

Theory-based studies on reactions in the troposphere

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The chemistry in the troposphere is highly varied, with a plethora of compounds reacting each in their specific way. In this contribution, we will discuss a set of compounds and their degradation pathways as they occur at ambient conditions. Emphasis lies on theoretical studies, with links to the available experimental data, discussing progress and challenges in the theoretical treatment.

The chemistry of stabilized Criegee intermediates, CI, has received significant attention lately, as they are potentially important for atmospheric SO₂ oxidation, affecting aerosol yields, and some of their reactions affect chamber and laboratory experiments. We will discuss the reaction rate and product formation for the reactions of CI with NO₂, acids, and O₃, and reaction trends in the unimolecular decay of CI; these reactions have all been shown to be competitive in some reaction environments. The available literature and the obtained results suggest that the steady state concentration of CI in the atmosphere will be strongly dependent on the environment, where especially warm, humid environments lead to rapid removal of CI.

The photo-dissociation of nitrophenols has been suggested as a possible HONO source in the troposphere. We present theoretical work on the OH and HONO formation from fragmentation of nitrophenol on the lowest-lying singlet and triplet potential energy surfaces, focusing on the product yields as a function of internal energy.

β-pinene is a ubiquitous monoterpene emitted in the troposphere by vegetation. Its atmospheric oxidation pathways have not yet been fully elucidated. We compare the results of recent chamber studies on this compound against model simulations using the MCM, or using a theory-based model. The experimental radical budgets indicate that the models remain incomplete, and possible pathways to rectify this are discussed.

The ¹³C kinetic isotope effect, KIE, induces slightly different decay rates for hydrocarbon isotopologues in the troposphere. This difference can be used as a chemical clock to estimate the age of air parcels. We discuss the difficulties encountered in the KIE *a priori* theoretical prediction of these KIE for the C₂H₆ + OH reaction, the best results available thus far, and possible steps to further improve the agreement with experimental values.