Analysis of α-acyloxyhydroperoxy aldehydes with electrospray ionization – tandem mass spectrometry (ESI-MS^n)

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The investigation of chemical composition and formation mechanism of the secondary organic aerosol (SOA) formed during the gas – phase ozonolysis of α – pinene has been the subject of numerous laboratory and field studies for the last two decades. Recently, it was concluded that high – molecular weight (HMW) compounds significantly contribute to the biogenic SOA mass. It is believed that the possible pathway leading to the formation of the observed HMW compounds involves gas phase reactions of the stabilized Criegee intermediate (SCI) with the primary productsof the ozonolysis reaction[1]. It has been also proposed that the extremely low - volatile α-acyloxyhydroperoxy aldehydes formed from the reaction of the SCI with carboxylic acids can induce the particle formation by acting as the nucleation precursors during SOA formation [1,2].

Popularization of the soft – ionization technique like electrospray ionization (ESI) enables to preserve molecular integrity of those HMW SOA components. However, due to lack of the appropriate standards, and therefore well established quantification methods, the detected HMW SOA components can be only tentatively identified. Structures in the majority of the studies published up – to date are based on either the elemental formula assignment using high resolution (HR) - MS and/or tandem mass spectra interpretation. Therefore, in order to improve the current methodology, new methods for identification of HMW SOA components needs to be introduced.

Results of the analysis of the α-acyloxyhydroperoxy aldehydes using ESI-MS^n and LC/MS will be presented. Fragmentation pathways of the 13 synthesized standards were investigated by tandem mass spectrometry and confirmed using deuterated compounds. The major fragmentation pathways were found to be common for all of the α-acyloxyhydroperoxy aldehydes, therefore it was possible to predict the mass spectra of this class of compounds. As a confirmation of this conclusion, one α-acyloxyhydroperoxy aldehyde synthesized using liquid phase ozonolysis of α-pinene in the presence of cis - pinonic acid was analyzed. Very good agreement of the predicted mass spectra and the experimental data was obtained. Those results underlines the possible applications of the developed methodology for the identification of the α-acyloxyhydroperoxy aldehydes in SOA formed from during the gas – phase ozonolysis of α-pinene.

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(2) Lee, S.; Kamens, R. M. *Atmos. Environ.* **2005**, *39*, 6822-6832.