

## PHOTOFRAGMENTATION PATHWAYS OF N-BUTYL BROMIDE

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Dissociation of organic halides has been used for studying ultrafast processes over the last three decades given their relative simplicity and the significance in atmospheric chemistry. Specifically, photofragmentation of alkyl bromides with UV light has attracted substantial attention because of the ozone depletion potential of Br atoms. This presentation summarizes our recent results on the ultrafast photodissociation mechanisms of n-butyl bromide resolved using femtosecond time-resolved mass spectrometry. Multiple dissociative pathways occur upon photo excitation of n-butyl bromide include C-Br scission, C-C dissociation, and hydrogen elimination leading to unsaturated carbon bonds. The dissociative A state is accessed via two UV photon adsorption of two UV pump photons. This state undergoes direct dissociation of the C-Br bond within 160 fs. Three photon excitation reaches the n-5p Rydberg state, where several competing fragmentation pathways are monitored. The fastest relaxations occur in states which are highly excited and have C-H dissociation leading to double and triple C-C bond formation with lifetimes of 500 fs. Dissociation on the ion-pair state occurs within 10 ps to produce the butyl radical. Additionally,  $\beta$  elimination of HBr from the parent molecule occurs within 4 ps. The depopulation of the 5p Rydberg state through internal conversion activates vibrations along the carbon backbone and produces an intermediate (bromopropyl radical) within 600 fs. The bromopropyl radical undergoes a concerted ring-closure and Br elimination into highly stable cyclopropane within 7.5 ps. The reaction pathways and potential energy curves were identified with the aid of density functional theory calculations. These results elucidate the elementary steps and mechanism which are fundamental in atmospheric chemistry and provide insight into how electronic photoexcitation is dissipated into the vibrational motions of the carbon backbone of simple hydrocarbons.