Characterization of Physical and Chemical Properties of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) aerosol

E. Kostenidou[1,2], E. Karnezi[3], R. Szmigielski[4] and S.N. Pandis[1,2,3]

[1]Department of Chemical Engineering, University of Patras, Patras, 26504, Greece
[2] Institute of Chemical Engineering Sciences, ICE-HT, Patras, 26504, Greece
[3]Department of Chemical Engineering, Carnegie Mellon University, PA, 15213, USA
[4]Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

Keywords: MBTCA, thermodenuder, PMF, OH.
Presenting author email: v_kostenidou@chemeng.upatras.gr

Secondary organic aerosol (SOA) is formed through the oxidation of volatile organic compounds (VOCs) by atmospheric oxidants such as O_3, OH radicals or NO_3. Monoterpenes may contribute as much as 50% to the total organic aerosol (Andersson-Skölld and Simpson 2001). Once SOA is formed in the atmosphere it can undergo multiple chemical processing such as fragmentation, functionalization and oligomerization. Organic acids constitute a major product of the O_3 and OH reactions with terpenes (Warnke et al., 2006). 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a highly oxidized tricarboxylic acid, has been proposed as the most relevant tracer compound for atmospheric terpene secondary organic aerosol (SOA) (Szmigielski et al., 2007; Zhang et al., 2010). Recently, Muller et al. (2012) showed that MBTCA is formed from the oxidation of pinonic acid and that this oxidation takes place in the gas phase. However, the physical and chemical properties of MBTCA particles are limited. To our knowledge this is the first time that MBTCA aerosol is studied in an environmental chamber.

MBTCA was synthesized in the Laboratory of Environmental Chemistry in the Institute of Physical Chemistry, Warsaw, Poland, following the approach of Szmigielski et al. (2007). Aerosol MBTCA was generated through an atomizer and characterized in the Patras ICE-HT smog chamber. Atmospheric levels of OH radicals were produced by HONO photolysis under UV illumination. An Aerodyne High Resolution Aerosol Mass Spectrometer (HR-AMS) and a Scanning Mobility Particle Sizer (SMPS) measured the particle phase, while a thermodenuder was used for the volatility characterization. The gas phase was monitored by a Proton Transfer Reaction Mass Spectrometer (PTR-MS).

The HR mass spectrum of the fresh MBTCA is shown in Figure 1. Some of the characteristic *m/z* values are 39, 41, 43, 44, 53, 55, 59, 67, 69, 96, 81, 83, 99, 100, 113, 114, and 141. Even after heating the particles to 120°C for 30 s the mass spectrum remained practically the same ($\theta < 12^o$). Applying the algorithm of Kostenidou et al. (2007), the AMS collection efficiency (CE) was around 1 and the fresh MBTCA density 1.8±0.1 g cm^{-3} clear. The T_{50} was estimated around 87°C, while an integrated volatility characterization was performed according to Karnezi et al. (2014) approach.

After exposure to OH radicals and UV illumination the aerosol O:C ratio decreased while the H:C ratio increased indicating fragmentation. Positive matrix factorization (PMF) applied to the chamber experiments revealed a second less oxygenated factor after OH addition (Figure 2).

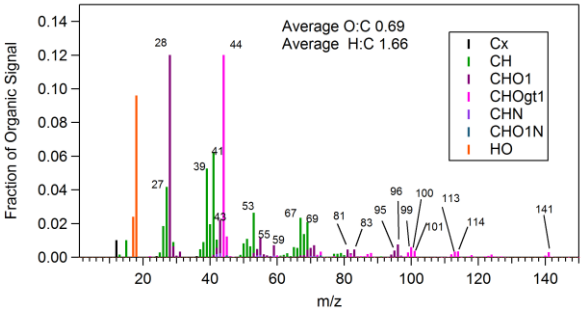

Figure 1. HR mass spectrum of fresh MBTCA.

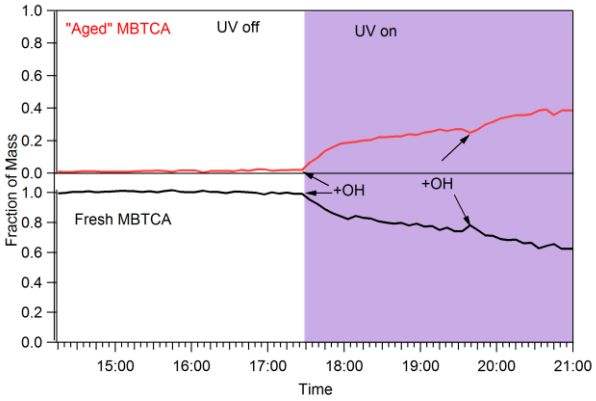

Figure 2. PMF analysis of the AMS organic aerosol spectra for an MBTCA photo-oxidation experiment.

Andersson-Skölld, Y., and Simpson, D. (2001) *J. Geophys. Res.* **106**:7357-7374.
Karnezi, E. et al (2014) *Atmos. Meas. Tech.*, **7**, 2953-2965, 2014.
Kostenidou et al. (2007) *Aer. Scien., Technol.,* **41**, 1002-1010.
Müller, L. Et al. (2012) *Atmos. Chem. Phys.*, **12**, 1483-1496.
Szmigielski, R. et al. (2007) *GRL*, **34**, 6 pp., L24811.
Warnke, J. et al. (2006) *Analyt. Bioanalyt. Chem.*, **385**, 34–45, 2006.
Zhang, Y. Y. et al. (2010) *Atmos. Chem. Phys.*, **10**, 7859–7873.