



Identification of products formed during the HO₂-initiated photo-oxidation of atmospherically relevant hydrocarbons

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Hydroxyl radical initiated oxidation of hydrocarbons in the atmosphere produces a diverse range of organic products which, depending on their vapour pressures, may be found in the gas, and/or particle phase. The identities of these secondary organic products, especially those in the particle phase, are not well known. We are using a smog chamber and a photochemical flow reactor to perform atmospherically important oxidation reactions under controlled conditions. The objective is to improve our knowledge of the chemical composition of the reaction products especially those in the particulate phase. Hydroxyl radicals are produced by photolyzing isopropyl nitrite in the presence of NO, and reactions are performed with or without pre-existing particles. Preliminary studies on the reactions of toluene, m-xylene, 1,3,5-trimethyl benzene and β -pinene have been undertaken. The concentrations of the hydrocarbon and NO_x are followed using a gas chromatograph (GC-FID) and a chemiluminescence analyzer respectively. A differential mobility analyzer (DMA) and condensation nucleus counter (CNC) are used to determine particulate size distributions, from which particle yields are obtained. Gas phase product analysis is carried out using a Sciex TAGA 6000E triple quadrupole mass spectrometer with an atmospheric pressure chemical ionization source (APCI): identification uses a library of compounds developed in-house. Particle phase product analysis is performed by collecting the sample on filters and either using solvent extraction followed by GC/MS analysis or using thermal desorption into the ion source of the TAGA. Both reaction systems are simulated by a kinetic box

model using a subset of the University of Leeds Master Chemical Mechanism (MCM) version 3.1, and a kinetically based gas-particle partitioning approach.

While comparison between the measurements and the model are encouraging in some areas, there are major discrepancies in others. The majority of the observed particulate phase products are not predicted by the MCM and conversely the species predicted are not generally observed. Many of the species identified in the particulate phase would be expected to preferentially partition into the gas phase. This suggests they are weakly bonded in the particulate phase but are decomposed prior to MS analysis.