C. R. Chimie 18 (2015) 742–751

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

South Europe-Japan Joint Forum on inorganic chemistry and its interfaces
(Strasbourg, France, 17 & 18 October 2014)

Sunlight-driven trifluoromethylation of olefinic substrates by photoredox catalysis: A green organic process

Munetaka Akita *, Takashi Koike

Chemical Resources Laboratory, Tokyo Institute of Technology, R1-27 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:
Received 26 December 2014
Accepted after revision 29 January 2015
Available online 18 June 2015

Keywords:
Photoredox catalysis
Trifluoromethylation
Visible light
Olefinic substrates

ABSTRACT

The principles and utility of photoredox catalysis in organic synthesis are described. After a brief description of the features of the two types of catalytic photoredox processes following the reductive quenching cycle (RQC) and the oxidative quenching cycle (OQC), the discussion is focused on organic transformations based on OQC, in particular the trifluoromethylation of olefinic substrates with electrophilic trifluoromethylating reagents furnishing solvolytic addition products and substitution products. It is concluded that catalytic photoredox systems are *green* from the point of view of harmfulness, safety, and energy source (visible light, including sunlight). Future prospects of photoredox catalysis will be also discussed.

1. Introduction

The sun provides huge and inexhaustible energy to the Earth, and the major component is visible light. It is needless to say that plants utilize the energy for their growth as well as for oxygen evolution [1]. Many scientists in various fields have made challenges to analyze and understand the mechanisms of the complicated biological and chemical systems and to develop chemical systems that mimic functions and reactions occurring therein, occasionally called "artificial photosynthesis" [2]. In the field of inorganic chemistry, electron transfer and energy transfer have been the major concerns and many excellent chemical systems have been developed so far [3]. In contrast, little attention has been paid to applications to catalytic transformations and attempts have been limited. For example, the reduction of *small inorganic molecules* such as proton and carbon dioxide giving hydrogen and carbon monoxide, respectively, has been studied to a considerable extent [3]. Such studies are invaluable from the viewpoint of energy storage, but much less attention has been paid to *catalytic organic transformations*. Although attempts at them have been made sporadically and the obtained results have been reported [4], they have not been studied systematically until recently. Taking into account this situation, we have made challenges toward developing catalytic organic transformations with two different strategies. One is *photoredox catalysis* (For selected reviews on photoredox catalysis see [5]), which is the subject of the present account, and the other is *bimetallic photocatalysis*, which was reviewed previously [6].

On the other hand, introduction of fluorine functional groups to organic skeletons causes dramatic changes of their properties such as liposolubility, water repellency, stability, and heat resistance and, in particular, various medical and agricultural fluorinated chemicals have been developed and launched by making use of these favorable properties [7]. For these purposes, many kinds of techniques for fluorination of organic compounds have been developed and even now new fluorination methods are demanded.

---

* Corresponding author.
E-mail address: matika@res.titech.ac.jp (M. Akita).

http://dx.doi.org/10.1016/j.crci.2015.01.013

We combined these two problems and set up development of novel trifluoromethylation methods of organic compounds involving carbon–carbon bond formation by the sunlight- or visible light-promoted photoredox catalysis as one of our research programs several years ago.

2. Photoredox catalysis

It has been recognized that photoreactions follow pathways different from those of thermal reactions so as to accelerate the reaction or even furnish different products [8]. Most of organic compounds, however, are colorless and, as a result, they cannot absorb sunlight (i.e. visible light). If one wants to utilize the sunlight energy (visible light), some photosensitizer should be added to absorb visible light. There are many kinds of photosensitizers ranging from organic dyes to metal complexes, and we have employed *metal photosensitizers* such as $[Ru(bipy)_3]^{2+}$ salts (**1a** in Fig. 1) and the isoelectronic cyclometalated pyridylphenyliridium complexes (e.g., $Ir(ppy)_3$ (**1b**)) [9]. Because their photophysical properties have been studied for many years, their features, including those of the photo-excited states, are now understood in detail. They have intense absorption bands in the region of visible light and the lifetime of the photo-excited states is of the order of the microsecond, which is long enough to interact with and activate organic molecules.

The key concept of *photoredox catalysis* is summarized in Scheme 1 [5]. The first event occurring upon visible light irradiation is metal-to-ligand charge transfer (MLCT) to form the singlet photo-excited species, which is converted into the triplet excited species ($\boldsymbol{M}^*$) via intersystem crossing in an almost quantitative yield. The resulting triplet species with a μs-order lifetime has a hole in the lower SOMO (the solid oval line) and a higher energy electron in the higher SOMO (in the dotted oval line), which can serve as an oxidant and a reductant, respectively. If an electron donor is present nearby (the upper cycle in Scheme 1), electron transfer from the donor to the hole generates the anionic metal species ($\boldsymbol{M}^-$) together with the oxidized cationic organic species ($\boldsymbol{D}^+$). The resultant anionic metal species may be oxidized by an acceptor in the reaction system to generate the reduced acceptor ($\boldsymbol{A}^-$) in addition to the original ground-state neutral metal species ***M***. Thus if an appropriate reaction system can be designed, a donor ***D*** and an acceptor ***A*** in the reaction system can undergo 1e-oxidation and 1e-reduction to form $\boldsymbol{D}^+$ and $\boldsymbol{A}^-$ during the catalytic cycle, respectively. This cycle is called *reductive quenching cycle* (*RQC*), because the photoexcited species $\boldsymbol{M}^*$ is reduced in the first step. But readers should note that the external substrate is oxidized in the first step of *RQC*. The catalytic cycle can also be initiated by transfer of the higher energy electron of the photoexcited species to an acceptor followed by oxidation of an external substrate, and this cycle is called *oxidative quenching cycle* (*OQC*; the lower cycle in Scheme 1).

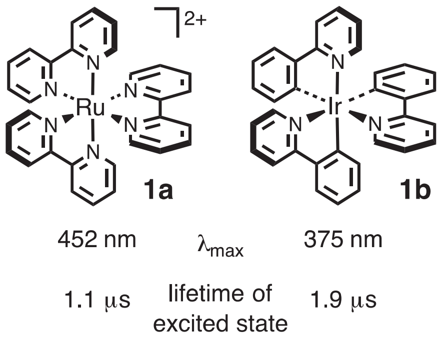
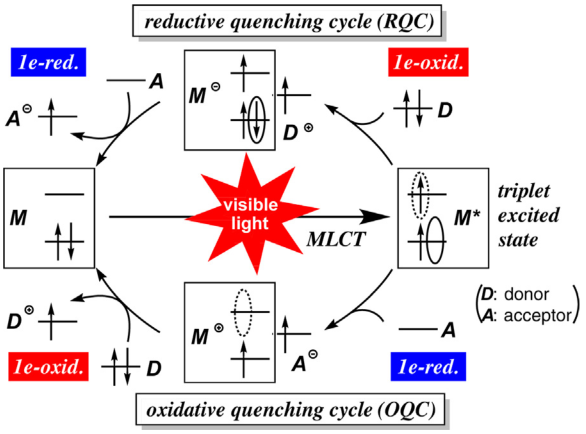


Fig. 1. Structures and photophysical properties of representative photoredox catalysts.



Scheme 1. (Color online.) Photoredox cycles: oxidative and reductive quenching cycles.

This photoredox system has been utilized for many transformations, including the reduction of small inorganic molecules as mentioned above. In those systems, however, *sacrificial* reducing/oxidizing reagents (e.g., trialkylamine) were added to supply/remove electrons to/from the reaction substrate. In the present photoredox systems, however, if the unique redox system can be combined with chemical reactions demanding these two redox functions, *no sacrificial redox reagents needs to be added*, in other words, the system is *redox-neutral*, as it will be described in the following sections.

Catalytic photoredox reactions developed in our laboratory during the last several years are summarized in Scheme 2 [10] (For a review, see also [5l–o]) and are divided into two categories, where the reactions follow either RQC or OQC. All reactions involve C-centered organic radicals as key intermediates, and we have found that the OQC system is particularly useful for *trifluoromethylation* of olefinic substrates (reactions 2b–g), which is the main subject of the present account. Before discussion of trifluoromethylation, one typical example following RQC will be briefly described in the next section.

3. Reactions mediated by reductive quenching cycle (RQC) [10a–d]

Generation of organic radicals under mild reaction conditions has remained to be a problem to be solved even now. During the course of our study, we revealed that hydrocarbyl radicals can be readily generated from the corresponding organoborates by the action of *photoredox*