



Aerosol and gas phase organic acids during aging of secondary organic aerosol from -pinene in smog chamber experiments

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Organic acids represent an important class of organic compounds in the atmosphere for both the gas and aerosol phase. They are either emitted directly from both biogenic and anthropogenic sources or formed as oxidation products from volatile organic compounds (VOCs) and precursors in the aqueous, gaseous and particle phase (Chebbi & Carlier, 1996)

Monoterpenes are a prominent class of VOCs with annual emissions of 127 Tg per year (Guenther et al., 1995). Because of their high formation potential of secondary organic aerosols, several compounds of this class, particularly α -pinene, have been investigated extensively in many laboratory studies.

Among other acids, *cis*-pinic and *cis*-pinonic acid have been found as products of α -pinene ozonolysis. Ma et al. (2007) published evidence that these organic acids are formed in the gas phase via Criegee Intermediates (CIs). Recently, 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) was identified by Szmigielski et al. (2007) as a product from α -pinene photooxidation, as well as diaterpenylic acid acetate (Inuma et al., 2009) and terpenylic acid (Claeys et al., 2009). These compounds could serve as tracers for α -pinene in ambient samples.

The present work sets its focus on the fate of α -pinene SOA organic acids under different aging conditions. (1) low NO_x concentration (2) high NO_x concentration (3) exposure to OH radicals in both dark and lighted environments. α -pinene SOA is produced by ozonolysis without OH scavenger in the PSI smog chamber. It consists of a 27m³ Teflon® bag that can be irradiated by four Xe arc lamps to simulate sunlight (Paulsen et al., 2004).

The organic acids are sampled with a wet effluent diffusion denuder (WEDD) and an aerosol collector (AC) for the gas phase and the aerosol particles, respectively. WEDD and AC samples are alternatively concentrated for 30 minutes on a trace anion concentrator (TAC) column (Dionex, Switzerland) and subsequently analyzed by ion chromatography coupled to mass spectrometry (IC/MS). This system is described in more details by Fisseha et al. (2004).

The results show that the *cis*-pinonic acid gas phase concentration increases rapidly in the presence of NO_x, while it stays more or less constant upon OH exposure. On the other hand, *cis*-pinic acid concentration in aerosol decreases in presence of NO_x but is nearly constant during OH exposure. 3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA) is also formed during ozonolysis and demonstrates a strong concentration increase for all aging conditions. This partially agrees with a recent publication of Szmigielski et al. (2007), where MBTCA is thought to be formed in the presence of NO_x, but this gives evidence that MBTCA can also be formed via another mechanism without NO_x. Moreover, after exposure of *cis*-pinonic acid to OH radicals produced in the dark, MBTCA is detected, confirming that *cis*-pinonic acid is involved in the mechanism formation of MBTCA.

The Master Chemical Mechanism (MCM) tends to overestimates the amount of organic acids formed. Therefore, inclusion of new reaction mechanisms and species that are not yet included will help to improve the present knowledge of the organic acids formation pathways.

Chebbi, A., & Carlier, P. (1996). *Atmos. Environ.*, 30, 4233-4249.

Claeys, M., et al. (2009). *Environ. Sci. Technol.*, 43, 6976-6982.

Fisseha, R., et al. (2004). *Anal. Chem.*, 76, 6535-6540.

Guenther, A., et al. (1995). *J Geophys Res.*, 100, 8873-8892.

Inuma, Y., et al. (2009). *Environ. Sci. Technol.*, 43, 280-285.

Jang, M. J., & Kamens, R. M. (1999). *Atmos. Environ.*, 33, 459-474.
Lee, S., & Kamens, R. M. (2005). *Atmos Environ.*, 39, 6822-6832.
Ma, Y., et al. (2007). *Phys. Chem. Chem. Phys.*, 9, 5084-5087.
Paulsen, D., et al. (2005). *Environ. Sci. Technol.*, 39, 2668-2678.
Szmigielski, R., et al. (2007). *Geophys Res. Lett.*, 34, L24811, doi:10.1029/2007GL031338.
Yu, J., et al. (1999). *J. Atmos. Chem.*, 34, 207-258.