Novel Decomposition Mechanism for Substituted Criegee Intermediates via Multistructural Semiclassical Transition State Theory

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The peculiar electronic structure of Criegee intermediates leads to interesting and surprising reactive patterns compared to other classes of molecules in the atmosphere. This work theoretically investigates the decomposition of a Criegee intermediate derived from leaf alcohol (*cis*-hex-3-eneol), leading to competition between the traditional pathway of 1,5-H abstraction and a new pathway leading to formaldehyde, explaining stoichiometric discrepancies found in previous experimental studies of the ozonolysis of leaf alcohol. A new multi-structural extension to semiclassical transition state theory, dubbed MS-SCTST, is developed to simultaneously treat multidimensional tunneling and multi-conformer effects.