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Ultraviolet photodissociation dynamics of the cyclohexyl radical

MICHAEL LUCAS, YANLIN LIU, JINGSONG ZHANG, Univ of California - Riverside — Cycloalkanes are important components in conventional fuels and oil shale derived fuels and the combustion of cyclohexane fuels leads to the production of benzene, a pollutant precursor. One of the pathways from cyclohexane to benzene is through sequential hydrogen loss, including the cyclohexyl radical as an intermediate. The ultraviolet (UV) photodissociation dynamics of the cyclohexyl ($c\text{-C}_6\text{H}_{11}$) radical was studied for the first time using the high- n Rydberg atom time-of-flight (HRTOF) technique in the range of 232-262 nm. The translational energy distributions of the H-atom loss product channel, $P(E_T)$'s, show a large translational energy release and a large fraction of average translational energy in the total excess energy, $\langle f_T \rangle$, from 232-262 nm. The H-atom product angular distribution is anisotropic with a positive β parameter. The most likely H-atom loss pathway is an axial H ejection from the β -carbon in cyclohexyl to form cyclohexene + H, which along with the positive β parameter, indicates that the transition dipole moment, μ , is perpendicular to the ring. The $P(E_T)$ and anisotropy of the H-atom loss product channel are significantly larger than those expected for a statistical unimolecular dissociation of a hot radical, indicating a non-statistical dissociation mechanism. The dissociation mechanism is consistent with direct dissociation on a repulsive excited state surface or on the repulsive part of the ground state surface to produce cyclohexene + H, possibly mediated by a conical intersection. Cyclohexyl is the largest radical so far showing a direct dissociation mechanism.

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