Tetrahedron Letters 59 (2018) 1651–1660

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Energy transfer or electron transfer?—DFT study on the mechanism of [2+2] cycloadditions induced by visible light photocatalysts

Mingyang Jiao[a], Yi-wen Ju[b], Bo-Zhen Chen[a,*]

[a] School of Chemical Sciences, University of Chinese Academy of Sciences, No. 19A, YuQuan Road, Beijing 100049, PR China
[b] College of Earth Science, University of Chinese Academy of Sciences, Key Laboratory of Computational Geodynamics, Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 9 January 2018
Revised 8 March 2018
Accepted 16 March 2018
Available online 17 March 2018

Keywords:
Visible light
Energy transfer
Electron transfer
Photocatalyst
[2+2] cycloaddition
Stereoselectivity

ABSTRACT

The intramolecular [2+2] cycloaddition of 1,3-dienes under visible light irradiation investigated by Yoon and his co-workers shows remarkably high yield and stereoselective differences under different photocatalysts. The reaction was speculated to be induced by energy transfer. However, the origin for these phenomena is still unclear. In this scene, the detailed mechanism for the [2+2] cycloaddition of 1,3-dienes under visible light has been investigated using density functional theory B3LYP and TPSSTPSS methods. The result shows that the reaction not only can be induced by energy transfer between photocatalysts and reactants, but also can be induced by electron transfer between them. The [2+2] cycloaddition induced by energy transfer is carried out along the potential energy surface (PES) of triplet excited states ($\mathbf{T_1}$) firstly, and then goes back to the singlet ground state ($\mathbf{S_0}$) via MECPs (minimum energy crossing points) between the PESs of the $\mathbf{S_0}$ and $\mathbf{T_1}$ states, forming the product in the $\mathbf{S_0}$ state. The [2+2] reaction induced by electron transfer proceeds along the doublet state PES of the cation radical reactant and the neutral four-membered ring product could be obtained by electron transfer from the corresponding reactant or reduced photocatalyst. The origin of stereoselectivity of the [2+2] reaction is attributed to the reaction mechanism difference under different photocatalysts.

Introduction

Cycloaddition products with four-membered carbon rings are key substances in the synthesis of natural products.[1] [2+2] cycloadditions under photo-irradiation are the most direct method to build four-membered carbon rings.[2–4] Because of low energy consumption, [2+2] cycloadditions under visible light have attracted the attention of many researchers, such as Yoon,[5–10] Bach[11–14] and Xiao.[15]

A lot of transition metal complexes, such as Ru, Ir and other transition metal complexes,[5–7,9,10,16] have been used to catalyze [2+2] cycloaddition reactions under visible light. Besides, organic compounds can also be used as photocatalyst to catalyze cycloaddition reactions.[12,17] It is generally believed that the mechanism of [2+2] cycloaddition induced by visible light has two possibilities: an energy transfer pathway (induced by energy transfer and subsequent [2+2] cycloadditions along the potential energy surface (PES) of the triplet excited state ($\mathbf{T_1}$)) and an electron transfer pathway (induced by electron transfer and subsequent anion/cation radical [2+2] cycloadditions).

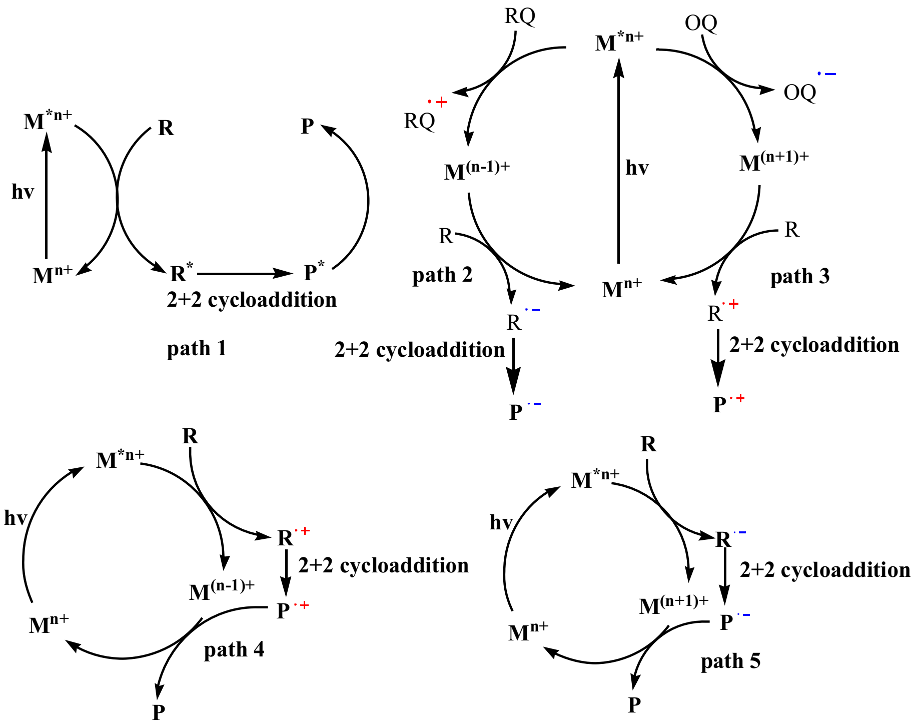
The energy transfer pathway happens as follows[18]: $\mathbf{M^{*n+}}$ (excited state transition metal complexes) can be formed under irradiation of visible light. During the process of $\mathbf{M^{*n+}}$ back to $\mathbf{M^{n+}}$, energies can be transferred to the reactant $\mathbf{R(S_0)}$, forming the reactant $\mathbf{R(T_1)}$ (path 1 in Scheme 1). Then, the [2+2] cycloaddition can be carried out along the PES of the $\mathbf{T_1}$ state.

The electron transfer pathway can be divided into two cases depending on the reaction system with and without a quenching agent. In the existence of a quenching agent, the reaction can be induced like this: at first, $\mathbf{M^{*n+}}$ is formed from $\mathbf{M^{n+}}$ under visible light. After it reacts with an oxidative/reductive quenching agent, $\mathbf{M^{(n+1)+}/M^{(n-1)+}}$ will be formed. $\mathbf{M^{(n-1)+}}$ may induce an anion [2+2] cycloaddition reaction (path 2 in Scheme 1), while $\mathbf{M^{(n+1)+}}$ may induce a cation [2+2] cycloaddition reaction (path 3 in Scheme 1). In the absence of quenching agents, $\mathbf{M^{*n+}}$ may act as an oxidative/reductive agent itself. That is, $\mathbf{M^{*n+}}$ reacts with reactant $\mathbf{R(S_0)}$ directly, producing $\mathbf{R^{\cdot+}/R^{\cdot-}}$ and $\mathbf{M^{(n-1)+}/M^{(n+1)+}}$. $\mathbf{R^{\cdot+}/R^{\cdot-}}$ undergoes a [2+2] cycloaddition reaction, forming cation/anion radical products $\mathbf{P^{\cdot+}/P^{\cdot-}}$. The neutral product $\mathbf{P(S_0)}$ will be produced after $\mathbf{P^{\cdot+}/P^{\cdot-}}$ reacts with $\mathbf{M^{(n-1)+}/M^{(n+1)+}}$. $\mathbf{M^{(n-1)+}/M^{(n+1)+}}$ goes back to $\mathbf{M^{n+}}$ simultaneously. All these constitute a cation/anion radical cycle (paths 4 and 5 in Scheme 1). In conclusion, only path 1 is the energy transfer pathway, paths 2–5 are all electron transfer pathways.

---

* Corresponding author.
E-mail address: bozhenchen@hotmail.com (B.-Z. Chen).

https://doi.org/10.1016/j.tetlet.2018.03.044



Scheme 1. Possible mechanism for [2+2] cycloadditions induced by visible light. path 1 and paths 2–5 are energy transfer and electron transfer pathways, respectively. R: reactants. M: photocatalysts. P: products. RQ: reductive quenchers. OQ: oxidative quenchers.

Yoon and his co-workers have investigated the [2+2] cycloaddition of 1,3-dienes under visible light irradiation.[7] Transition metal complexes $[Ru(bpy)_3]^{2+}$ and $[Ir(^{F}ppy)_2(^{tBu}bpy)]^{+}$ were selected as photocatalysts. A yield of 90% cyclobutane product was obtained in the absence of oxidative/reductive quenching agents. The reaction was speculated to be induced by energy transfer. Additionally, they found that the intramolecular [2+2] cycloaddition of **1R** (see Table 1) can be induced by $[Ir(^{F}ppy)_2(^{tBu}bpy)]^{+}$, not by $[Ru(bpy)_3]^{2+}$, while that of **5Re** (E isomer of **5R** shown in Table 1) can occur under either of them. For the [2+2] cycloaddition of **5Re**, the four-membered carbon ring product was formed as a 1:1 mixture of E and Z isomers at the presence of $[Ir(^{F}ppy)_2(^{tBu}bpy)]^{+}$, whereas the ratio of E/Z was higher than 10:1 under $[Ru(bpy)_3]^{2+}$. These facts aroused our curiosity about the reactions. Firstly, were the reactions induced only by the energy transfer? Can electron transfer also trigger the [2+2] cycloaddition? Secondly, why did the reaction show obviously stereoselectivities when $[Ru(bpy)_3]^{2+}$ was used as catalysts, while not when $[Ir(^{F}ppy)_2(^{tBu}bpy)]^{+}$ acted as catalysts?

Based on the issues above, the present study gives a computational investigation on intramolecular [2+2] cycloadditions of 1,3-dienes catalyzed by $[Ru(bpy)_3]^{2+}$ and $[Ir(^{F}ppy)_2(^{tBu}bpy)]^{+}$ under visible light. Herein we explored the reaction pathways along the PES of the $\mathbf{T_1}$ state and along the PES of the doublet state for ion radicals. Based on these calculated results, we could gain insights into experimental phenomena. To the best of our knowledge, no computational investigation was taken to show the mechanism of the reaction and to distinguish the energy transfer pathway and electron transfer pathway of [2+2] cycloadditions so far. We believe that our studies on the mechanism could be beneficial to experimental realizations.

Computational methods

All calculations were carried out using the Gaussian 09 program.[19] By comparing with the geometry structures optimized by a series of DFT methods (B3LYP,[20–23] TPSSTPSS,[24] M06L[25,26] and B3PW91[27,28]) and basis sets (LANL2DZ[29] and SDD[30–32] for metal atoms and 6-31G(d, p) for nonmetal atoms) for transition metal complexes $[Ru(bpy)_3]^{2+}$, we found that the geometry structure optimized by TPSSTPSS/BS1 is closest to the experimental data.[33] (BS1 denotes a mixed basis set of SDD for metal atoms and 6-31G(d, p) for nonmetal atoms). The details can be found in Table S1. Therefore, TPSSTPSS/BS1 was used to optimize the geometries of transition metal complexes $[Ru(bpy)_3]^{2+}$ and $[Ir(^{F}ppy)_2(^{tBu}bpy)]^{+}$. Based on Subotnik's researches,[34–37] DFT methods have their own limitations on calculations for the energy of excited states with charge transfer characters. However, no excited states with charge transfer characters are involved in our reaction systems. Considering the electronic correlation and system size, DFT calculations should be appropriate.

Geometries of other nonmetal substances were optimized at the B3LYP/6-31G(d, p) level. The vibrational frequency was calculated at the same level to confirm whether the optimized stationary point is a minimum (no imaginary frequencies) or a transition state (only one imaginary frequency). The intrinsic reaction coordinate (IRC)[38,39] pathways have been traced to confirm whether the transition state connects the reactant, intermediate, or product.

The improved energetic results were calculated by the single-point energy calculations with the solvent effects obtained by SMD[40] solvent model at TPSSTPSS/BS2. BS2 designates a mixed basis set of SDD for the Ru and Ir atoms and 6-311+G(d, p) for nonmetal atoms. The enthalpies and Gibbs free energies at 298 K and 1 atm at TPSSTPSS/BS2 level were gotten from TPSSTPSS/BS1 and B3LYP/BS1 frequency analysis calculations for transition metal complexes and nonmetal substances, respectively. The Gibbs free energies at the TPSSTPSS/BS2 level were used in the following discussion unless otherwise specified.

Results and discussion

In order to give an insight into the experimental phenomenon mentioned above, five reactants with different substituents