

Photodissociation of $\text{CF}_2\text{ICF}_2\text{I}$ and CF_2I_2 in solution probed by femtosecond infrared spectroscopy

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Photodissociation dynamics of $\text{CF}_2\text{ICF}_2\text{I}$ and CF_2I_2 in solution was investigated by probing the C-F stretching mode using femtosecond infrared spectroscopy after excitation with a 267-nm photon. Dissociation of the first I atom was faster than 0.3 ps after the UV absorption. All of the resulting haloethyl radicals undergo the secondary dissociation with two time constants; the radical from the *anti*- $\text{CF}_2\text{ICF}_2\text{I}$ in CCl_4 and in acetonitrile solutions dissociate with time constants of 175 ± 5 ps and 40 ps, respectively. The radical from *gauche*- $\text{CF}_2\text{ICF}_2\text{I}$ in both solutions dissociates with the same time constant of 7 ± 1 ns. Some portion of the radical from $\text{CF}_2\text{ICF}_2\text{Br}$ geminately rebinds and the remaining forms CF_2CF_2 with a time constant of 160 ns. A photodissociation mechanism that explains the conformer-dependent dissociation rate as well as solvent-dependent dissociation rate was suggested based on a potential energy surface calculated CASSCF.