Formation of highly oxidized molecules from cycloalkene ozonolysis observed in free-jet experiments

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The gas-phase reaction of ozone with C_5-C_8 cycloalkenes has been investigated in a free-jet flow system at atmospheric pressure and T = 297 ± 1 K. Highly oxidized RO_2 radicals with at least 5 O-atoms in the molecule and their subsequent reaction products were detected by means of NO_3^--CI-APi-TOF mass spectrometry. Formation of these RO_2 radicals can be explained via an autoxidation mechanism, ROO → QOOH and subsequently QOOH + O_2 → R´OO, starting preferentially from non-thermalized Criegee Intermediates after splitting-off an OH radical. The formation process is oxygen-limited even for close to atmospheric conditions. The total molar yield of highly oxidized products (predominantly RO_2 radicals) from C_5-C_8 cycloalkenes in air is 5.5 - 6.1 % affected with a calibration uncertainty by a factor of about two. For the most abundant RO_2 radical from cyclohexene, O,O-$C_6H_7(OOH)_2O_2$, determination of the rate coefficients for the reaction with NO, NO_2 and SO_2 yielded $(1.9 \pm 0.1) \times 10^{-11}$, $(1.0 \pm 0.1) \times 10^{-12}$ and $< 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The reaction of highly oxidized RO_2 radicals with other peroxy radicals (R´O_2) leads to detectable accretion products, RO_2 + R´O_2 → ROOR´ + O_2, which allows to acquire information on peroxy radicals not directly measureable with the ionization technique applied here. Additional experiments using CH_3COO^-(cluster) as the charger ion confirm conclusively the detection of highly oxidized RO_2 radicals and closed shell products. Other reaction products, detectable with this ionization technique, give a deeper insight in the reaction mechanism of cyclohexene ozonolysis.