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Secondary ozonides of endo-cyclic alkenes analyzed by Atmospheric Sampling Townsend Discharge Ionization Mass Spectrometry

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Development of ”soft” on-line techniques is important in order to avoid possible artifact formation of thermally labile oxidation products during analysis. We recently evaluated Atmospheric Sampling Townsend Discharge Ionization Mass Spectrometry (ASTDI-MS) in which sample air is introduced directly into the Townsend discharge source producing mainly O_2^+, NO^+ and NO_2^+ ions. Ion-molecule reactions of hydride abstraction, charge exchange and NO^+ addition result in mass spectra, which provide information about the functional group, including molar mass assignment of unknowns. Here we report the ASTDI and Collision Activated Dissociation (CAD) mass spectra of four secondary ozonides of endo-cyclic alkenes. Secondary ozonides (SOZ) of cyclohexene, 1-methylcyclohexene, 4-isopropyl-1-methylcyclohexene and d-limonene were cryo-synthesized by ozonolysis in pentane and purified on a silica gel column. The mass spectra obtained by ASTDI and CAD of the protonized SOZ showed characteristic losses evident of the ozonide structure. Oxygen was eliminated as e.g. O and O_2, and loss of (HCHO+HCHO) or $(O + CO_2)$ corresponded to the SOZ base-peak for the substituted cyclohexenes by ASTDI-MS. The CAD spectra of the protonized species by use of methane as chemical ionization gas, showed consecutive losses of three oxygen atoms. Elimination of hydroxy-methyl hydroperoxide (HMHP) was particular important for the protonized SOZ, unlike consecutive loss of (HCHO+HCHO) or $(O+CO_2)$. In addition, the spectra of d-limonene were characterized by an unique loss of H_2O_2. These losses appear to be useful for identification of SOZ in gas-phase ozonolysis mixtures of endo-cyclic alkenes, which makes ASTDI an alternative to other on-line techniques for analysis of SOZ in ozonolysis mixtures.