

Title: Enthalpy of Formation for Criegee Intermediates: A Correlation Convergence Study

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Abstract: Criegee intermediates, formed from the ozonolysis of alkenes, are thought to have a role in atmospheric chemistry, from forming acid rain to impacting the oxidizing capacity of the troposphere. Although numerous studies have been conducted since their discovery, the synthesis of these species in the laboratory has ushered in a new wave of studies on these species, both theoretically and experimentally. In many of these theoretical studies, high-order corrections for correlation energy are included to account for the mid multi-reference character found in these systems. Many of these studies include a focus on kinetics, therefore calculated energies must be accurate (<1 kcal/mol in error). However, it has been previously suggested that CCSDT(Q), typically used to assess the correlation energy convergence, gives a poor description of Criegee intermediates. In this study, we compute the enthalpy of formation for a small set of Criegee intermediates, including higher-order corrections for correlation energy up to CCSDTQ(P). Employing focal point analysis, the magnitude of different contributions to the energetics of these systems are compared. We hope that this data serves as a definitive reference for energy computations for these challenging molecules.