SINGLE PHOTON INITIATED DECOMPOSITION REARRANGEMENT REACTIONS (SPIDRR) OF ORGANIC MOLECULES MEDIATED BY THE Ni\(^{+}\) CATION

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The Bellert group at Baylor University has developed a novel method for performing single photon initiated decomposition rearrangement reactions (SPIDRR) of organic molecules mediated by a transition metal cation. The advantage that SPIDRR affords is the direct measurement of first order microcanonical rate constants, k(E), determined at resolved internal energies. Furthermore, the SPIDRR technique measures kinetic details of exothermic reactions where product production is limited only by submerged activation barriers (kinetic barriers that are at energies below the separated reactant limit). Thus, such reactions approach unit efficiency, are thermodynamically driven, and are of greater relevance to catalytic research. Direct measurements of k(E) values extend to isotopically labelled species that provide direct measurement of the kinetic isotope effect (KIE), furnishing unique insight into the mechanistic details of a reaction.

This talk presents results from the visible photon initiated, Ni\(^{+}\) induced decarbonylation reaction of propionaldehyde. Here a rather unique energy dependent behavior of the measured rate constants was observed and attributed to a dynamic competition between parallel reaction coordinates available to the photo-excited precursor. RRKM calculations in concert with high level DFT is used to support and further experimental results.