The Next Generation of SOA Models: Development and Application

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Functional Group Oxidation Model (FGOM)

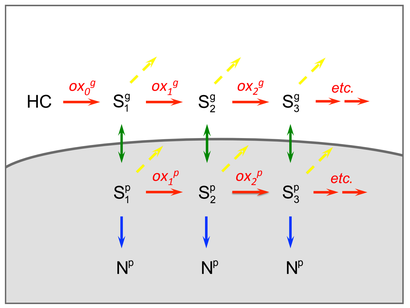
Three recent studies, 2D-VBS (Donahue et al., 2012), SOM (Cappa and Wilson, 2012), and FGOM (Zhang and Seinfeld, 2012), have been directed at a next generation of SOA models. They represent SOA formation and evolution in terms of the competition between functionalization and fragmentation. Each contains a set of parameters that are to be determined by fitting of the model to laboratory chamber data. The FGOM model is developed based on explicit chemical information in terms of the types of functional groups that result from the oxidation of a parent VOC.

Figure 1.

S_i^g -- The spectrum of gas-phase semivolatiles at the i^{th} generation.

S_i^p -- The spectrum of particle-phase semivolatiles at the i^{th} generation.

N^p – Nonvolatile products in the particle phase.



Fragmentation

- The probability of fragmentation of a compound is a function of its O:C ratio.
- Fragmentation is assumed to lead to one-carbon compound (C_1), together with a co-product (C_{n-1}) that has the same collection of functional groups but one fewer carbon atom than the parent compound.

S_i

Functionalization

- Addition of different combinations of four functional groups.
- Particle-phase oxidation reactions proceed in parallel with and via the same chemical mechanisms as in the gas phase.

Oligomerization

- Bimolecular reaction
- The elemental composition of non-volatile species is a parameter .

Volatility Estimation

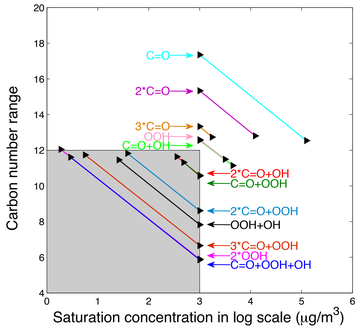
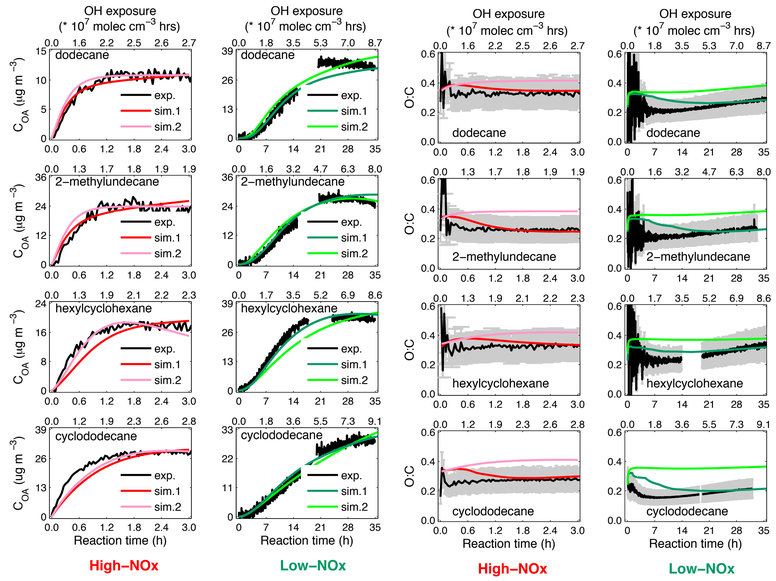


Figure 2. Carbon number range for products of OH oxidation of dodecane under low-NO_x conditions. The grey shaded region defines the particle phase "boundary" for compounds having twelve or fewer carbon numbers. The lines define the carbon number range and types of functional groups for oxidation products of dodecane under low NO_x conditions.

Application of the FGOM to C_{12} Alkanes

Free parameters in the FGOM	
f_v	- Characterizing the probability of fragmentation.
r_p	- The ratio of the particle-phase oxidative reaction rate constant to that in the gas phase.
k_a	- The accretion reaction rate constant in the particle phase.
$[C_x\ H_y\ O_z]$	- Carbon, hydrogen, and oxygen numbers of the non-volatile particle-phase products.

Figure 3. Simulated (colors) and observed (black) time-dependent total organic mass and O:C ratio from the photooxidation of four C_{12} alkanes under high (red) and low (green) NO_x conditions. Note that "sim.1" represents the full fitting of the six free parameters in the FGOM to the chamber data and "sim.2" refers to fitting by only two parameters, r_p and f_v, to the total organic mass concentration.



Conclusions

Organic aerosol yield depends most strongly on three variables: the probability of fragmentation to produce volatile compounds, oxidation reactions involving semi-volatile compounds in the particle phase, and irreversible particle-phase accretion reactions. The elemental composition of particles is dependent not only on the functionalization in the gas phase, but also, probably to as great an extent, on potential particle-phase chemistry. Comparison between the FGOM and SOM models reveals the potential importance of dehydration processes in shaping the aerosol chemical composition.

Statistical Oxidation Model (SOM)

The SOM model describes SOA formation as a statistical evolution in the space of numbers of carbon and oxygen atoms, n_C and n_O. It is assumed that the properties of the n_C / n_O pair can be represented by mean values that account for the actual distribution of functional groups within the group of molecules that make up an SOM species.

Free parameters in the SOM	
f	- Characterizing the probability of fragmentation
$dlVP$	- The decrease of vapor pressure per generation
n_O [% % % %]	- An array of the probabilities of adding 1, 2, 3 or 4 oxygen atoms per generation

Comparison of FGOM with SOM

Figure 4. Comparison of FGOM with SOM for low-NO_x dodecane SOA formation. The upper panel is the FGOM predicted SOA composition represented by saturation concentration and average oxidation state after 7(A), 14(B), 21(C), and 28(D) hours of reaction, respectively. The middle panel is the SOM predicted SOA composition at same time points as FGOM. The lower panel is the simulated results of these two models in the n_C vs. OS_C space. Both FGOM and SOM attempt to reproduce the observed chamber generated SOA properties, but via different mechanisms incorporated in the models.