PHOTOFRAGMENTATION DYNAMICS OF ICN⁻(CO₂)_n

JOSHUA P. MARTIN, JOSHUA P. DARR, W. CARL LINEBERGER, JILA and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309; ANNE B. MCCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

We report photofragmentation studies of mass-selected $ICN^{-}(CO_2)_n$ (n=0-18) cluster anions following 400, 500 and 600 nm excitation. Photodissociation of ICN^{-} following excitation *via* a 500 nm photon results exclusively in an I⁻ anionic photoproduct. However, excitation at either 400 nm or 600 nm results in 30% CN^{-} and 70% I⁻ anionic photoproducts. Complexation of ICN^{-} with two or more CO_2 molecules opens a third product channel, recombination of the chromophore on the ground state, a channel that is observable at all three photon energies. The product branching ratios for photodissociation of $ICN^{-}(CO_2)_n$ show sharp contrast to trends previously observed in dihalide studies of $IBr^{-}(CO_2)_n$ and $I_2^{-}(CO_2)_n$, but are strikingly similar to results found for $ICI^{-}(CO_2)_n$. Notably, a peak in the percentage of recombined photoproducts observed as a function of the number of solvent molecules shifts to larger n values as photon energy increases and does not reach 100% in the first solvation shell. It is likely that an intracluster reaction involving formation of the molecule $NCCO_2^{-}$ plays a significant role in the dynamics observed following excitation of the $ICN^{-}(CO_2)_n$ anion.