

Interactive comment on “Physico-chemical

characterization of secondary organic aerosol derived from catechol and guaiacol as a model substance for atmospheric humic-like substances” by J. Ofner et al.

J. Ofner et al.

grothe@tuwien.ac.at

Received and published: 12 October 2010

Answer to Referee #1:

We thank referee #1 for the friendly acknowledgement of our experimental study.

Comment: This paper describes a thorough analytical characterization of SOA formed in a smog chamber from catechol and guaiacol. Several analytical methods were used

C8565

to follow the formation and destruction of chemical functional groups in the SOA (IR and UV spectroscopy, mass spectrometry). The results suggest that high molecular weight compounds are formed in this reaction that may have some chemical signatures that resemble humic substances.

The formation is dependent on conditions, but not much has been discussed on this topic.

Answer: Our work on the formation and transformation of functional groups and structural elements is based on the environmental conditions, described in the paper. The primary aim is the characterization of a well defined HULIS model using spectroscopy and is not a kinetic study on particle formation. However, a discussion on kinetic parameters was added to the manuscript.

Revised, p. 17380, 21-26: *“During the aerosol formation process, the change of chemical bonds inside the aerosol particles has been studied by long-path FTIR spectroscopy using a 40 m White cell in the aerosol smog-chamber. Every 10 minutes 256 single scans were sampled. The medium residence time τ of catechol in the smog-chamber was calculated to 10 minutes by observing the decrease of the aromatic stretch vibration at 1510 cm^{-1} . Hence, during the first 10 minutes the precursor decays rapidly and products increase with approximately the same rate. After 30 minutes no further changes in the infrared spectrum are detectable. Thus, the SOA formation process of particles from catechol or guaiacol as precursors is completed after less than 30 minutes (Fig. 6). The chemical transformation of the precursor at the very beginning of the oxidation process (first 10 seconds) has been observed and discussed by Ofner et al. (2010). The formation of two main absorptions at 1690 and 1755 cm^{-1} in the carbonyl stretching region is reported. Where the band at 1690 cm^{-1} is occurring first and allocated to aryllic carbonyls and the band at 1755 cm^{-1} is following, indicating ring-opened olefinic carbonyls. The long-path FTIR spectra from the aerosol smog-chamber indicate that the full-grown particles do not undergo any further oxidation. This can be well inspected by the carbonyl stretching vibration (see figure*

C8566

6), which remains constant in shape and intensity. We conclude that the highly-polar, fully oxidized, gas-phase intermediates observed in the IR spectra are presumably the precursors of the SOA nucleation process.

According to the composition of the gas phase (N_2 , O_2 , CO_2 and O_3) and the chemical structure of the precursors, only vibrational modes containing carbon, oxygen, and hydrogen are expected. By the overlap of gaseous and solid products and gaseous educts, as well as other reactive or inert gas-phase species, a quantitative analysis of these data is hampered. “

Comment: The paper starts with a rather (too) long introduction that does not clearly outline the issues that will be discussed and does not provide a clear presentation of the hypothesis or goal of the study. I believe that the introduction can be cut by 30-50%.

Answer: A more detailed discussion of the relevant topics has been included, and the less relevant issues have been deleted from the introduction.

Deleted P 17372, lines 3-5: “However, formation pathways of SOA are still incompletely clarified, and details of the initiating reactions and therefore, the chemical transformation of the precursors by atmospheric oxidizing trace gases are hardly known.”

Deleted P 17372, lines 7-14: “Aerosol chamber studies have been applied to investigate particle formation and processing (Iinuma et al., 2004). The transformation pathways of this model substance have been well characterized by many authors, and various gaseous intermediates, such as pinonaldehyde, pinene oxide, norpinonaldehyde and 4-oxopinonaldehyde have been summarized in a recent overview (Yu et al., 2008), although the reported yields of pinonaldehyde span a range from 0.3 to 53 wt.% in the O_3 -reaction and 6-87wt.% in the OH-reaction.”

Deleted P 17373, line 21 – 17374, line 5: “In the recent past several field studies of SOA have been performed using aerosol mass spectroscopy (AMS) as a powerful tool identifying a myriad of compounds. However, the analyses of these data show

C8567

that complete single-molecule identification is a rather impossible task due to strong fluctuations of the chemical composition of the aerosol and due to the occurrence of isobar substances. At current, half of the particulate organic matter (POM) cannot be characterized as individual compounds. POM contains numerous types of organic molecules including hydrocarbons, alcohols, aldehydes, and carboxylic acids (Limbeck et al., 2005 and Kundu et al., 2010). Therefore, the more leading approach is the focussing on the reactive functional groups and fading out the aliphatic or aromatic rest. A new concept of laboratory and field measurements is needed, which aims at the understanding of the dynamic properties of SOA. Organic matter is semi-volatile and thus readily exchanges between gas and aerosol phase. Oxidation and oligomerization leads to larger molecules and thus changes the physical-chemical parameter of the aerosol completely.”

Revised text (shortened): P 17372, line 15 – P 17373, line 5: “The state-of-the-art model of atmospheric HULIS, since 20 years in use, is based on selected macromolecular structures with an aromatic or olefinic core (Mukai and Ambe, 1986). The large aromatic content of HULIS may origin from oxidative and non-oxidative particle-phase reactions of different precursors including aromatics (Kroll and Seinfeld, 2008). Gelencsér et al. (2003) report formation of light-absorbing organic matter from aromatic hydroxy-acids with hydroxyl radicals and suggest those products as HULIS. Hoffer et al. (2004) characterized the Fenton-reaction products of 3,5-dihydroxybenzoic acid with OH radicals as synthetic HULIS. Humic substances, especially commercial humic and fulvic acids (e.g. Suwannee River fulvic acid (SRFA)) seem to differ significantly from atmospheric HULIS, as reported by a detailed and critical review about the humic-like character of atmospheric HULIS (Graber and Rudich, 2006). Further, their preparation as aerosols in an aerosol smog-chamber is rather difficult. Thus, precursors are needed as in-situ model substances to generate SOA with HULIS qualities (Cowen and Al-Abadleh, 2009).”

New text was added on suggestion of referee #2. For the new text, please see the

C8568

answer to referee #2.

Comment: The experimental section is clear and it is followed by a very detailed results section. The conclusions are also clear, but are not discussed thoroughly in the atmospheric context.

Answer: SOA from those aromatic precursors should serve as model compound for some structural features of atmospheric HULIS, especially for the aromatic core structure. We have added more discussion of different atmospheric HULIS samples and related laboratory experiments with other model compounds (see answer to referee #2). On the other hand, SOA from a single compound like catechol, guaiacol or any other precursor, will never exhibit all features of natural samples. The conclusions were totally changed:

Revised, p. 17386, 18 – 17387, 29: *“SOA from catechol and guaiacol typically exhibits small particles with diameters between 40 and 90 nm, built up by a very fast formation process. Those particles have a nearly perfect spherical morphology, indicating their airborne formation by gas-to-particle conversion. Environmental conditions like solar radiation or relative humidity influence not only physical properties like aerosol size distributions or formation yields but also chemical properties like the total amount of oxidized sites and amount and types of functional groups.*

The difference between the H/C values is explained by the absence of aliphatic side chains in the SOA from catechol and guaiacol. Hence, SOA from those precursors represents the aromatic and olefinic oxidized core structure of atmospheric HULIS very well. Only saturated aliphatic parts of atmospheric HULIS are not represented.

Light absorption of those organic particles ranges from less than 200 nm up to 600 nm into the visible region and declines very smoothly. Thus, derived SOA samples are light brown coloured. This optical feature indicates absorption processes according to aromatic or olefinic structures with a large variety of chemically bound oxygen.

C8569

The chemical transformation from the gaseous precursor to the final aerosol particle is distinguished by the formation of different functional groups and disappearance of well defined structural elements of the entire benzene ring. The aromatic or olefinic structural element, an important attribute for atmospheric HULIS, still persists in the aerosol particle.

The variation of simulated sunlight or relative humidity results in various degrading structural elements like aromatic $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{H})$ stretch vibrations and pronounced oxygen containing functional groups, shifting $\nu(\text{C}=\text{O})$ vibrations.

SOA from catechol and guaiacol provides several features according to natural and synthetic HULIS and commercial proxies as discussed above. Especially the high molecular weight caused by the aromatic system and the polycarboxylic acidic functionality match those properties.

Due to the easy preparation it is applicable for lab-scale measurements of organic aerosol processing in an aerosol smog-chambers or aerosol flow reactors. Commercial HULIS proxies like SRFA need special and complex preparation techniques like ultrasonic nebulising or atomizing of solutions. The easy formation even in the dark or at different simulated environmental situations using only one precursor allows aerosol preparation with comparable properties. SOA could perform like SV- and LV-OOA using aerosol-smog-chamber experiments close to natural conditions. Different stable aged modifications of SOA from catechol and guaiacol could be obtained. Synthetic SOA from catechol and guaiacol produced in aerosol smog-chamber experiments fulfil the physical chemical characteristics of HULIS better than SRFA due to their analytical properties and can be used as atmospheric model substances for HULIS in laboratory experiments to study heterogeneous reactions with aromatic or olefinic cores. “.

Comment: I have expected to see more effort in characterizing actual atmospheric samples and comparing them to the SOA of this study to put it in an atmospheric context.

C8570

Answer: It was not the aim of our study to characterize natural HULIS samples. However, we have extended our discussion concerning the acceptability of SOA from catechol or guaiacol as a model compound for Atmospheric Aromatic HULIS. Therefore, we compare results from natural samples with laboratory experiments of different origin.

Added, p. 17383, 25: *"Same absorptions of carbonyls and aromatic rings were found for photodegraded tannic acid as a model for HULIS (Cowen and Al-Abadleh, 2009) or for SRFA (Hatch et al., 2009)."*

Added, p. 17384, 3: *"ATR-FTIR spectra of SOA from catechol and guaiacol exhibit absorptions reported for natural HULIS and used proxies like SRFA. The carbonyl and aromatic stretching region between 1600 and 1800 cm^{-1} is dominated by two bands at 1620 and 1716 or 1740. Those absorptions are reported for SRFA and for natural HULIS (Salma et al., 2010). Especially the $\nu(\text{C}=\text{O})$ at 1716 cm^{-1} of SOA catechol formed in the dark was found in BBOA (Salma et al., 2010). Most important functional groups of SOA from catechol and guaiacol seem to be carboxylic acids, carboxylic anhydrides and lactones or esters, shown by ATR absorptions at 1317 and 1295 cm^{-1} and TPP-MS. Those groups are reported for an ambient aerosol at a rural site with aromatic content of 17% (Courty and Dillner, 2009). Samburova et al. (2007) found high carboxylic and aryl fractions in HULIS samples. Aromatic acids with high-molecular weights were well correlated with HULIS by Stone et al. (2009). Carboxylic acids and their modifications are highly reported for natural HULIS, biomass burning aerosol and water-soluble organic carbon (WSOC) (Salma and L  ng, 2008; Kundu et al., 2010; Limbeck and Puxbaum, 1999; Kumagai et al., 2010). While Sun et al. (2010) report dimer formation based on C-O or C-C, ATR-FTIR spectra from catechol and guaiacol give also hints on formation of carboxylic acid dimers."*

Added, p. 17385, 22: *"The main m/z ratio of organic molecules in the particles of 200-450 is closer to natural HULIS samples than SRFA (Graber and Rudich, 2006) and is comparable to other SOA samples from photooxidation (Kalberer et al., 2004)."*

C8571

Added, p. 17386, 12: *"The O/C ratio between 0.3 and 1 is in good agreement with the reported O/C ratios for LV-OOA (low-volatile oxidized organic aerosol) and SV-OOA (semi-volatile OOA) (Jimenez et al., 2009). Further, the medium value of 0.6-0.7 fits the described oxidation state of atmospheric HULIS very well, although the measured H/C ratio of about 1 is lower than the reported 1.6-1.7 (Graber and Rudich, 2006). The H/C ratio is in good agreement with the widely used proxy SRFA (Dinar et al., 2006)."*

Comment: In addition to that authors do not discuss possible effects of the high concentrations used in the reaction, or compare to other experiments that tried to synthesize "artificial" HUMIC substances.

Answer: The high concentrations used in this study are required for a sufficient signal/noise ratio by our spectroscopic techniques, such as infrared spectroscopy (ATR and long-path absorption) and mass spectroscopy (TPP-MS). Those analytical methods inherently need elevated concentrations of final aerosols to be operated at the Bayreuth aerosol chamber and to archive interpretable spectra and results. However, the effect of the slightly elevated precursor concentrations has been discussed in the text.

Added p. 17384, 4: *"SOA was produced for FTIR and TPP-MS measurements at elevated concentrations, as described in the experimental section. This was not causing any identifiable discrepancies, when comparing with natural samples or other HULIS models."*

Comment: At the end, while the paper may provide a good baseline analytical work of these SOA, it reads like a technical report and does not move forward to test a real atmospheric issue.

Answer: We have extended the discussion in this paper significantly, and we are confident to fulfil the high standards of ACP. However, we may underline again this is not the analysis of field samples in a laboratory experiment but a physical-chemical laboratory model using selected pure model substances.

C8572

The completed references will be supplied in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17369, 2010.

C8573