

학술상1

MECHANISTIC UNDERSTANDING AND SYNTHETIC
APPLICATIONS OF SET PHTOCHEMICAL
REACTIONS OF IMIDE-ORGANOSILANE SYSTEMS

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Our studies in the area of single electron transfer (SET) photochemistry have led to the discovery of efficient processes, which result in regioselective formation of carbon-centered radicals. These processes take advantage of the high rates of nucleophile assisted desilylation of α -trialkylsilyl substituted cation radicals for the regioselective formation of carbon-centered radicals. The results of earlier laser flash photolysis studies probing the dynamics of decay of cation radical intermediates derived by SET oxidation of α -trialkylsilyl substituted donors showed that the rates of bimolecular desilylation of these intermediates exceed those for most other cation radical α -fragmentation processes (e.g., α -deprotonation). The high rates of nucleophile assisted α -desilylation serve as the basis for the design of efficient SET-induced photomacrocyclization reactions of polyether, polythioether, polyamide and peptidelinked phthalimides. Irradiation of trimethylsilyl-terminated substrates in these families promotes chemically efficient photocyclization reactions that produce polyfunctionalized macrocyclic products. The mechanistic route for these processes involves initial SET from the donor sites in the side chain to the excited phthalimide chromophore, leading to mixtures of interconverting zwitterionic biradical intermediates. In each case, nucleophile assisted desilylation occurs selectively on the zwitterionic biradical intermediate, in which the cation radical resides at the terminal α -silyl center, to produce neutral biradical precursors of the products.

Recent studies in our laboratories are designed to obtain information about factors that control the chemical efficiencies/regioselectivities and quantum yields of SET-promoted reactions of acceptor-polydonor systems. The results of this effort reveal that the relative energies of interconverting intermediate zwitterionic biradicals and the energy barriers for their α -heterolytic fragmentation reactions influence the chemical yields and quantum efficiencies of SET-promoted photocyclization reactions of acceptor-polydonor substrates. These studies which have led to a clear

mechanistic understanding of SET photochemical reactions of polydonor-substituted phthalimides.