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Supplement of

Relating hygroscopicity and optical properties to chemical composition and structure of secondary organic aerosol particles generated from the ozonolysis of α-pinene

C. Denjean et al.

Correspondence to: C. Denjean (denjean@tropos.de)

Supplementary material

1. Correction of the spectral attenuation coefficient (σ_{attn}) obtained with the aethalometer

σ_{attn} obtained with the aethalometer were corrected for various systematic errors. We applied the empirical correction described by Collaud Coen et *al.* (2010) which includes *R*, the attenuation effect due to light absorbing particles accumulating on the filter, $C_{ref,}$ the multiple scattering by the filter fibres and α, the scattering correction due to scattering of aerosols embedded in the filter:

$$\sigma_{abs}\,(\lambda, m) = \frac{\sigma_{ATTN}\,(\lambda, m) - \alpha(\lambda).\,\sigma_{scatt}\,(\lambda, m)}{C_{ref}.\,R}$$

R decreases with the gradual increase of attenuation due to the accumulation of absorbing particles embedded in the filter. As will be shown in the section 3.2., the attenuation modification during SOA measurement was very low, indicating weakly light absorbing particles. Thus, we assumed that R was equal to unity.

C_{ref} can be estimated by comparing σ_{attn} measured with the aethalometer measurements and σ_{abs} obtained from a non-filter based instrument (for example a photoacoustic photometer). However, simultaneous measurements with these two instruments were not possible during the reported experiments. Weingartner et *al.* (2003) estimated that soot particles coated with α-pinene-O_3 SOA were characterised by C_{ref} = 3.64 ± 0.98 and 3.90 ± 0.56 at 450 and 660 nm respectively. We used the average C_{ref} = 3.77 ± 2.11 of these values to correct σ_{attn} in this study.

α(λ) was deduced from the σ_{attn} measured by the aethalometer with non-absorbing ammonium sulfate particles according to the method described by Arnott et *al.* (2005) at the 7-wavelengths of the aethalometer. We used the value of $\alpha(\lambda) = 1.3\,.\,10^{-3}.\,\lambda^{5.6*10^{-1}}$ estimated by Denjean et *al.* (2014). The values of σ_{scat} at the wavelengths of the aethalometer other than

525 nm were derived from calculations based on Mie theory, measured size distributions and the constant CRI retrieved at 525 nm.

2. Quantification of the O:C at the surface of SOA from the XPS analysis

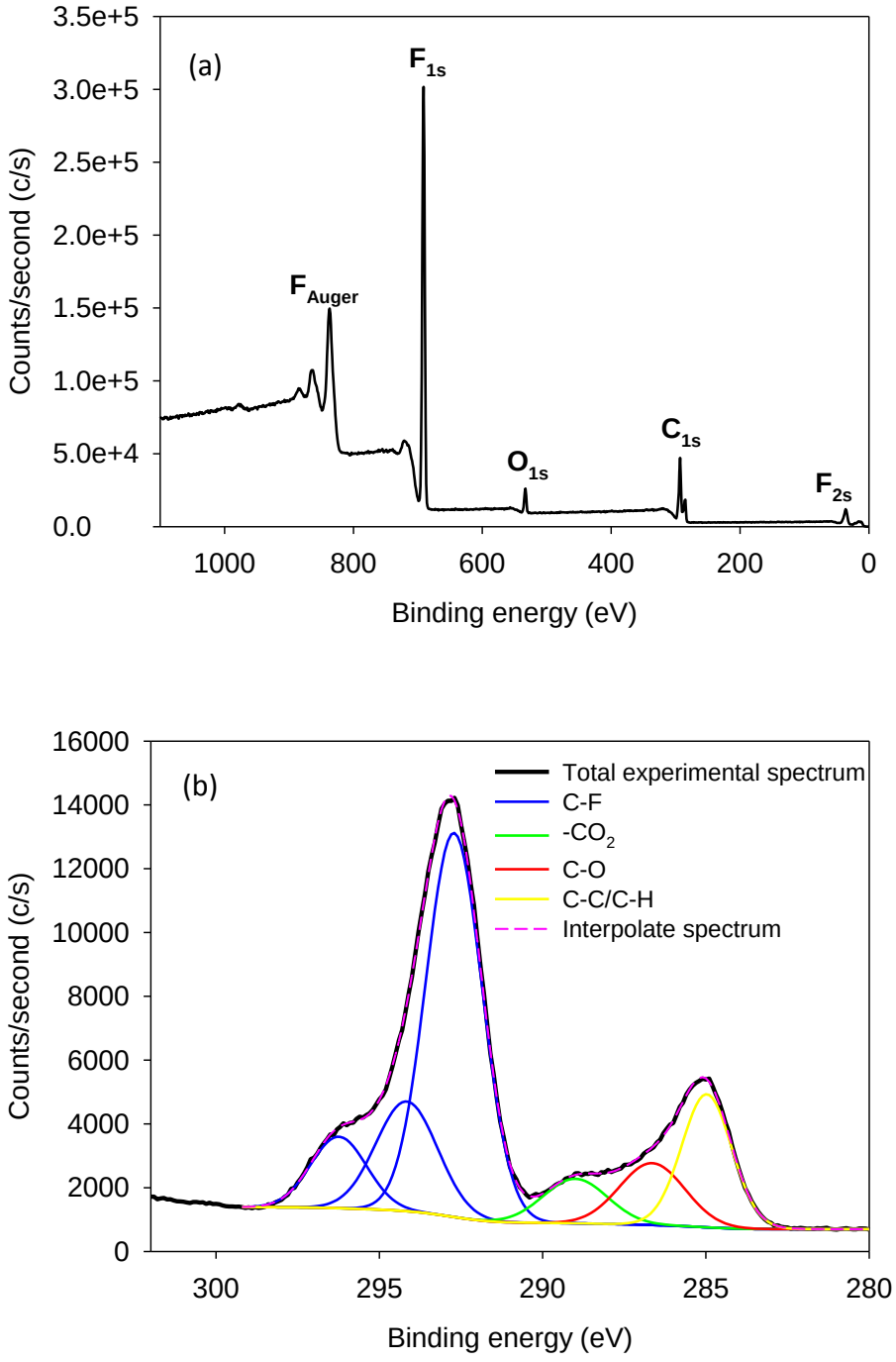

Figure S1. XPS spectra of SOA: (a) survey spectrum and (b) deconvolution of the high-resolution spectra C1s region. The reported three peaks represent different states of Carbon, respectively C-F, $-CO_2$, C-O, C-C and C-H.

3. Yields – literature comparison

The comparison between the steady-state aerosol yields determined in this study and the values reported in the literature is shown in Figure S2. To facilitate the comparison with the literature, we adjusted our yield data to a SOA density of 1.0 g m^{-3}. Our yields are in agreement with Hoffmann et al. (1997), but up to 2 times lower compared to other studies (Wang et al., 2011; Griffin et al., 1999; Cocker et al., 2001; Saathoff et al, 2009; .Shilling et al 2008). These differences are arise from instrumental and treatment uncertainties, as shown by the error bars. Shilling et al. (2008) investigated several possible artefacts and sources of error that could reasonably influence yield values. They suggested that different gas-phase chemistry or partitioning of species on the surface of the walls could occur within the chambers. However, our yields can be directly compared to the values reported by Wang et al. (2011) who performed experiments in a similar simulation chamber as ours. Our values are systematically lower than those reported by Wang et al. (2011) by approximately 20%. One major issue differentiating our experimental conditions is the initial concentration of ozone. Wang et al. (2011) performed experiments with an excess of ozone, while we used significantly lower ozone concentration to generate SOA. It is expected that a lower concentration of OH radicals was produced from our experiments during the ozonolysis of α-pinene, which could reduce the aerosol yield of the reaction.

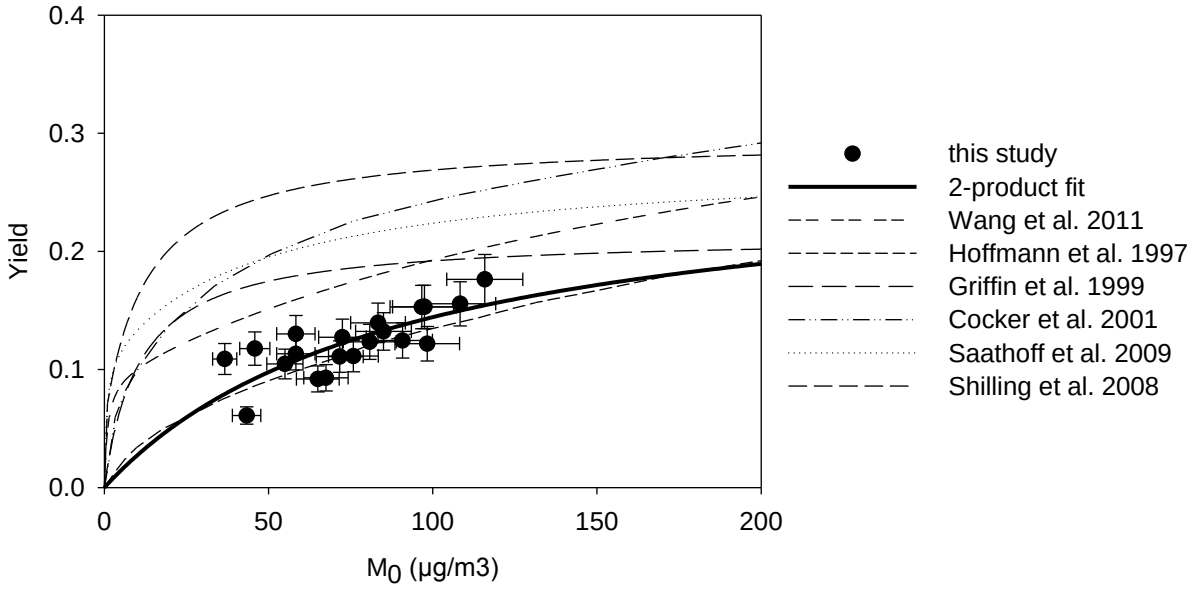

Figure S2. Comparison of aerosol yield obtained in this study to those of other studies for the dark ozonolysis of α-pinene. We adjusted our data to a SOA density of 1.0 g m^{-3} to facilitate the comparison with the literature. The solid black line shows the fit of our data for a two-product model $Y = M_0 \sum_i \frac{\alpha_i K_i}{1+K_i M_0}$ (Odum et al., 1996). We estimated α_1=0.275, α_2=0.001, K_1=0.011, K_2=0.001.

4. Absorption coefficient of SOA particles in the visible to near-UV region

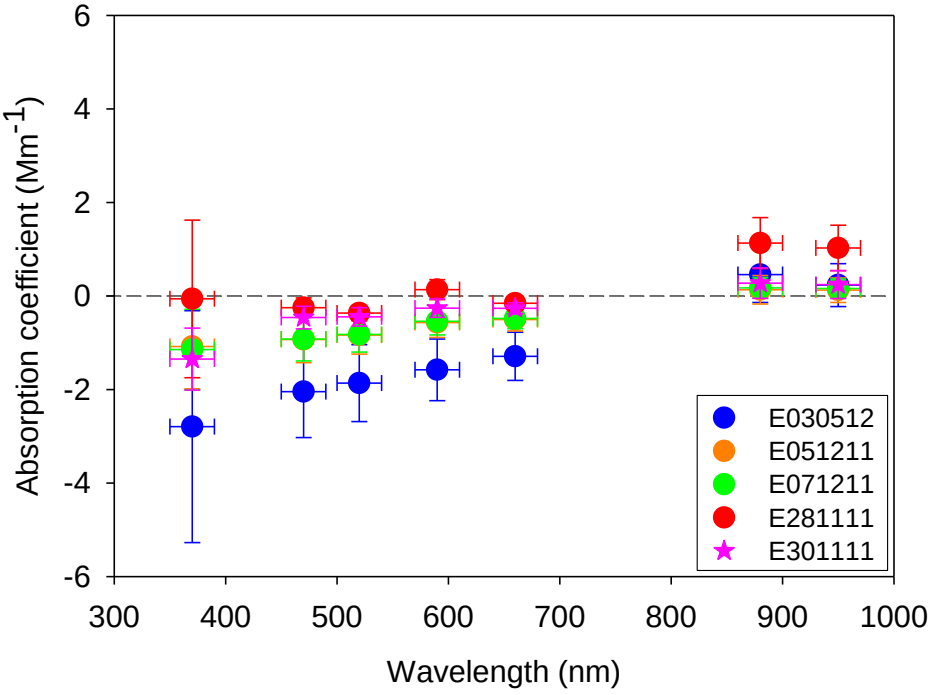

Figure S3: Wavelength dependence of the spectral absorption coefficients of α-pinene-O_3 SOA after 14 hours of reaction

5. Evolution of the SOA functionality during the reaction

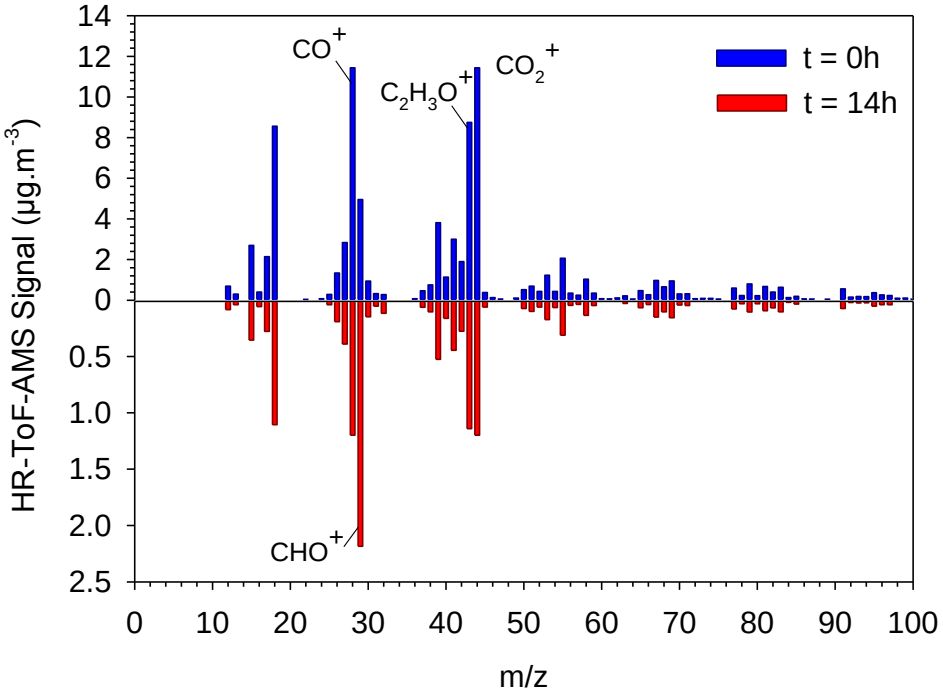

Figure S4. AMS mass spectra of α-pinene-O_3 SOA after 1 hour of reaction (red) and after 14 hours of reaction (blue).

The correlation between f_{44} and f_{43} for α-pinene-O3 SOA has been compared in Figure S5 to laboratory data obtained by Shilling et al. (2009) and ambient SOA ground and flight data from different sites, including Mexico city (Ng et al., 2010). Our data are within the triangular region of the typical ambient SOA, but exhibit higher f44 than Shilling et al. (2009). This discrepancy may be due to the use of OH scavengers by the latter. Previous laboratory studies have observed an increase of the O:C ratio of α-pinene-O3 SOA after OH exposure (Tritscher et al., 2011; Cappa et al., 2011; Qi et al., 2012; George and Abbatt, 2010; Donahue et al., 2012). Since f44 is the major contributor to the oxygen signal in the SOA spectra, this fragment may increase with OH exposure formation of carboxylic acids (Muller et al., 2012).

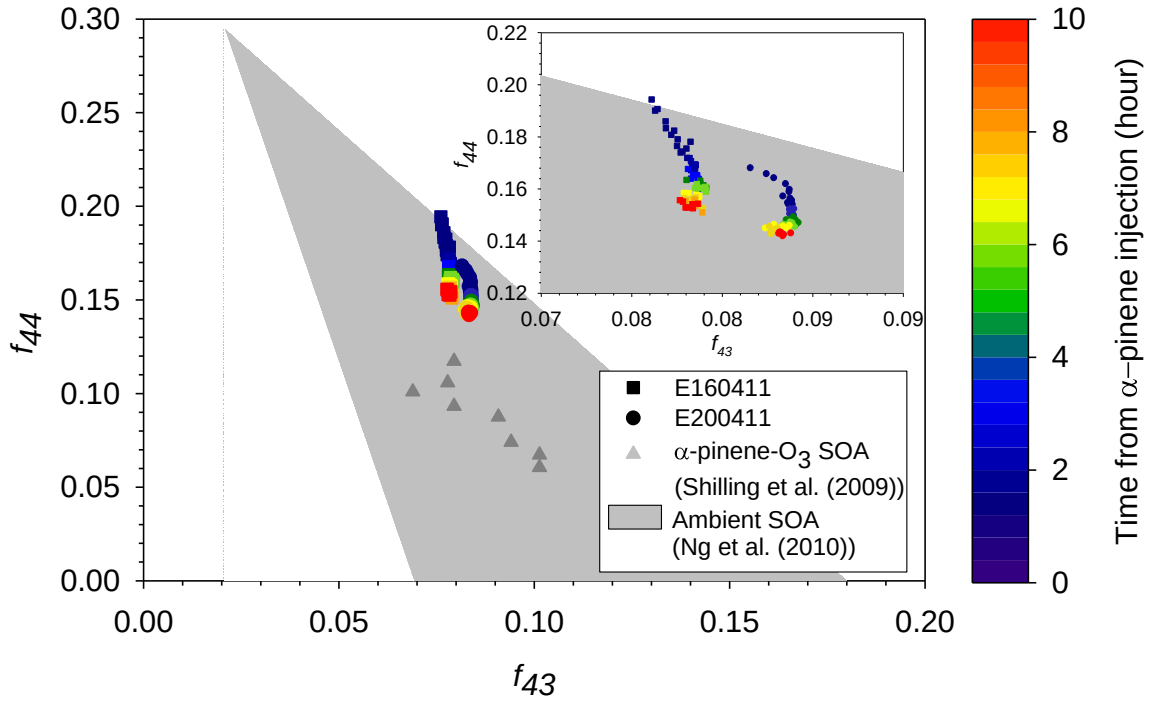

Figure S5. f_{44} as a function of f_{43} during the α-pinene-O_3 SOA reaction, including experimental data obtained in this study (symbols) and in Shilling et al. (2009), as well as typical ambient SOA (Ng et al., 2010).

6. Analysis of SOA particles by MET

Electron microscopy analysis was used to investigate the shape of SOA particles. SOA particles SOA particles were collected after 1 hour and 14 hours of reaction on copper TEM grids fixed on fibre glass filters (Whatman, 47 mm diameter, 0,7µm porosity). Analytical transmission electron microscopy (TEM) was performed with an instrument type JEOL 100CXII equipped with a X-ray energy-dispersive spectrometer (PGT Prism 2000 Si(Li)

detector and Avalon analyzer, Princeton Gamma-Tech, USA. In total, 50 particles have been analyzed by TEM. Figure S4 (Supplementary Material) shows an example of SOA particles after 1 and 14 hours of reaction. Only spherical particles have been observed in the samples.

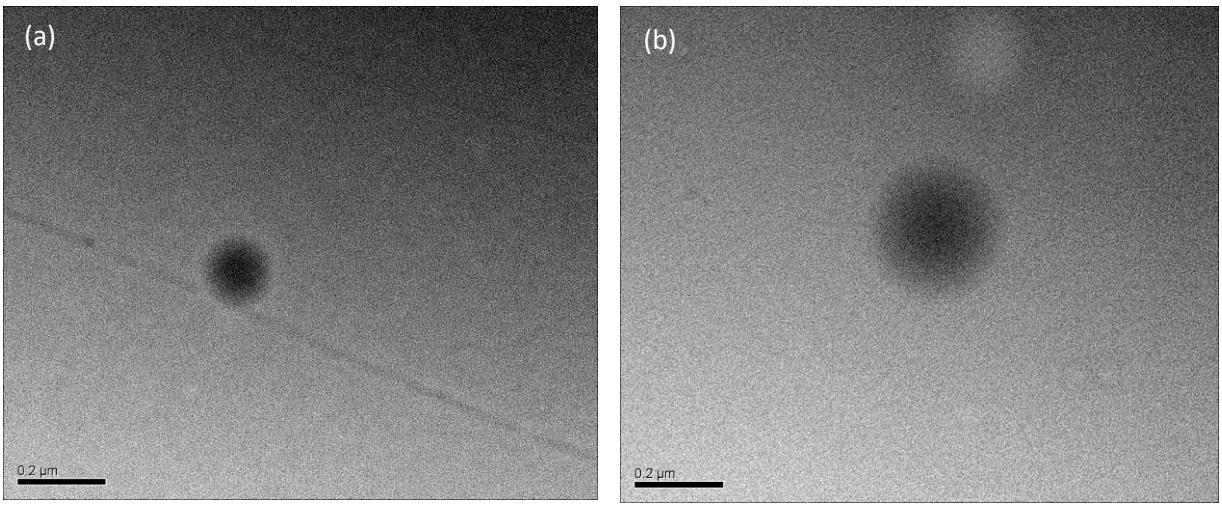

Figure S6. Examples of TEM images of α-pinene-O_3 SOA (a) after 1 hour and (b) 14 hours of reaction.