A self-generating approach for explicit mechanisms

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Why should we develop explicit organic chemical schemes?

VOC oxidation produces a large number of intermediates. These intermediates play a key role in the HOx and NOx budget and therefore in the tropospheric O$_3$ formation.

Secondary VOC are usually multifunctional species, i.e. having high water solubility and/or low vapor pressure. These organic intermediates may:

- modify the chemical and physical properties of aerosol by Secondary Organic Aerosols production
- modify cloud chemistry (e.g. acid formation) and microphysics (e.g. surface tension effect, properties of aerosol acting as CCN…)

Explicit scheme = reference scheme to test the relevance of simplified (reduced) schemes used in 3D models.

Objective tools to explore our ignorance through comparisons with observations.
From the parent species to the first generation

From the first to the second generation

NO $\rightarrow$ NO$_2$ conversion
HOx sink
NOx sink
From the parent species to the first generation

From the first to the second generation

NO → NO₂ conversion
HOx sink
NOx sink
How big are explicit chemical schemes?

Two problems:

- Explicit schemes are too large to be reasonably written by hand
- The quantity of physical and chemical data needed to develop explicit schemes is far in excess of available experimental data.

Data processing tools are required to:

- Assimilate all the data provided by laboratory studies
- Codify the various estimation methods
- Generate consistent and comprehensive multiphase oxidation schemes on a systematic basis
The chemical scheme generator

What we expect from a generator:

Automatic creation of fully-explicit schemes on the basis of a predefined protocol.

The protocol

Define the set of rules that lay out the choice of reaction pathways (and their associated rate constant).

1- When available, kinetic data taken from laboratory measurements are assigned

2- Otherwise, an estimation of the rate constant, stoichiometric coefficients and reaction products is performed using structure/activity relationships.
The chemical scheme generator

Generator = Expert system that
- assimilates physical and chemical data from laboratory experiments
- estimates the missing information based on structure/activity relationships

The protocol currently used:
- Conceptually similar to the MCM3 mechanism
- Most SAR implemented were borrowed from SAPRC99, MCM and NCAR MM
- Described in Aumont et al., ACP, 2005
**Low diagram of the generator**

**OH reaction**
- RH + OH → RO₂
- >C=C< + OH → >C(OH)C(O₂)<

**O₃ reaction**
- >C=C< + O₃ → >C=O + Criegee
- Criegee → products + OH

**NO₃ reaction**
- RCHO + NO₃ → R(O)OO
- >C=C< + NO₃ → >C(ONO₂)C(O₂)<

**Photolysis**
- RCHO + hν → R + HCO
- RONO₂ + hν → RO + NO₂
- ROOH + hν → RO + OH

**Thermal decomposition**
- RCO(OONO₂) → RCO(OO)+NO₂

**Peroxy alkyl chemistry**
- RO₂+NO → RO+NO₂
- RO₂+NO → RONO₂
- RO₂+NO₃ → RO+NO₂+O₂
- RO₂+HO₂ → ROOH + O₂
- RO₂+RO₂ → products

**Peroxy acyl chemistry**
- RCO₃+NO → R+CO₂+NO₂
- RCO₃+NO₂ → RCO(OONO₂)
- RCO₃+NO₃ → R+CO₂+NO₂+O₂
- RCO₃+HO₂ → RCO(ÖOH) + O₂
- RCO₃+HO₂ → RCO(OH) + O₃
- RCO₃+RO₂ → products

**Alcoxy chemistry**
- >CH(O.)+O₂ → >C=O + HO₂
- >CH(O.)C₂C(O.)< → >C(O.) C₂C(OH)<
- >C(O.)-R → >C=O + R

New reaction products added to the stack

VOCn  VOC2  VOC1

Radical?

C-H?

no

yes

new

RO2?

RCO3?

RO?

-C(O)OONO₂?

-Treat next species in the stack
The chemical scheme generator

**Input**
- Hydrocarbons
- Laboratory data

**Automatic generator** for VOC oxidation scheme
- Set of rules for simplification
- Lumping protocol

**Machinery**: structure/activity relationships

**Output**
- Explicit chemical schemes
- Reduced (simplified) chemical schemes
Chemical scheme reduction

(Near near) explicit scheme
(~70 primary species)

Reference scheme
359 660 species
2 270 159 reactions

Starting scheme

Automatic & systematic reduction

Reduced scheme
~150 species
~500 reactions

Ending scheme
Chemical scheme reduction

(Near near) explicit scheme
(~70 primary species)

Starting scheme

Pre-reduction: reference chemical scheme
359 660 species 2 270 159 reactions

Accuracy of the each reduction procedure can be quantified using the explicit scheme as a reference
See Szopa et al., ACP, 2005
Explicit scheme as an « exploratory vehicle » to explore the behavior of organic matter during oxidation

- where does the carbon go ? -
Modeling VOC oxidation: where does the carbon go?

Explicit modeling of octane oxidation

Chemical scheme:
- $1.2 \times 10^6$ species
- $7.5 \times 10^6$ reactions

Simulation conditions:
- $T=298$ K
- $[\text{octane}]_0 = 20$ ppb
- $[\text{NOx}]_0 = 10$ ppb

How does organic reactivity evolve after the first oxidation steps?

- Contribution to HOx, NOx, Ox budget at regional to global scale?
- How does strong emission sources affect the continental and remote troposphere?
Modeling VOC oxidation: where does the carbon go?

- Mixing ratio (ppbC) vs. Time (day)
  - Octane
  - CO+CO₂
  - Total secondary organics
  - Total simulated carbon

- Chain lengths of secondary organics
  - Total

- Number of functional groups borne by C₈ species
  - C₈
  - C₁ to C₇
  - C₁ to C₇

- Graphs showing changes in carbon distribution over time.
Most secondary organics are water soluble. How does organic matter evolve during cloud events?

What is the contribution of aqueous processes in:
- The removal of VOC
- Acids formation
- Organic aerosols formation (after cloud evaporation)
- The oxidant budget
Some secondary organics are non-volatile species. What is the fraction of the parent compound that leads to aerosols?

What is the contribution of organic condensation to:
- Hygroscopic behavior (CNN activation)
- Size distribution
- Optical properties

4 functional groups: typical species

![Chemical structures](image)

Number of functional groups borne by C8 species

- Time (day): 0 2 4 6 8 10 12

- Number: 0 20 40 60 80
How far should we go in the description of VOC oxidation?

Number of functional groups borne by C8 species

Mixing ratio (ppbC)

Time (day)
How far should we go in the description of VOC oxidation?

Evolution of organic functionalities during octane oxidation

![Graphs showing the evolution of functionalities over time](image)

\[
R_{i/C} = \frac{\text{Number of carbons bearing function } i}{\text{Total number of organic carbons}}
\]
How far should we go in the description of VOC oxidation?

Evolution of organic functionalities during octane oxidation

Evolution of nitrogen compounds and ozone during octane oxidation
Many questions surround the role of multifunctional organics in the chemistry of multiphase system.

The main difficulties:
description of the sources and sinks of a myriad of VOC that may partition to condensed phases.

Method:
extension of the self generating approach to model multiphase system.
Multiphase VOC oxidation: Development of data processing tools to generate kinetic schemes and thermodynamic equilibrium (LISA/NCAR)
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Explicit modelling of the gas/particle partitioning

GAS PHASE

COV

oxidation

+ox

COSVi

oxidation

+ox

CO+CO₂

AEROSOL PHASE

CONDENSATION:

absorption

Raoult’s law :

\[ P_i = \gamma_i x_i P_{vap} \]

P_{vap} are estimated for each intermediate using Myrdal & Yalkowski (97) structure/properties relationship (see Camredon et al., Atmos. Env., 2006)
Gradual change of organics during 1-octene oxidation

Simulation conditions:
T=298 K, [octene]₀ = 10 ppb, [NOx]₀ = 1 ppb (constant)
Evolution of organic functionalities during octene oxidation

\[
R_{i/C} = \frac{\text{Number of carbons bearing function } i}{\text{Total number of organic carbons}}
\]

- **Gas phase**
  - \(-\text{OH}\)
  - \(-\text{ONO}_2\)
  - \(-\text{CHO}\)
  - \(-\text{CO}^-\)

- **Aerosol phase**
  - \(-\text{OH}\)
  - \(-\text{ONO}_2\)
  - \(-\text{CHO}\)
  - \(-\text{CO}^-\)

Colors:
- Purple: ketone
- Green: carboxylic acid
- Yellow: PAN
- Red: nitrate
- Blue: hydroperoxide
- Orange: peracids
- Pink: aldehyde
- Blue: alcohol
Future developments …

CONDEENSE PHASE

- polymers
- oxidation
- polymerization
- inorganic

GAS PHASE

- COV
- oxidation
- oxidation
- CO+CO₂

CONDENSATION: absorption

H₂O

H₂O

inorganic

inorganic
AGU fall meeting, Poster, Tuesday morning

Explicit Modelling of SOA Precursors in Mexico City

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