



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. Only recently did Taatjes et al (2008) directly observe thermally stabilized Criegee intermediates (SCI), while work by Welz et al (2012) and others have finally started to elucidate the reaction kinetics and products of SCI with a subset of coreactants. Given the dearth of direct experimental data, theoretical analysis of the chemistry of SCI remains a prime source of information; in general, the predictions are in agreement with the scarce experimental data.

We present a set of modern theoretical studies on the chemistry of SCI, with emphasis on high-level quantum chemical calculations and theoretical kinetic analysis as a function of the substitutions in the SCI. A broad range of co-reactants is examined, as well as the unimolecular re-arrangement of SCI.

In the atmosphere, the fate of SCI was long assumed to be solely its reaction with H₂O, or unimolecular decomposition. However, recent re-analysis (Vereecken et al. 2012) of the available data shows that this view may need to be adjusted, with other fast bimolecular reactions playing a role in the atmosphere, with a strong dependence of the rates on the substituents in the SCI. Based on the new experimental and theoretical data, we re-evaluate the possible sinks of SCI in the atmosphere, putting forward a set of reactions that might have an impact in atmospheric or experimental reaction conditions. The reaction of SCI with SO₂ receives particular attention, as it is proposed in the literature to be of importance in the atmospheric formation of H₂SO₄ as an aerosol precursor.