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Photosensitized transformation of dicarboxylic acid in aerosols

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Ultraviolet or visible light absorbing organic constituents of atmospheric aerosols may act as photosensitizers for a number of processes. Photosensitizers may be primary organics from combustion sources or be formed in situ during oxidation in the atmosphere. The significance of photosensitized processes has been demonstrated by showing enhanced uptake of atmospheric oxidants to organic films or aerosol particles (George *et al.*, 2005, Stemmler et al., 2006, 2007). In this work, we focus on photosensitized reaction of organic aerosol constituents.

The aerosols were produced by nebulizing a solution containing ammonium sulfate, a dicarboxylic acid and benzophenone. The aerosol flow passed through a photoreactor with about 9 min. residence time, which was coupled to either a chemical ionization mass spectrometer (CIMS) in proton transfer mode or a High Resolution Time of Flight Aerosol Mass Spectrometer (AMS) and two Scanning Mobility Particle Sizer (SMPS). Separate experiments were performed in bulk aqueous solution using laser photolysis allowing monitoring the decay kinetics of the photosensitizer excited state. The decay of the triplet state of benzophenone was followed at 525nm.

Fig. 1 shows results from the bulk solution experiments, indicating that the benzophenone triplet is quenched in presence of both succinic and adipic acid.

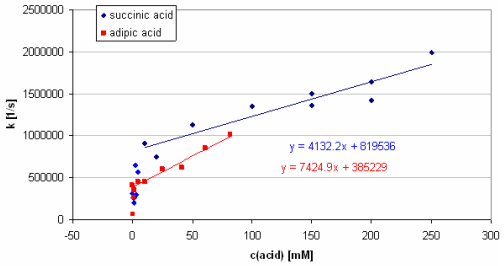

Figure 1. Benzophone triplet quenching kinetics in succinic and adipic acid solutions

Using the CIMS coupled to the aerosol photoreactor and with adipic acid aerosol present, we observed the characteristic fragmentation and an efficient ionization of the analyte. Adipic acid is seen mostly at m/z=147 and m/z=129. The peak m/z=129 indicates the loss of water, m/z=165 likely results from an additional attached water molecule. The presence of light between 300 and 400nm led to a reduction of adipic acid peaks.

Using the AMS, we observed changes to the ratio of m/z 44 to 43, with the changes being more pronounced in the case of succinic acid than in the case of adipic acid. This change in the 44 to 43 mass ratio is typically associated with the loss of carboxylic acid groups. A detailed analysis of the available data will allow extracting more information on potential products of the light induced reaction.

Overall, the results are a strong indication that the presence of a photosensitizer leads to light induced reactions of simple dicarboxylic acids.

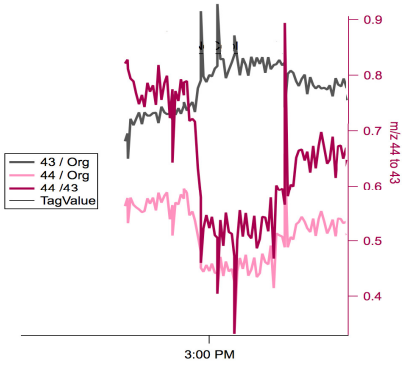

Figure 2. Result from the AMS measurements of the effect of light (switched on shortly before 3 pm) on m/z 44 and 43, both normalized to the total amount of organics, and on the ratio of m/z 44 to 43 (black line), for an aerosol containing succinic acid and a small amount of benzophenone.

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