Society has recently issued a Policy Statement on Global Climate Change [11] which states clearly that recent rapid changes in the Earth's climate are due to human activity, and that action is urgently needed to mitigate these risks. This statement goes on to make a number of specific chemistry relevant recommendations, including:

- Strengthening and fully funding a U.S. research program on the regional impacts of climate change, in order to enable design and implementation of effective mitigation and adaptation strategies
- Adopting national goals for rapid and deep reductions in CO_2 emissions through cap-and-trade regimes, carbon taxes, subsidies, and other strategies
- Research on low-emission energy technologies and energy-efficient processes

Many of these goals and recommendations are incorporated in the strategy of the M.I.T. Energy Initiative (MITEI). Established in 2006, MITEI 's objectives are to engage students, faculty, and staff throughout the Institute in an effort to help transform the global energy system, through innovative research, new educational programs, and reducing the energy intensity of M.I.T.'s own campus operations [12]. To help engage a broader spectrum of faculty, MITEI recently funded nineteen "seed" and "ignition" grants that are intended to help launch new or early stage projects that will produce enough results to be able to secure outside funding for further development [13]. Several of these projects are being carried out in M.I.T.'s Chemistry Department, *viz.*:

Prof. Catherine Drennan is studying the structure and functioning of enzymes in microorganisms that are able to utilize carbon monoxide, and even CO_2, as their carbon and energy source. Understanding these processes might enable us to remove CO_2 from the atmosphere and convert it to nontoxic, energetically useful molecules [14].

Prof. Keith Nelson is studying the fundamental properties of thermoelectric materials, which could lead to the design of devices for efficiently harvesting a portion of the waste heat from power generation and industrial processes [15].

Prof. Troy Van Voorhis plans to carry out molecular simulations of electron transport and excited state reactivity in materials. These simulations could lead to improved designs for photovoltaic and artificial photosynthetic devices [16].

The capture, conversion, and storage of solar energy in a practical and cost-effective way represents a major opportunity for chemistry to have an impact on the global energy system.

These examples are illustrative of the many opportunities that exist for chemistry to contribute to addressing the energy and climate challenges. Additional opportunities exist in the way that the chemical enterprise itself is carried out. One striking example concerns the use of fume hoods in chemistry laboratories. While essential to maintaining safe working conditions and complying with occupational and environmental regulations, fume hoods can be “energy hogs” because they draw large amounts of heated or cooled air, depending on the season, through their exhaust systems. A typical fume hood running 24 hours a day can consume as much energy as a single-family home in New England. Responding to students' investigation and concerns, M.I.T. has been promoting changes in the way that fume hoods are used as part of its Campus Energy Initiative [17], with potential energy cost savings up to $1 million every year. The need to modify usage patterns of fume hoods in order to conserve energy has recently gained national recognition [18].

"Green" strategies, products, and even life styles are finding increasing acceptance by business and the public, driven in no small measure by growing awareness of the gravity of the climate change issue and escalating energy prices [4]. Just as Green Chemistry has much to offer in meeting these challenges, this change in attitude may also provide some unique windows of opportunity for overcoming the barriers to its implementation. A recent workshop [19] identified a number of these barriers, including:

- perceived (if not actual) economic disadvantages
- lack of awareness among chemists, managers, and the public, and
- current educational systems and curricula do not address green chemistry, or sustainability issues in general, in an adequate manner.

The increasing frequency and severity of the environmental, economic, and social signals associated with energy costs, climate change, and food shortages may be leading to changes in all of these issues, which will ultimately prove beneficial for all of us. And just as the climate and energy challenge is global in scale, the international collaborations and networks that characterize Green Chemistry offer a model for the transboundary cooperation which is essential for addressing the former set of issues as well.

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SHORT COMMUNICATIONS