

UNIVERSITY OF RHODE ISLAND
Department of Chemistry Ph.D. Seminar

2:00 PM, Friday, March 03, 2023
Beaupre Room 105

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Investigating the Mechanisms and
Expanding the Reactivity of Cu(I)
Catalyzed [2+2]
Photocycloaddition Reactions of
Olefins

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Investigating the Mechanisms and Expanding the Reactivity of Cu(I) Catalyzed [2+2] Photocycloaddition Reactions of Olefins

Intermolecular and intramolecular [2+2] photocycloaddition reactions facilitate the generation of cyclobutane moieties which are otherwise difficult to synthesize. We have investigated how the structure and the ring strain of a substrate affect the reactivity and the rate of the Cu(I) catalyzed [2+2] photocycloaddition reactions. We have used norbornene and cyclohexene as models to explicate the mechanism of the Cu(I) catalyzed intermolecular photocycloaddition reactions by using X-ray and optical transient absorption techniques. The mechanism for norbornene shows an initial metal to ligand charge transfer (MLCT) state which lasts for 18 ns prior to reverse electron transfer. Cyclohexene shows a change in metal-ligand bond strength instead of undergoing charge transfer. The evidence of the change in bond strength is consistent with the proposed idea of Salomon and Kochi for the formation of a more strained *trans*-cyclohexene intermediate.

We have also worked to expand the scope of Cu(I) catalyzed intramolecular [2+2] photocycloaddition reactions using 1,6-heptadiene, 1,7-octadiene, and 1,8-nonadiene linear alkenes as model substrates. In previous studies, only 1,6-dienes have been shown to undergo Cu(I) catalyzed photocycloaddition. Using DFT/TD-DFT calculations and high energy resolution X-ray absorption spectroscopy to illuminate the structure-functional differences between photoreactive and nonreactive substrates, we have been able to sterically modify the structure of non-reactive substrates toward photoreactive trajectories. We have also verified this novel reactivity using NMR time-course studies.