

Reactivity of Halogenated Ethylene Ions using Photoionization and Collisional Activation

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The gas phase chemistry of isolated ethylene ions and of small clusters of these compounds displays many interesting features: isolated state decay, isomerization processes to unconventional species, nonadiabatic couplings etc. In this work, metastable ion decompositions, collisional activation and photoionization were used to measure the kinetic energy release distributions for the fragmentations of singly ionized 1,1- and 1,2-difluoroethylene and vinylbromide.

Metastable ion dissociations (MI) and collisionally activated dissociations (CAD) have been investigated using the accelerating voltage scan method with a forward geometry AEI-MS9 sector mass spectrometer. The associated kinetic energy release distributions (KERD) have been extracted via the Holmes-Osborne method. A retarding field technique coupled with a quadrupole mass filter allowed us to record KERDs from dissociative photoionization with the resonance lines at 21.21 eV (HeI) and 16.67 and 16.85 eV (NeI). On the same experiment a Lindau-type electron analyzer allowed us to perform photoion-photoelectron coincidence (PIPECO) experiments.

Four channels have been studied for the difluoroethylene ions: loss of F, HF, CF and CH₂F. Whereas the metastable HF loss shows only a high energy KERD starting at 0.4 eV, an additional low energy component clearly appears upon collisional activation. This component has been interpreted as resulting from the production, at higher internal energies, of the fluorovinylidene fragment cation. The KERD corresponding to the collisionally activated F loss displays two components, a statistical one and a non statistical one. This behaviour can be correlated to the breakdown diagram obtained by PIPECO. The non statistical component corresponds to the dissociation of the C state of the molecular ion and our data suggest that this leads to electronic excitation of the ionic fragment. The CF loss upon CAD is characterized by an average KER of 13 meV, whereas for the CH₂F loss, we observe an average KER of 0.25 eV to 0.32 eV, depending on the pressure conditions. These dissociation processes involve a nonadiabatic coupling between two potential energy surfaces.

Four channels have been studied in the dissociation of the vinylbromide cation, corresponding respectively, to the loss of Br, HBr, C₂H₃ and C₂H₂. The observed KERDs give us information on the statistical nature of these dissociations and on the internal energy deposited upon CAD.