LOW-PRESSURE YIELDS OF STABILIZED CRIEGEE INTERMEDIATES PRODUCED FROM OZONOLYSIS OF A SERIES OF ALKENES

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Ozonolysis of alkenes is an important oxidation pathway of alkenes in the troposphere because it is involved in the production of organic aerosol and OH radicals. The mechanism of ozonolysis of alkenes involves the formation of a primary ozonide (POZ), which then decomposes into a carbonyl and a high-energy carbonyl oxide (Criegee intermediate). Criegee intermediates are produced with a broad internal energy distribution. High energy Criegee intermediates decompose into atmospherically important compounds (e.g. vinoxy, OH radical). Stabilized Criegee intermediates (sCIs) undergo reactions to produce secondary ozonides and organic aerosols.

Cavity ring-down spectroscopy (CRDS) was utilized in combination with chemical titration with sulfur dioxide (SO_2) to quantify sCIs. The reaction is carried out under various flow and low-pressure conditions. Reference cross-sections of products and reactants are fitted with spectral features to obtain product number densities.

The yields of sCIs were measured at different low pressures and the nascent yields were determined by extrapolation to zero pressure. Endocyclic alkenes (cyclopentene and cyclohexene) show no sCI production at the pressures studied. However, acyclic alkenes show pressure-dependent sCI yields. Formaldehyde oxide (CH_2OO) from the alkenes studied (propene, 1-butene and isoprene) has a high nascent yield due to its relatively high energy barrier for dissociation. Cis-2-butene produces higher nascent sCI than trans-2-butene, possibly due to different syn- and anti-CI branching ratios, or different POZ conformations. There is an indication that alkenes larger than 2,3-dimethyl-2-butene would have higher nascent sCI yields. The information on low-pressure yields from the current studies can be used as a benchmark for theoretical calculations.