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Kinetics, mechanisms and products of reactions of Criegee intermediates.¹

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The atmospheric ozonolysis of alkenes such as isoprene produces Criegee intermediates which are increasingly recognized as important contributors to oxidation chemistry in the Earth's troposphere. Stabilized Criegee intermediates are conveniently produced in the laboratory by ultraviolet photolysis of diiodoalkanes in the presence of O₂, and can be detected by absorption spectroscopy using their strong electronic bands in the near ultraviolet region. We have used these techniques to study a wide range of reactions of Criegee intermediates, including their self-reactions, and reactions with carboxylic acids and various other trace atmospheric constituents. In collaboration with the Sandia National Laboratory group led by Drs C.A. Taatjes and D.L. Osborn, we have used photoionization and mass spectrometry methods, combined with electronic structure calculations, to characterize the products of several of these reactions. Our laboratory studies determine rate coefficients for the Criegee intermediate reactions, many of which prove to be fast. In the case of reactions with carboxylic acids, a correlation between the dipole moments of the reactants and the reaction rate coefficients suggests a dipole-capture controlled reaction and allows us to propose a structure-activity relationship to predict the rates of related processes. The contributions of these various Criegee intermediate reactions to the chemistry of the troposphere have been assessed using the STOCHEM-CRI global atmospheric chemistry model.

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