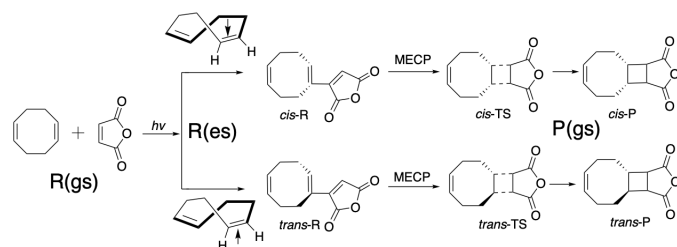# MECHANISTIC STUDY OF PHOTOCHEMICAL [2+2] CYCLOADDITION BETWEEN 1,5-CYCLOOCTADIENE AND MALEIC ANHYDRIDE

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One famous family of chemically recyclable polymers are produced from fused-ring cyclooctene monomers, and their chemical properties are highly tunable by modifying the functional groups from the monomers. The photochemical [2+2] cycloaddition is crucial to synthesizing such a fused-ring cyclooctene monomer, but its mechanistic details remain mysterious. Recently we observed a significant isomerization probability in the photochemical [2+2] cycloaddition between 1,5-cyclooctadiene and maleic anhydride, which produces more *trans*-fused-ring cyclooctene than the *cis* counterpart. In the present work, we investigated the photochemical mechanism (figure) of this reaction using density functional theory (DFT), with the aim of decoding when this isomerization happens and how it is correlated to the yields of products. We found that the isomerization occurs only at the first excited state after a charge transfer photoexcitation from 1,5-cyclooctadiene to maleic anhydride, and its activation barrier depends on the structure and orientation of the reactant complex. After the isomerization, the reactant complex barrierlessly reaches a conical intersection (CI) between the ground and the first excited states and quickly passes to the ground state of the product after climbing over an affordable activation barrier. Compared to a *cis* counterpart, the *trans* product exhibits a slightly lower total energy and a significantly lower activation barrier, indicating its *trans* configuration is favorable both thermodynamically and kinetically. Our model has been effectively extended to various functional groups and can be used to guide the rational design of photochemically synthesized fused-ring monomers.