Synthesis and glass formation properties of compounds representative of low-volatility secondary organic aerosol particles

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Secondary organic aerosol (SOA) particles arise from the atmospheric oxidation of volatile organic compounds (VOC). SOA particles consist of a myriad of organic compounds, but several key components have been identified (e.g. Hallquist et al., 2009). For example, in boreal forests α-pinene is one of the most important VOC precursors. Its gas-phase oxidation proceeds via pinonic acid, a semi-volatile compound, to the second-generation oxidation product 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA, see Fig.1), a low-volatility compound found predominantly in the aerosol phase (Jimenez et al., 2009; Müller et al. ACP 2012). Not much is known, however, about the physico-chemical properties and the phase state of 3-MBCTA. This knowledge is particularly important, because it has been suggested recently that SOA particles in boreal forests may exist in a glassy, i.e. amorphous solid state at room temperature under dry conditions (Virtanen et al., 2010). An amorphous semi-solid or solid state of organic aerosol particles has important atmospheric implications such as delayed gas-to-aerosol partitioning (Shiraiwa and Seinfeld, 2012; Zelenyuk *et al.*, 2012). However, the glass formation properties of key compounds of oxygenated organic aerosol such as 3-MBTCA have not been investigated until now. Here we describe the synthesis and physico-chemical characterization of 3-MBTCA.
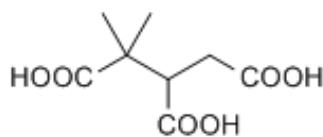

Fig.1: 3-MBTCA.

3-MBCTA was synthesized from methyl isobutyrate and dimethyl maleate in two steps with an overall yield of 78%. The compound was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, and mass spectrometry. The melting point of 3-MBTCA was found to be $T_m = 426$ K, in good agreement with literature data (Alder *et al.*, 1949). From knowledge of this T_m value a glass transition temperature of about $T_g = 299$ K has been predicted (Koop *et al.*, 2011). In the present study we were interested in confirming this value experimentally.

We have employed differential scanning calorimetry (DSC) to determine the temperature-dependent phase state behaviour of 3-MBCTA. In DSC experiments any substance has to be melted before it can be transferred into a glassy state. However, upon melting 3-MBTCA transformed into a lactone, implying that its T_g cannot be determined in the traditional way.

For this reason we have developed a novel spray diffusion drying technique in which a dilute aqueous solution of a water-soluble organic substance is atomized into aerosol particles that are then dried in several subsequent diffusion dryers. This drying may result in glass formation in each individual aerosol particle. The vitrified aerosol particles are then recollected in an impactor until enough mass has accumulated that their T_g can be determined by DSC.

The new technique has been tested using several reference compounds such as sugars or citric acid and the T_g values determined in this manner were in agreement with values obtained by previous methods. The experiments performed with 3-MBCTA show that its T_g is indeed above room-temperature supporting recent proposals of a glassy state of SOA particles. Such an amorphous solid state implies impedance of chemical reactions (Shiraiwa *et al.*, 2011) and the potential of such particles to act as ice nuclei at lower temperatures in the upper troposphere (Murray *et al.*, 2010).

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