Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "Modeling secondary organic aerosol formation through cloud processing of organic compounds" by J. Chen et al.

J. Chen et al.

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Response to anonymous reviewer 1: We thank the reviewer for comments. Changes have been made to address these comments.

Comment 1: p. 8953, l. 25: You should refer here to the modeling studies that applied the same multiphase mechanism as you did and could explain successfully oxalate concentrations [Sorooshian et al., 2006; Sorooshian et al., 2007]

Response: These two references have been added.

Comment 2: p. 8954, l. 15: The studies you cite for oligomerization reactions refer to reactions in concentrated particles, thus, not (necessarily) in dilute aqueous drops. You

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should either make this clear in this context that processes can occur in liquid particles or remove these citations here.

Response: The two references have been changed to Altieri et al. (2006).

Altieri, K.E., Carlton, A.G., Lim, H.J., Turpin, B.J., and Seitzinger, S.P., Evidence for oligomer formation in clouds: Reactions of isoprene oxidation products, Environ. Sci. Technol., 40, 4956-4960, 2006.

Comment 3: p. 8956, l. 11: (2) the assumption that aldehydes are converted fully to their corresponding acids is not true as it has been shown in lab studies [Carlton et al., 2006 and references therein]. You should state that your assumption may represent an overestimate of yields.

Response: The following words have been added on p.8956 (third paragraph of Section 2.1): "The assumption of full conversion of aldehydes of carbon number greater than four to their corresponding acids likely represents an upper-bound estimate of the yields of carboxylic acids from this reaction pathway (Carlton et al., 2006)."

Comment 4: p. 8957, l. 10: Does the vapor pressure (partitioning behavior) of the lumped compound groups represent an average value for the individual species or how were their physicochemical properties derived?

Response: The vapor pressure of the lumped compound groups was estimated based on the average structure of compounds in a group. This method was documented in Pun et al. (2002), which is cited on line 18 of that page.

Comment 5: p. 8959, l. 5 ff: The assumption of constant RH, T, LWC etc certainly represents a rough simplification to the system but allows an efficient model simulation. Can you elaborate a bit on the trends you might expect if these values vary?

Response: Sensitivity studies have been conducted to investigate the effects of relative humidity (RH), temperature in clouds (T), liquid water content of clouds (LWC), and reduced photolysis rates in clouds as compared to clear sky conditions on the zero-

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dimensional model results. The following words have been added as the last paragraph of Section 3.1.

"Sensitivity analyses also were performed to study the effects of RH, temperature in clouds, cloud water content, and reduced photolysis rates in clouds as compared to clear sky conditions on the zero-dimensional model results. It was found that variations in cloud water content have the most significant effect on the model results, with variations in other factors only having minor effects. When cloud water content is reduced from 0.5 g m(-3) to 0.1 g m(-3), the increase of SOA prediction considering aqueous-phase organic reactions averaged over 48 hours decreases to 11% for Scenario 1 and 5% for Scenario 2. This suggests clearly that the magnitude of cloud water content needs to be taken into account when results from various model simulations are compared."

The sensitivity analyses also lead to the modification of the third paragraph of Section 3.2. The third paragraph of Section 3.2 is now as follows:

"The average relative increase across the domain is smaller than that from the zero-dimensional model simulation for Scenario 1 in which strong monoterpene emissions are considered. The zero-dimensional model simulation represents an ideal situation in which a site is influenced by biogenic monoterpene emissions and is exposed to clouds for three hours in the afternoon (12.5% of the time of each day). Examination of the meteorological inputs for the chosen episode indicates that resolved clouds occupy approximately 10-20% of surface area during the episode. In addition, CMAQ internally calculates sub-grid convective clouds. Therefore, on average, each grid has the probability of 10-20% of being exposed to cloud processing, which is close to the cloud exposure time used in the zero-dimensional model. However, the average cloud liquid water content during the episode is about 0.2 g m(-3), which is smaller than the 0.5 g m(-3) used in the zero-dimensional model simulation. If cloud liquid water content in the zero-dimensional simulation is assumed to be 0.2 g m(-3), the SOA prediction averaged over 48 hours considering aqueous-phase organic chemistry is reduced to

approximately 18% higher than that without aqueous-phase organic chemistry for Scenario 1. In addition, locations influenced strongly by monoterpene emissions may not be necessarily exposed to cloud processing. These two reasons are believed to explain a much smaller relative SOA increase in the three-dimensional model simulation compared to the zero-dimensional simulations if SOA formation from aqueous-phase organic chemistry in clouds is considered."

Comment 6: p. 8961, l. 27: You state that SOA formation in clouds is less important for aromatics than for monoterpenes. In general, e.g. the OH concentration in more polluted scenarios is smaller. Could this fact explain this trend or is it more related to the reactivity of aromatics vs. monoterpenes?

Response: The OH concentration in more polluted scenarios is smaller. The predicted amount of organic compounds (from the gas-phase chemistry mechanism) that are subject to the aqueous-phase processing is smaller for the aromatic compounds. The reactivity of aromatic products in cloud droplets is smaller than that of monoterpene products. A combination of these factors explains this trend. These words have been added to the end of the third paragraph of Section 3.1.

"The reasons for this include smaller OH concentrations in Scenario 2, smaller predicted concentrations of aromatic products (from the gas-phase chemistry mechanism) that are subject to the aqueous-phase processing, and smaller reactivity with OH in cloud droplets for aromatic products compared to monoterpene products."

Comment 7: p. 8965, l. 28: It should be made clear here that the presented multiphase mechanism predicts water-soluble organics that can be further oxidized in cloud droplets. Previous SOA studies on deliquescent particles (with a relatively small volume compared to drops) predict the formation of other products that form particulate mass due to their low-volatility. Thus, SOA formation on deliquescent particles and in cloud droplets is caused by different organics that are formed in different chemical reactions.

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Response: The presented multiphase mechanism treats one SOA formation pathway in cloud droplets (i.e., further oxidation of water-soluble organics by OH). This pathway can potentially occur in deliquescent particles. It does not exclude other pathways for SOA formation on deliquescent particles. In that paragraph of the original manuscript: "Such treatment would need to consider the interactions of different ions and molecules in the particles, which poses significantly more difficulty than processes in the cloud droplets" has been modified to "To treat similar processes in deliquescent particles, the present multiphase mechanism needs to be revised to consider interactions of different ions and molecules in the particles." (second to last paragraph)

Comment 8: Table 4: Is 'Scenario 1' and 'Scenario 2' used for the same scenarios that are called 'urban' and 'rural' in Table 5? (If so, use consistent terms)

Response: "Scenario 1" represents the rural case and "Scenario 2" represents the urban case. Table 5 has been modified ("urban" changed to "Scenario 2" and "rural" changed to "Scenario 1") so that consistent terms are used.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8951, 2007.

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