Quantitative detection of RO\textsubscript{2} radicals and other products from cyclohexene ozonolysis with NH\textsubscript{4}\textsuperscript{+} and acetate Chemical Ionization Mass Spectrometry

Wiebke Scholz (1), Bernhard Mentler (1), Lukas Fischer (1), Torsten Berndt (2), Armin Hansel (1,3)
(1) Institute for Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria, (2) Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Dept. (ACD), 04318 Leipzig, Germany, (3) Department of Physics, University of Helsinki, Helsinki 00014, Finland

The performance of the novel ammonium chemical ionization time of flight mass spectrometer (NH\textsubscript{4}\textsuperscript{+}-CI3–TOF) utilizing NH\textsubscript{4}\textsuperscript{+} adduct ion chemistry to measure quantitatively first generation oxidized product molecules (OMs) as well as highly oxidized organic molecules (HOMs) was investigated for the first time. The gas-phase ozonolysis of cyclohexene served as a first test system. Experiments have been carried out in the TROPOS free-jet flow system at close to atmospheric conditions. Product ion signals were simultaneously observed by the NH\textsubscript{4}\textsuperscript{+}-CI3-TOF and the acetate chemical ionization atmospheric pressure interface time of flight mass spectrometer (acetate-CI-API-TOF). Both instruments are in remarkable good agreement within a factor of two for HOMs. For OMs not containing an OOH group the acetate technique can considerably underestimate OM concentrations by 2-3 orders of magnitude.

First steps of cyclohexene ozonolysis generate ten different main products, detected with the ammonium-CI3-TOF, comprising 92% of observed OMs. The remaining 8% are distributed over several, minor products that can be attributed to HOMs, predominately to highly oxidized RO\textsubscript{2} radicals. Summing up, observed ammonium-CI3-TOF products yield 4.9 x 10\textsuperscript{9} molecules cm\textsuperscript{-3} in excellent agreement with the amount of reacted cyclohexene of 4.5 x 10\textsuperscript{9} molecules cm\textsuperscript{-3} for reactant concentrations of [O\textsubscript{3}] = 2.25 x 10\textsuperscript{12} molecules cm\textsuperscript{-3} and [cyclohexene] = 2.0 x 10\textsuperscript{12} molecules cm\textsuperscript{-3} and a reaction time of 7.9 s. For the first-time carbon closure could be achieved with a single instrument. NH\textsubscript{4}\textsuperscript{+} adduct ion chemistry based CIMS techniques offer a unique opportunity for complete detection of the whole product distribution including also peroxy radicals, and consequently, for a much better understanding of oxidation processes.