

Competing Pathways from the 266 nm Photodissociation of Primary, Secondary and Tertiary Alkyl Iodides

Michael A. Todt, Alex Rose, Kiana Leung, and H. Floyd Davis*

Department of Chemistry and Chemical Biology

Baker Laboratory, Cornell University, Ithaca, NY 14853-1301, USA

Abstract

The 266 nm photodissociation dynamics of representative gaseous primary, secondary, and tertiary alkyl iodides were compared through studies of 1-iodopropane, 2-iodopropane, and t-butyl iodide. Two complementary detection methods, vacuum ultraviolet photoionization, and 100 eV electron impact ionization, were employed using a rotatable source crossed molecular beams apparatus with fixed detector. The photochemistry of 1-iodopropane was found to be similar to methyl and ethyl iodide, with 72% of the iodine atoms excited $I^*(^2P_{1/2})$ and 28% ground state $I(^2P_{3/2})$, with no evidence ($< 0.3\%$) for production of HI + propene. Significantly different behavior was found for photodissociation of the secondary and tertiary iodides, with C-I bond fission leading primarily to ground state $I(^2P_{3/2})$, and significant HI ($v > 3$) production via fast 1,2-elimination. The HI yield was found to be $9 \pm 2\%$ for 2-iodopropane and $12 \pm 2\%$ for t-butyl iodide. The anisotropy (β) parameters for all observed channels, including HI elimination, approached the limiting value of 2, indicating that all channels occur rapidly following initial excitation to 3Q_0 . The roles of increasing methyl substitution at the α -carbon atom in enhancing nonadiabatic behavior ($1^\circ < 2^\circ < 3^\circ$) in alkyl iodide photodissociation, and the occurrence of secondary spontaneous decomposition of the alkyl radicals following C-I bond fission, are discussed.