

# **A self-generating approach for explicit mechanisms**

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# Why should we develop explicit organic chemical schemes ?

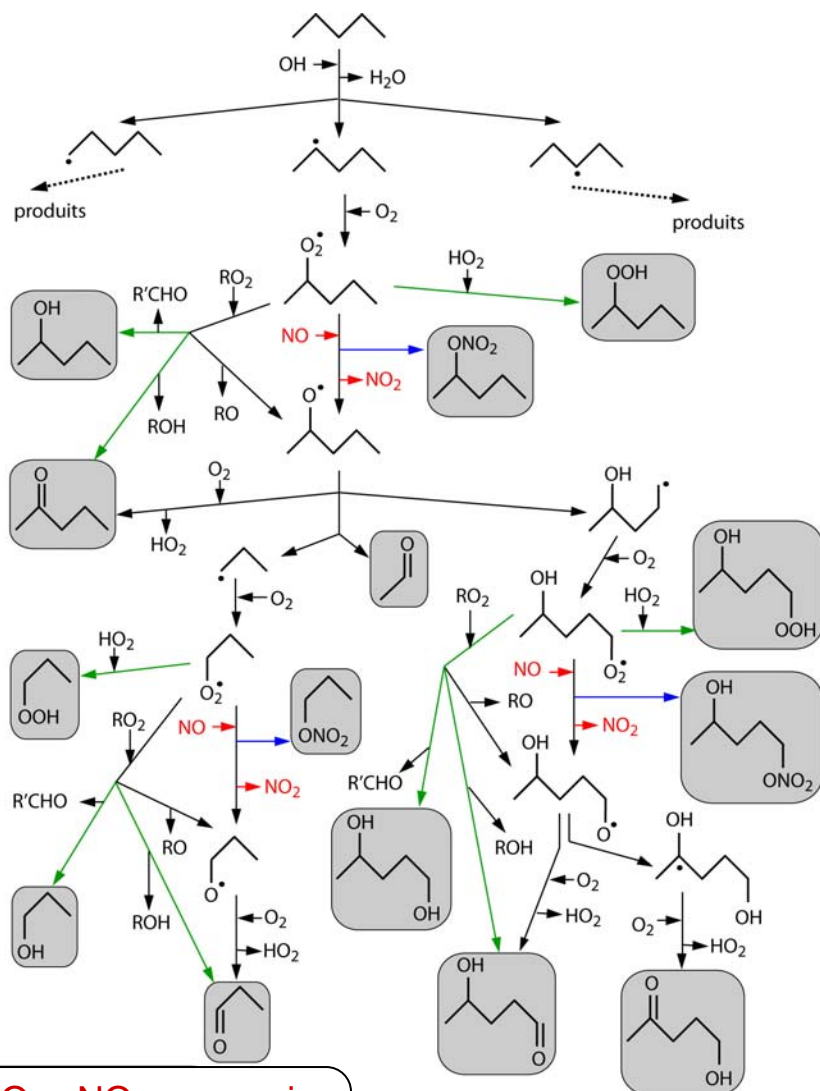
VOC oxidation produces a large number of intermediates. These intermediates play a key role in the HOx and NOx budget and therefore in the tropospheric O<sub>3</sub> formation.

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.

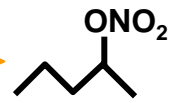
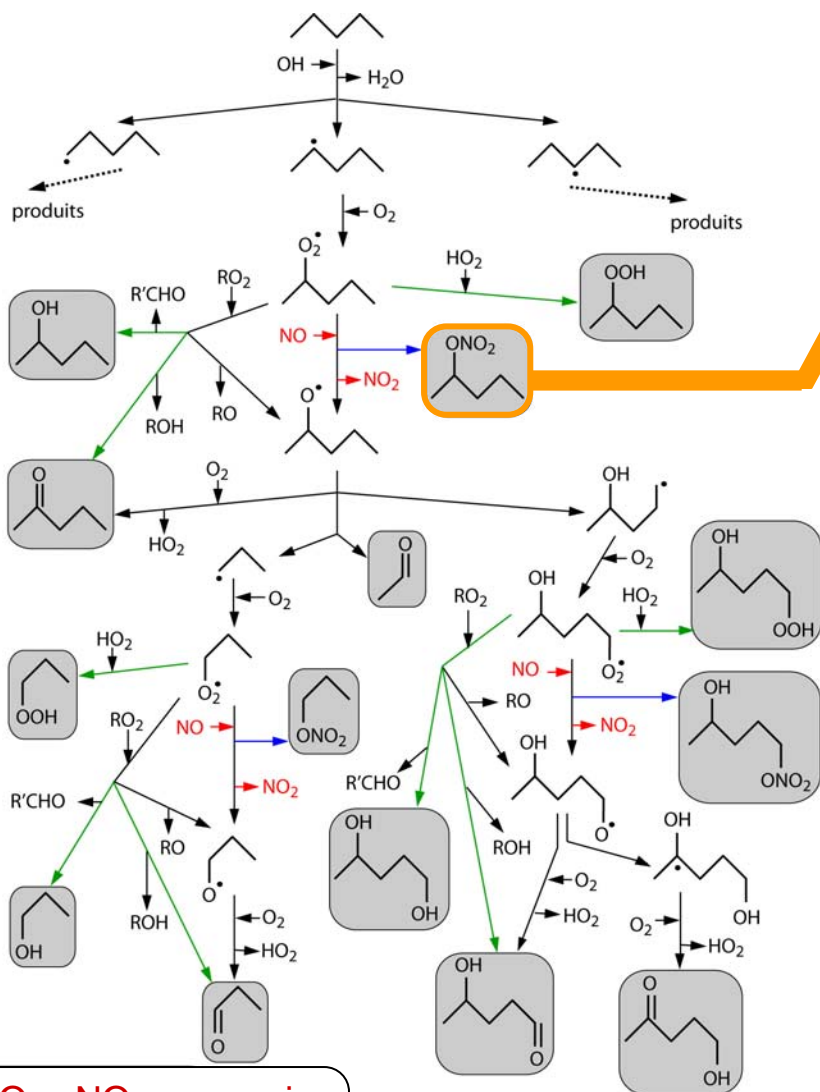
Objective tools to explore our ignorance through comparisons with observations



NO → NO<sub>2</sub> conversion  
HOx sink  
NOx sink

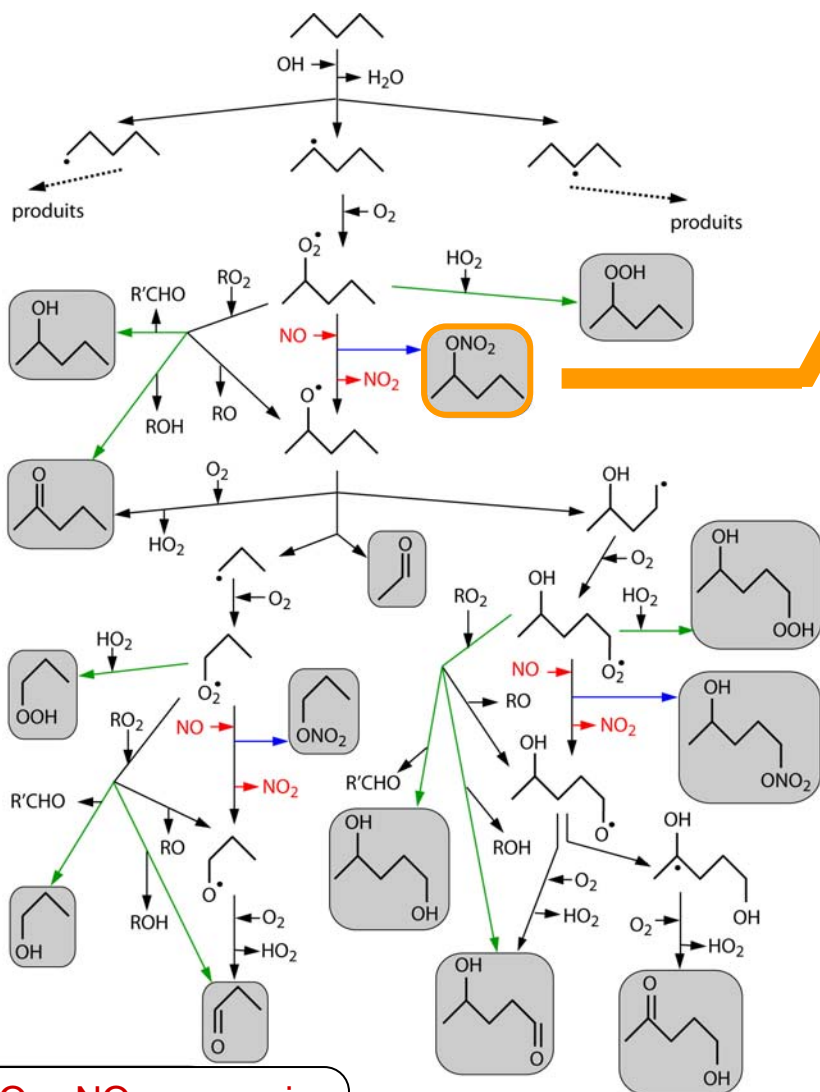
From the parent species to the first generation

From the first to the second generation

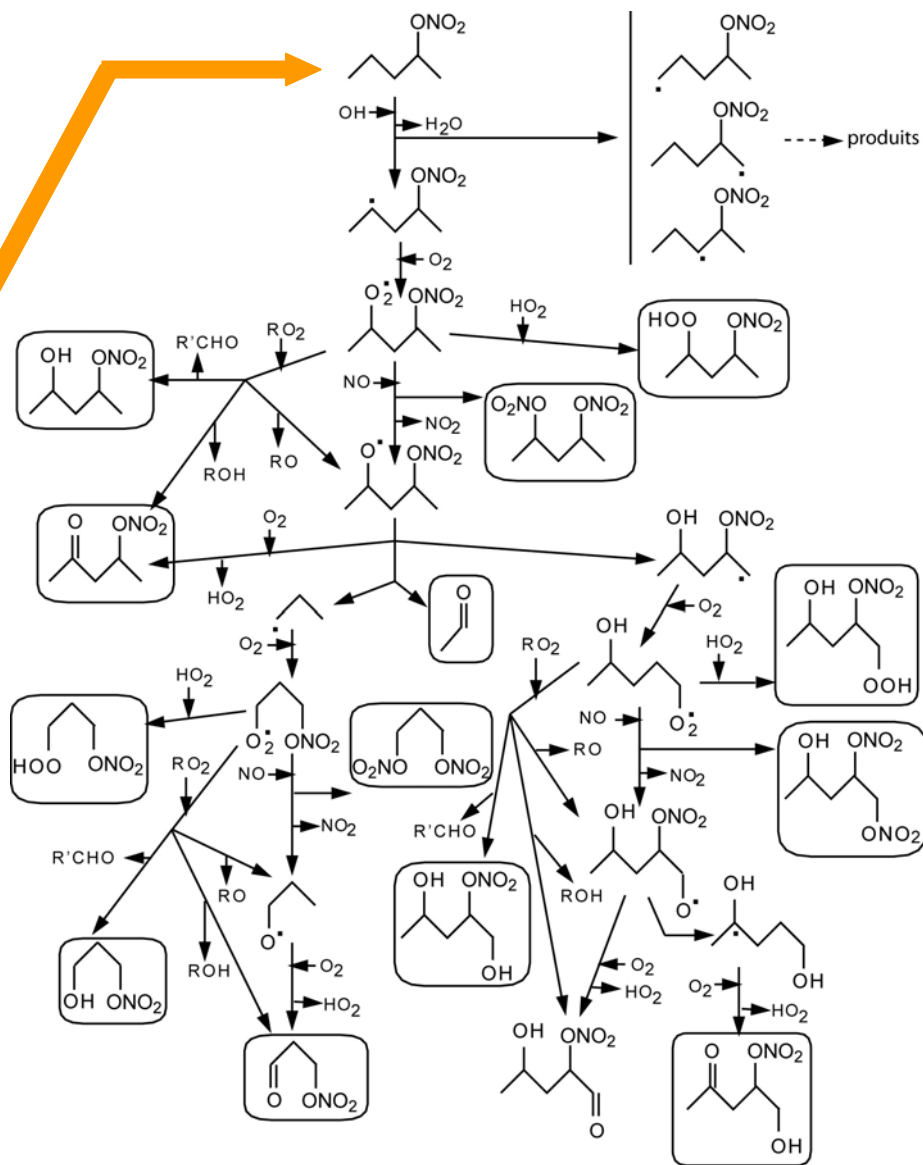


NO → NO<sub>2</sub> conversion  
 HOx sink  
 NOx sink

## From the parent species to the first generation

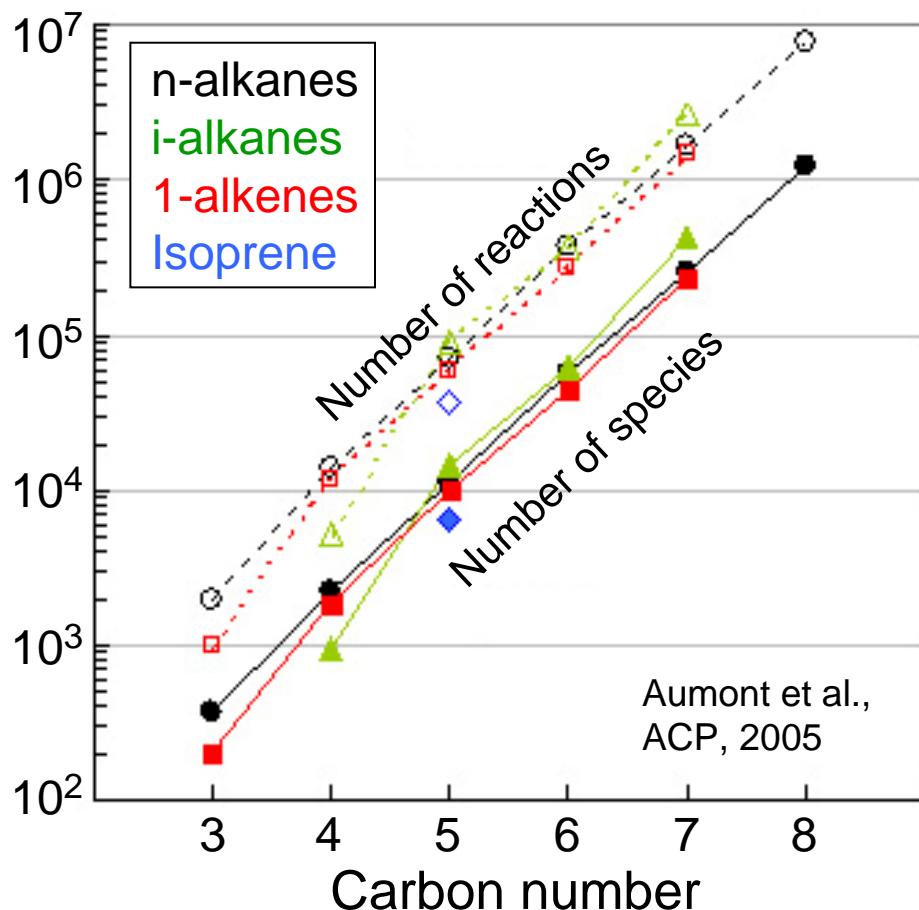


## From the first to the second generation



NO → NO<sub>2</sub> conversion  
 HO<sub>x</sub> sink  
 NO<sub>x</sub> sink

# How big are explicit chemical schemes ?



➔ A fully explicit description leads to schemes dealing with an exorbitant number of species

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

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## ✘ What we expect from a generator :

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

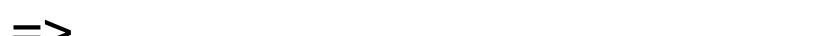
starting point



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## ✘ The protocol

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

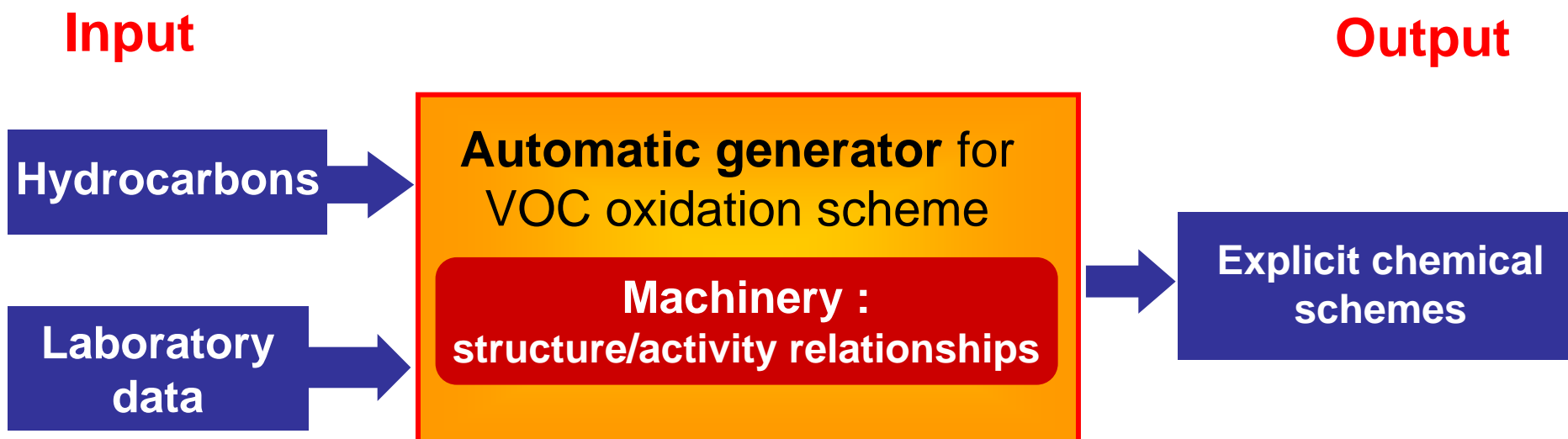
- 1- When available, kinetic data taken from laboratory measurements are assigned
- 2- Otherwise, an estimation of the rate constant, stoichiometric coefficients and reaction products is performed using structure/activity relationships.

# The chemical scheme generator

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Generator = Expert system that

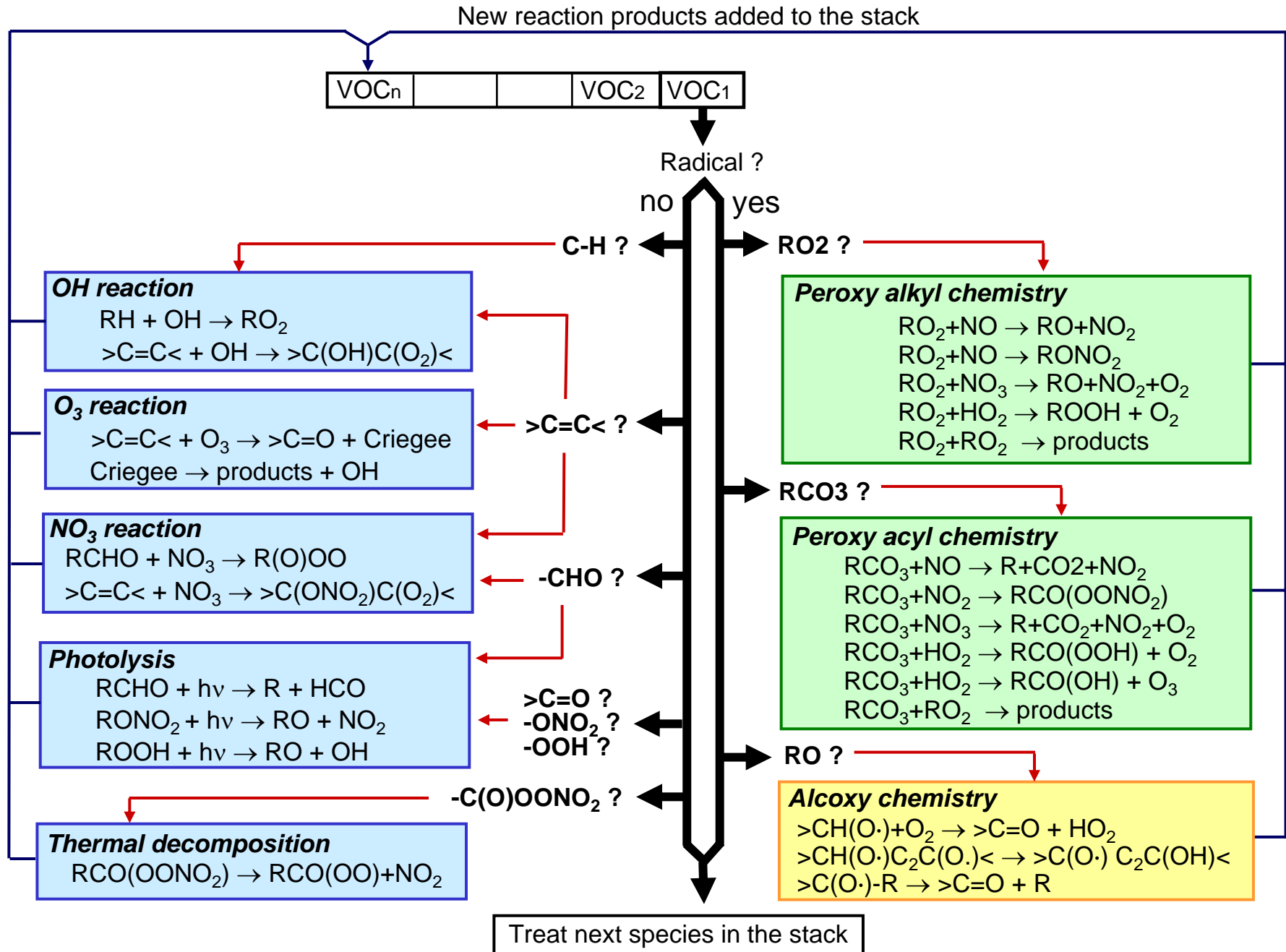
- assimilates physical and chemical data from laboratory experiments
- estimates the missing information based on structure/activity relationships



## The protocol currently used :

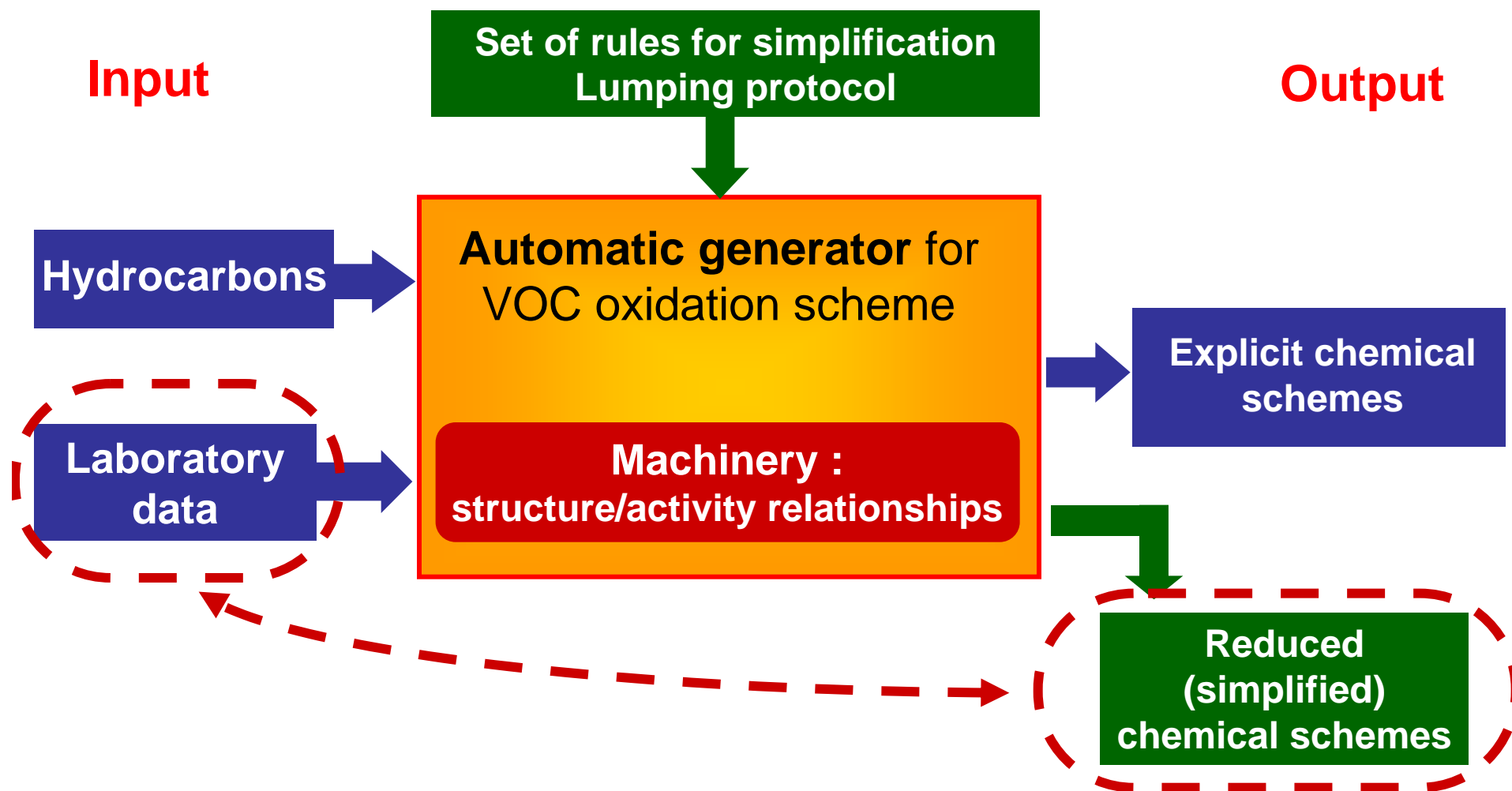
- Conceptually similar to the MCM3 mechanism
- Most SAR implemented were borrowed from SAPRC99, MCM and NCAR MM
- Described in Aumont et al., ACP, 2005

# Low diagram of the generator



# The chemical scheme generator

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# Chemical scheme reduction

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

Reference scheme  
359 660 species  
2 270 159 reactions

Starting scheme

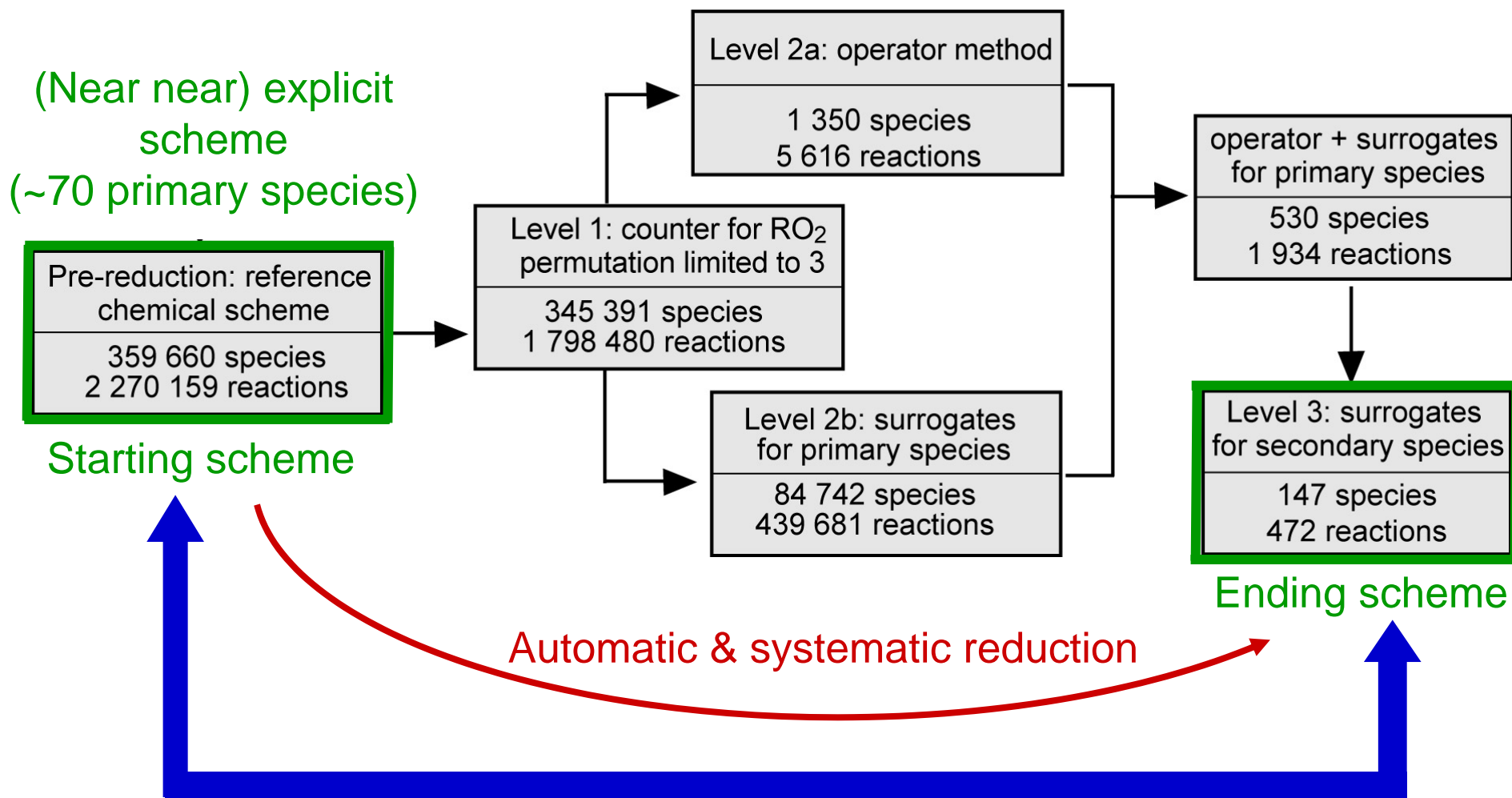
Reduced scheme  
~150 species  
~500 reactions

Ending scheme

Automatic & systematic reduction

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graph LR; A["Reference scheme  
359 660 species  
2 270 159 reactions"] -- "Automatic & systematic reduction" --> B["Reduced scheme  
~150 species  
~500 reactions"]
```

# Chemical scheme reduction



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 ?

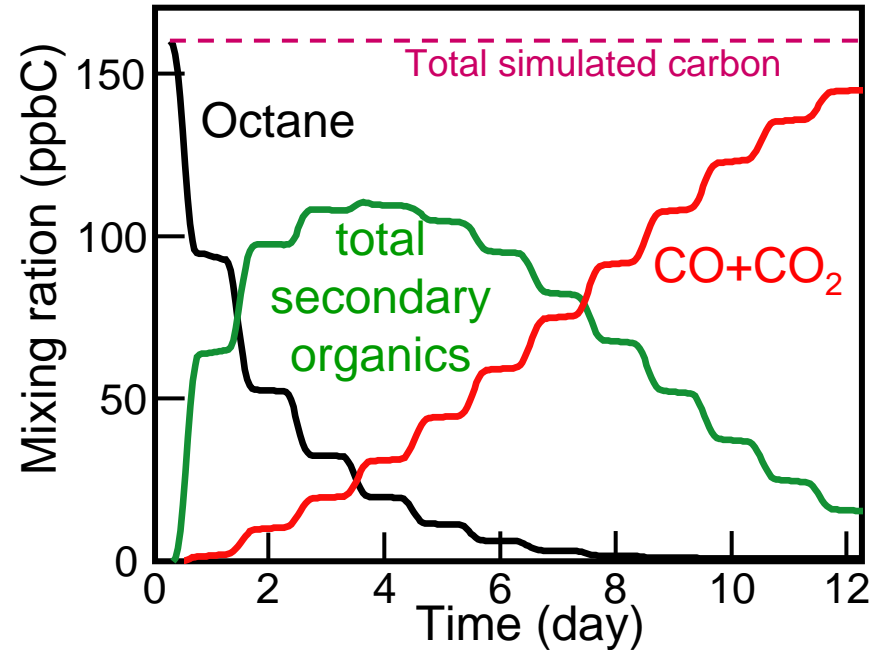
## Explicit modeling of octane oxidation

### Chemical scheme :

$1.2 \times 10^6$  species  
 $7.5 \times 10^6$  reactions

### Simulation conditions :

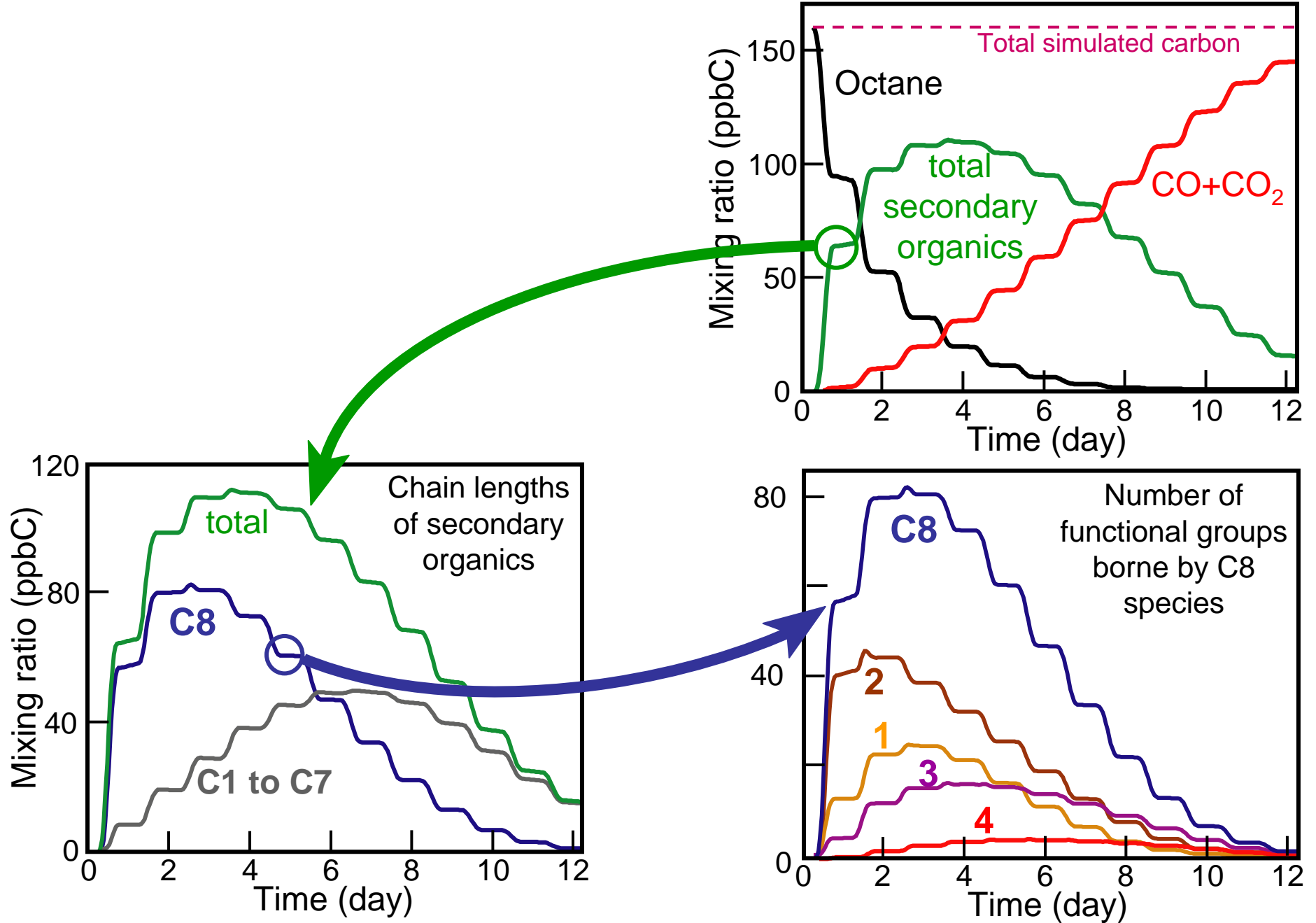
$T = 298$  K  
 $[\text{octane}]_0 = 20$  ppb  
 $[\text{NO}_x]_0 = 10$  ppb



## How does organic reactivity evolve after the first oxidation steps ?

- Contribution to HO<sub>x</sub>, NO<sub>x</sub>, 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 ?

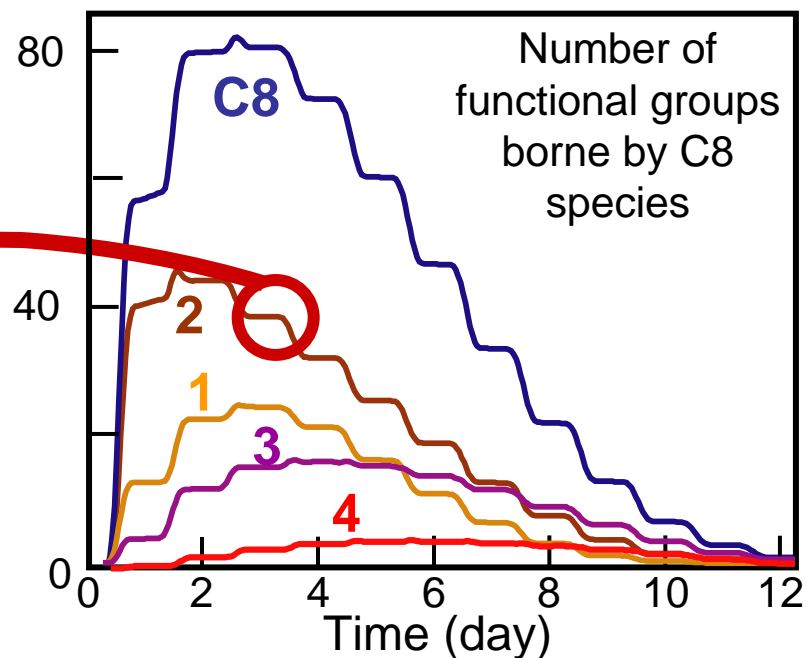
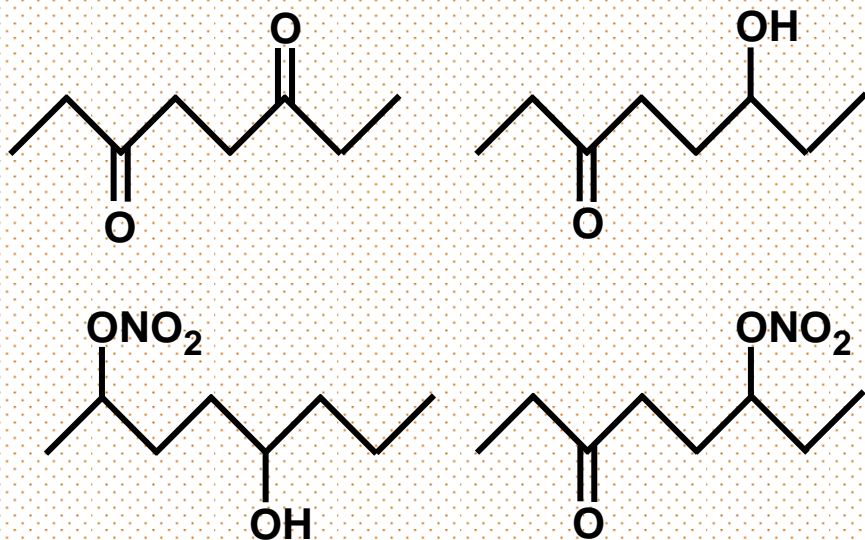


## Most secondary organics are water soluble. How does organic matter evolve during cloud events?

What is the contribution of aqueous processes in:

- The removal of VOC
- Acids formation
- Organic aerosols formation (after cloud evaporation)
- The oxidant budget

### 2 functional groups : typical species

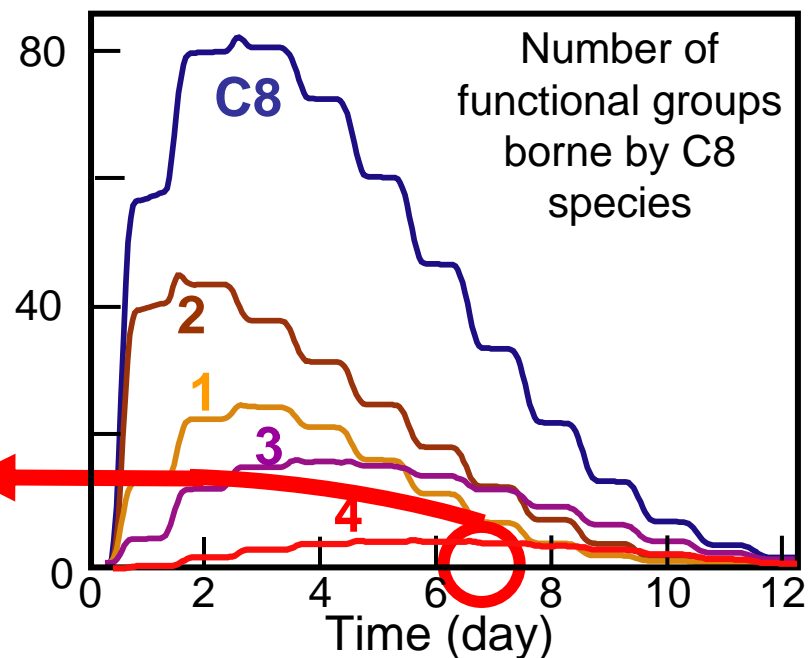
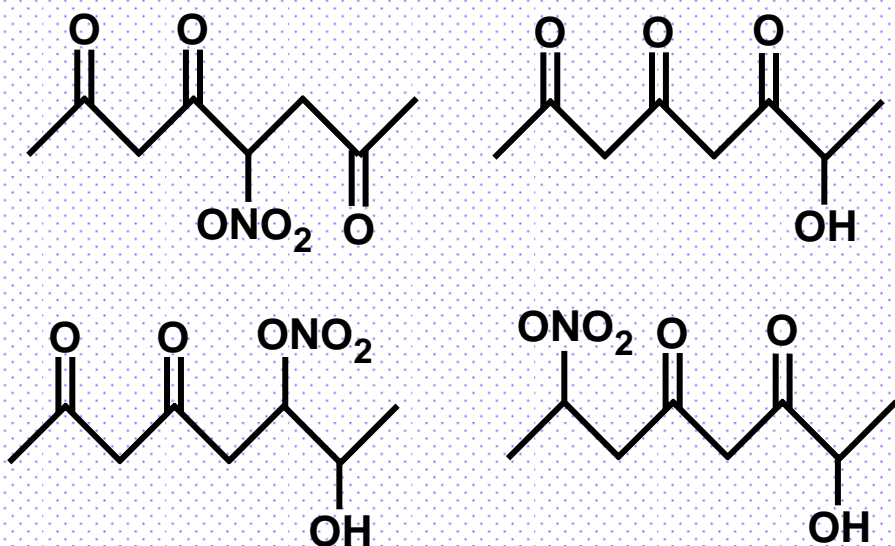


Some secondary organics are non-volatile species. What is the fraction of the parent compound that leads to aerosols ?

What is the contribution of organic condensation to:

- Hygroscopic behavior (CNN activation)
- Size distribution
- Optical properties

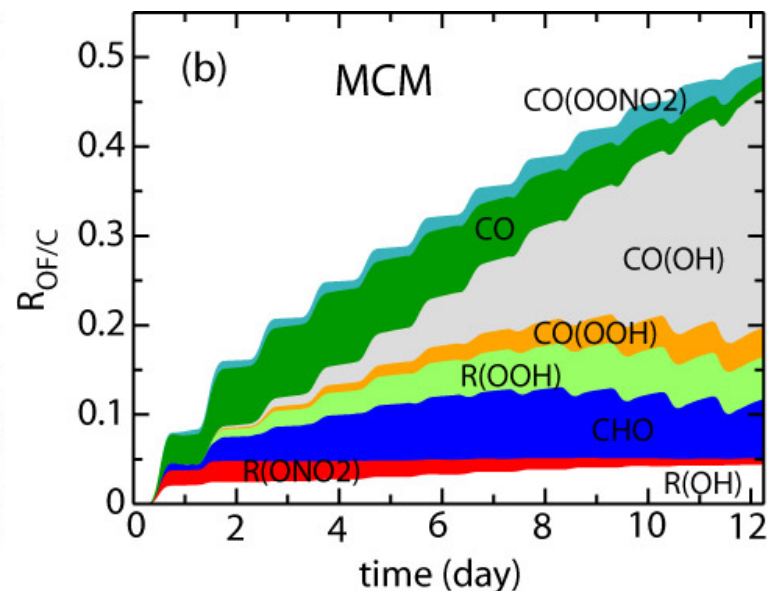
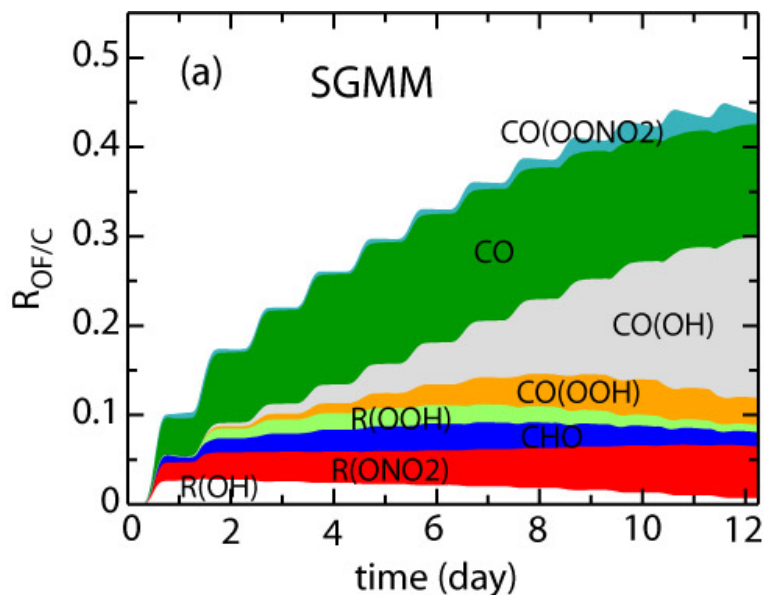
**4 functional groups : typical species**





# How far should we go in the description of VOC oxidation ?

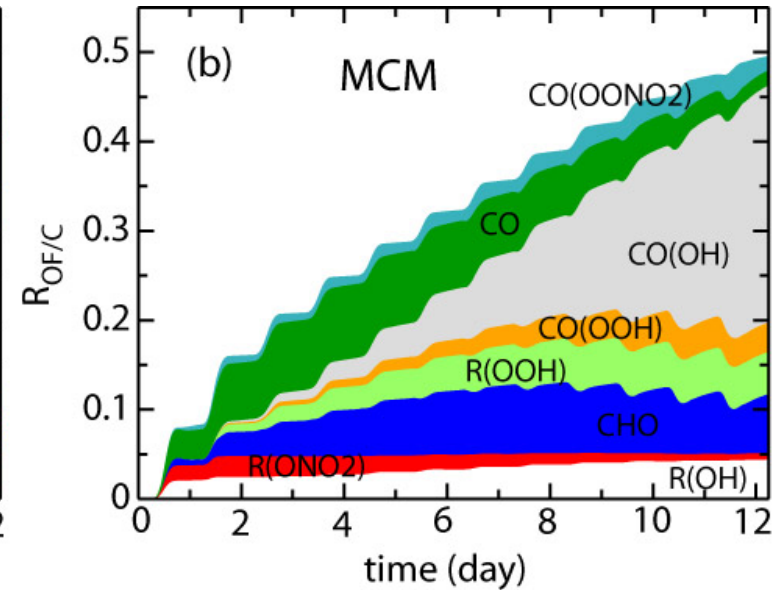
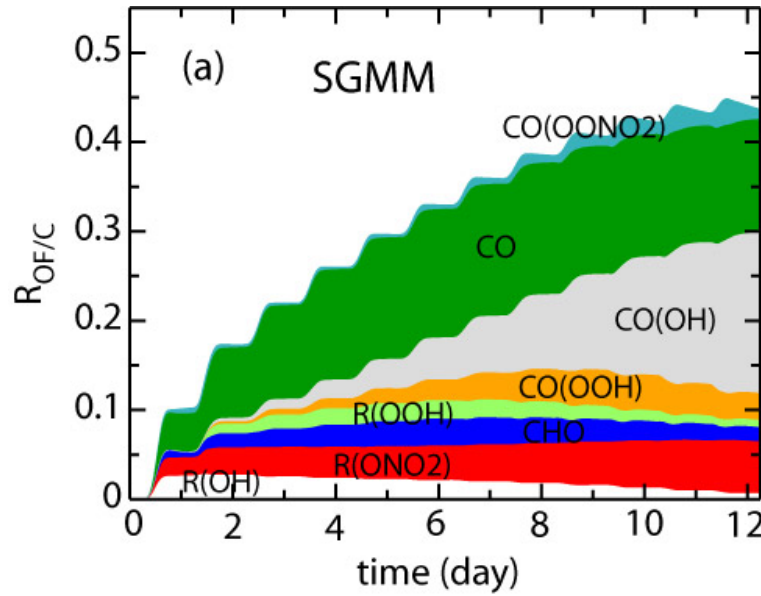
Evolution of organic functionalities during octane oxidation



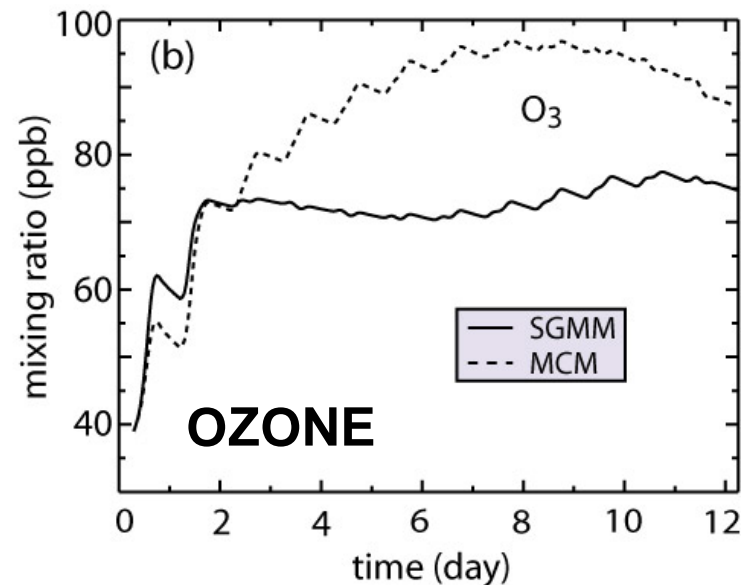
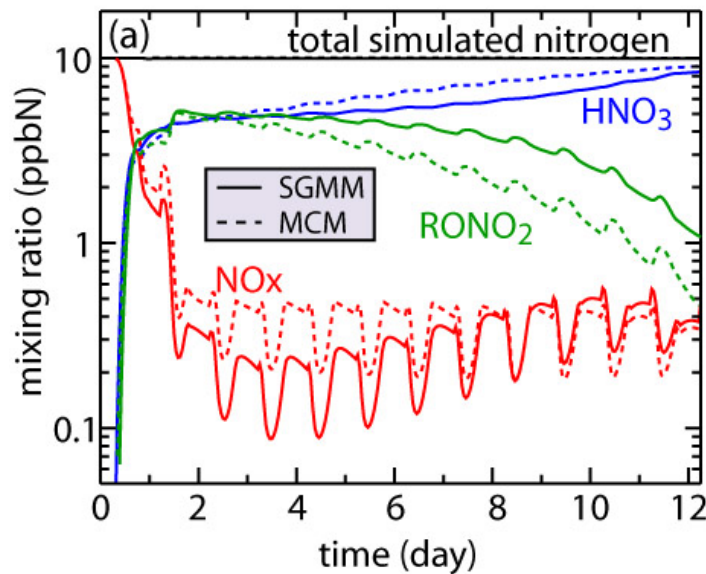
$$R_{i/C} = \frac{\text{Number of carbons bearing function } i}{\text{Total number of organic carbons}}$$

# How far should we go in the description of VOC oxidation ?

Evolution of organic functionalities during octane oxidation

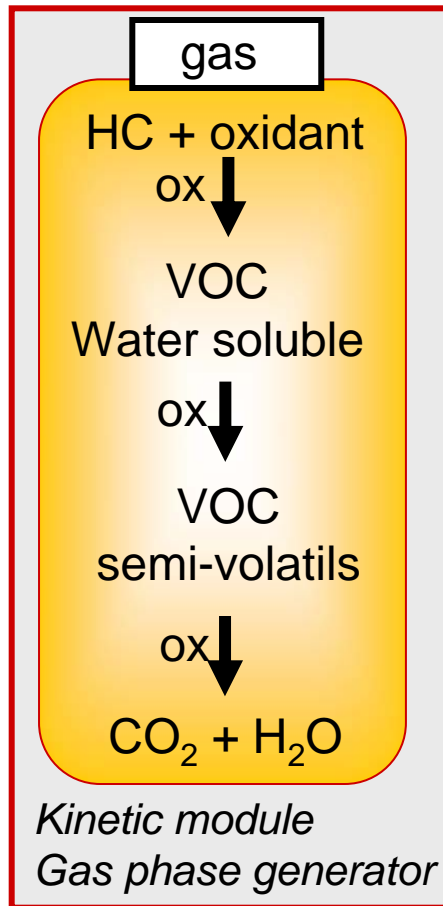


Evolution of nitrogen compounds and ozone during octane oxidation



# Multiphase VOC oxidation : Development of a data processing tools to generate kinetic schemes and thermodynamic equilibrium (LISA/NCAR)

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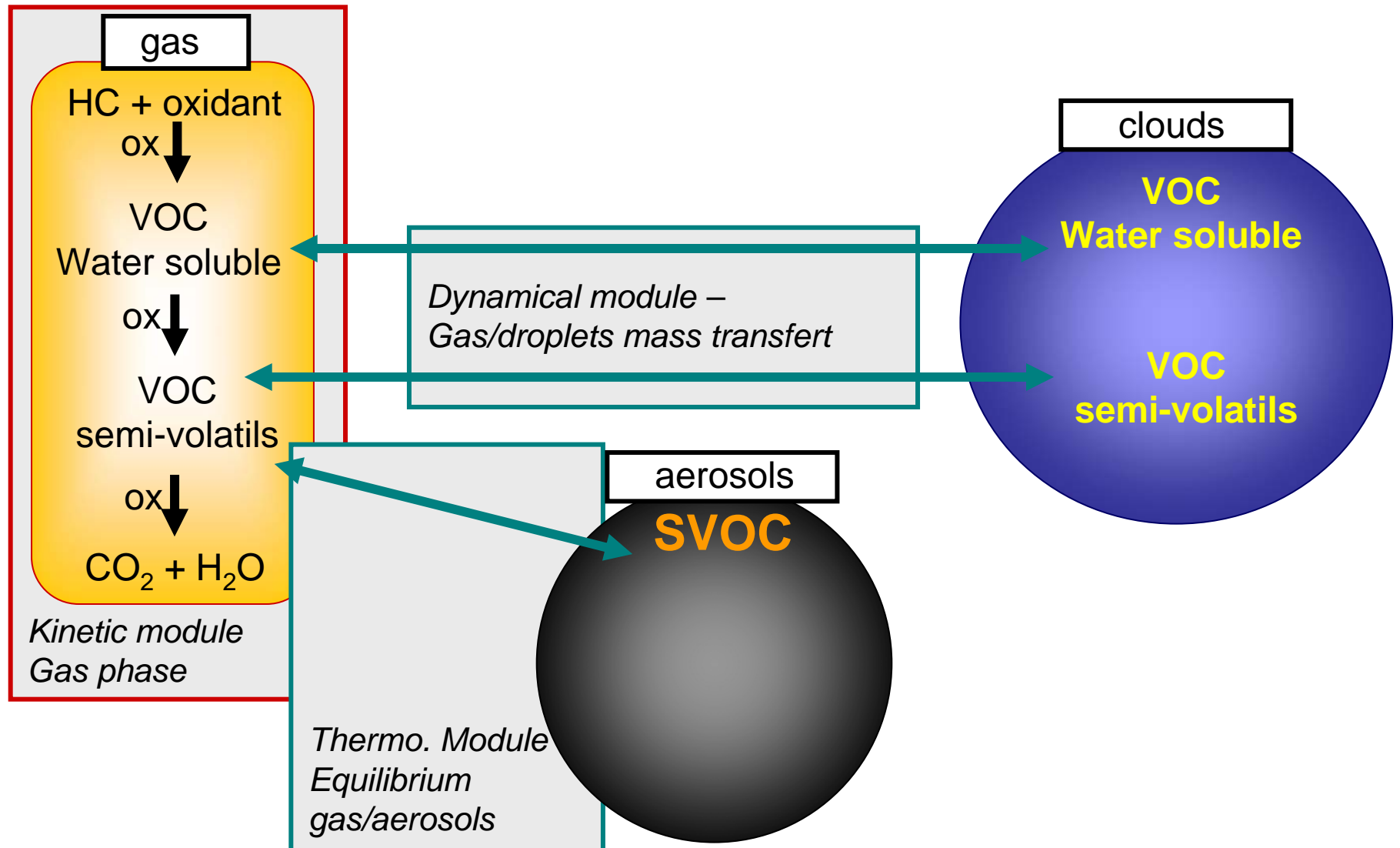


Many questions surround the role of multifunctional organics in the chemistry of multiphase system

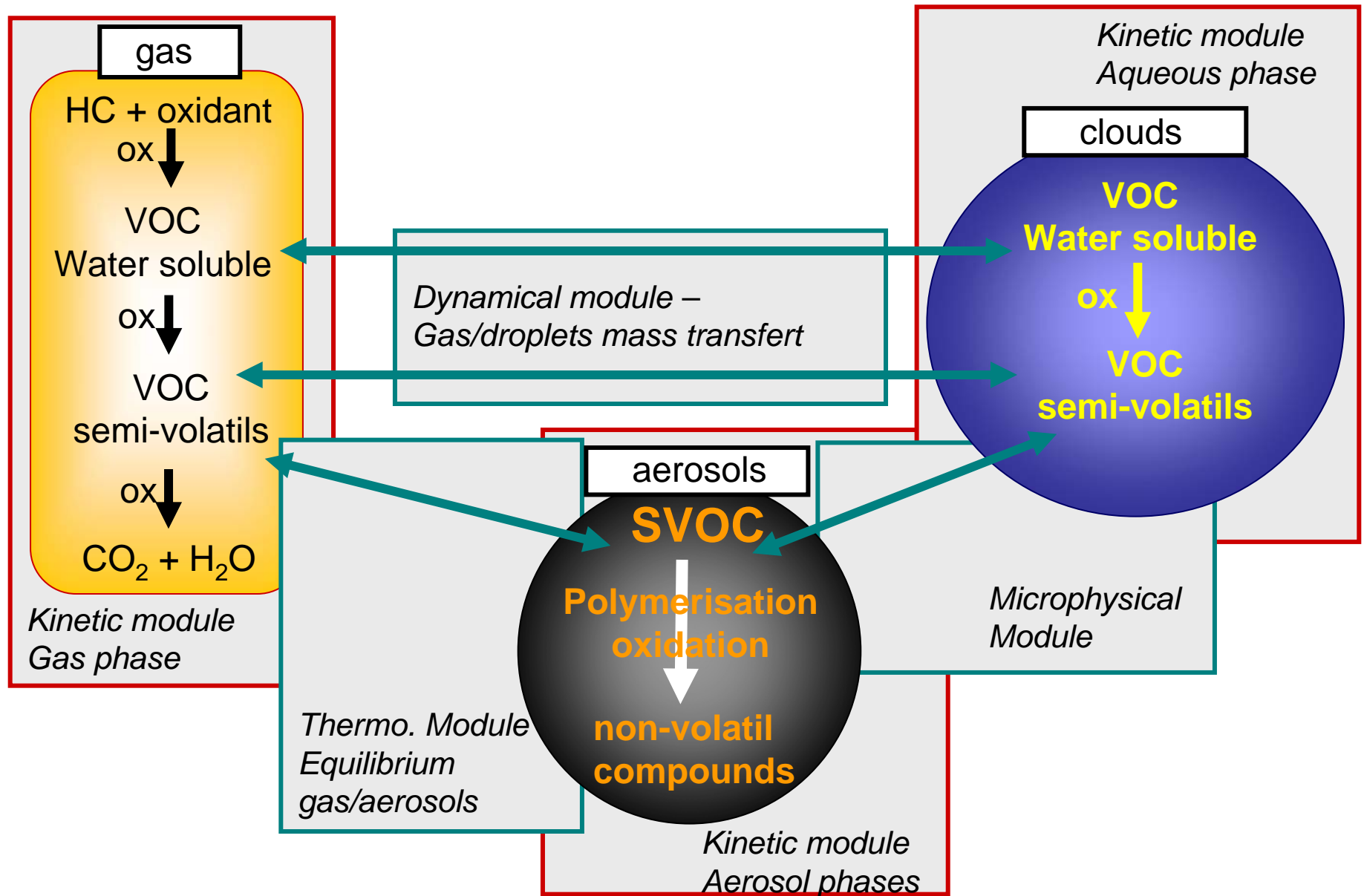
The main difficulties :  
description of the sources and sinks of a myriad of VOC that may partition to condensed phases.

**Method :**  
**extension of the self generating approach to model multiphase system**

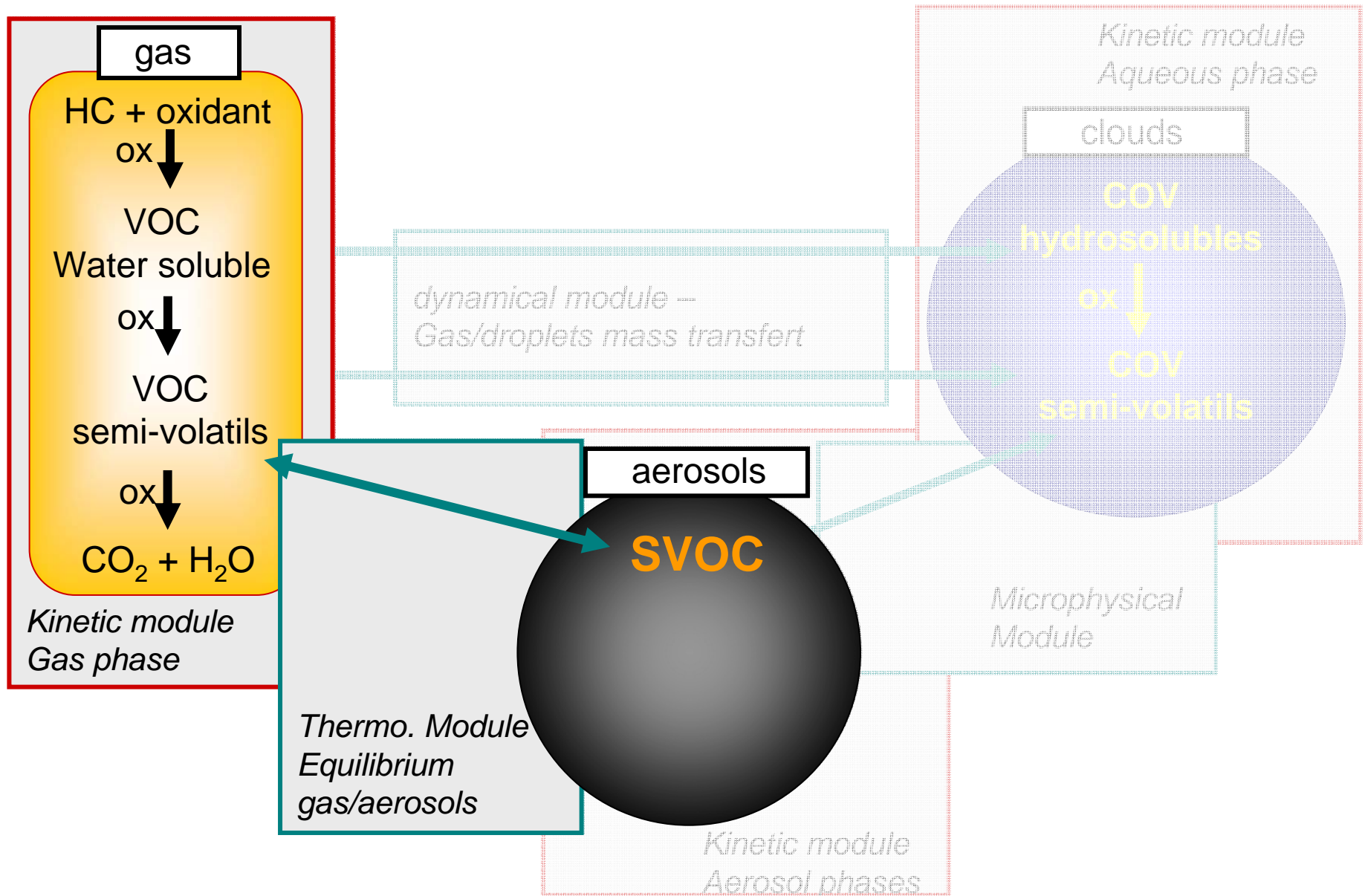
# Multiphase VOC oxidation : Development of a data processing tools to generate kinetic schemes and thermodynamic equilibrium (LISA/NCAR)



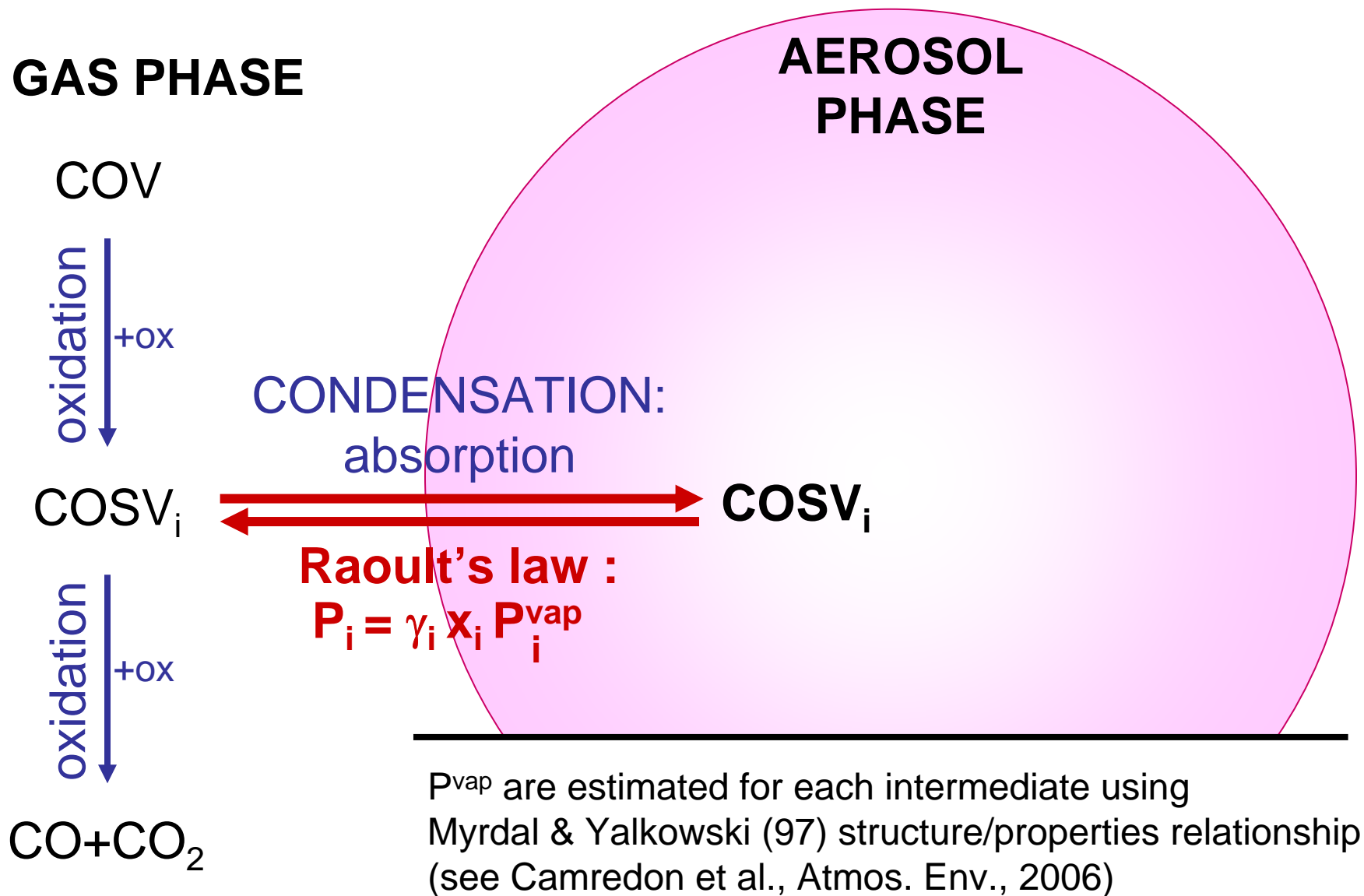
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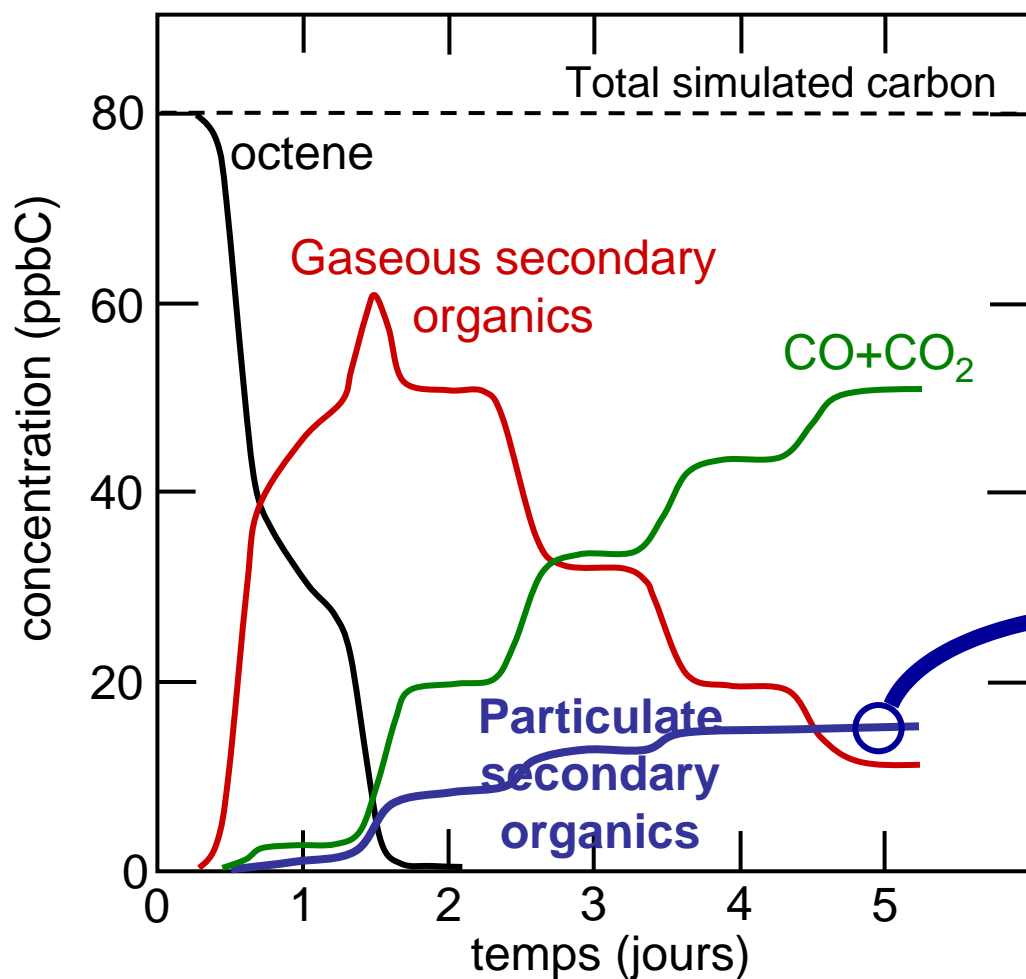
# Multiphase VOC oxidation : Development of a data processing tools to generate kinetic schemes and thermodynamic equilibrium (LISA/NCAR)



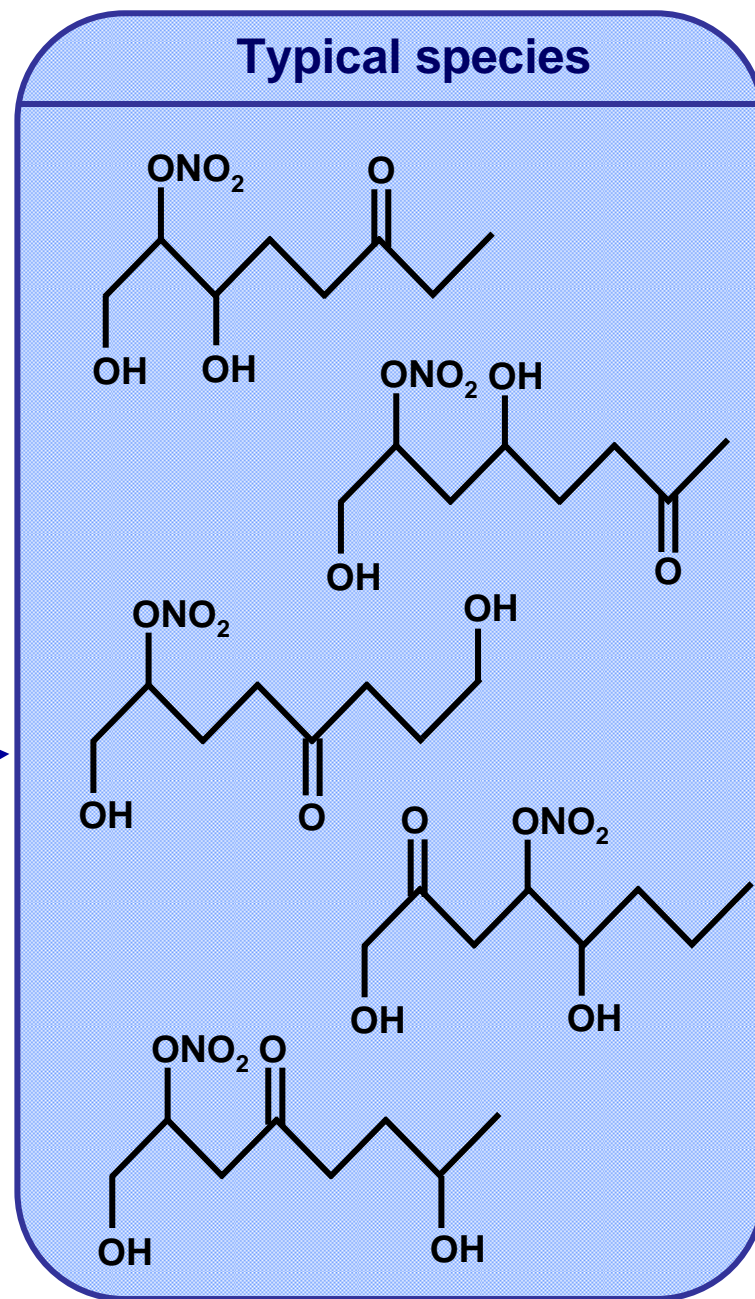
# Explicit modelling of the gas/particle partitioning



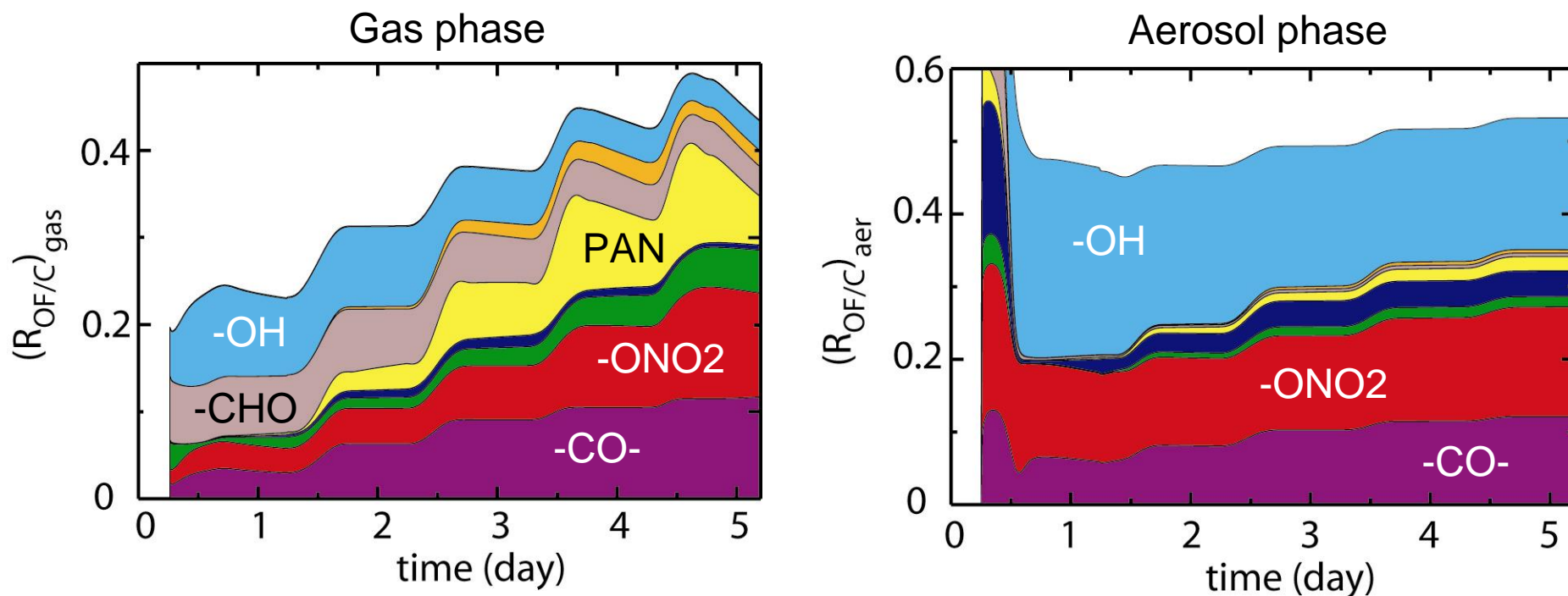
# Gradual change of organics during 1-octene oxidation



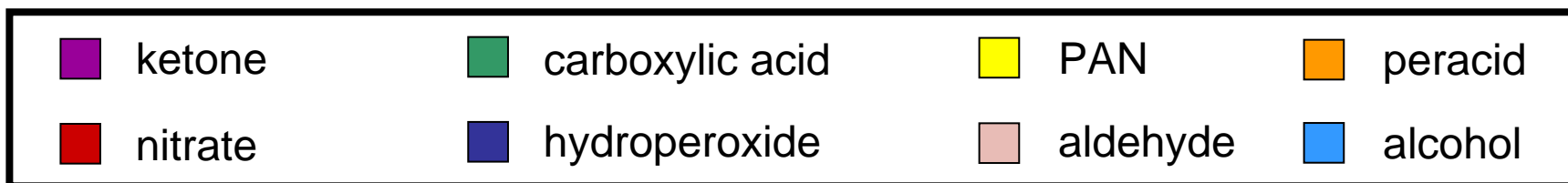
Simulation conditions :  
 T=298 K, [octene]<sub>0</sub> = 10 ppb,  
 [NO<sub>x</sub>]<sub>0</sub> = 1 ppb (constant)



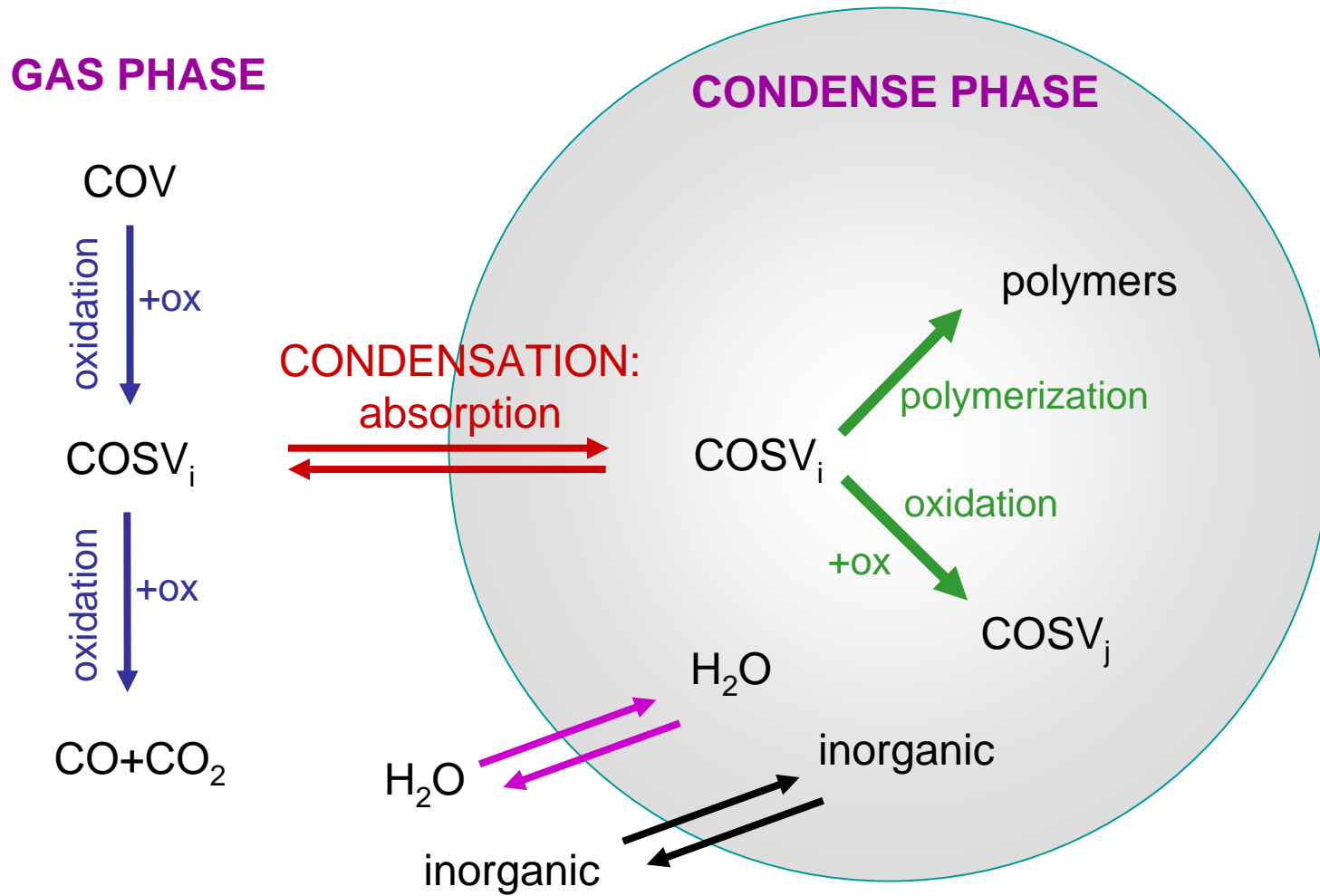
# Evolution of organic functionalities during octene oxidation



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



# Future developments ...



Advertisement :

**AGU fall meeting, Poster, Tuesday morning**

Explicit Modelling of SOA Precursors in Mexico City

J. Lee-Taylor, S. Madronich, G. Tyndall, B. Aumont, M. Camredon

