CAPTURE AND CHARACTERIZATION OF NASCENT UV PHOTODECOMPOSITION PRODUCTS WITH MASS-SELECTIVE CRYOGENIC TRAPPING TECHNIQUES

OLIVIA MOSS, PAYTEN HARVILLE, TIM SCHLEIF, EVAN H PEREZ, MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

The photodecomposition pathways of polyatomic molecules are important processes ranging from UV photodamage of biopolymers to the transformations undergone by aerosols in the troposphere. This typically occurs in complex environments in which chromophores are embedded in electrolyte solvents. In this poster, we will present an experimental scheme in which target molecular ions are complexes with ions and solvent molecules and exposed to UV light in a temperature controlled ion trap. The nascent photoproducts are then cooled and tagged with H₂ molecules so that their structures can be established by comparison of their vibrational band patterns with those calculated for candidate structures. We demonstrate this approach on the photodecarboxylation of the conjugate base of benzoylbenzoic acid, a proxy molecule widely used to simulate radical photoinitiation by UV excitation at the air-water interface. We cool and trap the phenide carbanion photoproduct as well as a radical anion generated by loss of HCO_2 from the deprotonated scaffold. We will discuss the dependence of the branching ratios for CO_2 loss vs solvent loss in the BBA-M²⁺-(solvent)_n complexes with M=Mg and Ca and solvent = CH₃CN and H₂O. Analysis of the frequency dependence of the product branching ratios supports a model in which some of the UV photon energy remains trapped in an electronically excited state, potentially revealing formation of triplet states long invoked to rationalize their propensity to act as radical photosensitizers.