Secondary Organic Aerosols (SOA) are major constituents of the troposphere, with mass often exceeding sulfate, nitrate, and soot combined, and with impacts on human health, urban and regional photochemistry, precipitation patterns, and directly or indirectly on climate. SOA are by-products of the photo-oxidation of hydrocarbons, both anthropogenic and biogenic, but attempts to describe the chemistry of their formation have fallen short by 0.5-2 orders of magnitude. Implementation of SOA in atmospheric models is still in its infancy and recently[1][2] include parameterizations of chamber-derived yields and volatility distributions without specific information on SOA chemical composition[1][3].

We are developing a model of the explicit gas phase chemistry of hydrocarbons leading to the formation of SOA[1][4]. Chemical pathways and kinetics are obtained from compilations of laboratory measurements, or derived from these using various structure-activity relations. The model predicts the chemical identity of the products as well as their properties relevant to gas-particle partitioning. The model is being evaluated with observations in Mexico City (MILAGRO, 2006) of SOA mass (µg m⁻³) and atomic ratios (oxygen and nitrogen to carbon ratios, O/C and N/C). The major chemical constituents of SOA are identified as β-hydroxy nitriles and ketones from long-chain alkanes as observed in chamber studies[5][6], and nitro-catechols from aromatics. The importance of nitrogen-containing molecules is noteworthy in our model results, although measurements by aerosol mass spectrometry (AMS) suggest lower values[7][8].

B. Model: The “Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere” (GECO-A)

• Aliphatic chemistry is represented explicitly via structure-activity relationship[9].
• Aromatic chemistry is ring-opening is from Leeds MCM[10] mechanism.
• Saturation vapor pressures are computed using group contributions.[11]
• No in-aerosol chemistry.

2 sets of assumptions reduce mechanism size:

a) Species with vapor pressures < 10⁻¹⁰ atm added exclusively to aerosol phase
   → no further gas phase reactions
b) Longer-chain species lumped into chemically similar isomers

Mechanism size for Mexico simulations:

- 1.15 M species (∼ 300 K non-radicals)
- 6.3 M gas-phase reactions
- Computational time on workstation: 0.5x real time

C. Mexico City Model

• The explicit mechanism is used in a 0-D (box) model with diurnally-varying temperature, solar cycle, emissions, deposition, and boundary layer height.

Model Meteorological Conditions

Model-obs comparison: Inorganic species in Mexico City, March 2006

D. Aerosol Mass Yields and Carbon #

As carbon number rises, gas-phase NMHC abundance drops.

Volatility also drops .... resulting aerosol mixture is highly diverse in terms of chain length.

E. Predicted Aerosol Functionality

Sensitivity Study: all species with C>10 are represented by one long-chain NMHC per run.

Each run (except base case) adds the same quantity of NMHC carbon.

C* ratios are smaller than observed[13] from AMS (0.4-0.9)
N/C ratios are larger than observed[14] from AMS (0.01).

Large regional impacts:
Net production continues for several days despite dilution and evaporation.

Examples of major contributors

Straight-chain NMHCs n-alkanes & n-alkenes
Monofunctional nitriles e.g. pentadecane-2-nitrile
Delta-hydroxy-nitriles R-CH(ONO₂)-2(CH₂)-CH(ONO₂)-CH₃
Beta-hydroxy-carbonyls R-CH(ONO₂)-CO-CH₃
Tri-functional chains R-CH(ONO₂)-CO-CH₃(CH₂)₆
R-CH(ONO₂)-CO-CH₃(CH₂)₃
Substituted Aromatic 2-methyl-6-dinitro-pheno
Precursor: toluene

3.5-dimethyl-6-nitro-catechol
Precursor: m-xylene

Aromatic ring-opened products

2,3-epoxy 4-hydroxy-2-methyl-5-nitroso-6-oxo-heptane
Precursor: m-xylene

6-hydroxy-1,4,5,6-tetranitro-2,3-dioxo-1-cyclo-octene
Precursor: 1,2,4-trinitrobenzene

CH₂CO(ONO₂)+(CH₂)₆CO
Precursor: various aromatics

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