1-7-2. Pioneering of Photoreactions by Electron Transfer and Photoinduced Electron Transfer

Overview

The development of photoreactions via photoinduced electron transfer has become the mainstream of synthetic organic chemistry. This is because highly reactive species such as radical cations, radical anions, and radicals can be easily generated under mild conditions (room temperature) simply by light irradiation, enabling the cleavage and formation of covalent bonds that are difficult to achieve with thermal reactions. In particular, reduction and oxidation reactions by photoinduced electron transfer (photoredox reaction) have been actively studied. Recently, the combination of photoredox reactions with transition metal catalysts, electrodes, flow reactors, and so on, has been further developed.

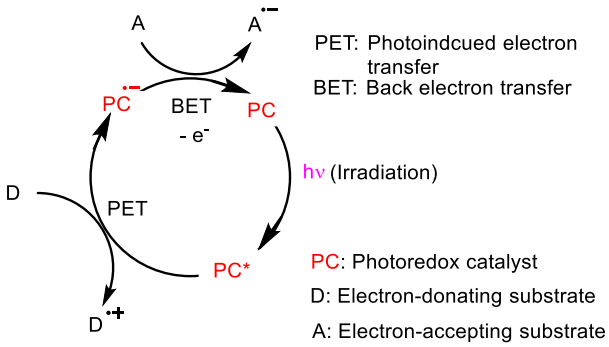

Figure 1. Photoredox reaction.

Current Status and Frontiers

The development of novel synthetic organic reactions based on photoredox reactions has become a major theme in synthetic organic chemistry, involving researchers who have been using transition metals. In Japan, a large number of researchers have pioneered and led this field since the 1970s; refer to Section "1-7-1. Radical Ions" in the Photochemistry Div Report described in Japanese for an overview until the mid-2000s. URL: https://division.csj.jp/div-report/02/0210701.pdf Next, we will introduce some examples of research developments since the 2010s.

1. Photoreactions using one-molecule photoredox catalysts

Numerous examples of photoreactions using photoredox catalysts are known, such as addition reactions of alkenes via radical cations and radical reactions of aliphatic carboxylic acids via photoinduced decarboxylation. One-molecule photoredox catalysts such as Fukuzumi catalyst, Ir catalyst, and 4CzIPN are used in these reactions, which can be reduced or oxidized by photoexcitation of a single molecule. Many derivatives of these catalysts have been synthesized and used for photoredox reactions.

2. Photoreactions combining one-molecule photoredox catalysts and transition metal catalysts

The radical species generated by the abovementioned photoredox reactions are trapped by transition metals such as Ni and Pd, and reactions using the generated organic transition metal complexes have been attempted. For example, it is known that a new carbon-carbon bond can be formed by trapping alkyl radicals generated by photoredox reactions with Ni and cross-coupling the resulting alkyl Ni complex with aryl bromide.

3. Reactions via photoinduced LMCT transition

Reactions utilizing electron transfer from ligands to metals by photoexcitation of organometallic complexes (LMCT transitions) are being actively developed. In particular, electron transfer from ligands such as bipyridine to transition metals such as Ni and Cu changes the valence and the reaction proceeds.

4. Photoreactions using two-molecular photoredox catalysts

Some unique reactions using two-molecular photoredox catalysts, in which two molecules are used and can be reduced and oxidized by photoexcitation, have been known. Although Japanese researchers have long been studying "redox photosensitized reactions," there have been few examples of such reactions, and their advantages have not been clear. Various two-molecular photoredox reactions, including photoinduced decarboxylative and photoinduced deboronative reactions, have been developed, and their advantages such as the fact that the reduction and oxidation potentials of catalysts can be easily changed by simply replacing molecules and that back electron transfer can be suppressed have been found (Yoshimi et al.). For example, direct photoinduced decarboxylation of benzoic acid has been successfully achieved using these catalysts, but photoinduced decarboxylation does not proceed due to fast back electron transfer when one-molecule photoredox catalysts are used.

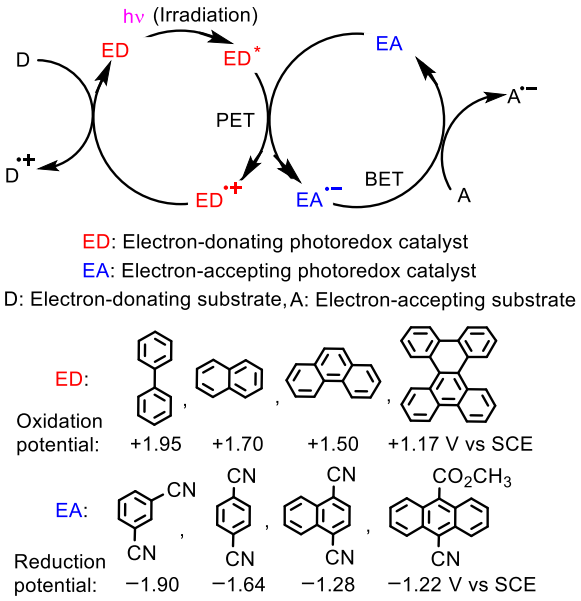

Figure 2. Two-molecule photoredox reaction.

References

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Future Perspectives and Directions

Issues to be solved or realized by the end of the decade: Realization of organic photoreactions at the industrial level, Expansion of photoreactions using sunlight, Synthesis of useful organic compounds using carbon dioxide and sunlight, and Development of photoreactions that can proceed only in flow reactors.

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