

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 C_6H_4 , C_4H_3 , and C_2H_2 photofragments show the presence of two decomposition channels. The only C_6H_5 decomposition channel observed at 248 nm corresponds to CH bond fission from the cyclic radical producing *ortho*-benzynes. 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 C_6H_5 radical and subsequent fragmentation to *n*- C_4H_3 and C_2H_2 . 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^a predicts a second H loss process that occurs after C_6H_5 decyclization resulting in the linear C_6H_4 photofragment. This channel cannot be unambiguously discerned from the $C_6H_4^+$ time of flight data, but is believed to take place since decyclization is observed.

^aL. K. Madden, L. V. Moskaleva, S. Kristyan, and M. C. Lin *J. Phys. Chem. A* **1997**, 101, 6790.