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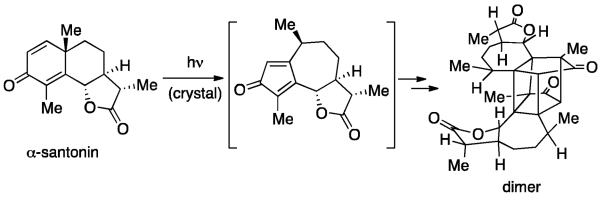
Editorial for the Special Issue on Photocatalysis

Light-driven organic chemical transformations are at the center of the terrestrial energy cycle. Photosynthesis captures a small fraction of the solar energy striking the surface of the planet by producing organic compounds, which ultimately sustain life on earth through nutrition and through the chemical fuels that provide humans with heat and electricity. Scientists have long sought strategies to similarly use the energy content of sunlight in the direct production of sustainable electricity or high energy materials for energy storage. These efforts over many decades encompass a broad, interdisciplinary effort to use photochemistry to harness solar energy in usable forms.

The utilization of light energy in synthetic chemistry, however, has proceeded at a somewhat slower pace until quite recently. This is not to say that photochemical synthesis is a "new" field. The ability of light to drive elegant reaction chemistries has fascinated organic chemists for as long as we have been able to synthesize organic structure in a controlled fashion.[1] The finding in 1834 by Trommsdorff that crystals of the anthelminthic α-santonin would turn yellow and burst upon exposure to sunlight was the first reported example of an organic photochemical reaction (eq 1).[2] An understanding of the fundamental mechanisms and selection rules for this and other photochemical reactions would not emerge until decades later, but by the 1970s, many photochemical processes involving light were well-known and could be deployed in organic synthesis.[3]



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An important feature of photochemical reactions that has attracted the interest of synthetic chemists is the characteristic reactivity of electronically excited organic molecules. These intermediates are subject to different selection rules than their ground-state counterparts, which allows access to processes that are not available via thermal activation even when catalysts are employed (Figure 1A vs B). However, most simple organic molecules are colorless and can be photoactivated only by using relatively short wavelength ultraviolet light. These high energy photons are sufficiently reactive that they can cause the uncontrolled fragmentation of many bonds in a complex molecule. Thus, useful photochemical synthesis was often limited to highly conjugated organic substrates that could absorb longer wavelength, lower energy light. In select circumstances, catalysts could lower the activation barriers needed for the photochemical process (Figure 1C),[4] but this approach is not general.

This limitation, however, can be addressed by utilizing sensitization. *Photosensitizers* are molecules that mediate photochemical reactions by first absorbing light and then using that energy to activate a less photoactive reactant toward some chemical transformation. Effective photosensitizers feature (1) symmetry-allowed absorption features that enable a strong interaction with light and (2) relatively long excited-state lifetimes that facilitate bimolecular reactions with substrate molecules. Photosensitizers are typically catalytic species that are returned unchanged in the overall balanced reaction; in these cases, the term "photosensitizer" and "photocatalyst" can be used interchangeably.

The activation of organic substrates by an electronically excited sensitizer, however, can occur via a variety of different mechanisms. This is true whether the catalyst is transition metal centered or fully organic. One common mechanism of photoactivation involves *energy transfer* events. These processes couple the electronic relaxation of the sensitizer to the simultaneous excitation of the substrate, with conservation of spin. Most often, bimolecular energy transfer events occur from the long-lived triplet state of a photoexcited sensitizer, and this process is referred to as *triplet sensitization* (Figure 1D). This sensitization is particularly useful when generation of the same species by direct photoexcitation is not efficient (e.g., accessing the triplet state of stilbene),[5] thereby allowing processes to occur much more facilely. Synthetically useful organic reactions involving energy transfer from excited-state transition-metal complexes are only beginning to be reported, but the use of organic triplet sensitizers in this context has a long and important history. Particularly relevant is the generation of electronically excited singlet oxygen, which can be accomplished using a variety of visible light absorbing organic dyes.[6]

In addition to energy transfer, another mechanism by which an electronically excited photosensitizer can activate an organic substrate involves an *electron transfer* step, which may be oxidative or reductive in nature. If initially oxidative, such sensitizers abstract an electron from neutral species to generate reactive radical cations (Figure 2A) or from anionic species to generate reactive radicals. If initially reductive, neutral species give rise to radical anions (Figure 2B) and cation species to radicals. After participation in a transformation through one or multiple steps, regeneration of the sensitizer by donation of an electron to or abstraction of an electron from a reaction intermediate, respectively, closes the cycle such that the sensitizer is a catalyst.

In the recent literature, this activation mode has been described as *photoredox catalysis*. In earlier literature, the term *photoinduced electron transfer* (*PET*) was used more frequently to describe the same phenomenon. Thus, the seminal papers prior to 2000 that provide much of the conceptual background for this field will generally refer to what we would now call photoredox catalysis as *PET sensitization*. Although catalytic ruthenium and iridium polypyridyl complexes have come to dominate this literature, increased redox activity is a common property of excited state molecules. Classically, a variety of

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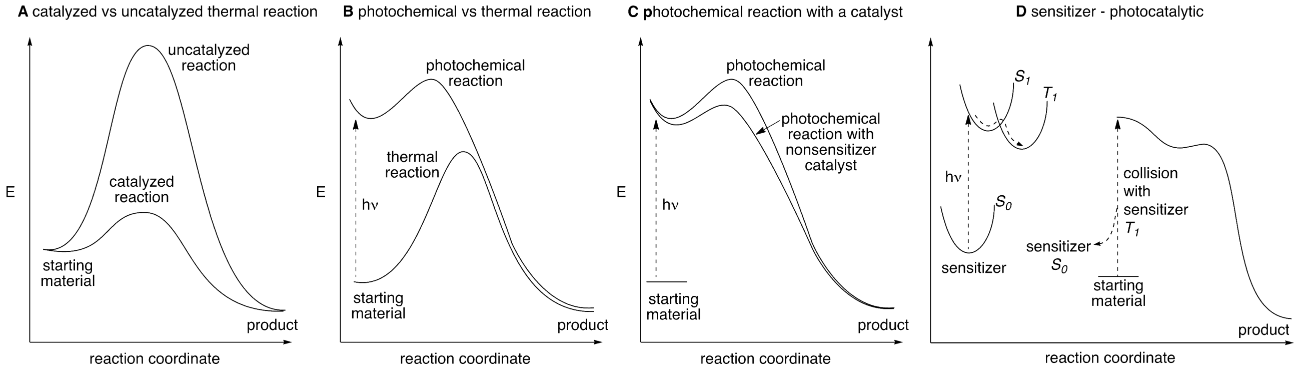

Figure 1. Reaction coordinate diagrams thermal (A) vs photochemical reactions (B) and photochemical reactions with a catalyst (C) and with a sensitizer/photocatalyst (D).

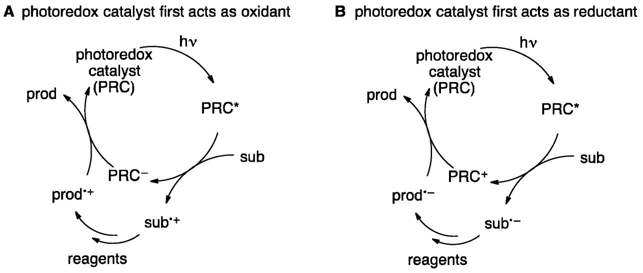

Figure 2. Photoredox catalytic cycles.

organic sensitizers including electron-deficient arenes and aromatic ketones were used to catalyze these reactions.

Recently, photochemical synthesis, and particularly photocatalytic synthesis, has enjoyed renewed attention among synthetic chemists. This Special Issue of the *The Journal of Organic Chemistry* has been commissioned to highlight some of the interesting research directions that have emerged from this ongoing effort. Much of this work has been based upon the use of photocatalysts that are activated using visible light. A central motivation for the use of visible light in photochemical synthesis has been the accessibility of the equipment required for these experiments. The light sources commonly used in this new generation of methods are often available at nominal cost, and in the case of consumer white lightbulbs, are already present in any research lab. Moreover, standard borosilicate glassware is transparent to visible light, obviating the need for quartz glass to accommodate short-wavelength UV. Thus, photocatalytic strategies involving visible light have easily been adopted by a large and growing cohort of researchers in various areas of synthetic chemistry.

The rapidity of growth in this area, however, has resulted in confusion over terminology and experimental descriptions. A collection of competing terms has been used to describe similar phenomena; the explicit definitions of these terms are not entirely interchangeable and have occasionally been applied unevenly in the literature. This editorial presents an opportunity to propose some standards that we hope will be respectful of both common usage and historical background.

Increasingly over the past decade, the term *photoredox catalysis* has been commonly applied to this class of reactions. As described above, this nomenclature implies a mechanism involving a photochemically induced electron-transfer step. In studying the mechanisms of photocatalytic reactions, the feasibility of electron transfer relative to energy transfer can sometimes be surmised by considering the energetics of these steps, which can be deduced by considering the relative excited state triplet energies and redox potentials of the donor and acceptor molecules. The rates of these reactions are generally fast only when the overall transfer, either of energy or electrons, is thermodynamically reasonable. However, it can often be challenging to unambiguously determine whether a given reaction occurs via energy or redox transfer, and reactions that are characterized as "photoredox" reactions have sometimes been later shown to be energy transfer reactions instead.

We submit, therefore, that the most general term applicable to this entire field is *photocatalysis*, which does not imply any particular mechanism of activation. The use of this nomenclature, unfortunately, has not been without some recent controversy of its own. One point of continuing disagreement is what is implied to be "catalytic" in a photocatalytic process. If a photosensitizer is not directly involved in bond-forming steps and is instead simply a precatalyst for the generation of reactive electrons or holes, can it be considered a catalyst? Does the term "photocatalysis" imply that a reaction must be catalytic in photons in some way?

One could mount a defense of this nomenclature based on any of a number of arguments. For instance, it is supported by IUPAC conventions: a "photocatalyst" is defined as a species that can produce chemical changes in a reaction partner upon absorption of light.[7] The IUPAC definition is quite permissive and does not imply any particular mode of interaction between the photocatalyst and its reaction partners. More importantly, however, the term "photocatalysis" is already broadly used to describe the activity of photoactive semiconductor materials in a variety of applications, ranging from water purification to solar energy conversion. This terminology, therefore, connects contemporary research efforts in photochemically enabled synthesis to this broader, interdisciplinary field that relies on quite similar mechanistic principles and physical considerations.

With respect to the experimental conditions, we have encountered a tremendous diversity in how different researchers report their procedures. Recognizing that most researchers understand that illumination is often rate-determining and that reaction rates can be increased by increasing exposure to light via several means (increased intensity, additional light sources, differently shaped reactor vessels), a set of minimum experimental descriptors can be formulated. A description of the light sources is crucial including type of lamp (manufacturer/model number is desirable), information regarding intensity (e.g., wattage), any available information regarding spectral distribution (spectral data, $\lambda_{\max}$), and for commercial reactors, a manufacturer/model number. In addition, the distance from the light source to the irradiation vessel is key to reproducing the protocol and to estimating the role of heating. Finally, the material of the reaction vessel needs to be specified if it is anything other than standard borosilicate glass.

Contemporary photocatalysis has proven to be incredibly powerful, allowing ready access to reactive species that are either difficult to generate via conventional methods or where such methods prohibited the development of selective processes. In this Special Issue, we are pleased to present 50 contributions from 12 countries showing the vitality of this field, the creativity of its practitioners, and the breadth of transformations that this approach permits. Three contributions on photocatalysis by means of energy transfer and 40 contributions on photocatalysis by electron transfer have been included. Photoredox transformations are net redox neutral when an electron is transferred from or to the substrate transiently and then is ultimately returned, regenerating the photoredox catalyst. Twenty-one contributions focus on such processes covering a range of chemistries including cycloadditions, alkene additions, cross-coupling reactions, substitutions reactions, and even C—H activation reactions. However, it is possible to add an external oxidant that ultimately regenerates the photocatalyst resulting in a net oxidation of the substrate molecule. This type of transformation has seen broad application with a range of oxidants including oxone, persulfates, nitromethane, tetrahalogens, and molecular oxygen. Fifteen contributions focus on this type of chemistry including oxygenation reactions, cyclizations, and fragment couplings. The use of an external reductant to regenerate the photocatalysts and drive a net reduction of the substrate is also feasible and is highlighted with four contributions in this Special Issue. Notably, radical chain propagation processes have been described as the major or competing mechanism in five of the above cases. Intermixed within the above categories are several examples involving dual catalysis where a photoredox catalyst is combined with organometallic, chiral phase-transfer, Lewis acid, or chiral hydrogen-bonding catalysts. Seven further articles provide valuable overviews of the field or address mechanism and catalyst development. These latter two areas are particularly at the frontier of the field. While there has been much experimental study of the mechanisms of these transformation, tools to study the reactive intermediates are limited and the description of electron paramagnetic resonance spectroscopy (EPR) presents a promising direction for processes involving open-shell intermediates. The presence of excited states causes a quantum increase in the complexity of electronic structure calculations, and two articles show how researchers are starting to tackle the relevant issues. The development of new catalyst systems will have a major impact on the field. Three contributions describe different approaches to new catalyst systems including coreactants to expand the range of chemistry available and photoredox catalysts with greater efficiency or lesser environmental footprints.

In summary, the papers of this Special Issue illustrate the wide range of strategies that are being used to harness the power of light in organic chemical transformations. Much has been accomplished in terms of discovering new reaction pathways orthogonal to thermal reaction chemistry, and the prospect for the discovery of additional new reaction types remains strong, especially when interfaced with additional catalyst modes.[8] We hope that you find this Special Issue highlighting contributions in the rapidly growing field of photocatalysis both informative and inspiring.

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Notes

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