

## Mechanistic Insights into the Tropospheric Ozonolysis of Alkenes: Closed Shell and Radical Product Yields

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The gas-phase reaction of alkenes with ozone has been the subject of considerable research interest over several decades owing to its key role in the Earth's tropospheric chemistry. Ozonolysis of alkenes not only leads to removal of hydrocarbons from the atmosphere but also the formation of a wide range of functionalised oxygenated products including carbonyls, organic acids and hydroperoxides, many of which are semi-volatile and can contribute to the formation of secondary organic aerosol [1]. Alkene-ozone reactions are widely recognised as a significant non-photolytic source of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals, initiating further oxidation and contributing to the overall tropospheric HO<sub>x</sub> budget, which can be dominant under certain conditions.

We report radical (OH, HO<sub>2</sub> and RO<sub>2</sub>) and stable co-product yields for a range of small C<sub>2</sub>-C<sub>6</sub> alkenes (ethene – isoprene). Experiments were performed in the European Photoreactor (EUPHORE), using a range of instrumentation including chemical ionisation-reaction time-of-flight mass-spectrometry (CIR-TOF-MS) and laser-induced fluorescence (LIF) to measure stable VOC/oVOCs and radical products respectively [2]. Alkene/ozone reactions were investigated with and without the presence of radical scavengers, in order to suppress side reactions and to obtain reaction rate coefficients, primary/secondary carbonyl and stabilized Criegee intermediate yields. Radical concentrations were measured directly, and interpreted through detailed chemical box modelling drawing upon the Master Chemical Mechanism (MCMv3.2; <http://mcm.leeds.ac.uk/MCM>) with mechanistic updates from the recent literature and our results.

Directly measured OH yields are found to be broadly in agreement with the existing literature and are entirely consistent with the widely accepted hydroperoxide mechanism. HO<sub>2</sub> yields measured in the absence of an OH scavenger are biased high owing to interference from the decomposition of β-hydroxyalkyl RO<sub>2</sub>, formed from the OH + alkene reactions, within the LIF instrument [3]. In the presence of a suitable OH scavenger, the measured HO<sub>2</sub> yields are lower than those inferred in some other recent studies, but in good agreement with those implemented in MCMv3.2 under dry conditions. Mechanistic insights and implications for atmospheric radical levels are also presented.

### References

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