

Formation and decomposition of Criegee Intermediates in the new explicit chemistry modeling tool MCM/GECKO-A

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Unsaturated organic compounds constitute the majority of organic emissions at the global scale. They are emitted to the atmosphere from a range of natural and anthropogenic sources, notably biogenic emissions of isoprene and monoterpenes. Alkenes can significantly contribute to the total OH sink in both urban and forested environments and are highly reactive with tropospheric ozone. The ozonolysis of unsaturated hydrocarbons proceeds via the concerted addition of ozone to the C=C double bond to form a primary ozonide (POZ), which is promptly fragmented to form two pairs of carbonyls and Criegee Intermediates (CIs). CIs play an important role in tropospheric chemistry because their decomposition can be a direct, non-photolytic source of OH radicals via the vinylhydroperoxide channel (VHP) and of HO₂ radicals via a “hot” acid/ester intermediate. Thermally stabilized CIs (SCIs) can also act as oxidants in bimolecular reactions, mainly with water vapour and sulfur dioxide^{1,2}.

MCM/GECKO-A is the next generation of detailed chemical schemes for tropospheric chemistry. This tool aims at building a benchmark organic chemistry mechanism using a state of the art automated generation tool. As most of the species chemistry described with such a tool is unmeasured, their oxidation kinetics and mechanisms must be estimated following predefined protocols based on up to date experimental data and empirical estimation methods^{3,4}.

In this framework, a new description of ozonolysis reactions and the fate of CIs will be included in the set of rules guiding the auto-generation process. We propose here a new protocol describing the formation and decomposition of CIs with an emphasis on carbonyl and radical yields (HO_x, RO₂ and SCI). This protocol needs to provide a way of estimating (i) fragmentation branching ratio of the POZ and (ii) CI evolution branching ratios between stabilization, VHP formation and decomposition. Using a newly assembled database of experimental carbonyl, OH and SCI yields, we evaluate the accuracy of available estimation methods^{4,5}. A new protocol is built following this evaluation with the aim of including recent mechanistic developments and achieving better statistical performances.

References

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