

Down Down Down: Vinyl Hydroperoxide Stabilization

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With growing interest in the chemistry of Stabilized Criegee Intermediates (SCI) in Earth's atmosphere, we require increasingly accurate knowledge of the stabilization dynamics of ozonolysis products. A challenge to this understanding is the succession of weakly bound wells following the highly exothermic ozone alkene reaction. Based on conflicting data on the pressure dependence of stabilization reactions, we have hypothesized that stabilization into more than one well is important, including the SCI but also the subsequent vinyl hydroperoxide (VHP). High-level multireference computational calculations confirm that the VHP does indeed have a relatively tight dissociation transition state and thus is potentially vulnerable to stabilization. However, the calculations also reveal a stable complex following this transition state corresponding to a strong hydrogen-bonded complex between the products. This lowers the transition-state energy and thus confounds stabilization, at least for VHP with low carbon numbers. In order to constrain the chemistry of this complex reaction, we have performed master-equation calculations on a sequence of SCI-VHP systems, using the high-level multireference calculations for the two-carbon base system as our guide but progressively increasing the carbon number to probe the effect of increasing degrees of freedom on the stabilization behavior. The results reveal that stabilized VHP may well be important in the atmosphere, but that the overall ozonolysis potential energy surface still hides some mysteries.