



Reactions of stabilized Criegee Intermediates

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Carbonyl oxides (Criegee intermediates) were proposed as key intermediates in the gas phase ozonolysis of alkenes in 1975 by Rudolf Criegee. Despite the importance of ozonolysis in atmospheric chemistry, direct observation of these intermediates remained elusive, with only indirect experimental evidence for their role in the oxidation of hydrocarbons, e.g. through scavenging experiments. Direct experimental observation of stabilized CI has only been achieved since 2008. Since then, a concerted effort using experimental and theoretical means is in motion to characterize the chemistry and kinetics of these reactive intermediates.

We present the results of theoretical investigations of the chemistry of Criegee intermediates with a series of coreactants which may be of importance in the atmosphere, in experimental setups, or both. This includes the CI+CI cross-reaction, which proceeds with a rate coefficient near the collision limit and can be important in experimental conditions. The CI + alkene reactions show strong dependence of the rate coefficient depending on the coreactants, but is generally found to be rather slow. The CI + ozone reaction is sufficiently fast to occur both in experiment and the free troposphere, and acts as a sink for CI. The reaction of CI with hydroperoxides, ROOH, is complex, and leads both to the formation of oligomers, as to the formation of reactive etheroxides, with a moderately fast rate coefficient. The importance of these reactions is placed in the context of the reaction conditions in different atmospheric environments ranging from unpolluted to highly polluted.