

Research Highlight

Secondary organic material (SOM) produced by the oxidation of biogenic volatile organic compounds is a major global contributor to the mass concentrations of organic components of atmospheric particles. Chemical mechanisms of SOM production are typically developed in focused laboratory studies but widely used in the complex modeling context of the atmosphere. Given this extrapolation, a stringent testing of the mechanisms is important. Chamber experiments have contributed greatly to our knowledge of important endpoints relevant to climate and air quality, such as SOM yield and composition. Particle mass yield is a typical standard for model-measurement comparison. Particle composition expressed as O:C and H:C elemental ratios can serve as a higher dimensional constraint. A paradigm that uses the two constraints is presented in this study for SOM production from an important C5-C10-C15 terpene sequence, namely isoprene, α -pinene, and β -caryophyllene. The model MCM-SIMPOL is introduced based on the Master Chemical Mechanism (MCM v3.2) and a group contribution method for vapor pressures (SIMPOL). The O:C and H:C ratios of the SOM are measured using an Aerosol Mass Spectrometer (AMS).

As shown in Figure 1 (panels a1 and a2), measurement and model were in good agreement with respect to particle mass yields from isoprene and α -pinene oxidation. However, a higher dimensional comparison between the in situ O:C and H:C measurements and the corresponding predicted values (panels b1 and b2) revealed important disagreements. The model had to be evolved by including chemical pathways that moved the SOM composition in the direction of $\Delta(\text{H:C}) < 0$ and $\Delta(\text{O:C}) < 0$ without significantly altering the particle mass. In this light, the present study concludes that the model-measurement gap can be significantly reduced by a newly proposed reaction pathway (Figure 2): the particle-phase decomposition of organic hydroperoxides and subsequent oligomerization involving free radicals. Such free-radical oligomerization, though well-known in other fields of research, has not been widely considered in previous thinking of SOM production pathways. The products might in many ways resemble the humic-like substances that figure prominently in atmospheric organic material.

For β -caryophyllene, some additional measurement-model gaps are apparent in Figure 1 (panels a3 and b3). Most notably, MCM-SIMPOL overpredicts the particle mass yield. The measurement-model gaps are possibly related to the poor constraining of secondary ozonides (SOZs) in the model. The high fraction of predicted particle-phase SOZs is not congruent with our concurrent molecular product analysis. Rather than the MCM chemistry that produces SOZs, the stabilized Criegee intermediate seems not to rearrange in SOZs at 40% RH but rather to react with gas-phase water. Another factor is that SIMPOL possibly underestimates the vapor pressure of the SOZs, thereby including them as particle-phase species when instead they remain in the gas phase, if they form.

For climate-related modeling such as the aerosol direct effect, mass-based modeling is the norm. In this regard, the model might be concluded as acceptably accurate based on the one-dimensional model-measurement comparison on yield; yet, the further analysis proves that the model mechanism is missing important particle-phase chemistry that possibly controls the physical properties of the particles. It is crucial to use multidimensional data constraints for testing the accuracy of the chemical mechanisms related to the climate models, especially because the range of conditions sampled by a model greatly exceeds the range of conditions that can be reasonably studied in a laboratory environment. In this case, model extrapolation can be accurate only in the case that the underlying chemical mechanism is also accurate. High

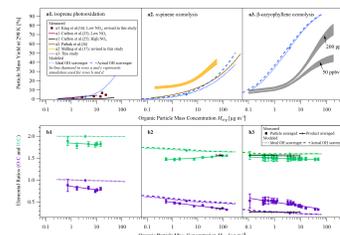


Figure 1. Measurements and predictions. The first row shows particle mass yields at 298 K. The second row shows the modeled and measured particle-average O:C and H:C ratios for increasing particle mass concentrations.

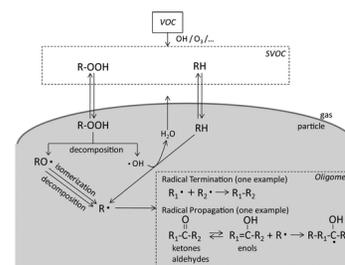


Figure 2. Proposed dehydration and oligomerization reaction sequence. The decomposition of organic hydroperoxides (R-OOH) produces radicals that initiate the sequence. Abbreviations in the figure include: VOC, volatile organic compounds (e.g., isoprene, α -pinene, β -caryophyllene); SVOC, semivolatile organic compounds (produced by the oxidation of VOCs); R#, alkyl radical; RO#, alkoxy radical; R-OOH and RH are SVOC molecules.

confidence of this latter result can be achieved only by stringent testing against multidimensional endpoints.

Reference(s)

Chen Q, Y Liu, N Donahue, J Shilling, and S Martin. 2011. "Particle-phase chemistry of secondary organic material: modeled compared to measured O:C and H:C elemental ratios provide constraints." *Environmental Science & Technology*, , 10.1021/es104398s.

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Aerosol Life Cycle