

# Chemical reactivity and aerosol forming potential of anthropic Volatile Organic Compounds

*from chemical structure to properties*

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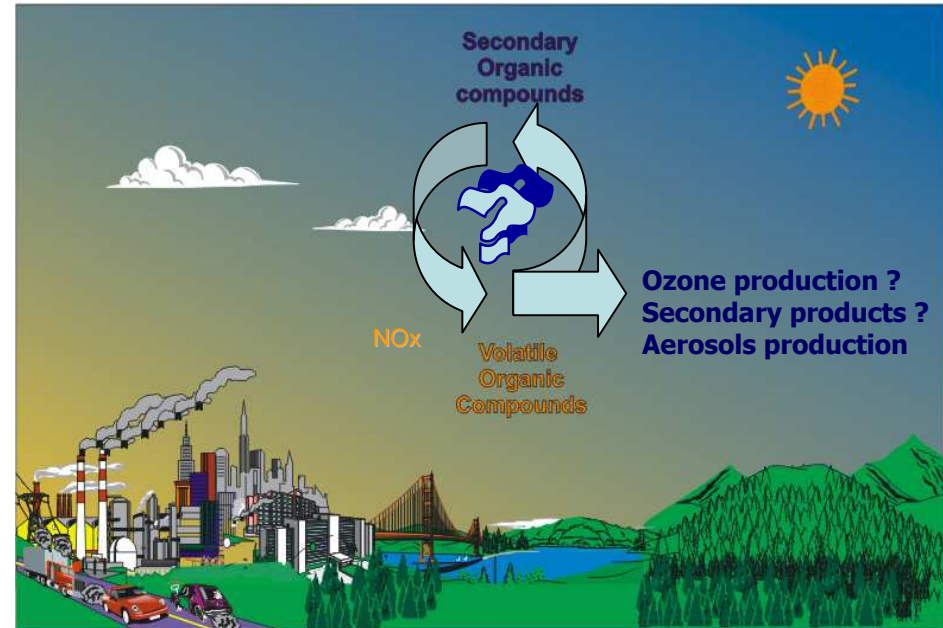
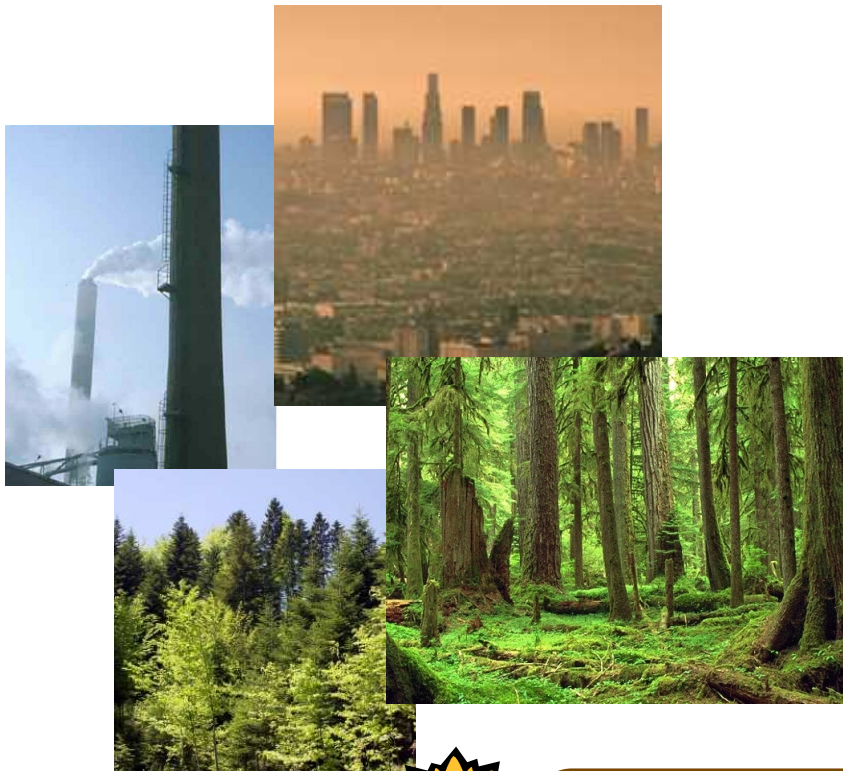
- **VOCs are a blend of hundreds of volatile organic compounds some of which are chemically reactive,**
- **VOCs are emitted from a variety of sources,**
  - motor vehicles,
  - chemical plants, refineries, other industries,
  - consumer and commercial products,
  - architectural coatings ...
- **Anthropic VOCs emission are changing with the increasing use of new products, alternatives fuels/solvents, new industrial processes...**

**Because of this diversity, it is necessary to be able to draw rules to link chemical structure and atmospheric effects**

# *Plan*

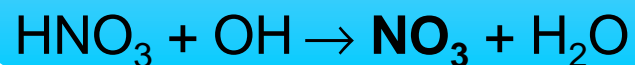
- Oxidizing capacity of the atmosphere
  - how fast they are removed ?
  - how many photo-oxidant are produced ?
- Secondary aerosol formation

# Atmospheric Oxidation of the VOCs

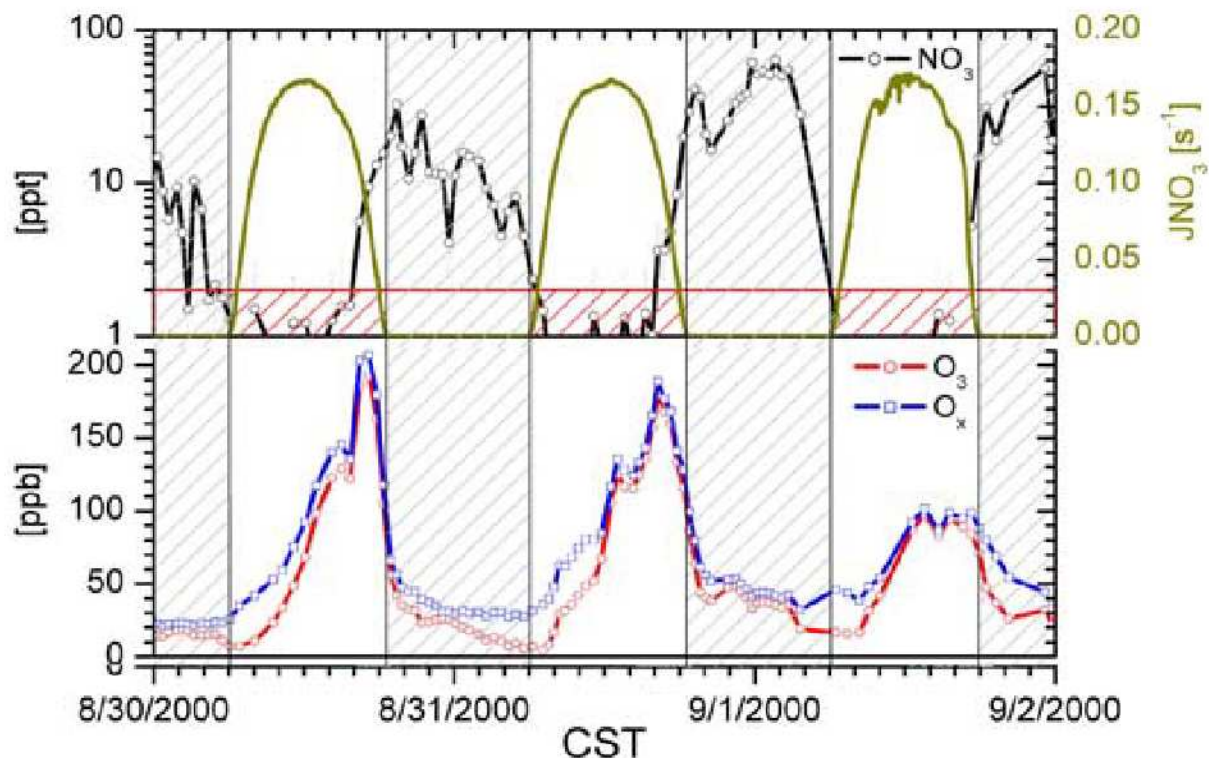
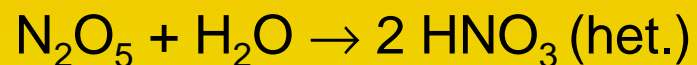
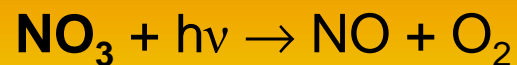


# Nitrate Radical ( $\text{NO}_3$ )

## $\text{NO}_3$ sources :





## Puits de $\text{NO}_3$ :





Geyer et al,  
JGR, 2003  
(Ground  
measurement,  
Houston, Texas)

# *NO<sub>3</sub> induce a night-time chemistry...*

composé	 $\tau_{\text{NO}_3}$ <b>at night</b> [NO <sub>3</sub> ]= 10 ppt	 $\tau_{\text{OH}}$ ([OH]= 2.10 <sup>6</sup> molécules.cm <sup>-3</sup> )	$\tau_{\text{O}_3}$ [O <sub>3</sub> ] = 30 ppb
	3-methylpentane	23 days	1 days
Acétaldéhyde	18 days	10 hours	755 years
2-methylbutanal	1,7 days	4 hours	-
Pentene	3 days	4,5 hours	1,7 days
Trans-2-butene	3 hours	14 min.	42 min.
6-methyl-5-hepten-2-one	<b>9 min.</b>	53 min.	1 hours
Acétate de cis-3-héxényl	<b>4,5 hours</b>	2 hours	7 hours
$\alpha$ -pinene	<b>11 min.</b>	3 hours	5 hours
$\beta$ -pinene	<b>27 min.</b>	2 hours	1,1 days
2-carene	<b>4 min.</b>	2 hours	2 hours

... but  $\text{NO}_3$  can also be a daytime oxidant

compounds	$\tau_{\text{NO}_3}$ <b>daytime</b> [NO <sub>3</sub> ]= 0,2 ppt	$\tau_{\text{OH}}$ [OH]= 0.1ppt	$\tau_{\text{O}_3}$ [O <sub>3</sub> ] = 30 ppb
3-methylpentane	3,2 years	1 day	-
Acétaldehyde	2,5 years	10 hours	755 years
2-methylbutanal	0.25 years	4 hours	-
Pentene	152 days	4,5 hours	1,7 days
Trans-2-butene	6,3 days	14 min	42 min
6-methyl-5-hepten-2-one	8 hours	53 min	1 hours
Acétate de cis-3-héxényl	10 days	2 hours	7 hours
$\alpha$ -pinene	<b>9 hours</b>	3 hours	5 hours
$\beta$ -pinene	23 hours	2 hours	1,1 days
2-carene	<b>3 hours</b>	2 hours	2 hours

## *What about new compounds ?*

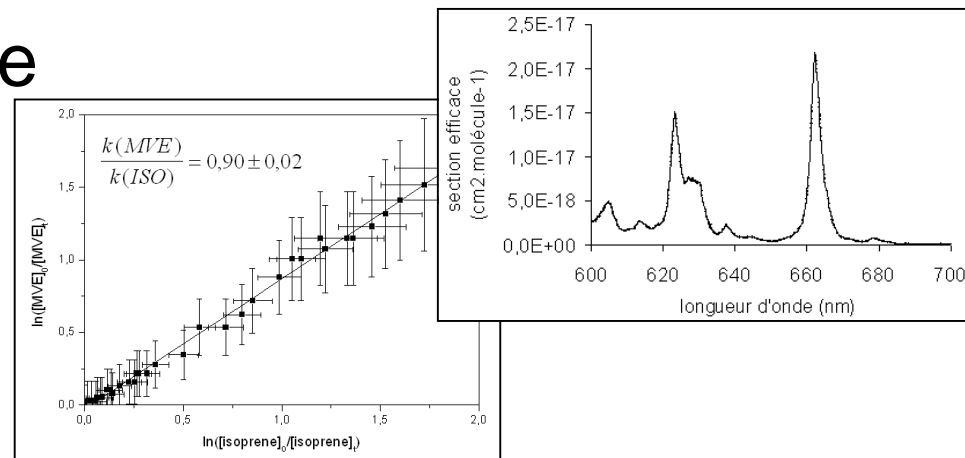
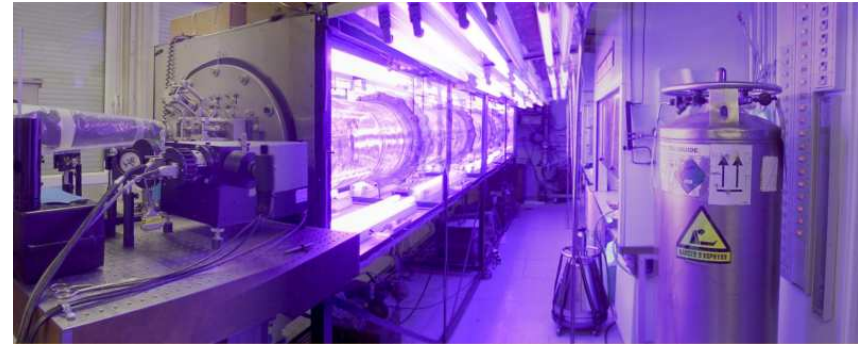
- **Vinyl ethers** (new solvents, motor oil additives, manufacturing of coatings, synthesis intermediates...)
- **Unsaturated acetates** (new fumigants, synthesis intermediates, monomer for polymer production, emission from new fuel use...)

Only few kinetics and mechanistic studies

***Need for data to rationalize our understanding of the gas phase chemistry of new oxygenated compounds***

# Kinetic and mechanistic studies of the $\text{NO}_3$ induced oxidation scheme

- Use of simulation chambers
- Relative and absolute studies
- Products and pathways identification



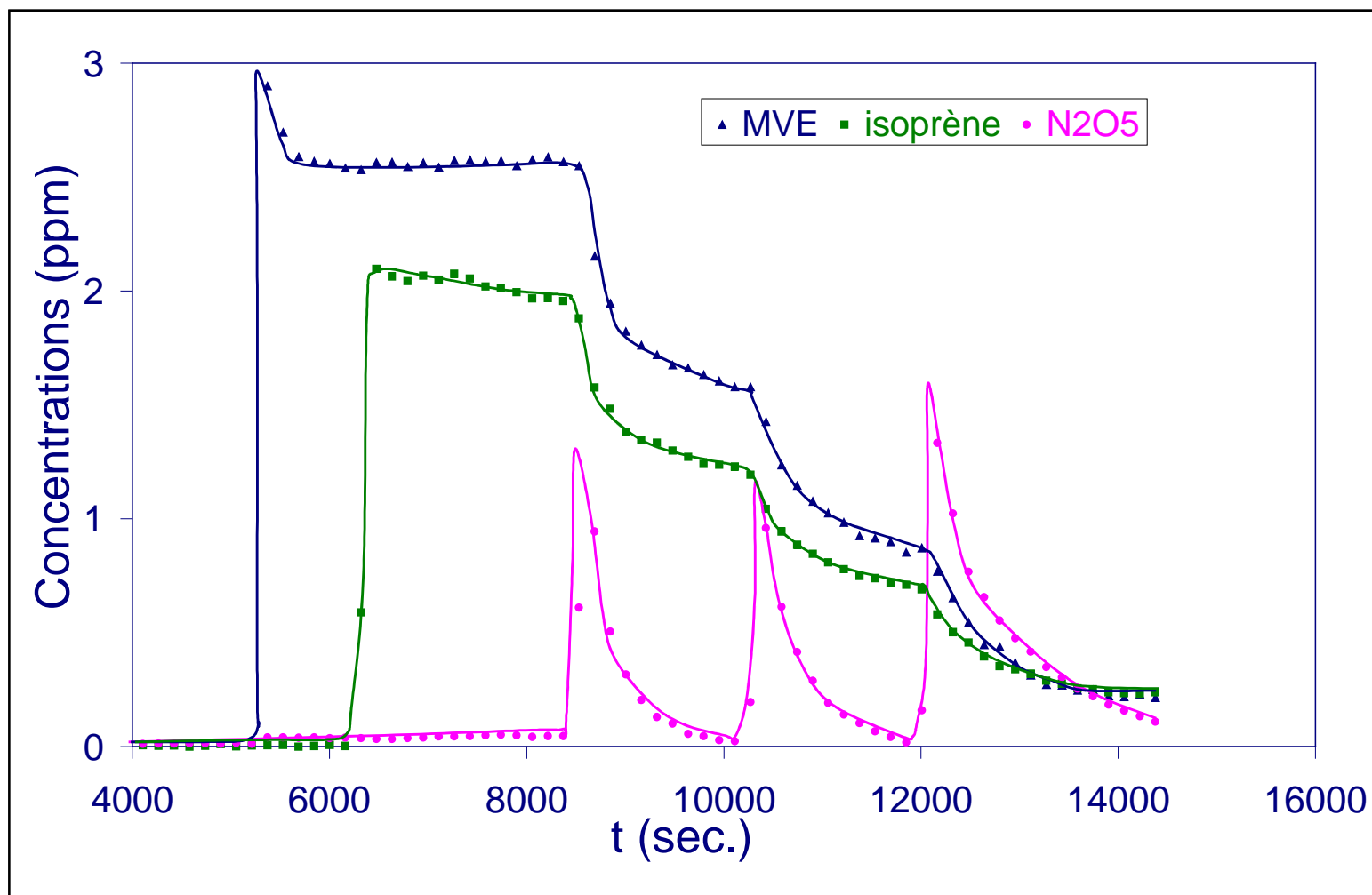
## *A serie of vinyl ether ...*

- A homogeneous serie of vinyl ether

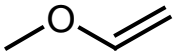
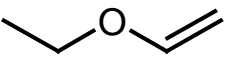
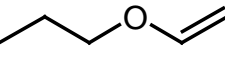
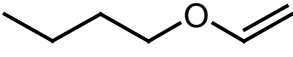


- Some studies (*Thiault 2002, Klotz et al. 2004, Zhou, 2006*)

# Vinyl ether experiment



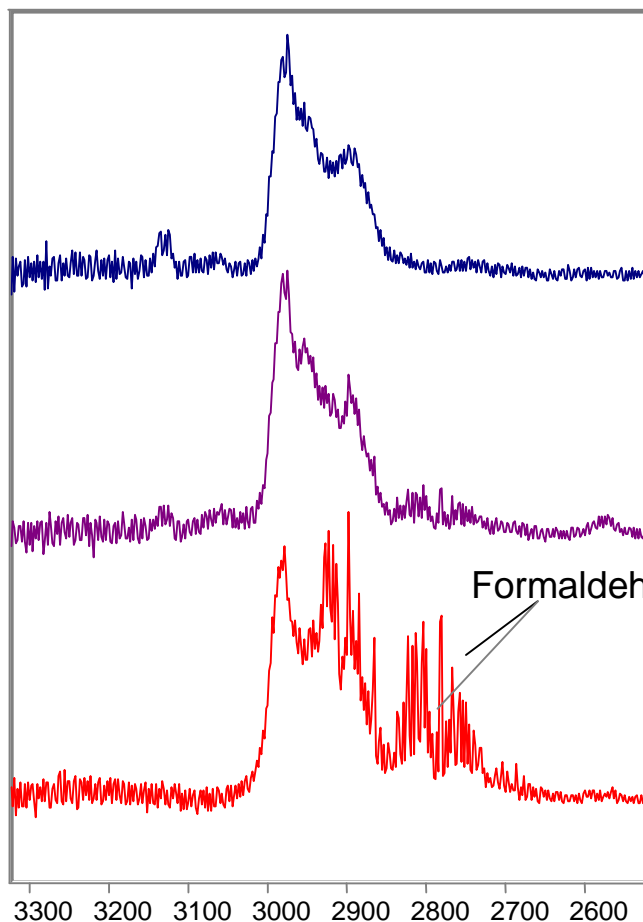
# Kinetics

Composé	k (*)	k <sub>moyen</sub> (*)	Autres travaux (*)
MVE 	7,6 ± 0,4 6,1 ± 1,1 6,3 ± 0,5	<b>7,2 ± 2,9</b>	4,68 (Grosjean et al., 1992) (Estimation)
EVE 	15,1 ± 3,3 13,8 ± 1,5 14,5 ± 2,5	<b>13,1 ± 5,3</b>	17 ± 13 (Pfrang et al., 2006) 14.0 ± 3.5 (Zhou et al., 2006)
PVE 	13,3 ± 1,8 12,8 ± 1,6 12,4 ± 2,0 15,1 ± 1,7	<b>13,3 ± 5,9</b>	18.5 ± 5.3 (Zhou et al., 2006)
BVE 	15,8 ± 1,8 18,9 ± 1,6 16,5 ± 1,4	<b>17,0 ± 7,3</b>	21.0 ± 5.4 (Zhou et al. 2006)

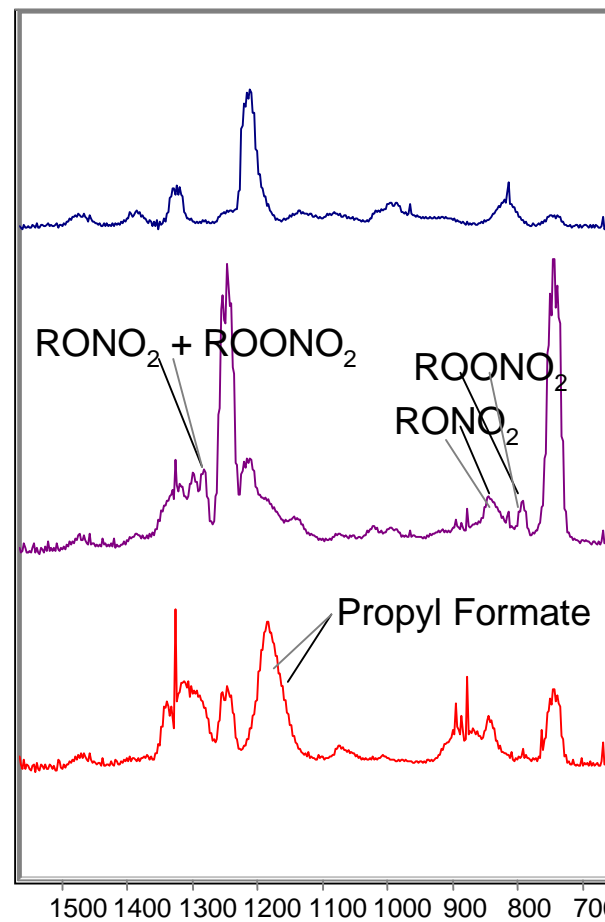
(\*) :  $10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$

Scarfogliero et al, 2006  
Journal of Physical Chemistry A

# Products Identification from FTIR monitoring

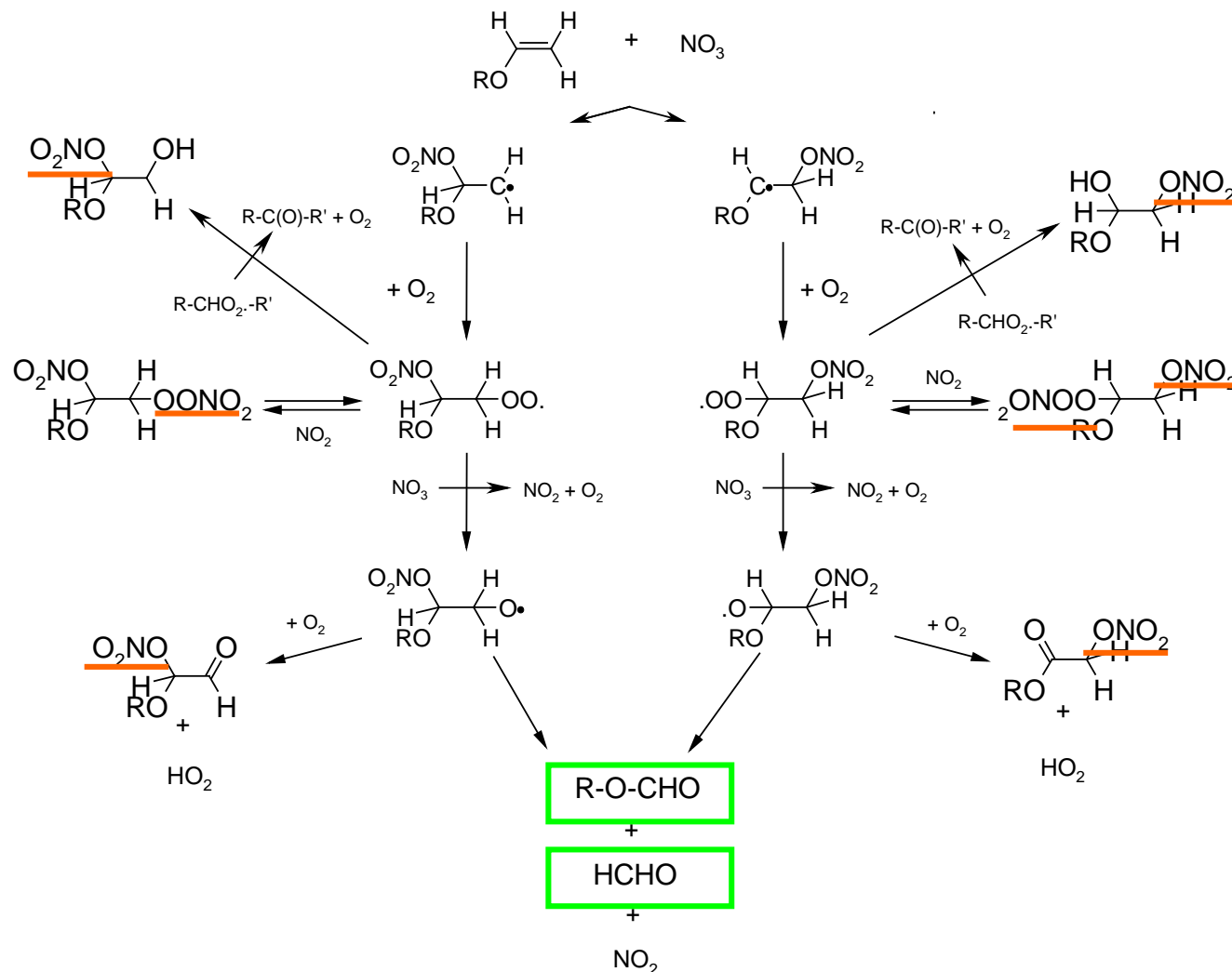


$\sigma$  (cm<sup>-1</sup>)

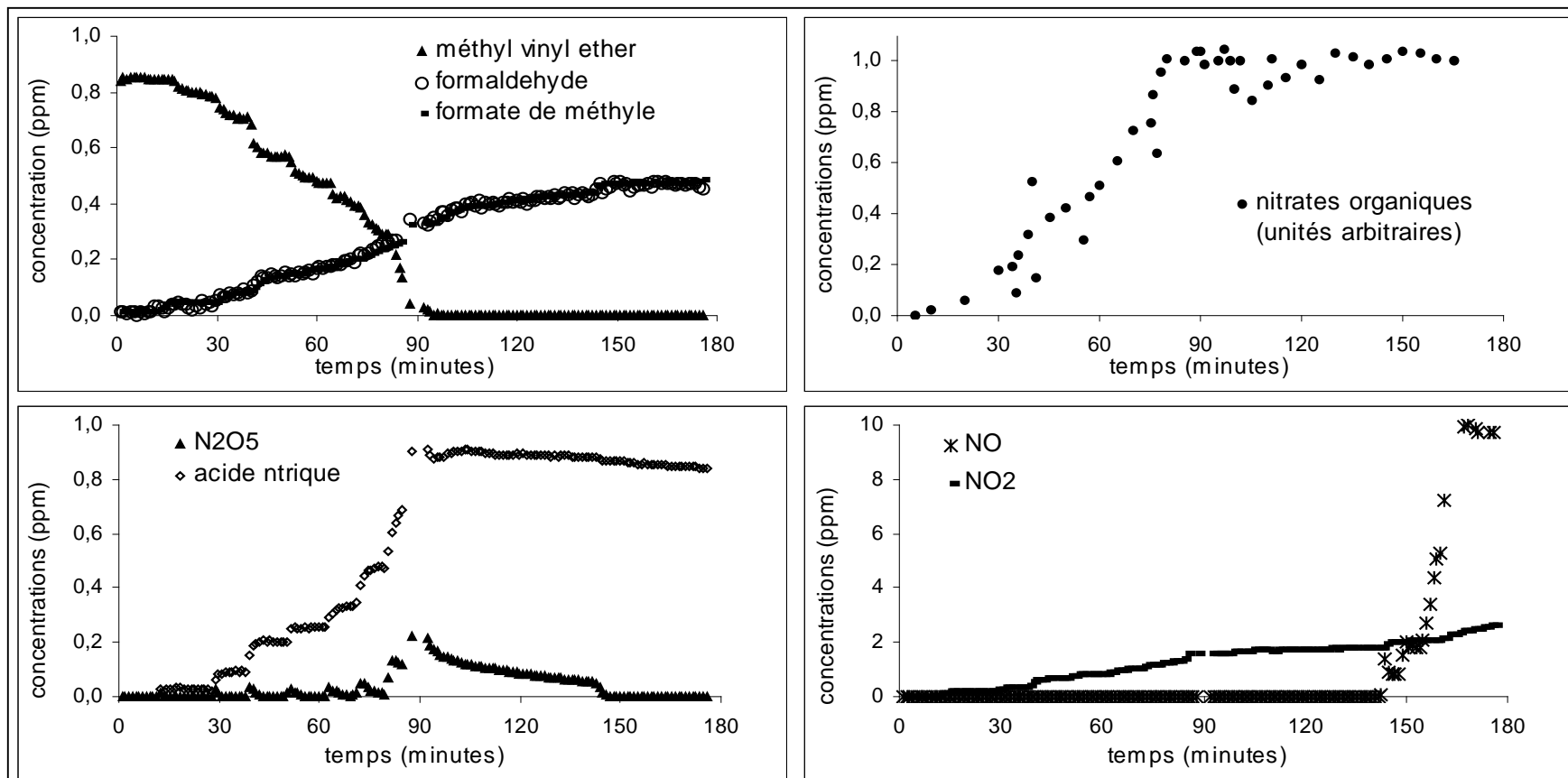


$\sigma$  (cm<sup>-1</sup>)

# Chemical Scheme

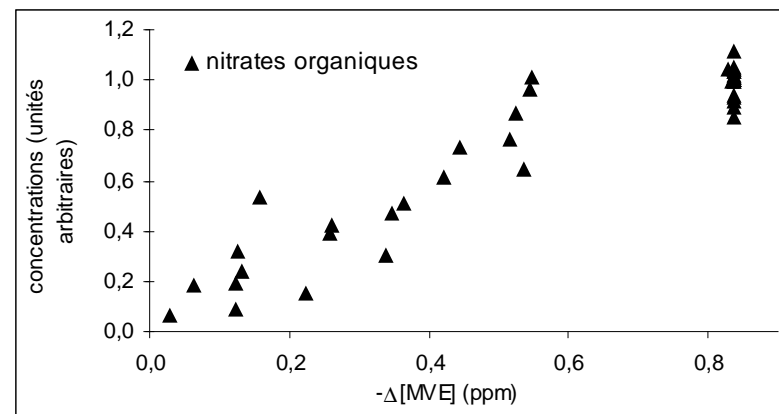
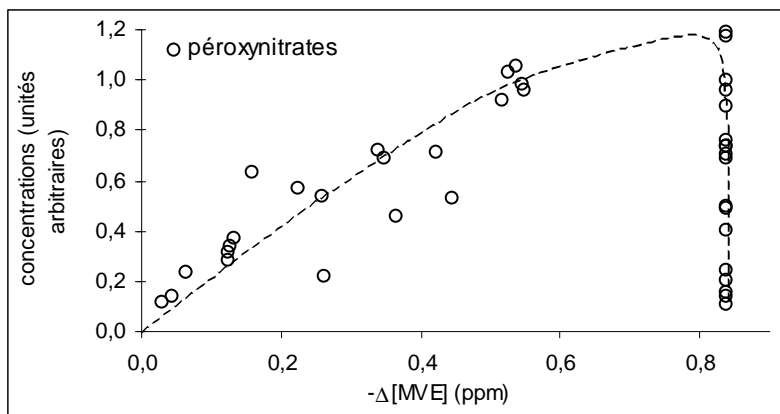
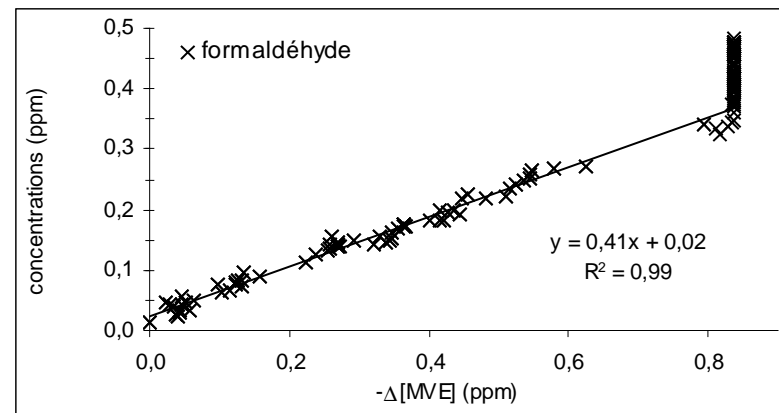
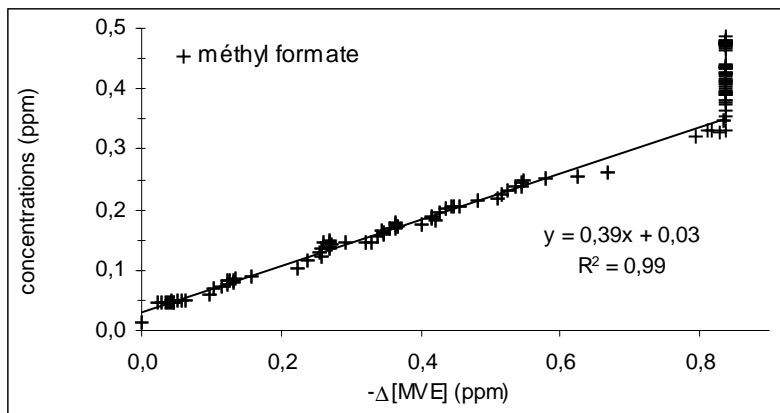


# Products study experiments



NO injection at the end to destroy peroxy nitrates

# Products study experiments : Yield



## Products Yields

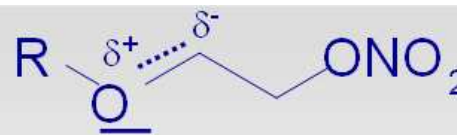
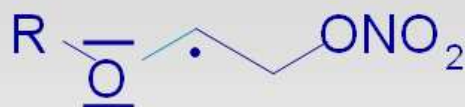
vinyl ether	Primary yield (%)		final yield (%)	
	HCHO	alkyl formate	HCHO	alkyl formate
methyl	46 ± 9	45 ± 9	52 ± 14	53 ± 9
ethyl	54 ± 14	46 ± 8	68 ± 13	60 ± 7
propyl	51 ± 16	45 ± 15	50 ± 16	48 ± 6
butyl	44 ± 8	44 ± 7	47 ± 8	50 ± 4

# Kinetics

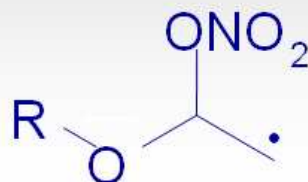
X 100

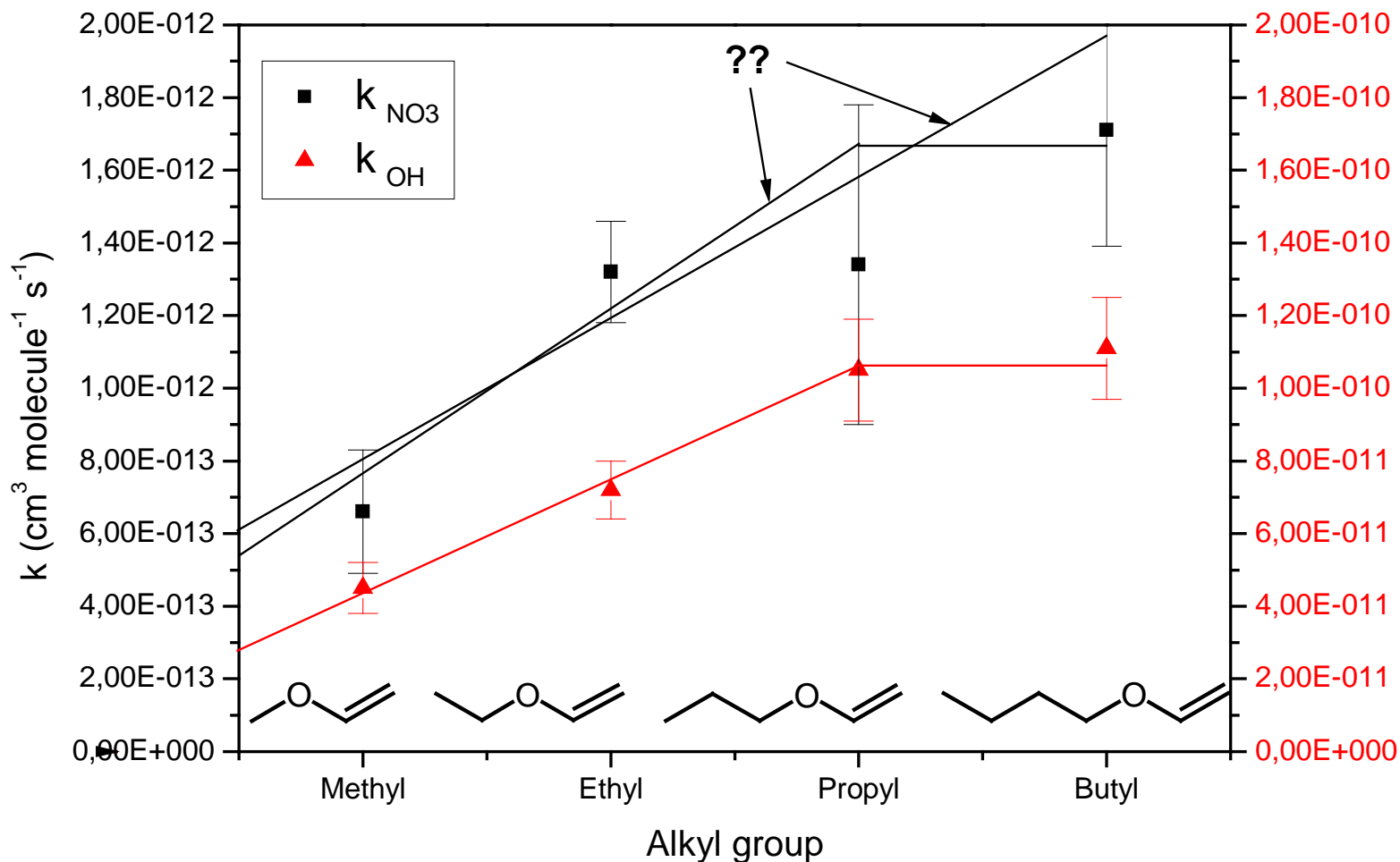
Alkyle group	Alkenes <sup>(a)</sup> (R-CH=CH <sub>2</sub> )	Vinyl ethers <sup>(a)</sup> (R-O-CH=CH <sub>2</sub> )
CH <sub>3</sub>	(9,5 ± 0,8).10 <sup>-15</sup> (b)	(7,2 ± 1,5).10 <sup>-13</sup>
C <sub>2</sub> H <sub>5</sub>	(13,5 ± 4,1).10 <sup>-15</sup> (c)	(13,1 ± 2,7).10 <sup>-13</sup>
C <sub>3</sub> H <sub>7</sub>	(15 ± 5).10 <sup>-15</sup> (d)	(13,3 ± 3,0).10 <sup>-13</sup>
C <sub>4</sub> H <sub>9</sub>	(18 ± 7).10 <sup>-15</sup> (d)	(17,0 ± 3,7).10 <sup>-13</sup>

External Addition



Internal Addition

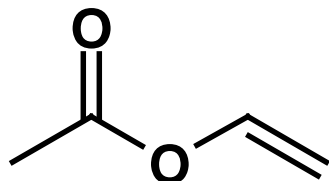




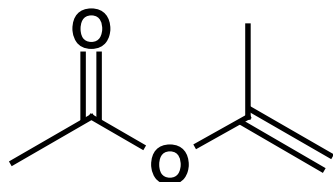
Electron donor (mesomeric and inductive) effects increase the reactivity of the double bond

## *A serie of unsaturated acetates ...*

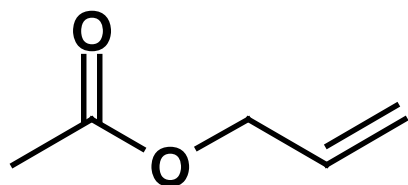
- A homogeneous serie



**Vinyl acetate**



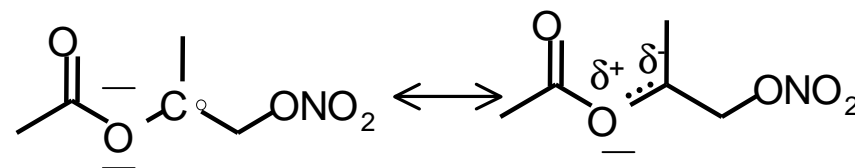
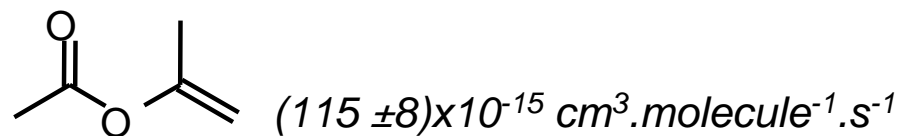
**Isopropenyl acetate**




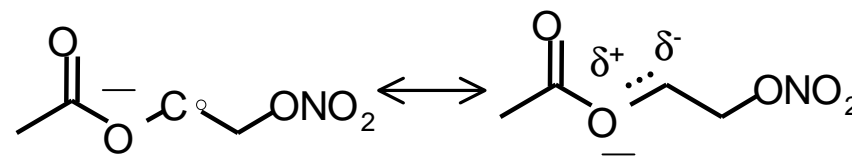
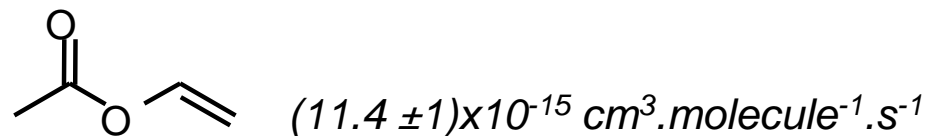
**Allyl acetate**


- Very few studies (*Grosjean et al. 1992 (SAR)*)

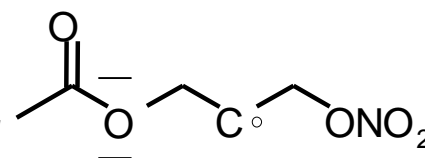
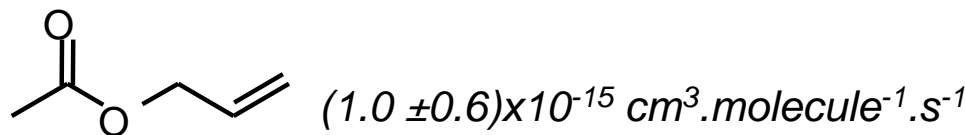
# $k_{\text{acetate} + \text{NO}_3}$




  
 $\times 10$




  
 $\div 10$



# Atmospheric Lifetimes

	$\tau_{\text{NO}_3}$ [NO <sub>3</sub> ] = 50 ppt (polluted)	$\tau_{\text{NO}_3}$ [NO <sub>3</sub> ] = 2 ppt (rural)	$\tau_{\text{OH}}$ [OH] = 2×10 <sup>6</sup> moléc.cm <sup>-3</sup>	$\tau_{\text{O}_3}$ [O <sub>3</sub> ] = 50 ppb
<b>Methyl vinyl ether</b>	<b>20 min</b>	<b>8 hours</b>	3 hours (a)	1 hours (a)
<b>Ethyl vinyl ether</b>	<b>9 min</b>	<b>4 hours</b>	2 hours (a)	
<b>Propyl vinyl ether</b>	<b>10 min</b>	<b>4 hours</b>	1.5 hours (a)	
<b>Butyl vinyl ether</b>	<b>8 min</b>	<b>3 hours</b>	1.5 hours (a)	
<b>Vinyl Acetate</b>	20 hours	21 days	3 hours (b)	70 hours (c)
<b>Isopropényle Acetate</b>	<b>2 hours</b>	<b>2 days</b>	2 hours (e)	-
<b>Allyl Acétate</b>	7 days	160 days	5 hours (f)	-

a : Thiault et al., 2002, b: Grosjean et al., 1992, c: Grosjean et al., 1998, d: Fantechi et al., 1998, e: Ferrari 1995, f: Picquet 2000

- Vinyl Ethers very reactive with NO<sub>3</sub>
- Acetate lifetime can vary over a wide range with NO<sub>3</sub> but not really with OH

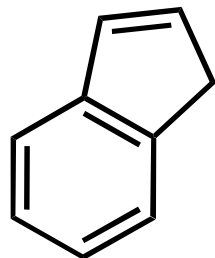
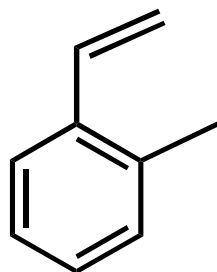
# Secondary aerosol formation

- Organic material contributes from 10 to 90% to total fine aerosol mass
- SOA formed by gas-to-particle conversion of oxidation products of VOC.
- Complexe mixtures (dicarboxylic acids, ketoacids, polyols ...)
- Environmental effects :
  - direct and indirect radiative forcing
  - visibility reducing
  - toxicity

***Good knowledge of their formation processes  
and chemical composition is needed !***

## *SOA from Aromatic compounds*

- Intensively emitted by anthropogenic sources
- Known to be precursors of SOA (Odum et al., 1997, Forstner et al. 1997)
- Two target compounds : *2-methyl Styrene* and *Indene*



polymer combustion,  
biomass burning, cigarette  
smoke

- Strong similarities in chemical structures
- Only one kinetic study (Kwok et al., 1996) – no mechanistic study

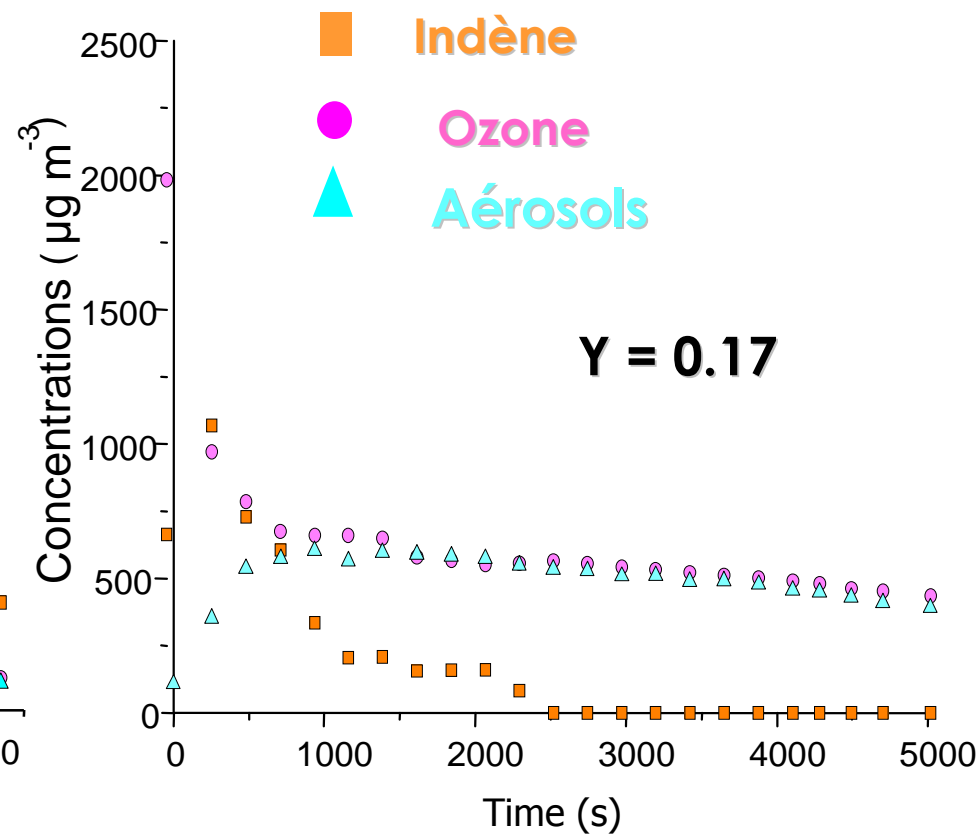
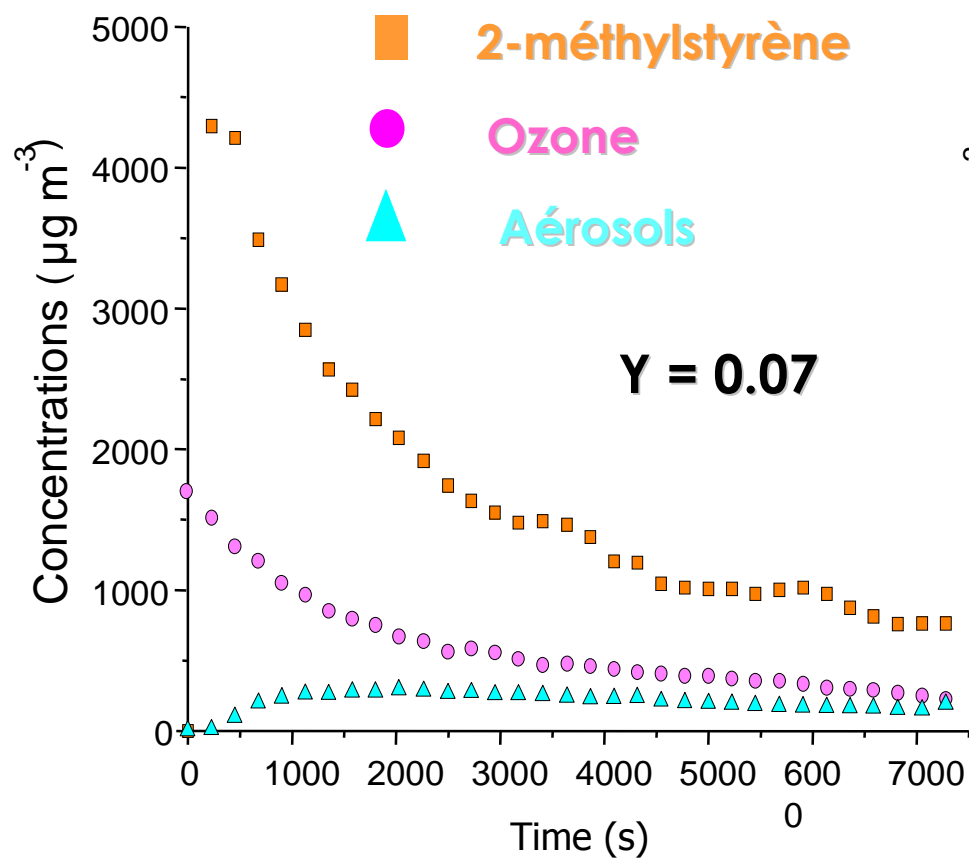
# *SOA production from indene and Me-Styrene : comparative study*

- Production of SOA in simulation chamber...
- ... from ozonolysis reaction ...
- ... under dry conditions.

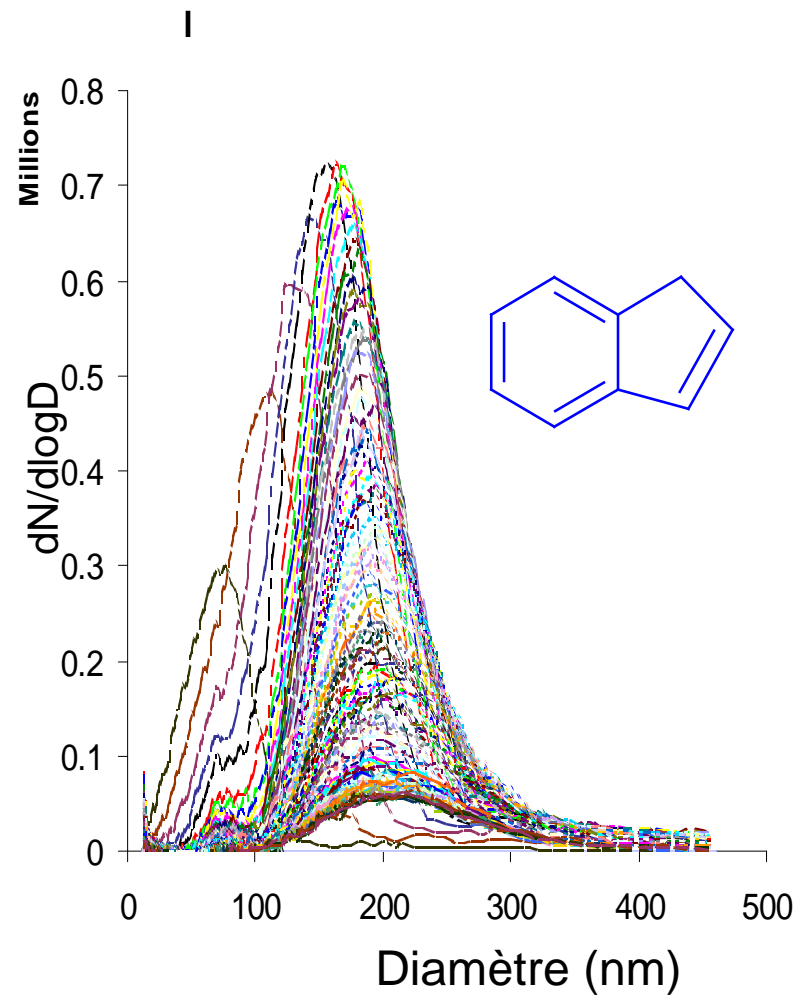
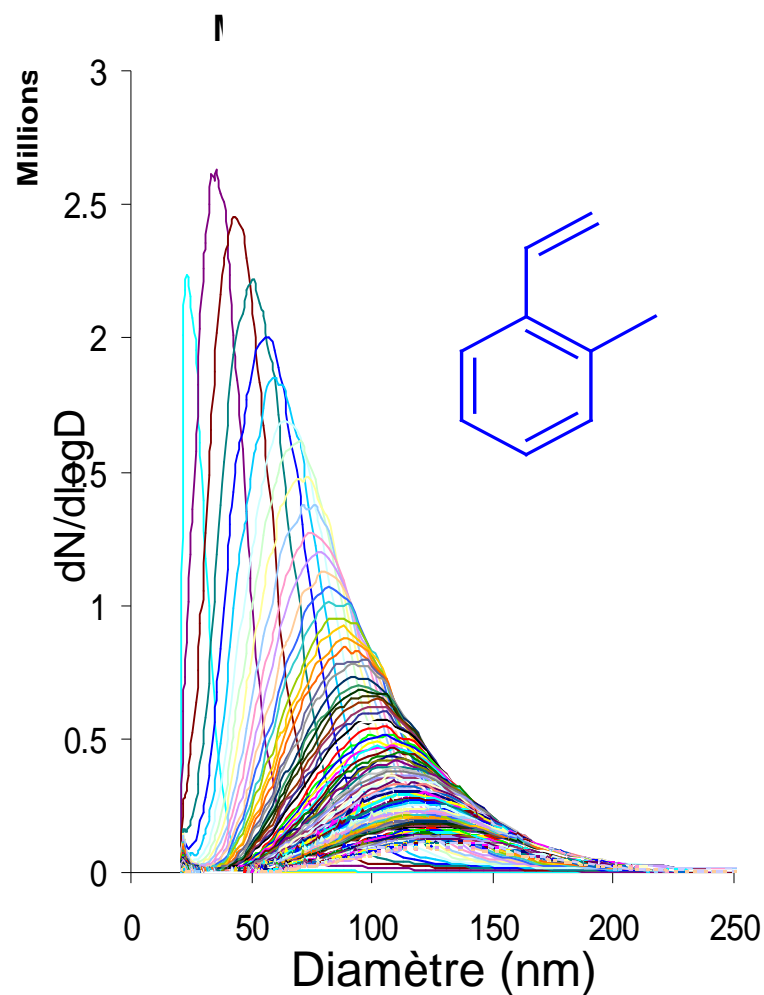
## Chemical/Physical analysis ...

- Particles number and size monitored by SMPS (TSI 3022A/3081)
- ... in gas phase : long-path FTIR
- ... in particulate phase : sampling on glass-fiber filters + Supercritical Fluid extraction with BSTFA + direct coupling with GC/MS (SFE-GC-MS)

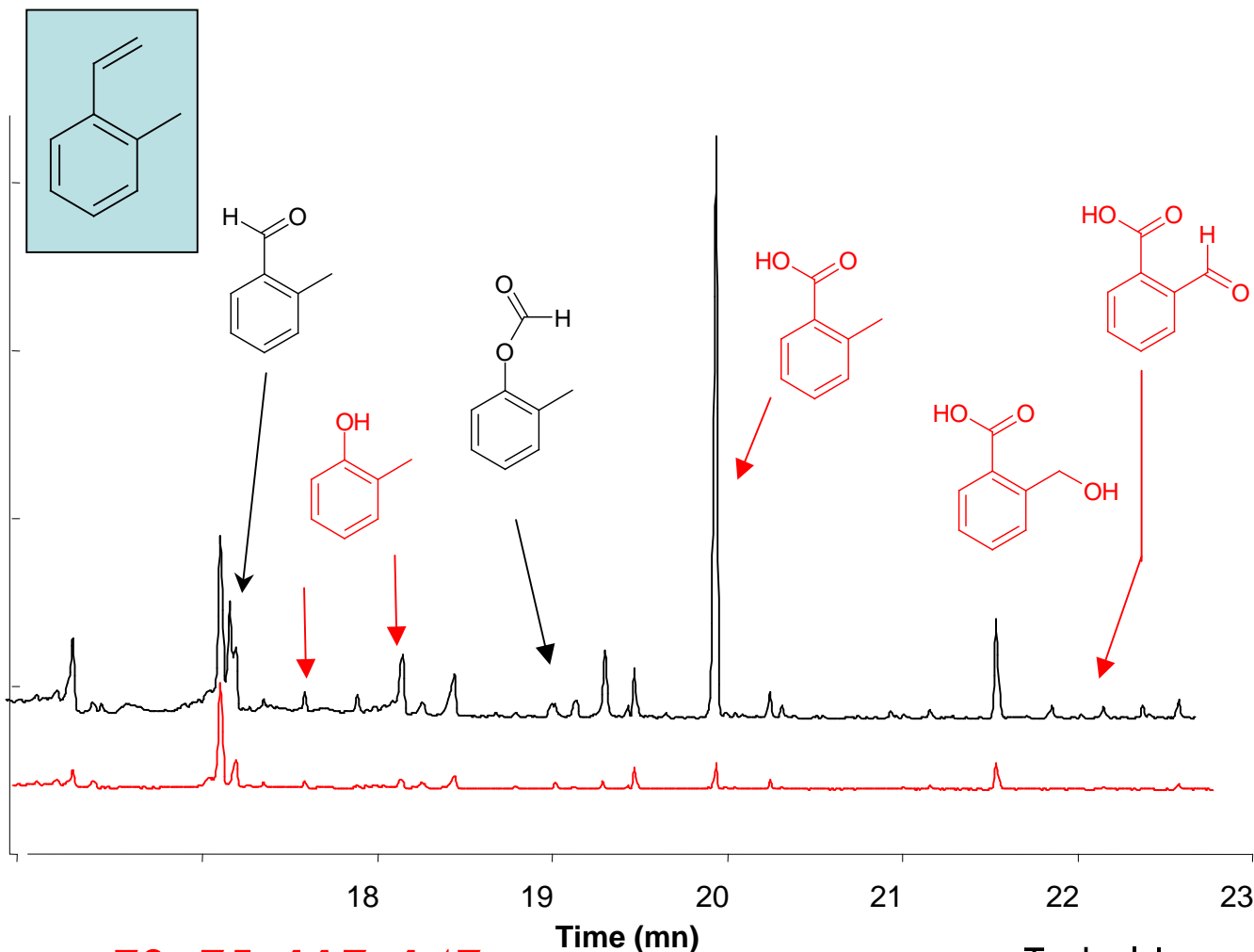
# SOA production from indene and Me-Styrene : comparative study



# SOA production from indene and Me-Styrene : comparative study



# Composition of SOA produced from Me-Styrene ozonolysis



Laboratoire Inter-universitaire  
des Systèmes Atmosphériques

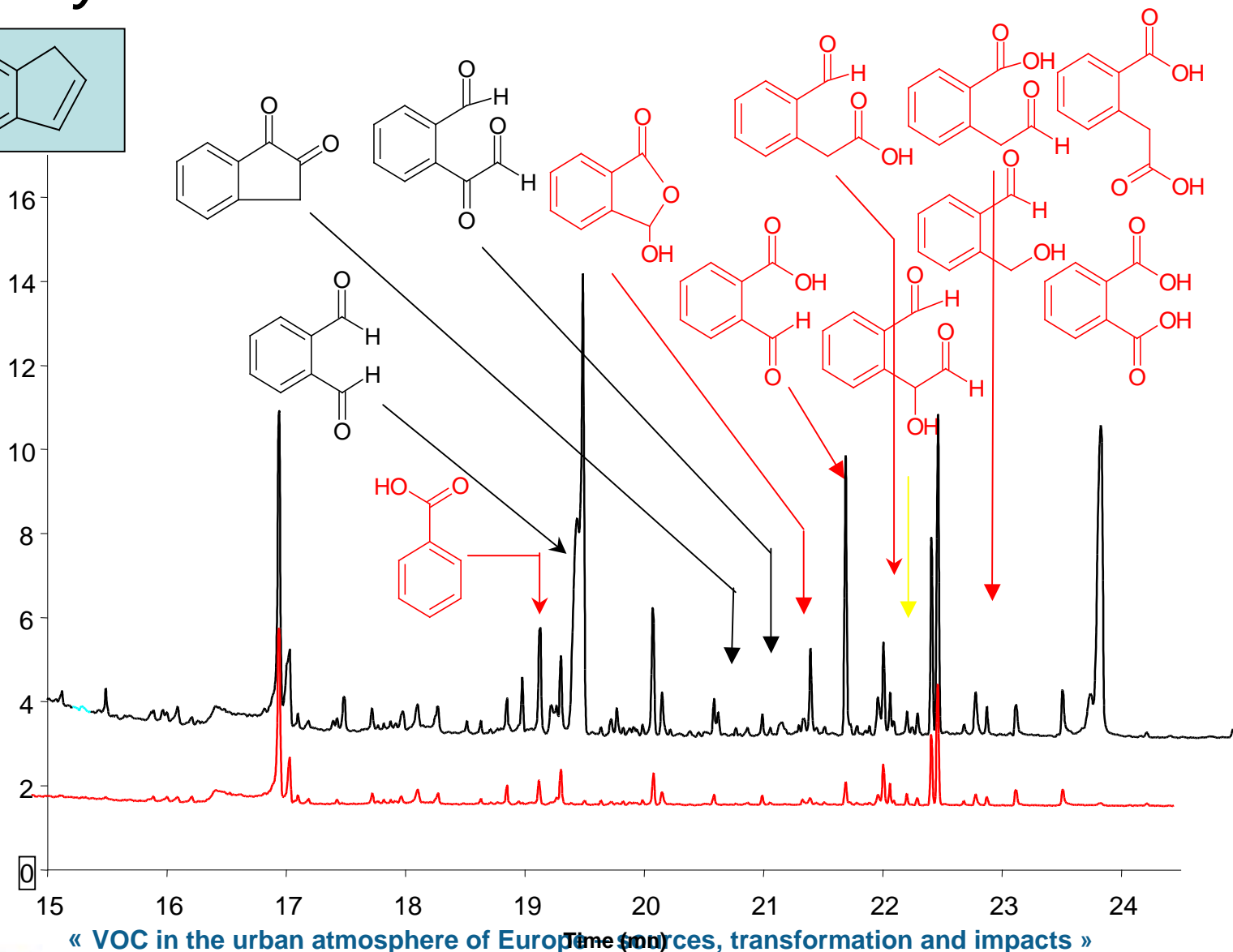
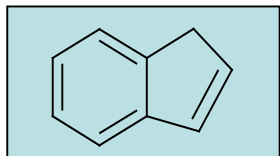
Ions: 73+75+117+147

Total Ions

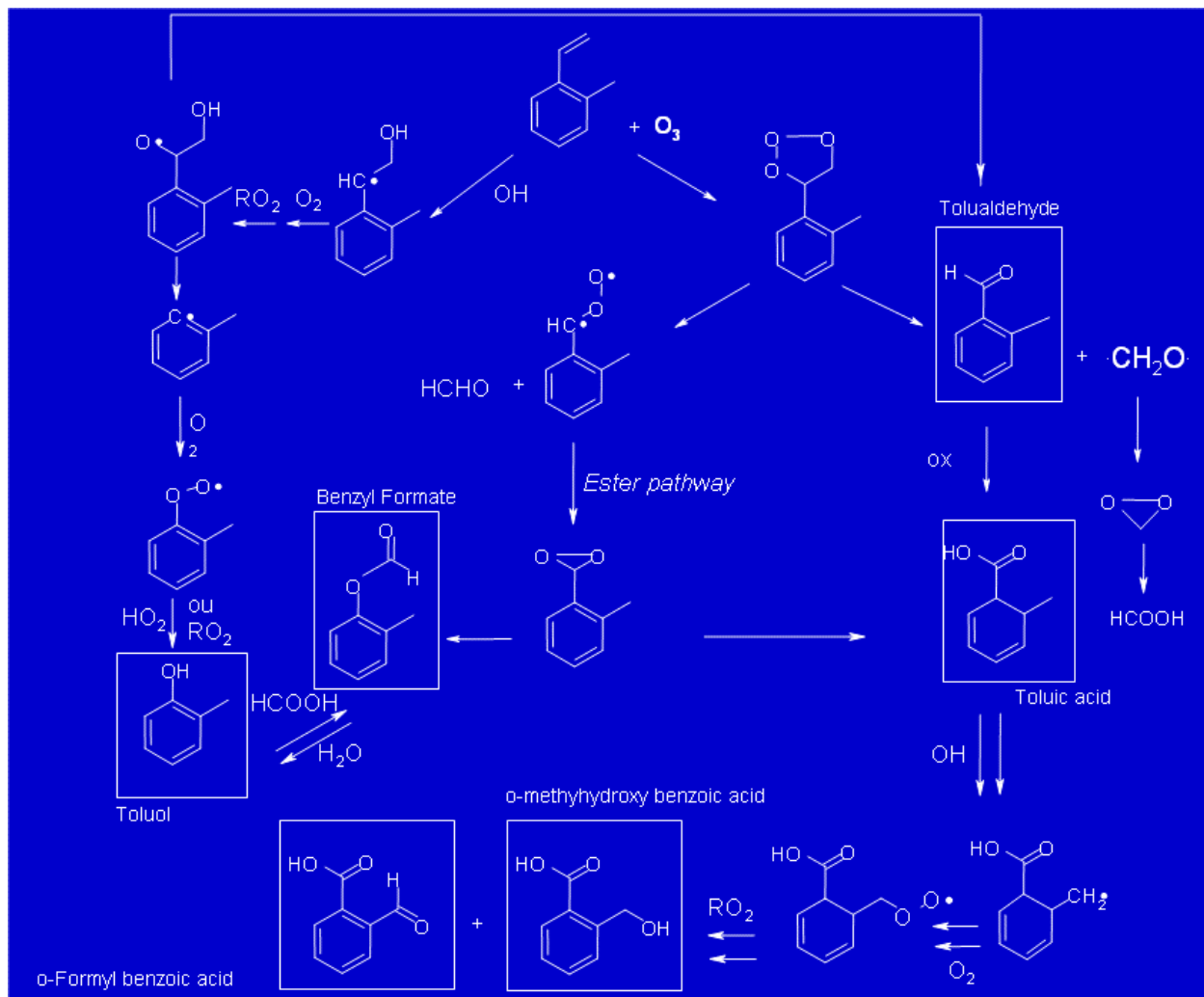
« VOC in the urban atmosphere of Europe – sources, transformation and impacts »

Wroclaw, Poland, 25-26 Sept. 2007 - JF Doussin

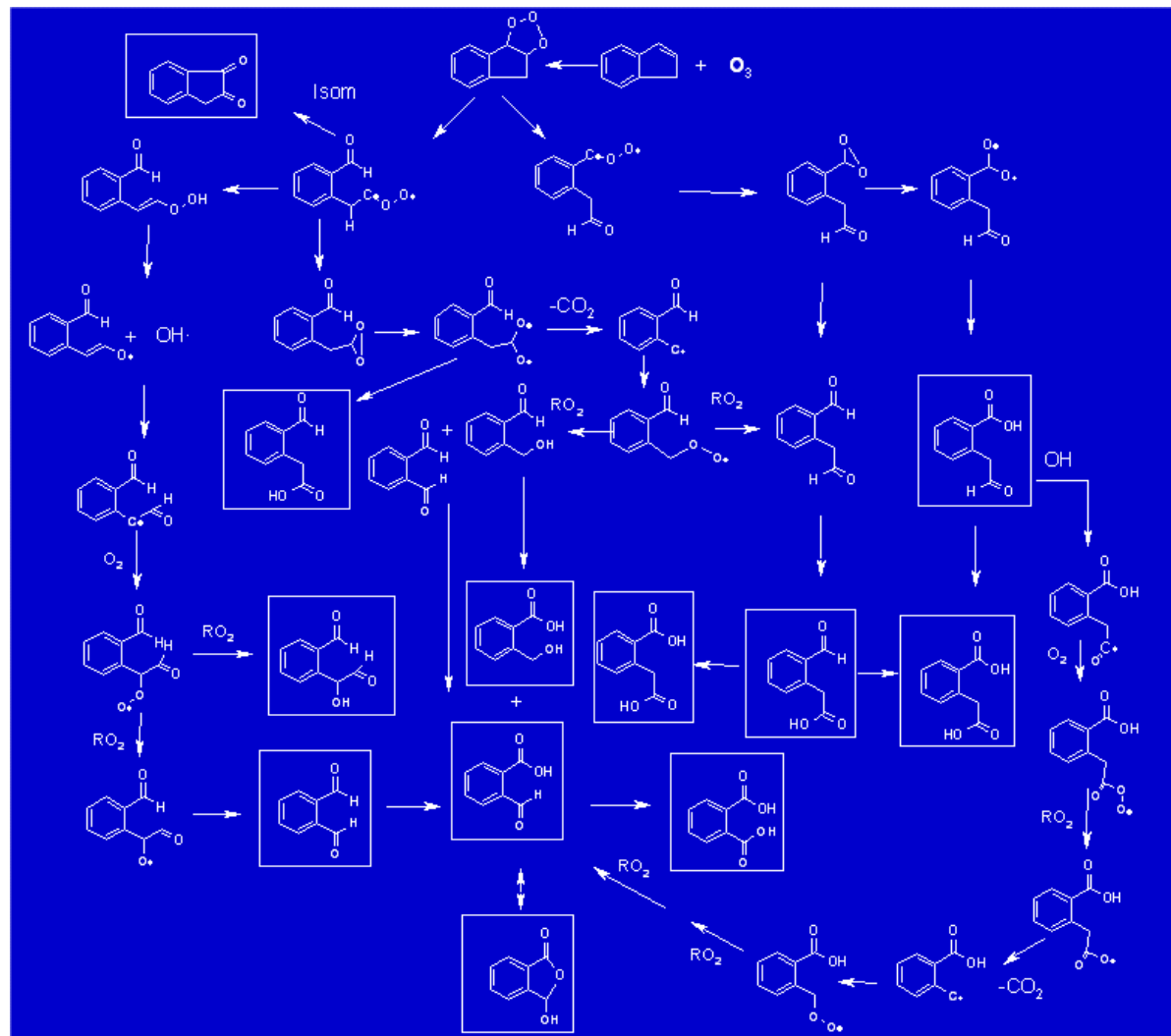
# Composition of SOA produced from Indene ozonolysis



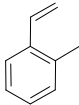
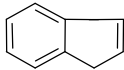
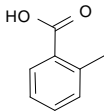
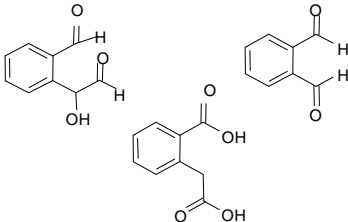
# Composition of SOA produced from Me-Styrene ozonolysis



# Composition of SOA produced from Indene ozonolysis



# SOA production from indene and Me-Styrene : comparative results

	Me-Styrene	Indene
<b>Structure</b>		
<b>Rate Constant with O<sub>3</sub> (molec<sup>-1</sup>.cm<sup>3</sup>.s<sup>-1</sup>)</b>	(1.5±0.3)×10 <sup>-17</sup>	(14±2)×10 <sup>-17</sup>
<b>Mass yield (%)</b>	7 %	17 %
<b>Aerosol Mass (mg.m<sup>-3</sup>)</b>	310	850
<b>Max size (nm)</b>	100	250
<b>Analyzed SOA (%)</b>	54 ±17 %	36 ±7 %
<b>Typical identified species</b>	Mono-fonctionnal 	Poly-fonctionnal 



## *Conclusion*

- Small change in the structure may induce large effects on the impacts of the considered VOC
- Simple structure analysis rules can be used to roughly forecast the reactivity/impact of new VOCs : ex use of allyl acetate may be an alternative to vinyl acetate at local scale
- These rules may be useful for the building of Structure-Activity Relationship

# Acknowledgment



Introp

## MOST

«**Multiphase Chemistry of Oxygenated Species in the Troposphere** »

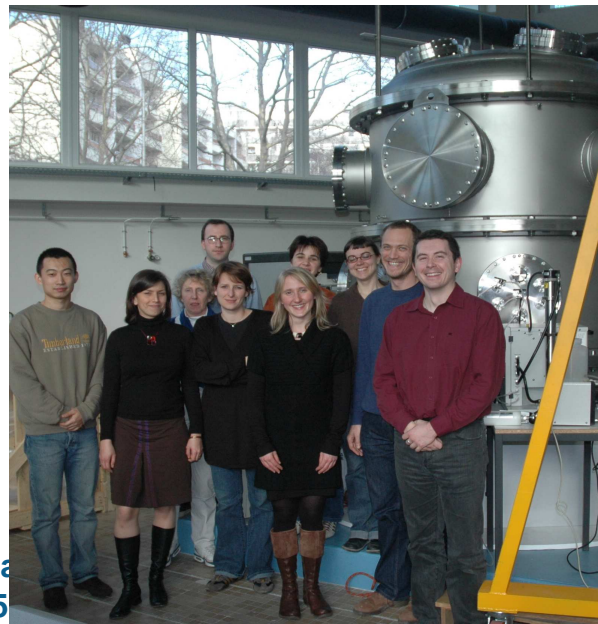
EVK2-. 2001-00114



*Liberté . Egalité . Fraternité*

RÉPUBLIQUE FRANÇAISE

French Ministry of Environment



« VOC in the urban a  
Wroclaw, Poland, 25

formation and impacts »