



Radical Yields from the Ozonolysis of Small (C2-C6) Alkenes

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Unsaturated VOCs, alkenes, are emitted to the atmosphere from a wide range of anthropogenic and natural sources. They are significant primary pollutants in the boundary layer, contributing to total VOC emissions in urban air, where they may account for up to 30% of the total OH sink, however a key fate for alkenes is reaction with ozone, which may form the dominant loss pathway depending on local conditions, and leads to the non-photolytic production of OH, HO₂ and RO₂ radicals. Radical formation via ozonolysis is of interest as it may substantially influence the radical budget in urban and rural environments. While there are a number of quantitative indirect OH yield measurements from ozonolysis in the literature, obtained for example through the use of radical tracers / scavenger species, very few direct observations have been reported. Moreover, reported yields for HO₂ and RO₂ production have been largely inferred through the observation of associated stable products using assumed mechanisms. Gas-phase alkene-ozone reactions also generate a range of degradation products, notably secondary organic aerosol precursors, which together with many other products remain largely unidentified for biogenic alkenes.

We present a comprehensive analysis of detailed simulation chamber experiments in which the total radical production and degradation products of alkene ozonolysis reactions have been directly observed for ethene, propene, methylpropene, 1-butene, trans/cis-2-butene and 2,3-dimethyl-2-butene. The experiments were carried out in the European photoreactor EUPHORE (Valencia, Spain), with instrumentation including chemical-ionization-reaction time-of-flight mass-spectrometer (CIR-TOF-MS) and laser-induced fluorescence (LIF) to measure stable VOC and radical products respectively. Alkene/ozone reactions were investigated with and without the presence of a radical scavenger, in order to suppress side reactions and to obtain reaction rate coefficients, primary carbonyl and stabilized Criegee yields. Radical concentrations were measured directly, and interpreted through detailed chemical box modelling drawing upon the Master Chemical Mechanism (MCMv3.1) with mechanistic updates from the recent literature and our results. Reaction rate coefficients, radical yields and stable product yields are compared with those simulated, and the implications for atmospheric oxidant levels are presented.