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Laser driven hydrogen transfer reactions in atmospheric chemistry[1]

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Ozonolysis of alkenes, an important non-photolytic source of OH radicals in the troposphere, proceeds through energized Criegee intermediates that undergo unimolecular decay to produce OH radicals. In this work, infrared laser activation of cold methyl-substituted Criegee intermediates is utilized to drive hydrogen transfer from the methyl group to the terminal oxygen, followed by dissociation to OH radicals. State-selective excitation of the Criegee intermediates in the CH stretch overtone region combined with sensitive OH detection reveals the infrared spectra of CH_3CHOO and $(CH_3)_2COO$, effective barrier heights for the critical hydrogen transfer step, and rapid decay dynamics to OH products. Complementary theory provides insights on the infrared overtone spectra as well as vibrational excitations, structural changes, and energy required to move from the minimum energy configuration of the Criegee intermediates to the transition state for the hydrogen transfer reaction.

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