

Competitive Bond Rupture in Photodissociation of Bromoacetyl Chloride, 2- and 3-bromopropionyl Chlorides: Adiabatic versus Diabatic Dissociation

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Competitive bond dissociation mechanisms for bromoacetyl chloride, 2- and 3-bromopropionyl chlorides following the transition $^1[n(O)\rightarrow\pi^*(C=O)]$ at 234-235 nm are investigated, yielding branching ratios of C-Br/C-Cl bond fission to be 0.47, 0.24, and 0.098, respectively, by using (2+1) resonance-enhanced multiphoton ionization (REMPI) technique equipped with velocity ion imaging. The fragment branching ratios depend mainly on dissociation pathway and orbital distance between Br and C=O chromophore. The C-Cl bond fission is anticipated to follow an adiabatic potential surface, for a strong diabatic coupling between the $n(O)\pi^*(C=O)$ and $n_p(Cl)\sigma^*(C-Cl)$ bands. In contrast, the C-Br bond fission is subject to much weaker coupling strength between $n(O)\pi^*(C=O)$ and $n_p(Br)\sigma^*(C-Br)$, and a diabatic pathway is preferred for bromoacetyl chloride and 2-bromopropionyl chloride leading to the excited state products. For 3-bromopropionyl chloride, the available energy can not reach the excited state products such that the C-Br bond fission has to proceed via an adiabatic pathway with severe suppression by nonadiabatic coupling. The fragment translational energies and anisotropy parameters for the three molecules are also analyzed and appropriately interpreted.

References:

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