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Photodissociation dynamics of ethyl ethynyl ether: A ketenyl radical precursor MARIA KRISCH, JOHANNA MILLER, LAURIE BUTLER, University of Chicago, HONGMEI SU, RICHARD BERSOHN[1], Columbia University, JINIAN SHU, Lawrence Berkeley National Laboratory — We investigate the photodissociation dynamics of ethyl ethynyl ether at 193.3 nm with crossed laser-molecular beam photofragment translational spectroscopy and laser-induced fluorescence. We establish ethyl ethynyl ether as the first clean precursor to the ketenyl radical, a key species in combustion reactions. One major bond fission channel was observed for the system, cleavage along the HCCO-C_2H_5 bond, leading to ground state C_2H_5 (ethyl) radicals and HCCO (ketenyl) radical products in two distinct electronic states. We observed neither cleavage of the other C-O bond nor molecular elimination to form C_2H_4 + CH_2CO (ketene). Ketenyl radicals formed in the higher recoil kinetic energy channel could be either $\tilde{X}(^2A")$ or $\tilde{A}(^2A')$ state ketenyl radical. We assign the lower recoil kinetic energy channel to the spin forbidden $\tilde{a}(^4A")$ state of the ketenyl radical, reached through intersystem crossing. Laser-induced fluorescence from the ketenyl radical peaks after a 20 μs delay, indicating that it is formed with a significant amount of internal energy and subsequently relaxes to the lowest vibrational level of the ground electronic state, a result consistent with the product assignment.

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