



Quantitative detection of RO₂ radicals and other products from cyclohexene ozonolysis with NH₄⁺ and acetate Chemical Ionization Mass Spectrometry

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The performance of the novel ammonium chemical ionization time of flight mass spectrometer (NH₄⁺-CI3-TOF) utilizing NH₄⁺ 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 NH₄⁺-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 RO₂ radicals. Summing up, observed ammonium-CI3-TOF products yield 4.9×10^9 molecules cm⁻³ in excellent agreement with the amount of reacted cyclohexene of 4.5×10^9 molecules cm⁻³ for reactant concentrations of $[O_3] = 2.25 \times 10^{12}$ molecules cm⁻³ and $[cyclohexene] = 2.0 \times 10^{12}$ molecules cm⁻³ and a reaction time of 7.9 s. For the first-time carbon closure could be achieved with a single instrument. NH₄⁺ 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.