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Analysis of reversibility and reaction products of glyoxal uptake onto ammonium sulfate aerosol

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Glyoxal, the smallest alpha-dicarbonyl, is an oxidation product of both biogenic and anthropogenic volatile organic compounds (Fu et al. JGR 113, D15303, 2008). Despite its low molecular weight, its role in secondary organic aerosol (SOA) formation has gained interest and a recent study suggested that it accounts for more than 15% of SOA in Mexico City (Volkamer et al. GRL 34, L19807, 2007). Despite numerous previous studies, questions remain regarding the processes controlling glyoxal uptake onto aerosol, including the role of acid catalysis, degree of reversibility, and identity of aerosol phase reaction products.
We present results of chamber aerosol studies (Galloway et al. ACPD 8, 20799, 2008) and laboratory studies of bulk samples aimed at improving the understanding of these processes, in particular formation of oligomers and organosulfates of glyoxal, as well as the formation of imidazoles (carbon-nitrogen containing heterocyclic aromatic compounds) under dark and irradiated conditions. The relevance of these classes of reaction products extends beyond glyoxal, as evidence of oligomers and organosulfates other than those of glyoxal have been found in ambient aerosol (Surratt et al. JPCA 112, 8345, 2008; Denkenberger et al. Environ. Sci. Technol. 41, 5439, 2007).

Experiments in which a chamber air mass was diluted after equilibration of glyoxal uptake onto ammonium sulfate seed aerosol (relative humidity 60% and glyoxal mixing ratios of 25-200 ppbv) shows that under these conditions uptake is reversible. The most important condensed phase products are hydrated oligomers of glyoxal, which are also formed reversibly under these conditions.

Our studies show that organosulfates were not formed under dark conditions for neutral or acidified aerosol; similarly, Minerath et al. have recently shown that formation of a different class of organosulfates (alkyl sulfates) also proceeds very slowly even under acidic conditions (Environ. Sci. Technol. 42, 4410, 2008). The masses assigned to sulfate esters in previous work (Liggio et al. Environ. Sci. Technol. 39, 1532, 2005) via low resolution AMS studies were assigned as glyoxal oligomers in our study via high resolution AMS spectra. However, organosulfates were identified under irradiated conditions, and we present attempts to identify the specific species via comparison with lab synthesized organosulfates. The influence of irradiation on organosulfate formation is still under investigation.

Under irradiated conditions we see clear evidence for active oxidative photochemistry. The aerosol phase becomes increasingly oxidized and oxidation products, such as organic acids, similar to those observed in studies using bulk samples by Carlton et al. (Atmos. Environ. 41, 7588, 2007) are formed. Overall uptake is reduced under our experimental conditions, likely due to increasing temperature and decreasing relative humidity.

We also report observation of imidazoles (carbon-nitrogen containing aromatic heterocycles) resulting from reaction of glyoxal with the nitrogen component of the ammonium sulfate seed aerosol. The imidazoles form irreversibly under dark and irradiated conditions, in ammonium sulfate and acidified ammonium sulfate (pH∼1) aerosol. The molecular framework of imidazoles is very stable as a result of the aromaticity. The primary imidazole product, which has a low vapor pressure estimated at 0.0014 Torr, is predicted to be present as a (protonated) cation, owing to its basicity (pKB = 7). It is thus likely not a candidate for repartitioning to the gas phase. Evidence for participation of ammonium in reactions with glyoxal using bulk samples has recently been reported by Noziere et al. (JPCA 113, 231, 2008; ACPD 9, 1, 2009).

This study reveals the complex chemistry occurring within ammonium sulfate seed aerosol even for systems with greatly reduced complexity compared to atmospheric aerosol. The results increase our understanding of the contribution of glyoxal to SOA formation processes. More specifically, these results provide valuable insights into important aerosol processes, such as organosulfate and oligomer formation, as well as the formation of aromatic nitrogen containing heterocycles from reaction of a carbonyl with ammonium sulfate aerosol.