

Ab initio molecular design for [2+2] photocycloaddition and metathesis reactions

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Well-known [2+2] photocycloaddition reactions of two olefins leading to a cyclobutane ring formation is thermally forbidden in the ground state due to Woodward-Hoffman rules and typically occurs only after sensitization to the triplet state. Direct excitation to the lowest lying singlet states requires UV light and leads to fragmentation of the system. Compared to photocycloadditions, photocycloreversions are still a subject of ongoing reactions. The reversion is an important step in the metathesis reaction [1], which represents a viable way for transferring double bond. Photocycloreversion is particularly attractive in the context of photoredox catalysis [2], because ring cleavage can be also achieved both in a cationic or anionic state via photoredox catalysis using e.g. flavinium salts as the catalyst. [3] Theoretical description of the photocycloreversion is, however, difficult due to complicated electronic structure of intermediates. We study the formation and fragmentation of [2+2] systems using *ab initio* molecular dynamics in ground and excited states. Using accelerated molecular dynamics approaches we evaluate the free energy profiles for the reactions and we estimate reaction barriers. We also benchmark DFT approaches against high-level multi-reference calculations. Finally, we perform a screening of the systems in the chemical space, trying to identify potential candidates for further experimental identification.

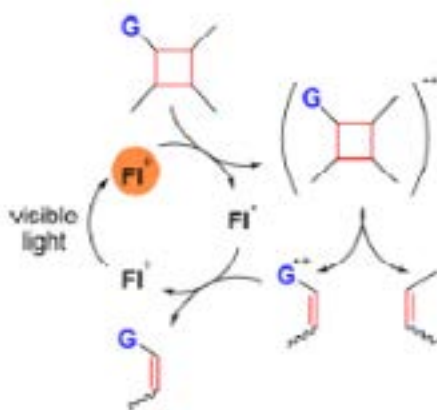


Figure : Flavinium salt facilitates the electron transfer from or to the cyclobutane moiety, upon which the ring cleavage can take place. [4]

Recent Publications

1. Poplata, S.; Tröster, A.; Zou, Y.; Bach, T. *Chem. Rev.* **2016**, 116, 9748–9815.
2. Mojr, V.; et al. *Chem. Commun.* **2015**, 51, 12036–12039.
3. Muchová, E.; Bezek, M.; Suchan, J.; Slaviček, P. *In preparation for IJQC.*
4. Hartman, T.; Cibulka, R. *Org. Lett.* **2016**, 18 (15), 3710–3713

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