PHOTODISSOCIATION DYNAMICS OF THE PHENYL RADICAL VIA PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY

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Photofragment translational spectroscopy was used to study the photodissociation dynamics of the phenyl radical at 193 and 248 nm. Time of flight data collected for the C₆H₆, C₅H₆, and C₄H₂ fragments show the presence of two decomposition channels. The only C₆H₆ decomposition channel observed at 248 nm corresponds to CH bond fission from the cyclic radical producing ortho-benzylene. The translational energy distribution peaks at 0 kcal/mol and is consistent with no exit barrier for the H loss process. At 193 nm photodissociation, however, H loss was observed to be the minor channel, while the major decomposition pathway corresponds with decyclization of the C₆H₆ radical and subsequent fragmentation to n-C₅H₅ and C₄H₂. These two momentum matched photofragments have a translational energy distribution that peaks around 9 kcal/mol, indicative of a process that proceeds through a tighter transition state. Previous theoretical work on the unimolecular decomposition of the phenyl radical predicts a second H loss process that occurs after C₆H₆ decyclization resulting in the linear C₅H₄ photofragment. This channel cannot be unambiguously discerned from the C₅H₄⁺ time of flight data, but is believed to take place since decyclization is observed.