In-cloud chemistry of organic species

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Laboratoire CHIMIE Provence

Tropospheric Clouds

- ☞ **Surface cover : about 60% of the Earth's surface**
- ☞ **Lower troposphere : first 4-6 km altitude**
- ☞ **A small fraction (about 10%) of clouds precipitate (rain)**
- ☞ **Significantly influenced by surface emissions**

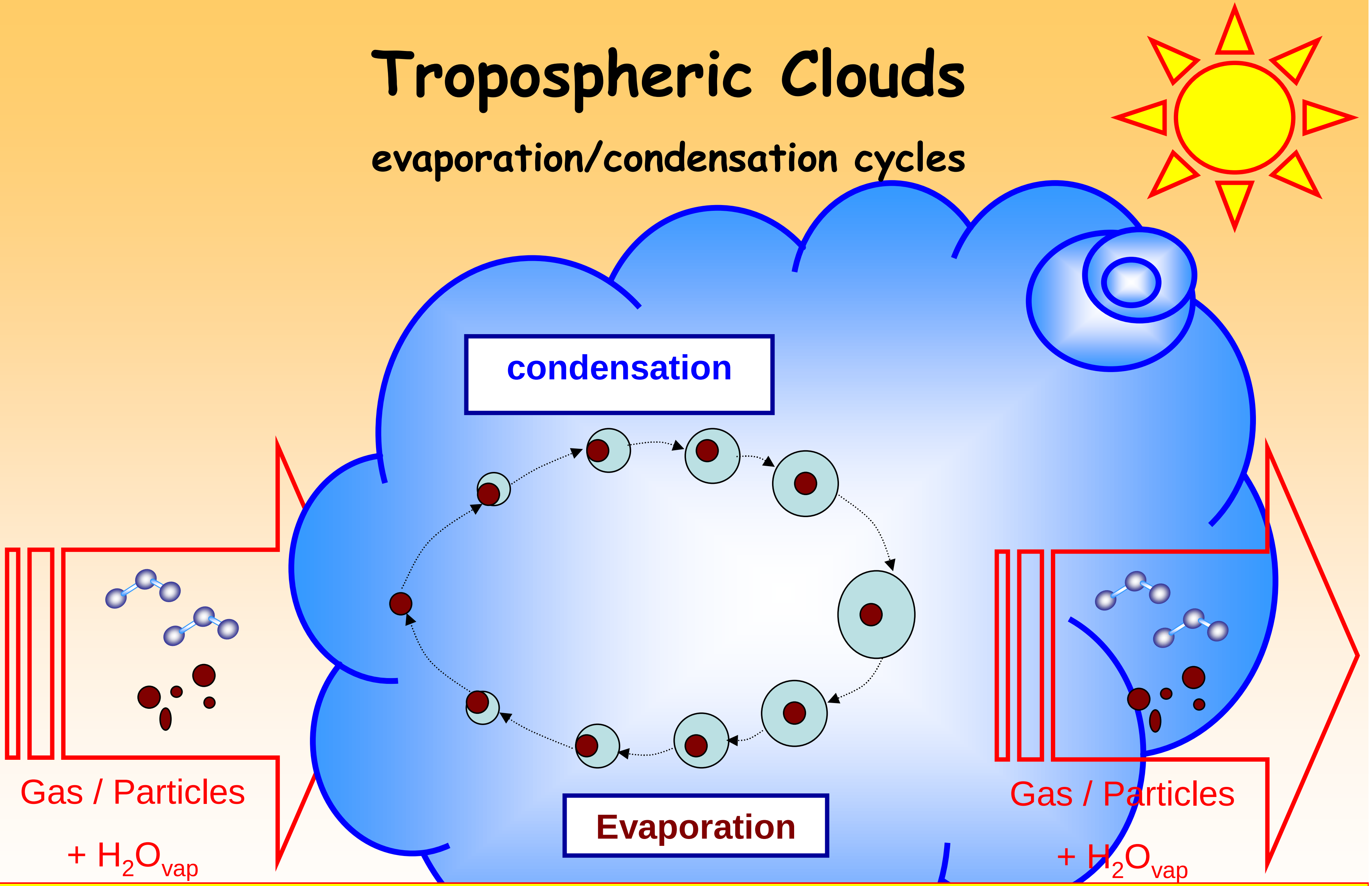
Cloud water droplets → Chemical photoreactors

Monod *et al*., 2005
Herrmann et al., 2005
Altieri *et al*., 2007

Carlton et al., 2007
Liu *et al*., 2009
El Haddad *et al*., 2009…

Tropospheric Clouds

evaporation/condensation cycles

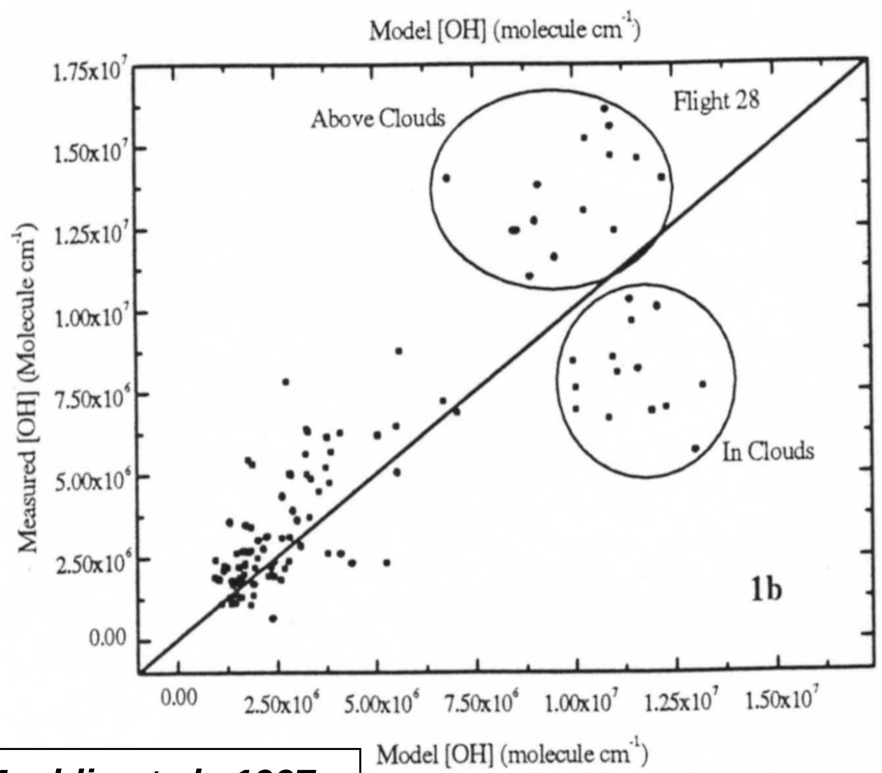


In-cloud chemistry impacts :

gas phase composition ? Particles ?

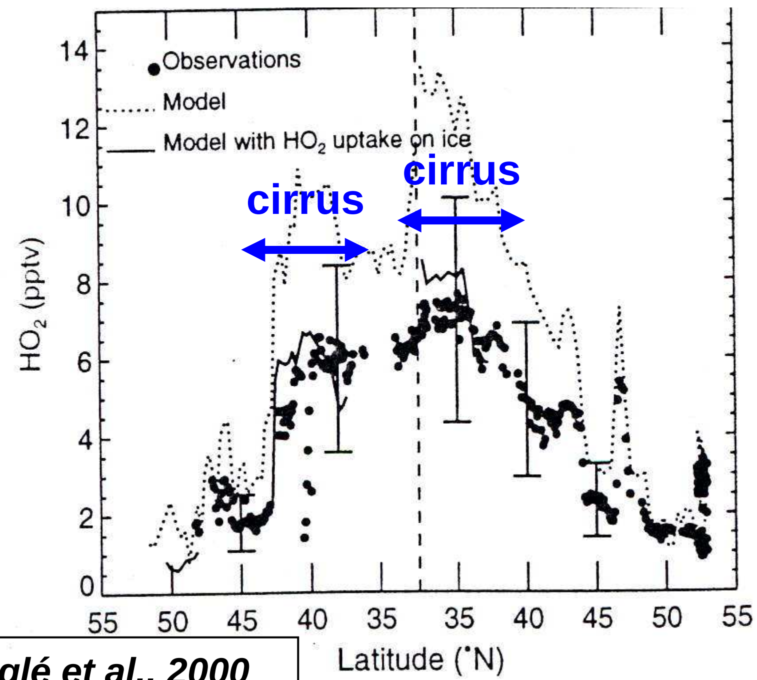
Field evidence

OH flight measurements



Mauldin et al., 1997

HO_2 flight measurements



Jaeglé et al., 2000

Impact on radical chemistry

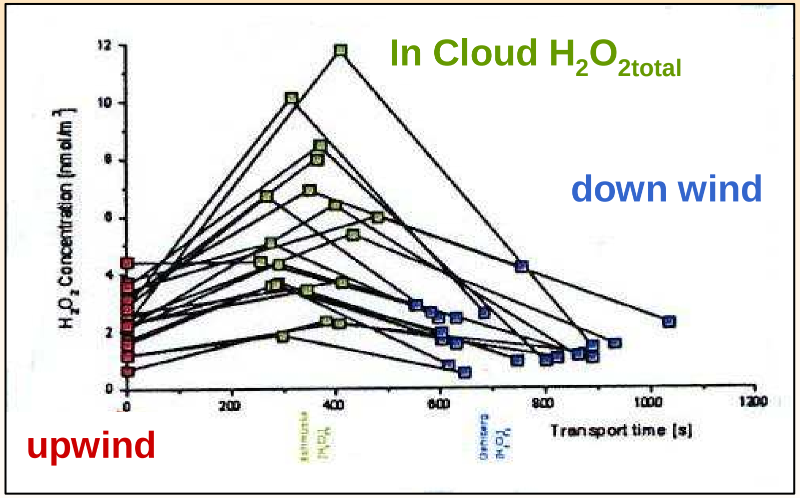
Impact on the gas phase composition ?

Hydroperoxides

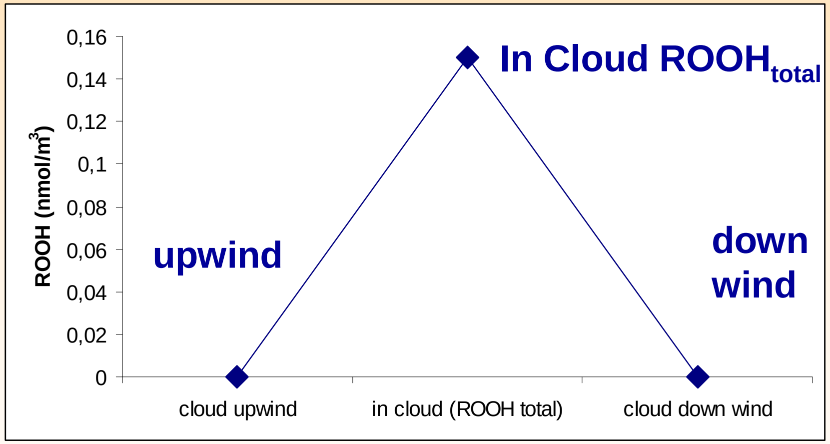
Field evidence

H_2O_2 and ROOH formation in an orographic cloud Schmücke mountain (Germany)

H_2O_2



Total ROOH



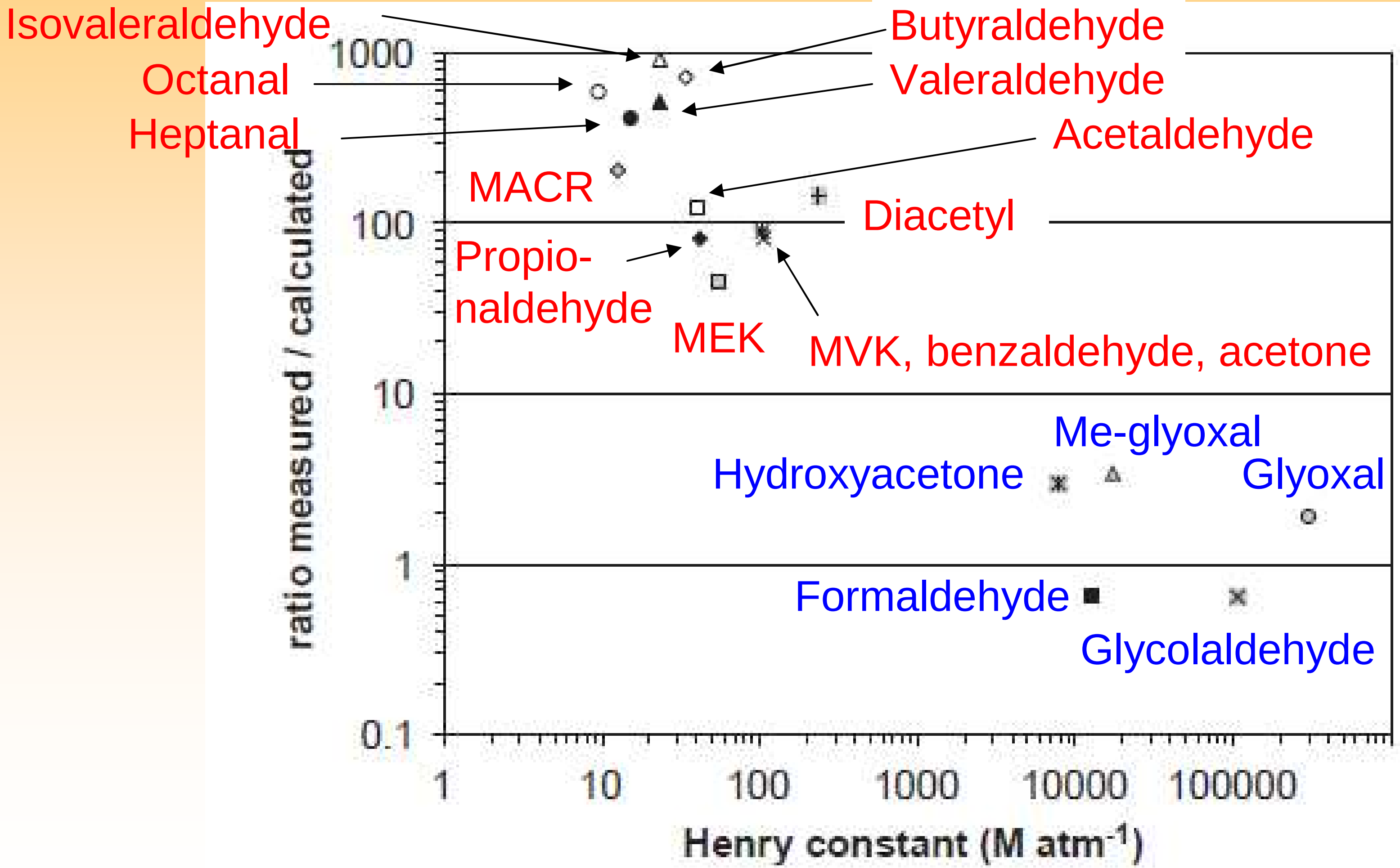
$CH_3OOH + H_2C(OH)OOH + CH_3CH(OH)OOH$

Jaeschke et al., 2003; Valverde-Canosa, 2005

Impact on the gas phase composition ?

VOCs Field evidence

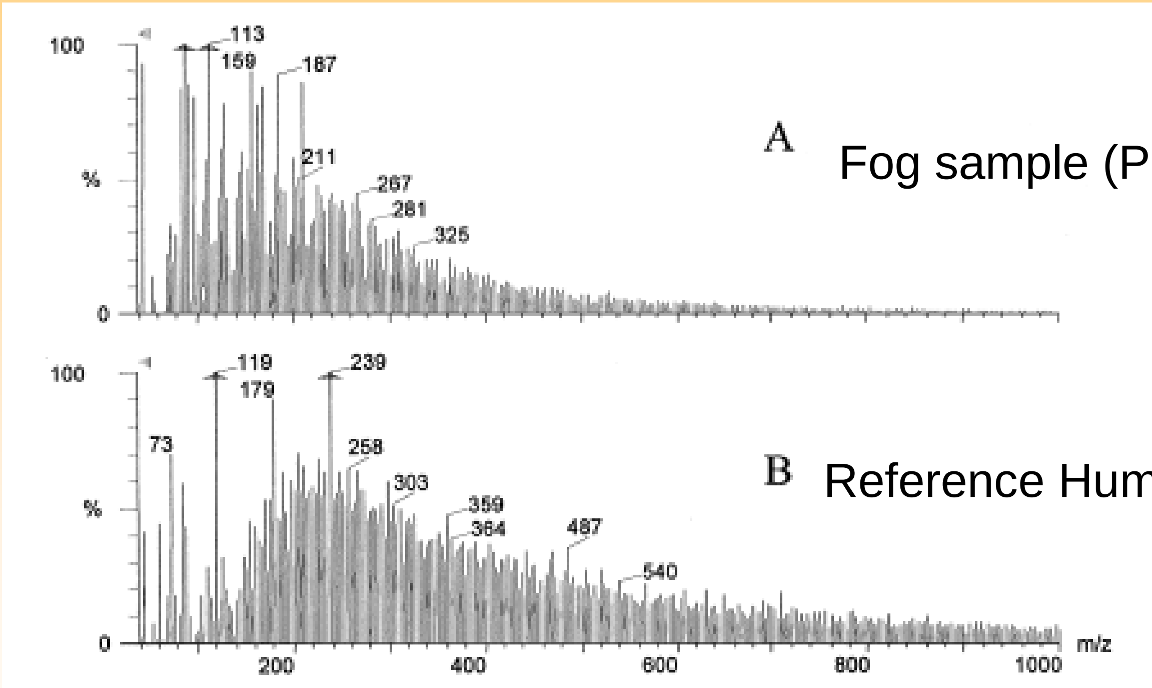
phase partitioning : liquid phase / interstitial gas phase
In an orographic cloud at the Schmücke mountain (Germany)



Van Pinxteren et al., 2005

Field measurements

Humic-like substances in fog



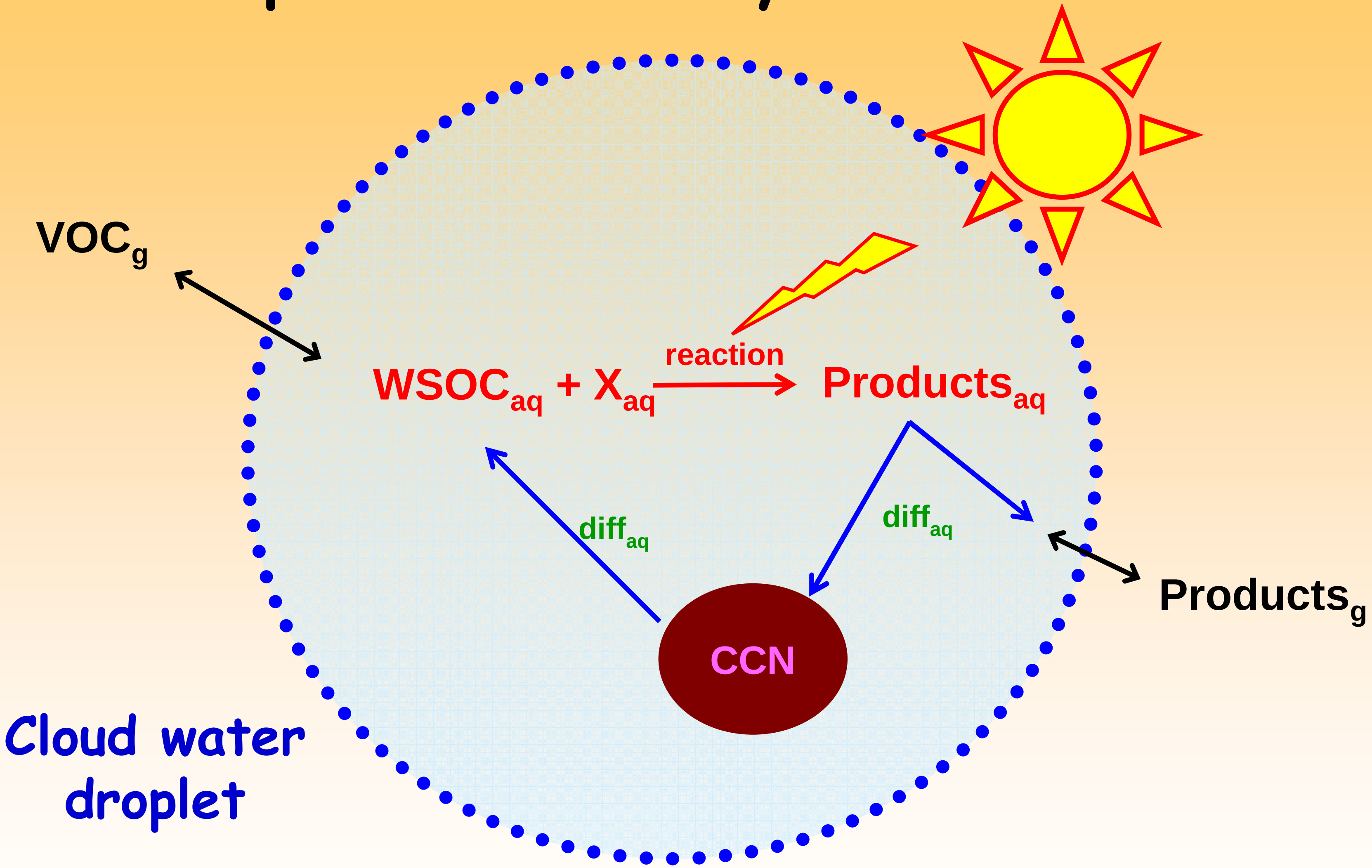
A Fog sample (Po Valley)

B Reference Humic acids

Mass spectrum signal by ESI$^-$ ionisation

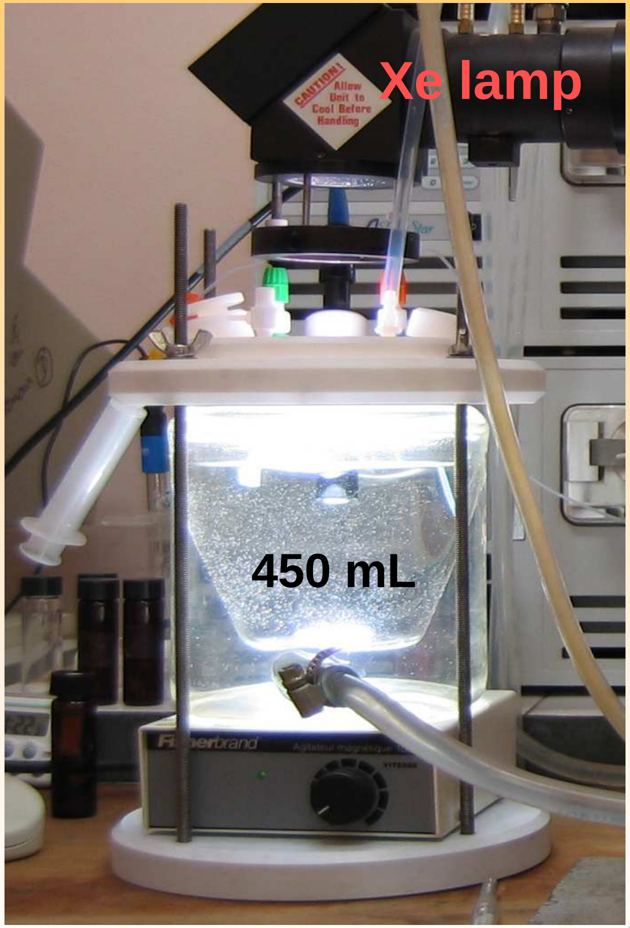
Krivàcsy et al., 2000

Multiphase Reactivity of OC in Clouds



Kinetics and mechanisms of photooxidation of OC in the aqueous phase ?

Aqueous phase simulation chamber



Production of $^{\bullet}OH_{aq}$

- ☞ $H_2O_2 + h\nu \rightarrow 2\ ^{\bullet}OH$
- ☞ $HNO_2 + h\nu \rightarrow\ ^{\bullet}OH + NO$

Fenton

Acetaldehyde
Propionaldehyde
Butyraldehyde
Valeraldehyde
Acetone
Me-Et-Ketone
Me-*i*-But-Ketone
Me-glyoxal

Methacrolein
Me-Vin-ketone
Me-hydroperoxyde
Et-hydroperoxyde
N-Me-pyrrolidone
Phenol
Et-*t*-But-Ether
n-But-acetate
Methanol
Ethanol

Reaction

WSOC + $^{\bullet}OH_{aq} \rightarrow$ Products

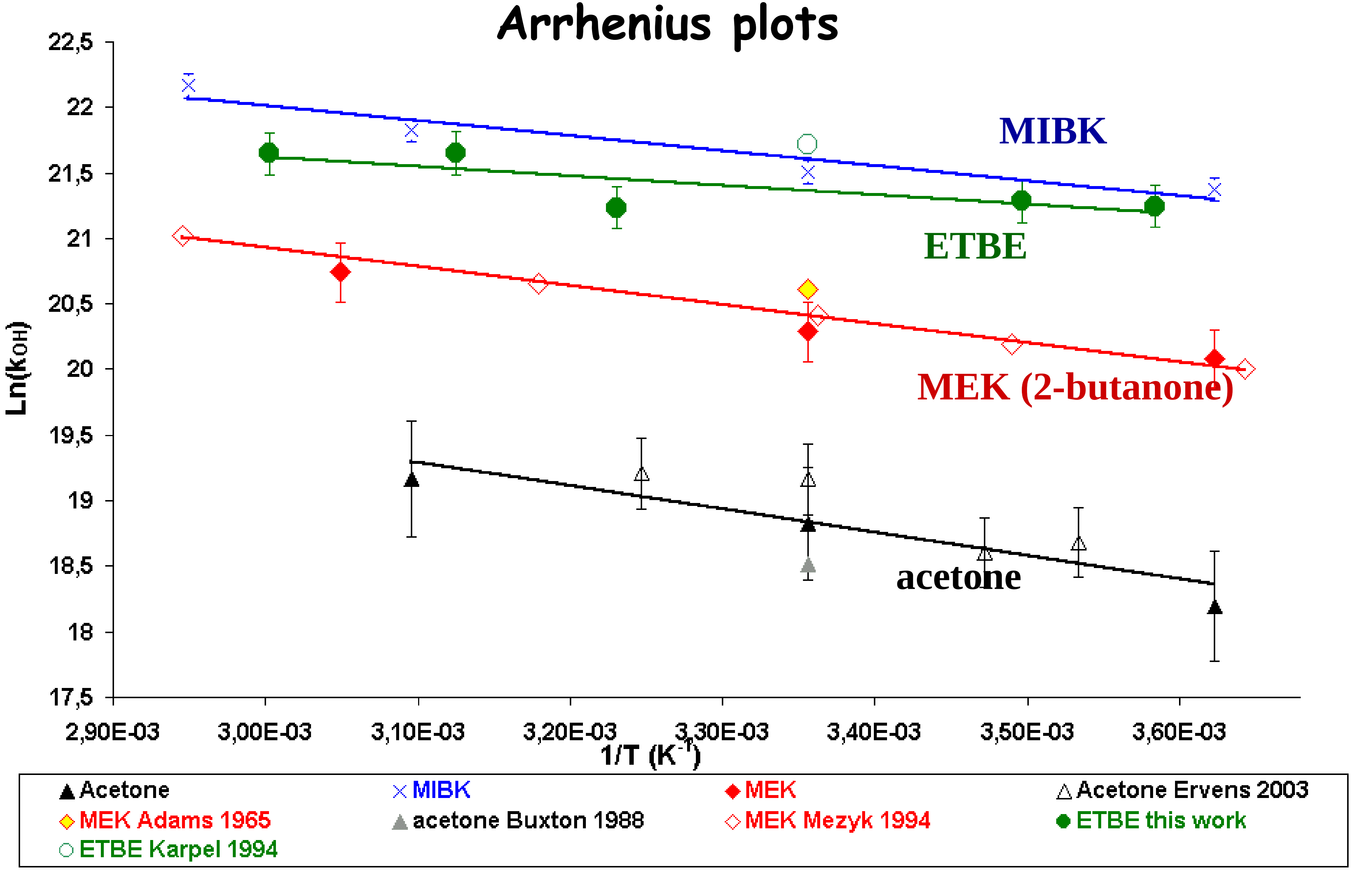
Aqueous phase chemical analyses

HPLC-UV (2,4-DNPH)	carbonyls
HPLC - Fluo (POPHA + peroxydase)	H_2O_2 and ROOH
GC-FID	alcohols, ethers, esters, ketones
Ionic chromatography	organic acids
HPLC-MS/MS	Identification of organic compounds
APCI-MS/MS and ESI-MS/MS	High weight organic compounds

RESULTS

1) Kinetics

Relative Kinetics towards OH radicals



Monod et al., 2005

Aqueous phase SAR

alkanes, alcohols, organic acids, bases and polyfunctionals

$$RH_{aq} + OH_{aq} \rightarrow \text{products} \qquad k_{298} ?$$

Data base: 72 compounds

44 references (Buxton *et al.* (Review) 1988; Ervens *et al.* 2003; George *et al.* 2003; Monod *et al.* 2005…)

Parameterisation of each chemical group, in the α– and β– positions (Atkinson 1987; Kwok and Atkinson 1995)

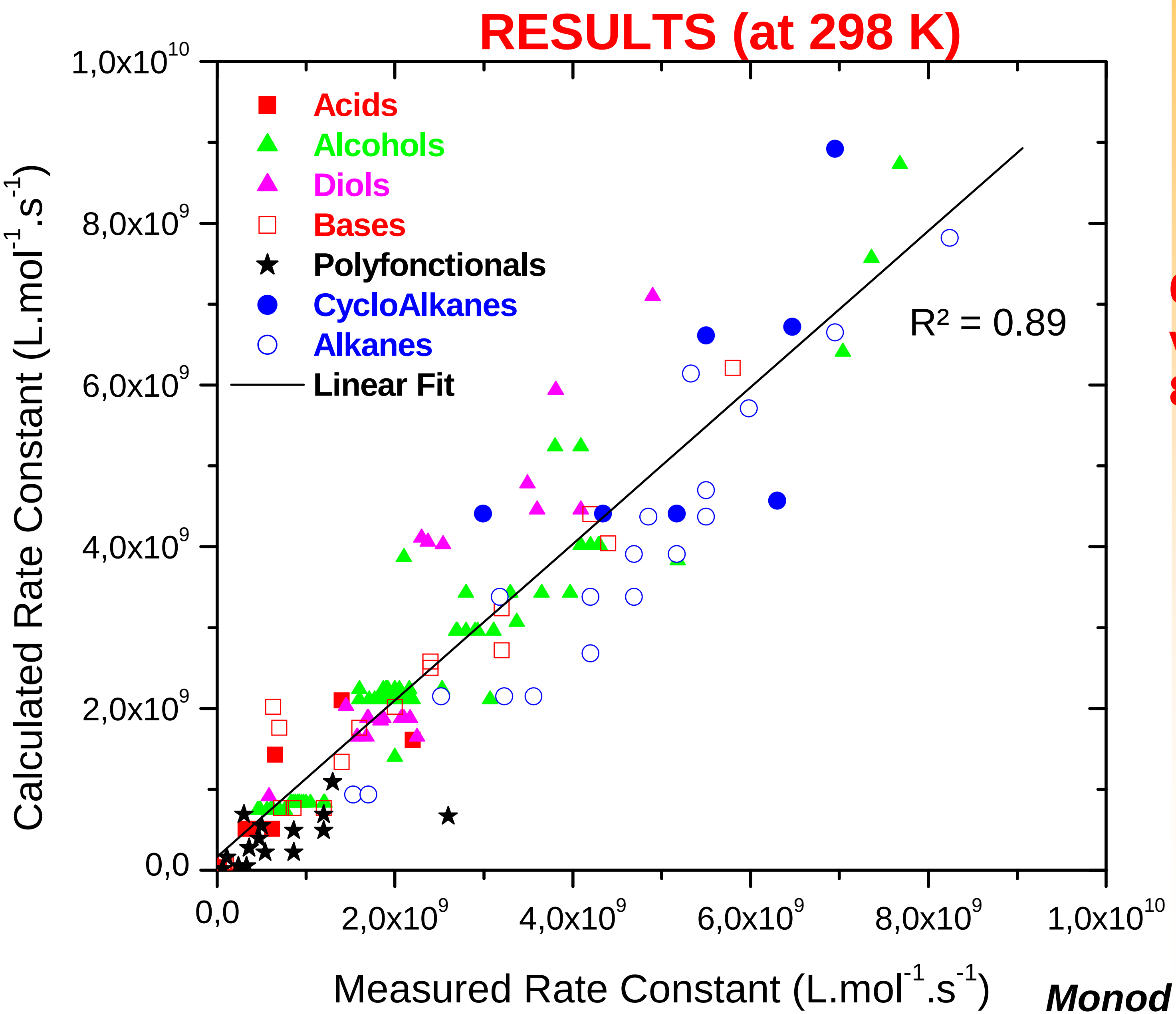
$$k = \sum_{i=1}^{n} \left(k(i) \times \prod F(\alpha - group) \right) \times \prod G(\beta - group)$$

group rate constants

substituent factors

Monod and Doussin, 2008

Aqueous phase SAR



60% of k_{est} values are within 80% of k_{exp}

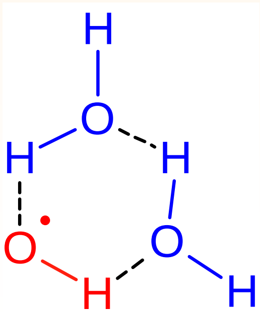
Monod and Doussin, 2008

Aqueous phase SAR

RESULTS (at 298 K)

Kinetic rate constants

	Aqueous $(L.mol^{-1}s^{-1})$	Gas (Kwok and Atkinson, 1995) $(cm^3.molec^{-1}s^{-1})$
k(OH)	6.9×10^7	0.14×10^{-12}
$k(CH_3)$	3.5×10^8	0.14×10^{-12}
$k(CH_2)$	6.5×10^8	0.93×10^{-12}
k(CH)	4.7×10^8	1.9×10^{-12}



(Rudakov *et al*., 1981, 1982, 2006)

Monod and Doussin, 2008

Aqueous phase SAR

RESULTS (at 298 K)

Kinetic rate constants ($L.mol^{-1}s^{-1}$)

k(OH)	6.9×10^7
$k(CH_3)$	3.5×10^8
$k(CH_2)$	6.5×10^8
k(CH)	4.7×10^8

$k(OH) / k_{Total}$ =	7%	methanol
	4.3%	*t*-butanol
	2.5%	ethanol
	< 2%	other alcohols

(Asmus *et al*., 1973)

Monod and Doussin, 2008

Life times

$$WSOC_{aq} + OH_{aq} \xrightarrow{kaq} prod$$

$$\tau_{life\ (aq)} = 1/\ (k_{aq}[OH_{aq}])$$

$$VOC_{g} + OH_{g} \xrightarrow{kg} prod$$

$$\tau_{life\ (g)} = 1/\ (k_{g}[OH_{g}])$$

τ_{life}	aqueous phase	gas phase
	$[OH_{aq}] = 10^{-13}$ M	$[OH_{g}] = 10^{6}\ cm^{-3}$
Acetone	1 day	1 month
Formic acid	1 day	1 month
Methanol	3 h	15 days
NMP	1 h	6 h
ETBE	2 h	3.5 days

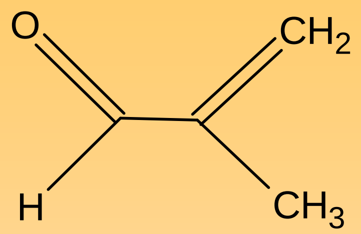
→ **Drastic reduction in the aqueous phase**

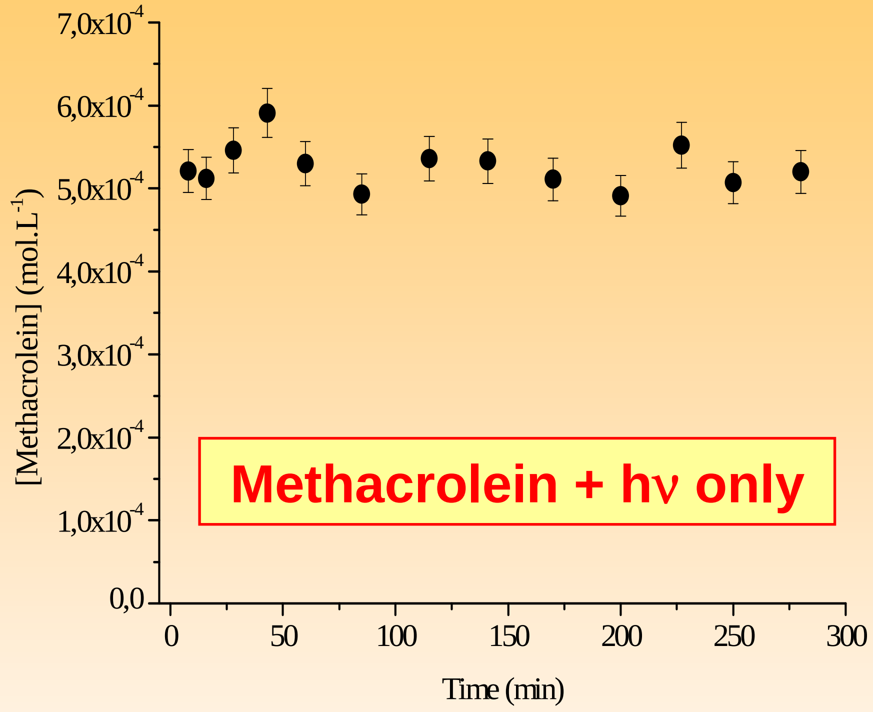
Monod et al., 2005

RESULTS

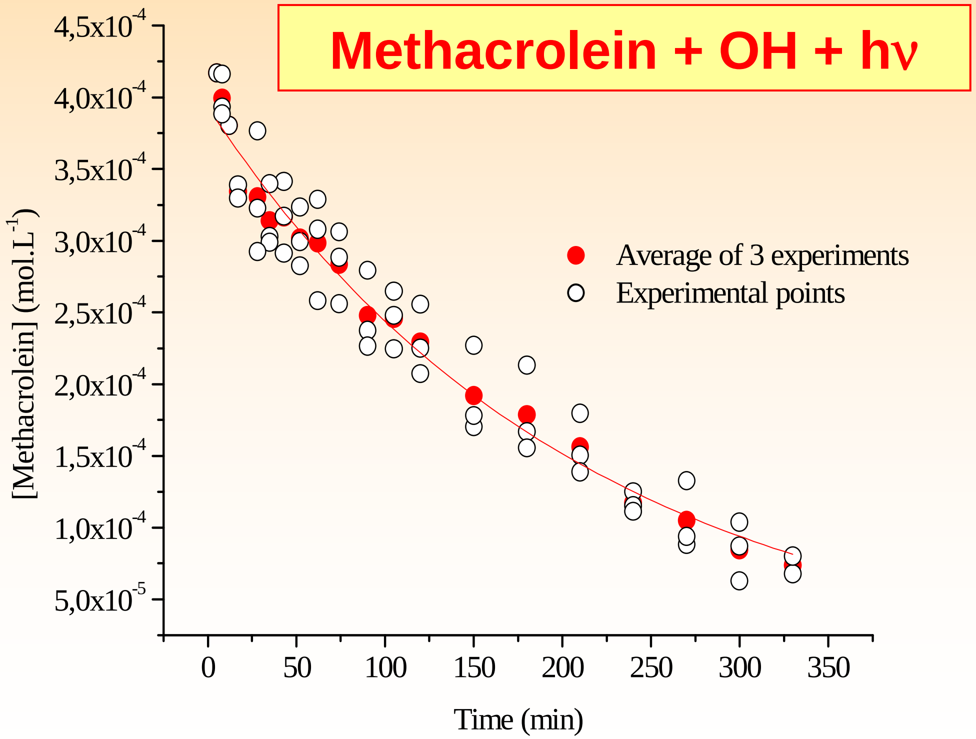
2) Chemical Mechanisms

Photooxidation of methacrolein in the aqueous phase





No degradation with UV only



Degradation caused by OH radicals

Good reproducibility

Initial concentrations :

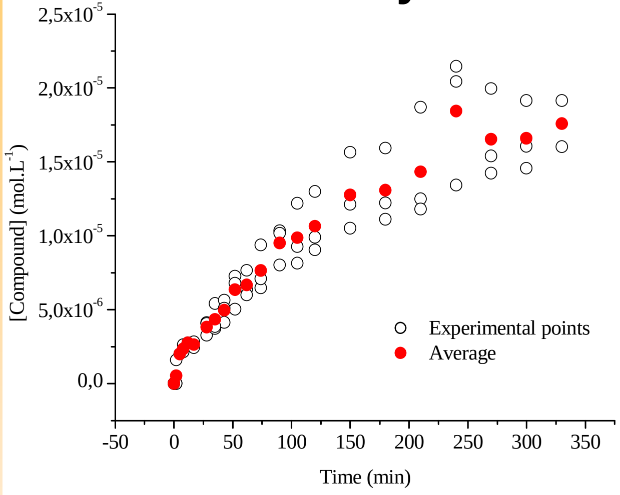
[Methacrolein] = 4.10^{-4} M

$[H_20_2] = 6.10^{-2}$ M

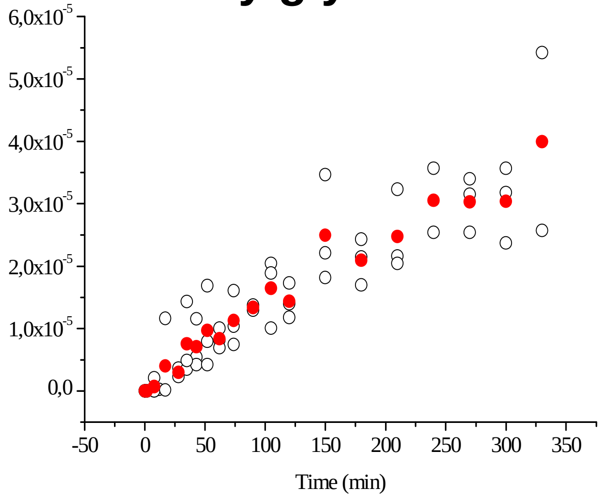
Liu et al., 2009

Photooxidation of methacrolein in the aqueous phase

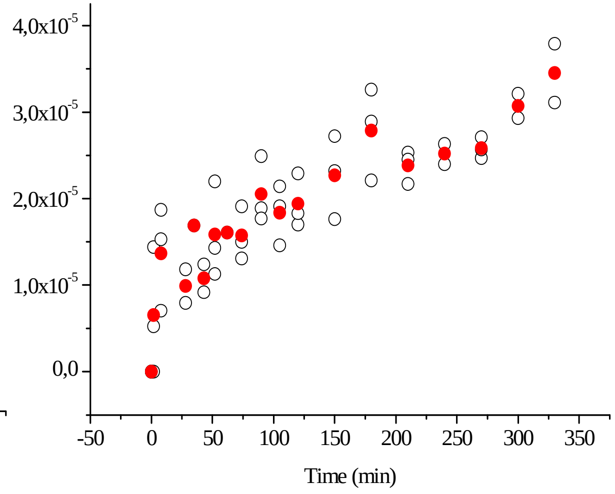
Formaldehyde / time

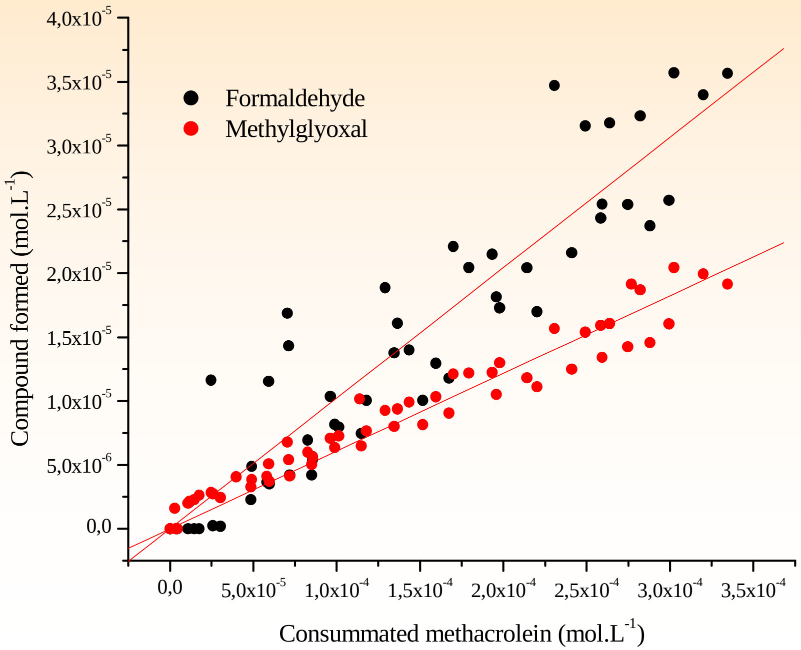


Methylglyoxal / time



Hydroxyacetone / time





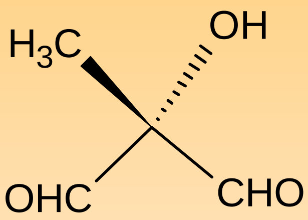
- **Formaldehyde / Δ MACR**
- **Methylglyoxal / Δ MACR**

Liu et al., 2009

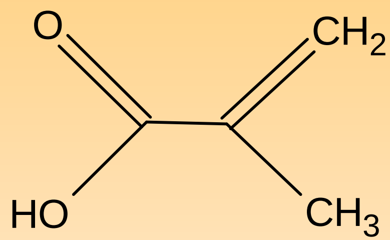
Photooxidation of methacrolein in the aqueous phase

…And also :

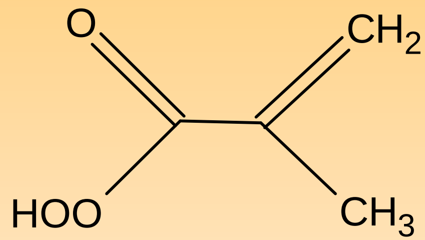
Acetic, Oxalic, Pyruvic, Glyoxalic acids …



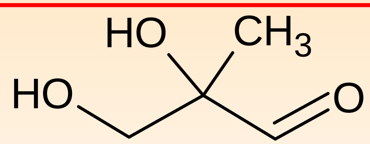
hydroxy(methyl)propanedial



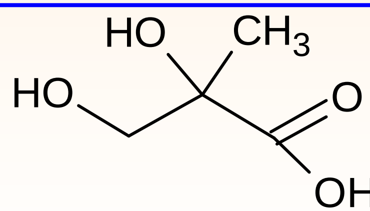
Methacrylic acid



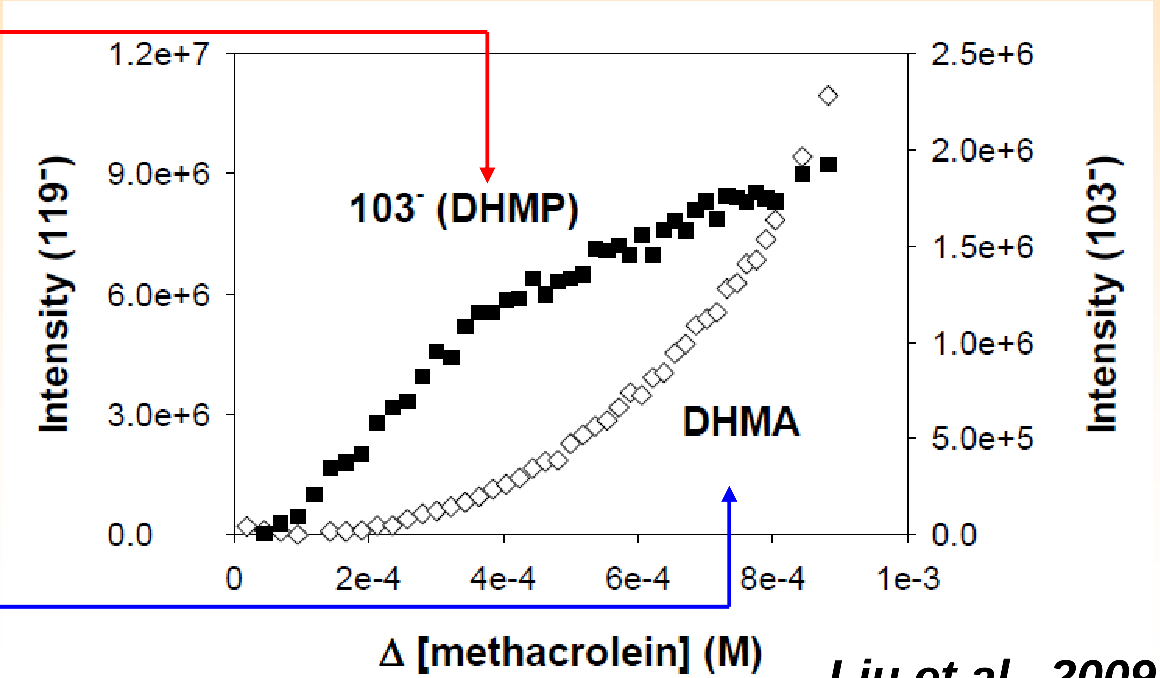
Peroxymethacrylic acid



2,3-dihydroxy-2-methylpropanal



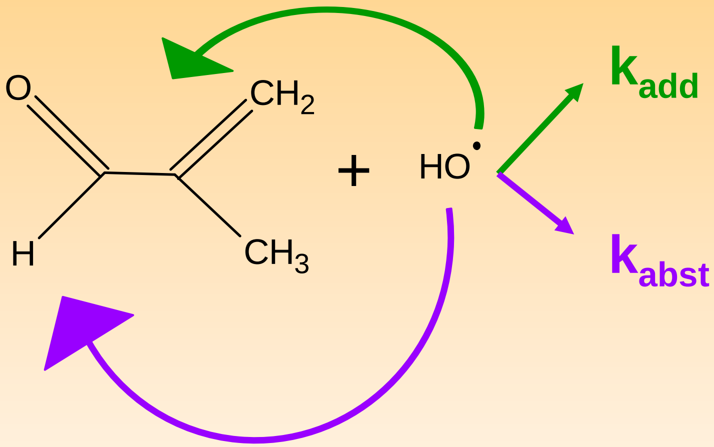
2,3-dihydroxymethacrylic acid



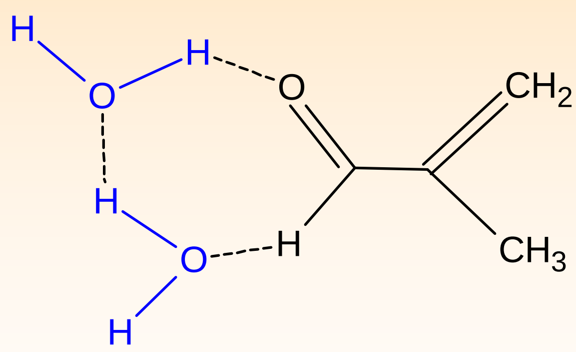
Liu et al., 2009

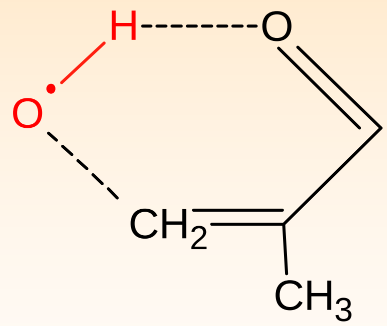
Photooxidation of methacrolein

Mechanism



k_{abst} / k_{Total}	
5 (± 3) %	40 - 50 %
Aqueous	**Gas**
This work	Pimentel and Arbilla, 1999; Orlando *et al*., 1999; Chuong and Stevens, 2004





Mellouki *et al.* (2003) ; Smith and Ravishankara (2002); H. Sidebottom (today !)

Liu et al., 2009

Photooxidation of methacrolein in the aqueous phase

Carbon yields

Reaction product	Molar yield %	Carbon yield %
Me-glyoxal	9 (± 2)	25 - 57
Formaldehyde	12 (± 2)	
Hydroxyacetone	15 (± 6)	
Acetic acid	17 (± 6)	
Methacrylic acid	0.7(± 0.4)	
HMM + DHMP	3 – 11	
Peroxymethacrylic acid	4 (± 3)	
DHMA, Pyruvic, Oxalic, Glyoxylic acids	Secondary products	

Other reaction products ?

Liu et al., 2009

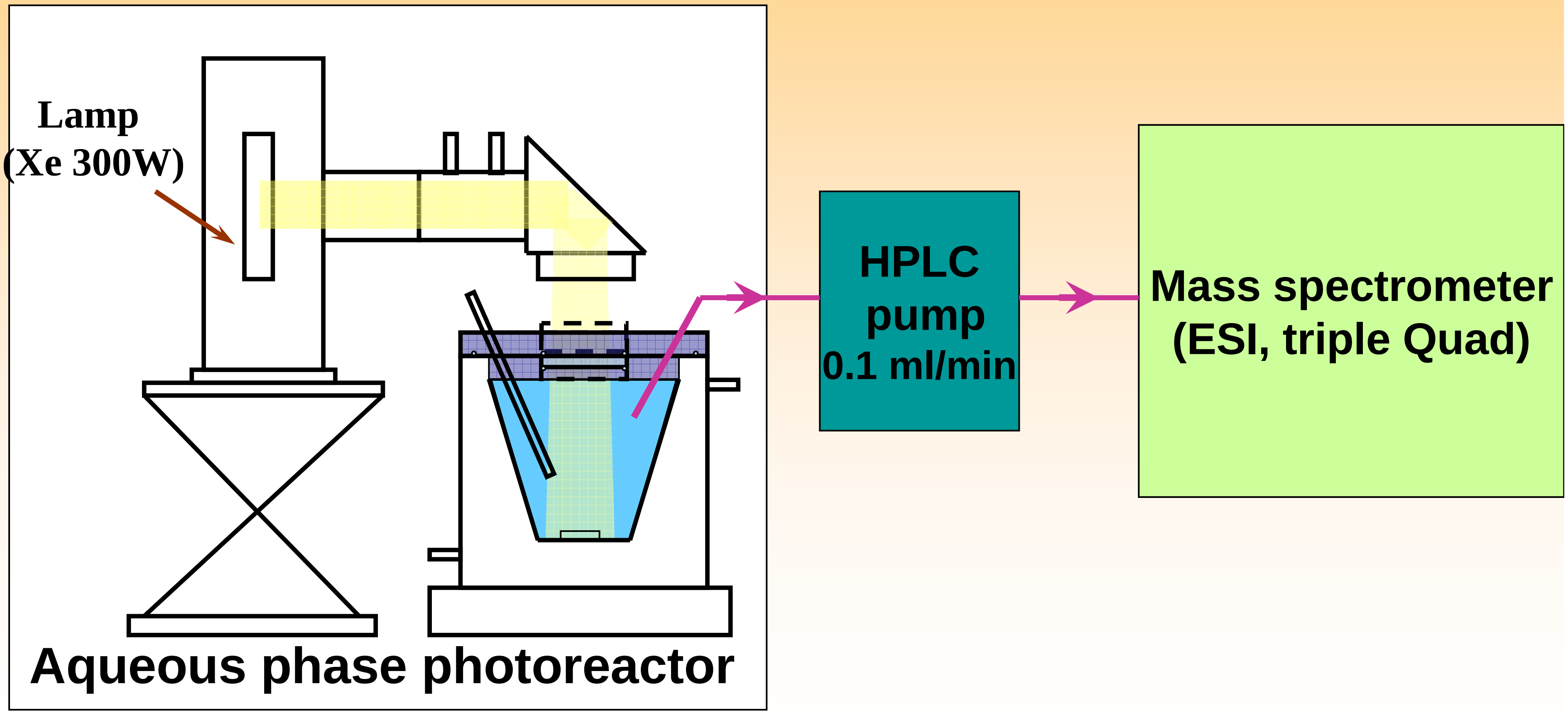
Chemical mechanisms WSOC + OH

Reaction products chemical analyses

Reaction	Carbon balance
CH_3OH + OH	> 93%
CH_3CHO + OH	> 90%
Acetone + OH	> 95%
$CH_3C(O)CH_2C(CH_3)_3$ (MIBK)	< 30%
N-Methylpyrrolidone+ OH	< 55 %
Methacrolein + OH	< 57 %

Other reaction products ?

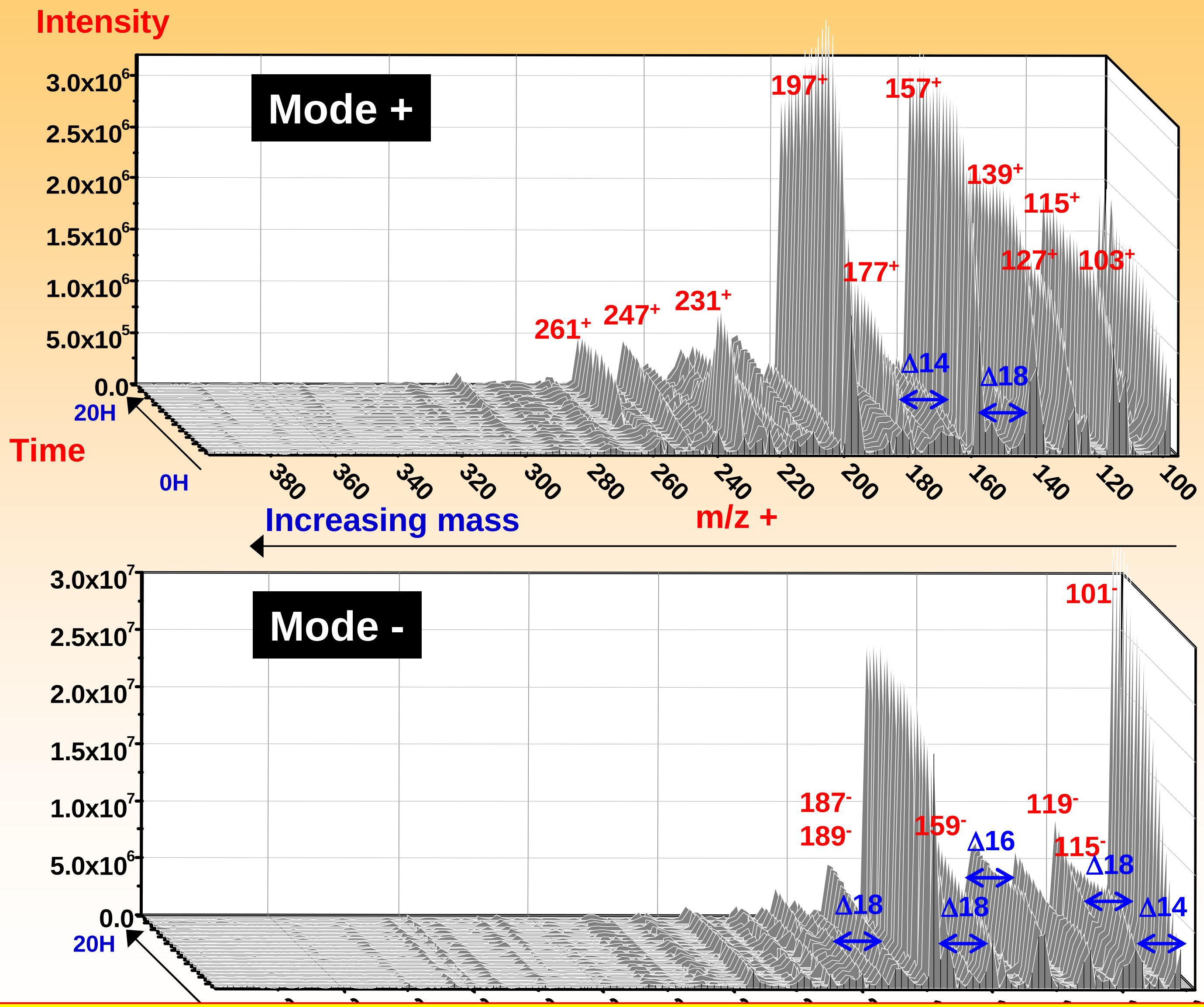
On-line mass spectrometer on the aqueous phase simulation chamber



Poulain et al., 2007

Photooxidation of methacrolein

Photoreactor-ESI-MS Results



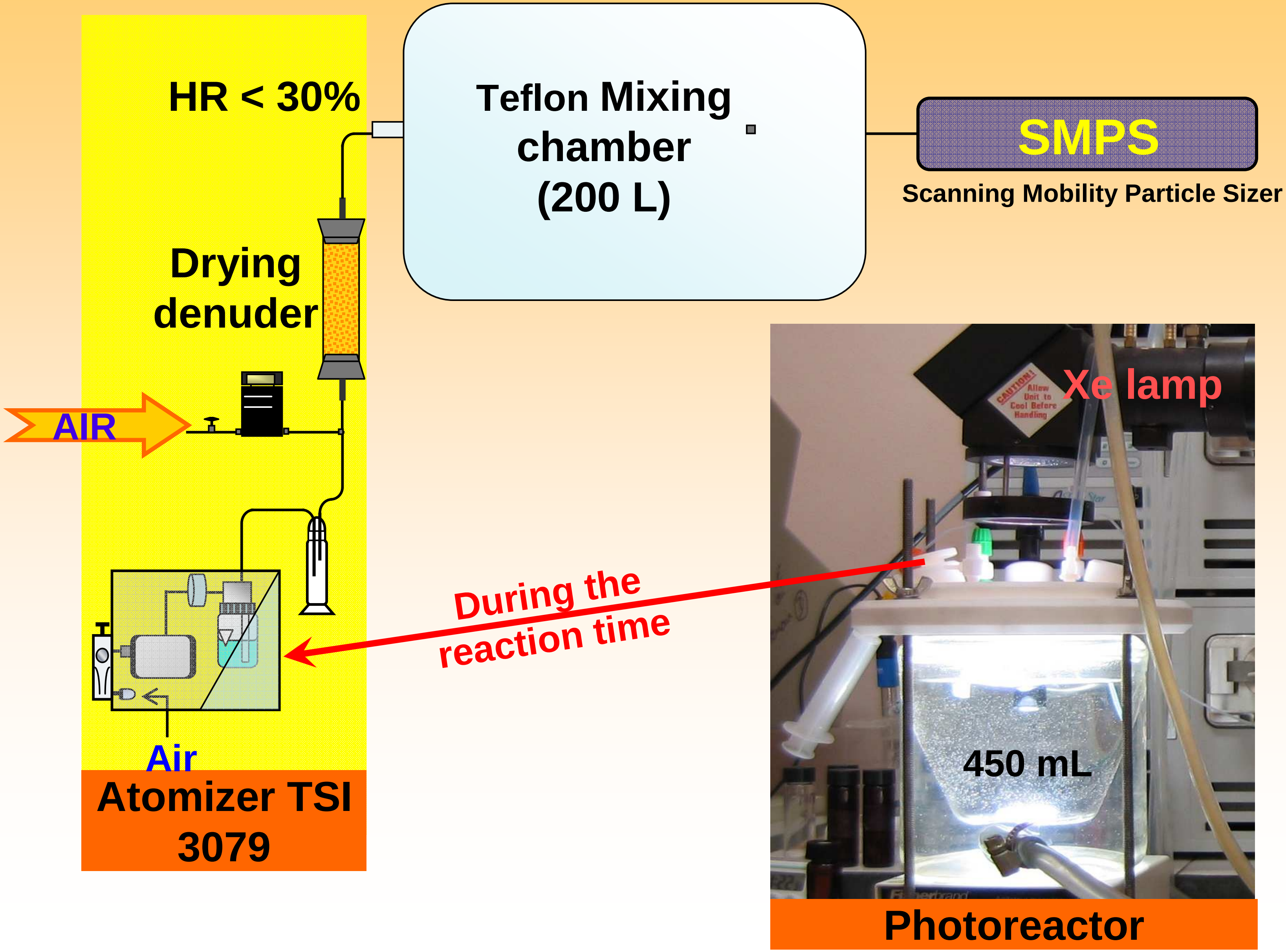
~ 50 additional reaction products!! 100 – 400 a.m.u.

ESI-MS / MS and HPLC-MS

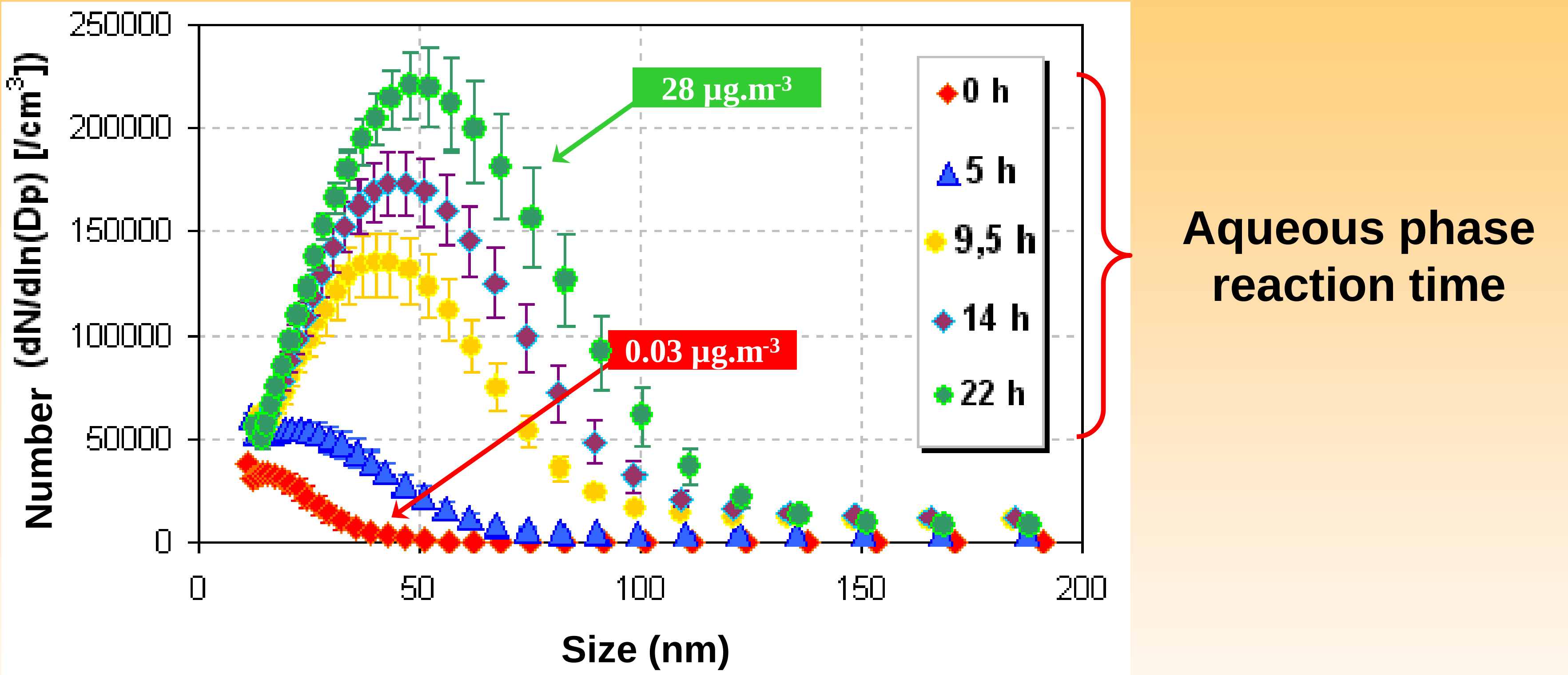
- Multifunctional products
- 2 series of oligomeres

Formation of SOA when water evaporates ?

Particle generation
Nebulization of reacting solutions



Particle generation
Results

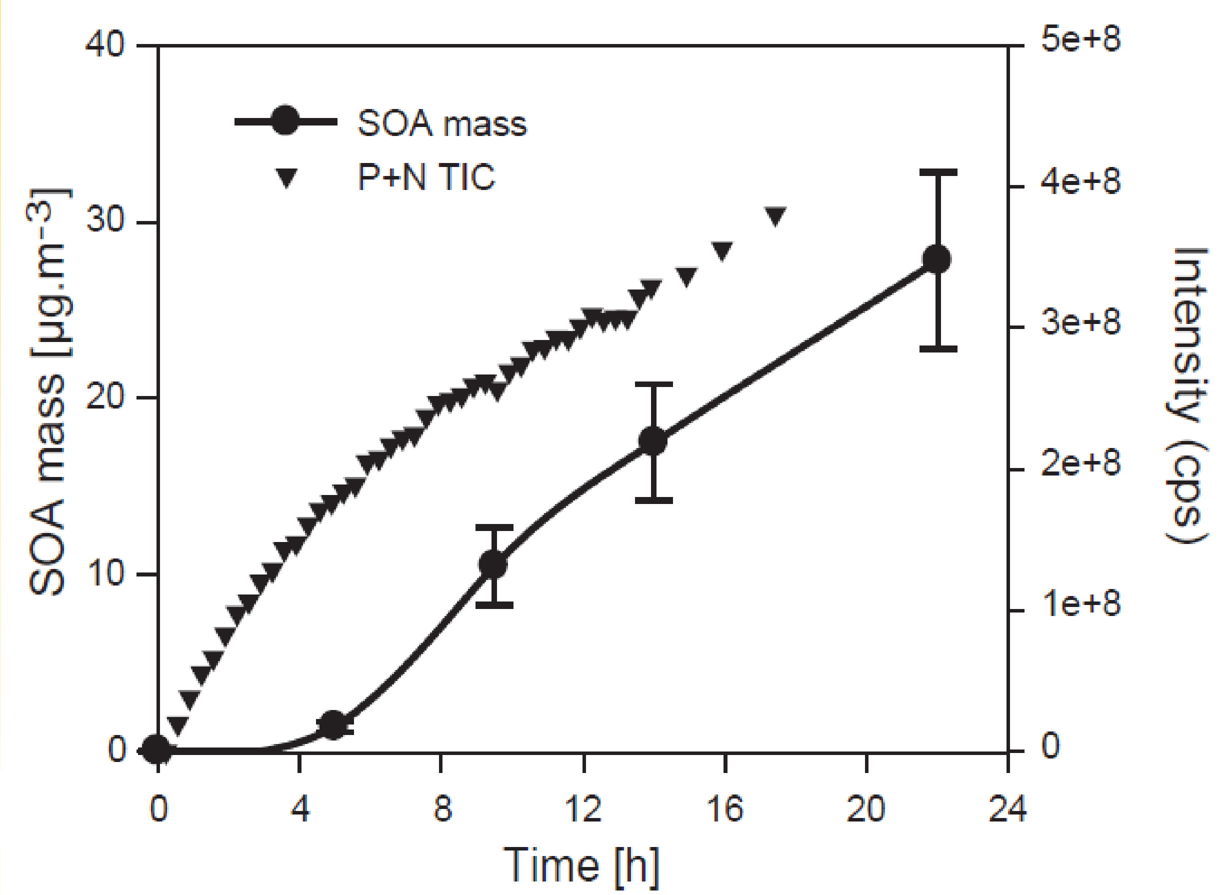


Aerosol: nb and size significantly increase with reaction time

El Haddad *et al*., 2009; Michaud *et al*., 2009

Particle generation

Results

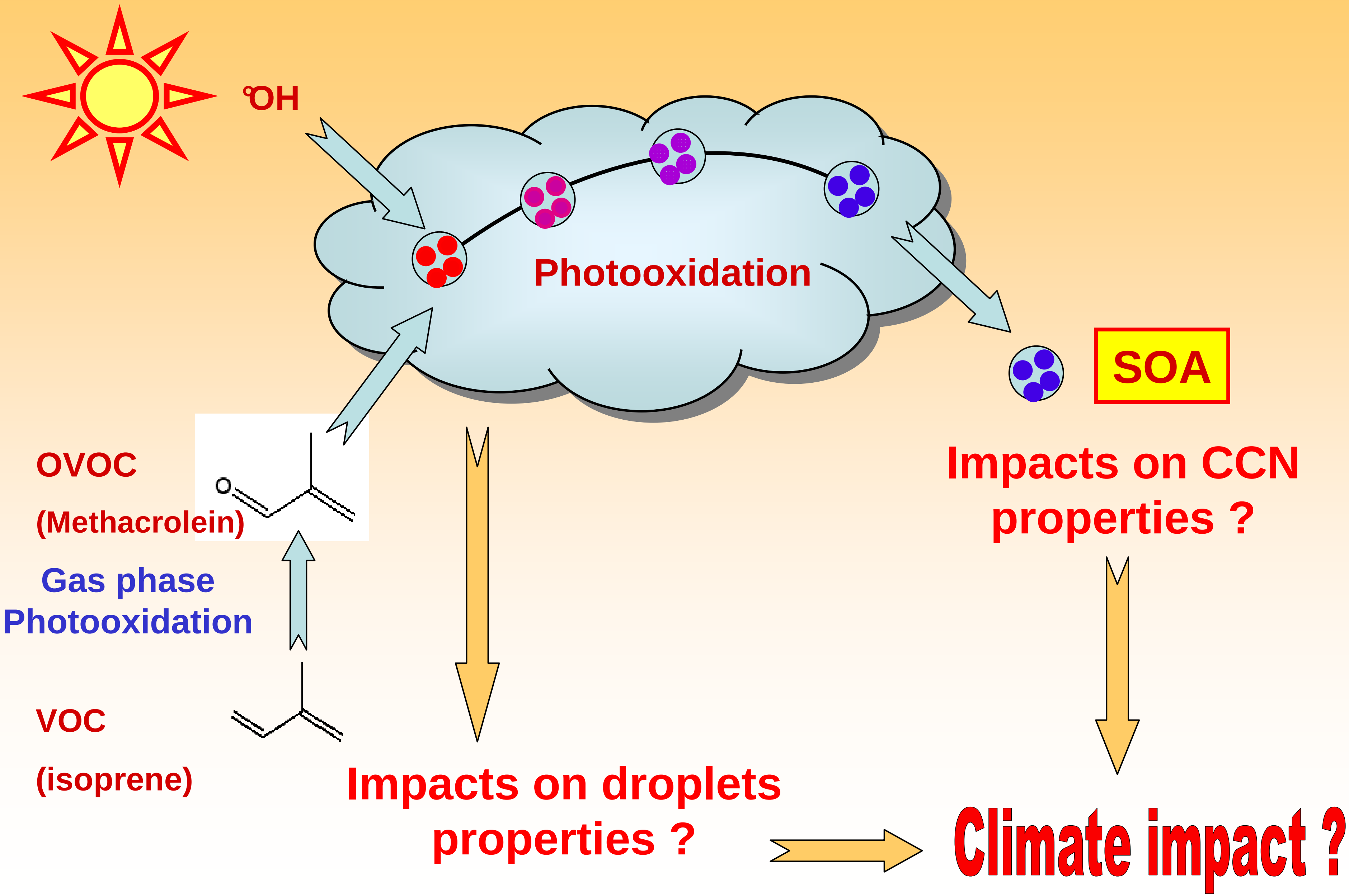


Correlation with the production of HW molecules in the solution

SOA yield : 2 – 12% >> 1-4 % isoprene$_{gas}$ photooxidation

El Haddad *et al*., 2009; Michaud *et al*., 2009

CONCLUSIONS



Aknowledgements

Students

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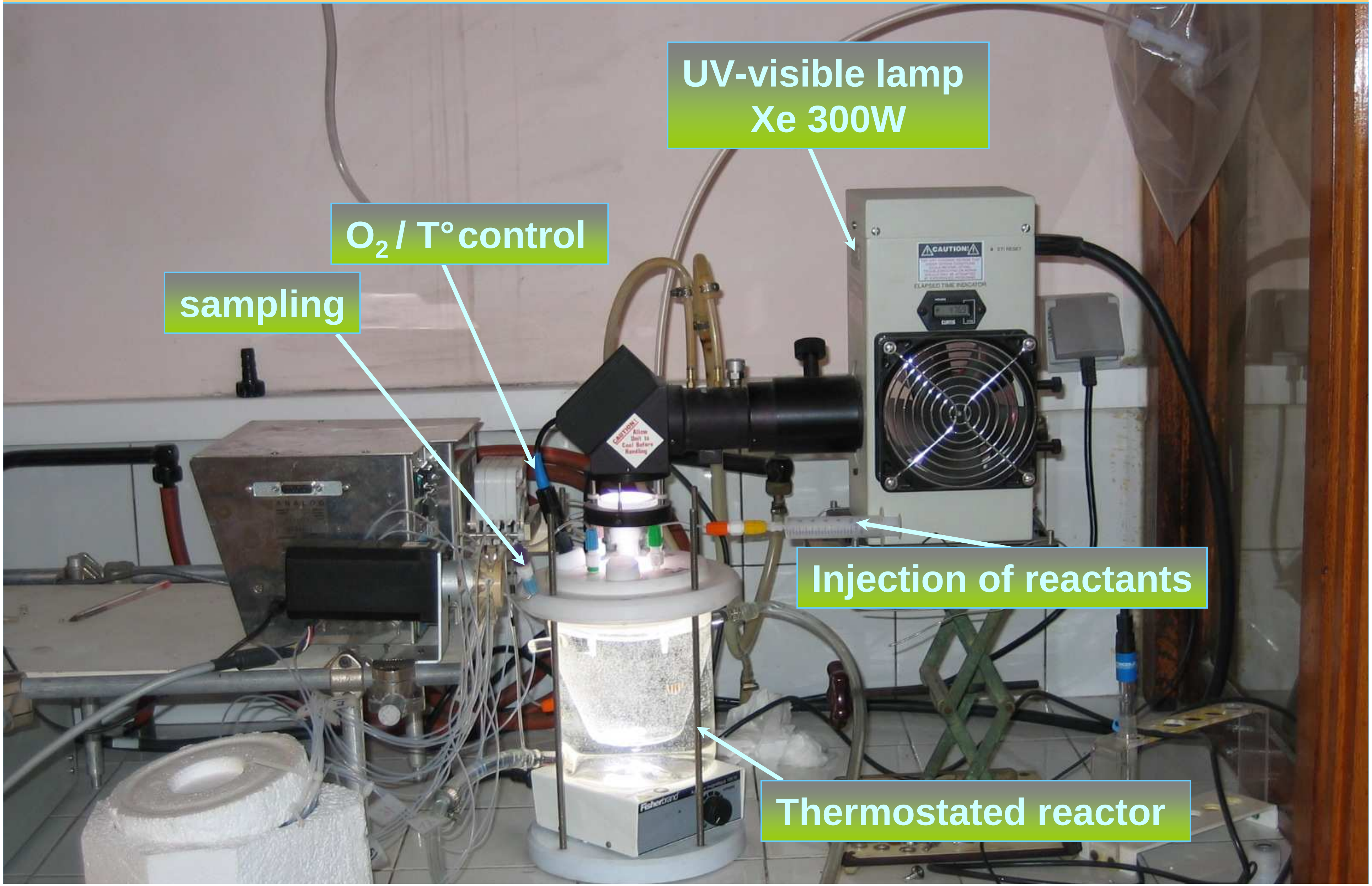
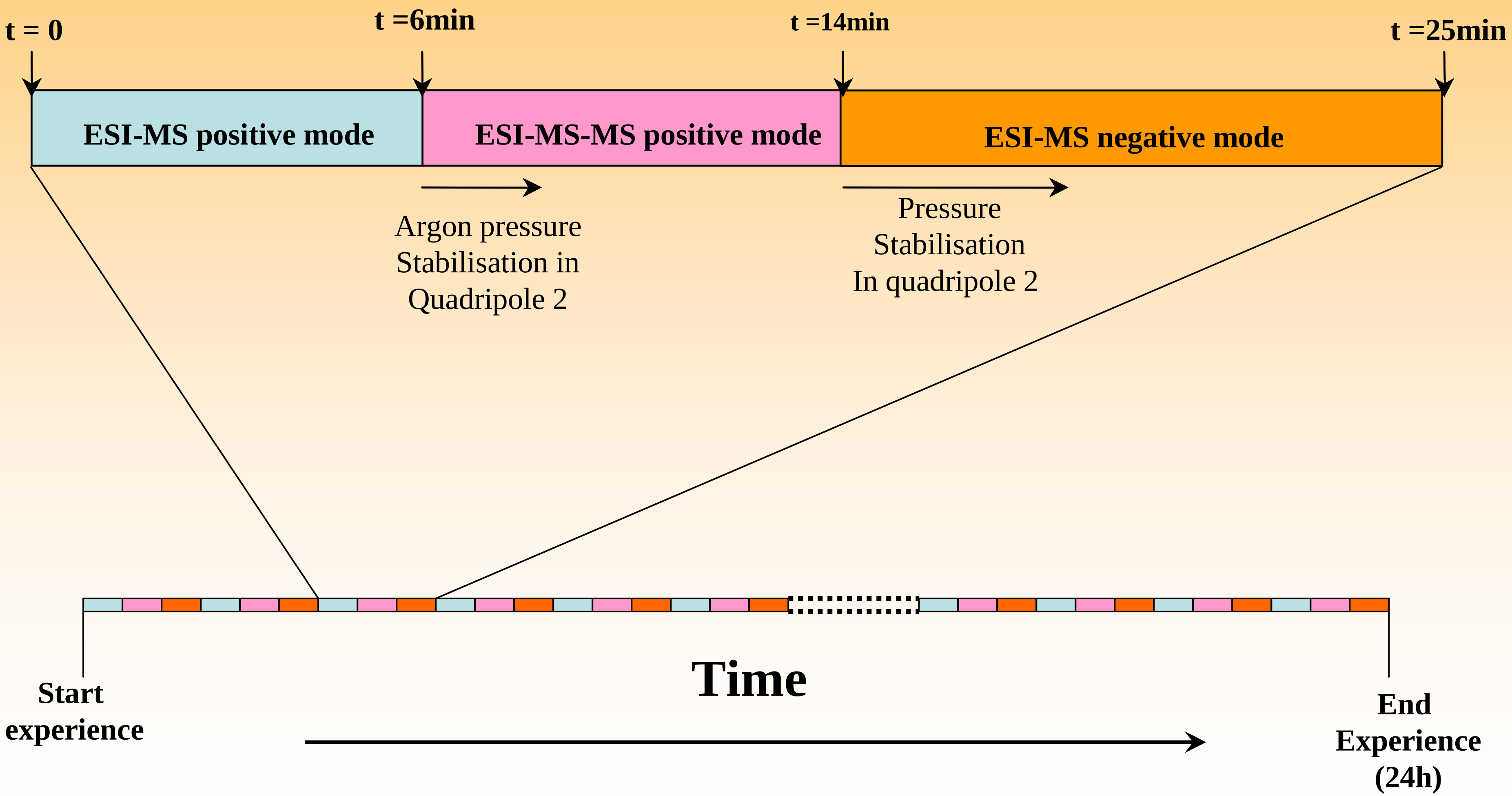
Bénédicte Picquet-Varrault
Didier Voisin

Aqueous phase simulation chamber



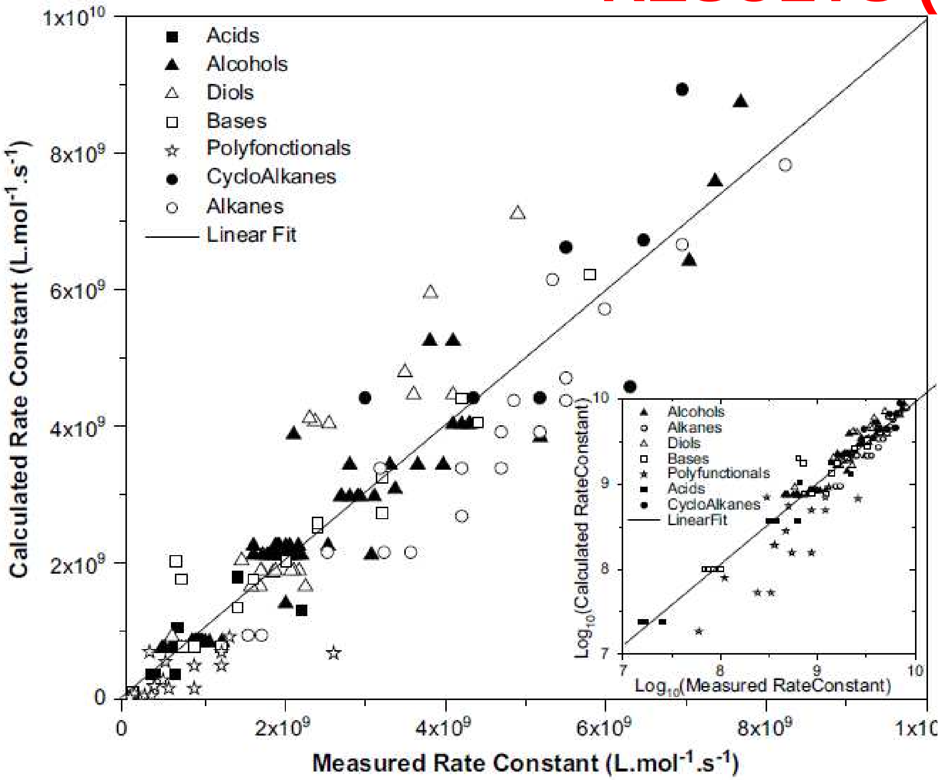
MS conditions

scan range :20-1000 mass units



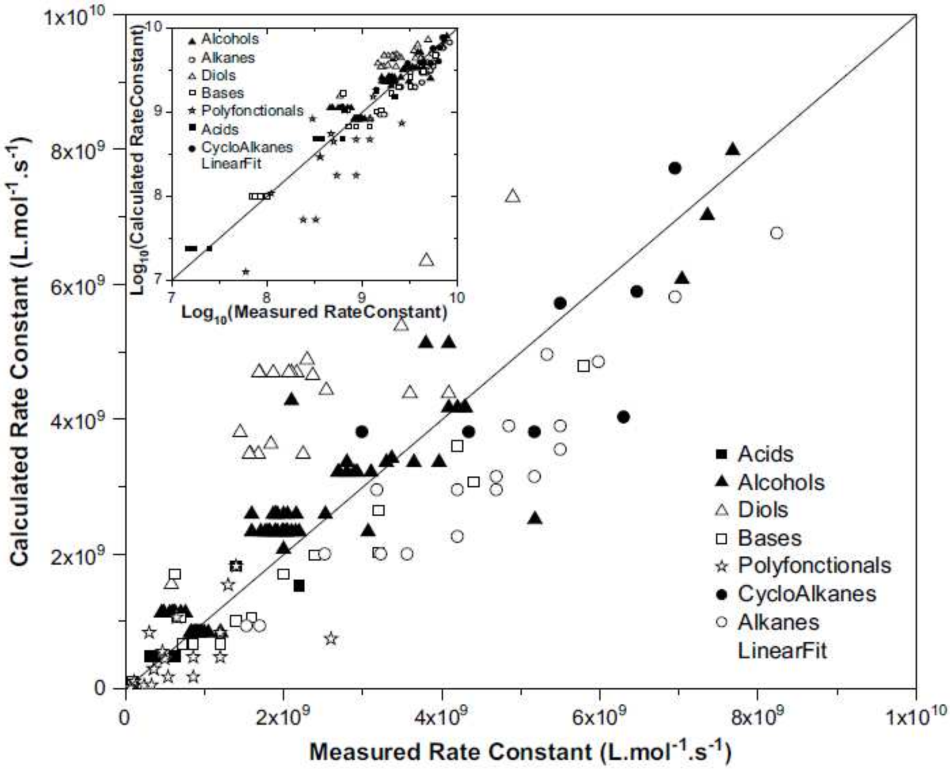
Aqueous phase SAR

RESULTS (at 298 K)



β-effect

no β-effect



Monod and Doussin, 2008

Aqueous phase SAR

RESULTS (at 298 K)

Kinetic rate constant

Parameter	Value	Units
$k(OH)$	6.9×10^7	$L\,mol^{-1}\,s^{-1}$
$k(CH_3)$	3.5×10^8	$L\,mol^{-1}\,s^{-1}$
$k(CH_2)$	6.5×10^8	$L\,mol^{-1}\,s^{-1}$
$k(CH)$	4.7×10^8	$L\,mol^{-1}\,s^{-1}$

Neighbouring effect parameters

Parameter (α-position)	Value	Parameter (β-position)	Value
$F(-CH_3)$	1.33	$G(-CH_3)$	1.17
$F(-CH_2-)$	1.21	$G(-CH_2-)$	1.1
$F(-CH-)$	1.11	$G(-CH-)$	1.05
$F(-C-)$	1	$G(-C-)$	1
$F(-OH)$	2.1	$G(-OH)$	0.44
$F(-COOH)$	0.07	$G(-COOH)$	0.7
$F(-COO^-)$	0.24	$G(-COO^-)$	1.23
$C(C4)$	0.6	$C(C6)$	1
$C(C5)$	0.8	$C(C7)$	0.9

Monod and Doussin, 2008

Aqueous phase SAR

RESULTS (at 298 K)

Parameter (α-position)	Value	Parameter (β-position)	Value
F(-CH_3)	1.33	G(-CH_3)	1.17
F(-CH_2-)	1.21	G(-CH_2-)	1.1
F(-CH-)	1.11	G(-CH-)	1.05
F(-C-)	1	G(-C-)	1
F(-OH)	2.1	G(-OH)	0.44
F(-COOH)	0.07	G(-COOH)	0.7
F(-COO^-)	0.24	G(-COO^-)	1.23
C(C4)	0.6	C(C6)	1
C(C5)	0.8	C(C7)	0.9

Inductive electron donnors

Group	***R***	F
OH	-1.89	+0.46
COOH	+0.66	+0.44
COO^-	+0.40	-0.27

Resonance (*R*) and Field (*F*) values as defined by Swain and Lupton (1968) .

Monod and Doussin, 2008

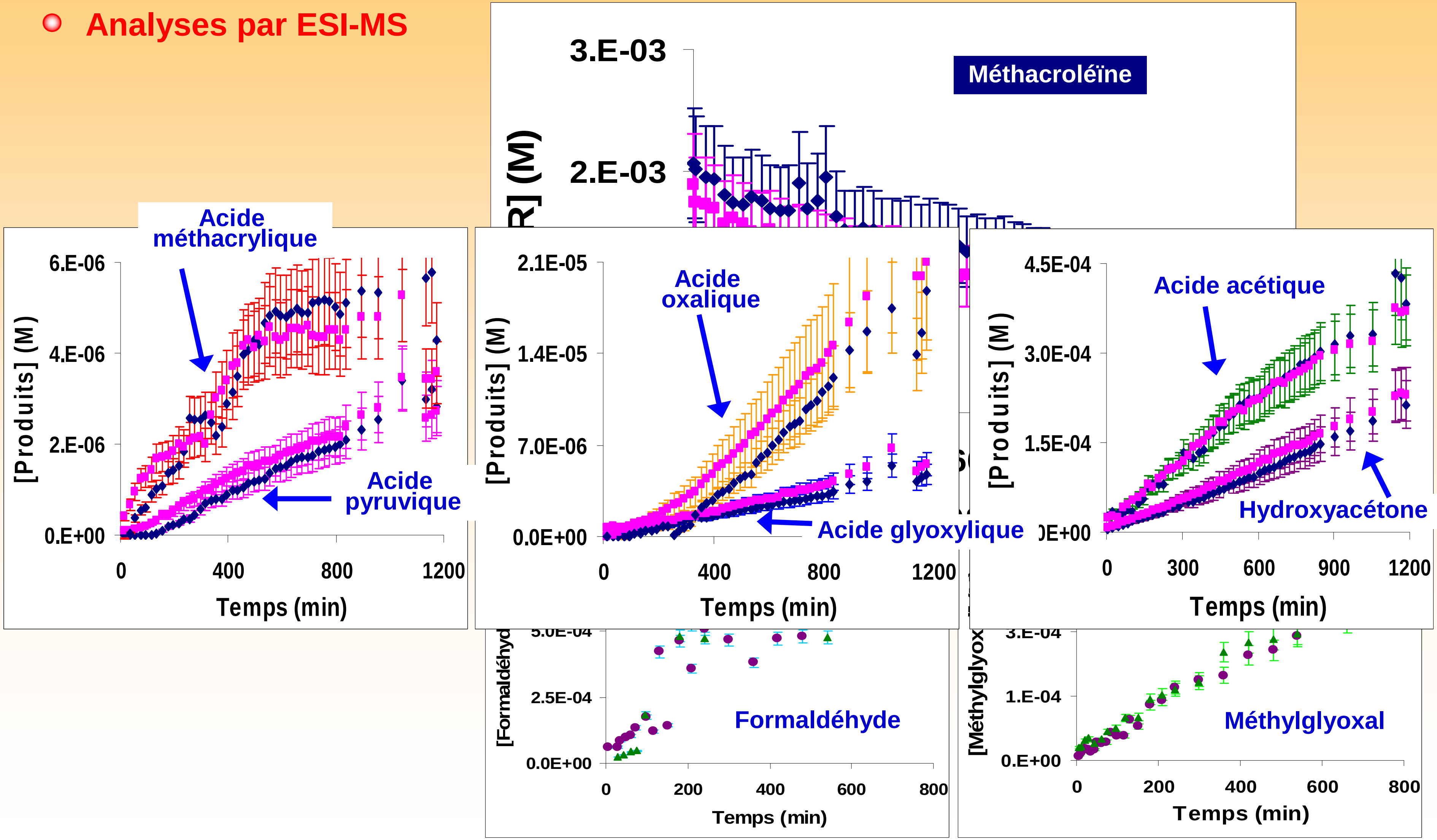
Phase aqueuse

Suivi de l'évolution de méthacroléïne et des produits formés

Expérience à pH libre

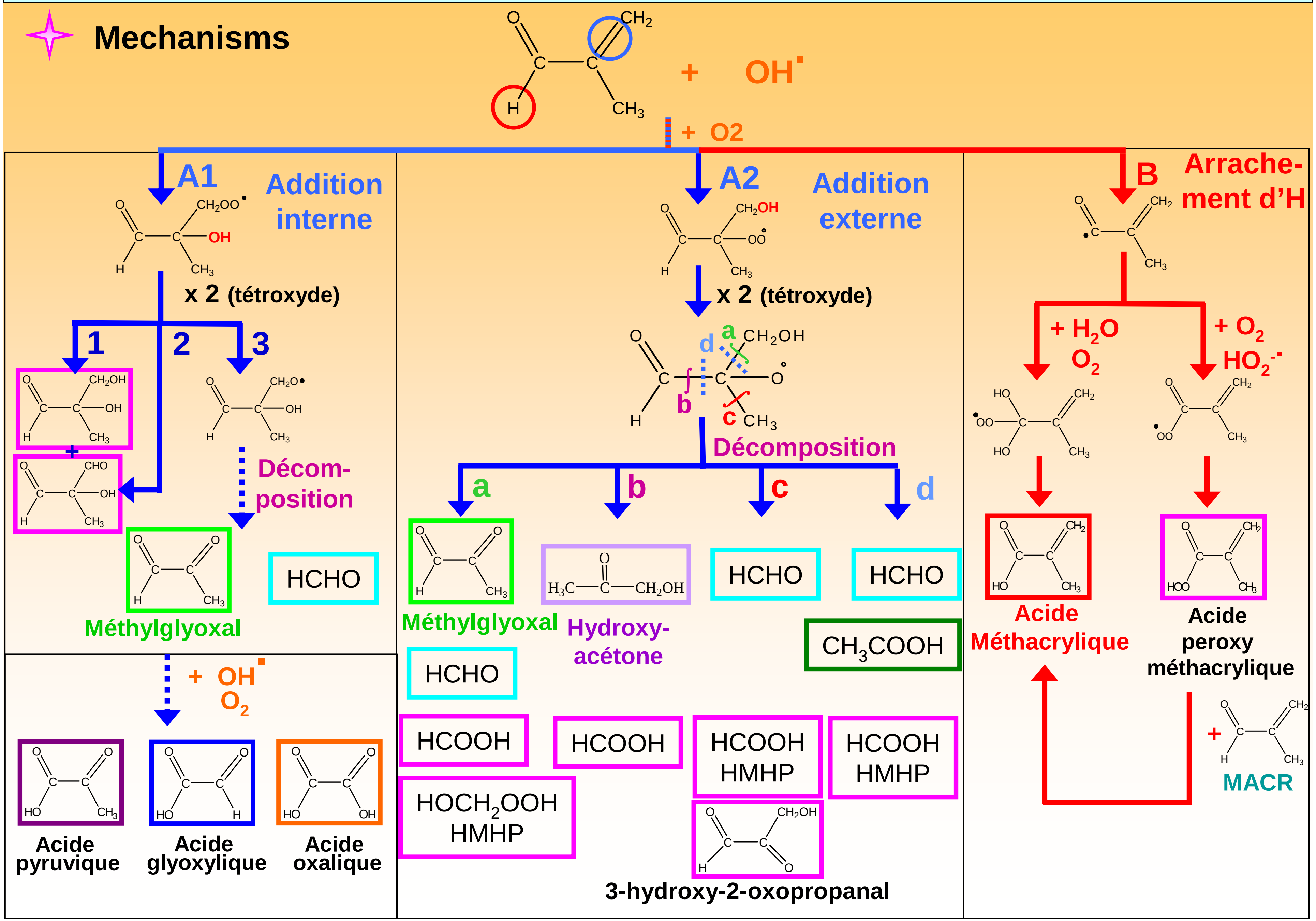
Méthacroléïne

- **Analyses par ESI-MS**



Phase aqueuse

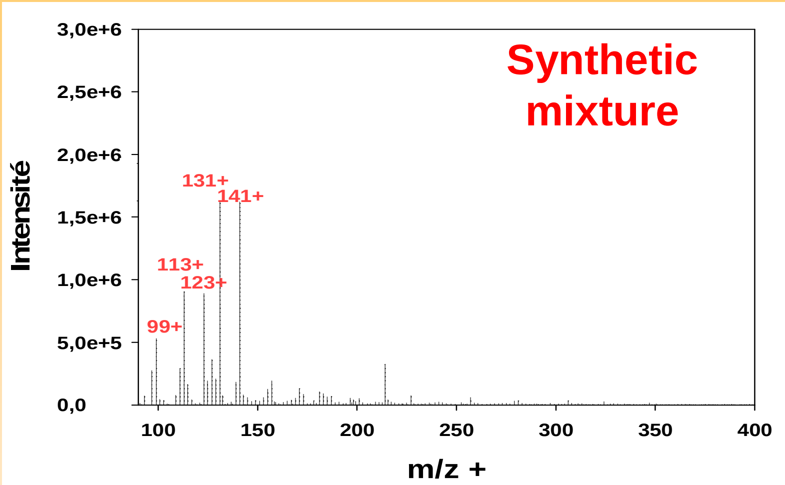
Mechanisms

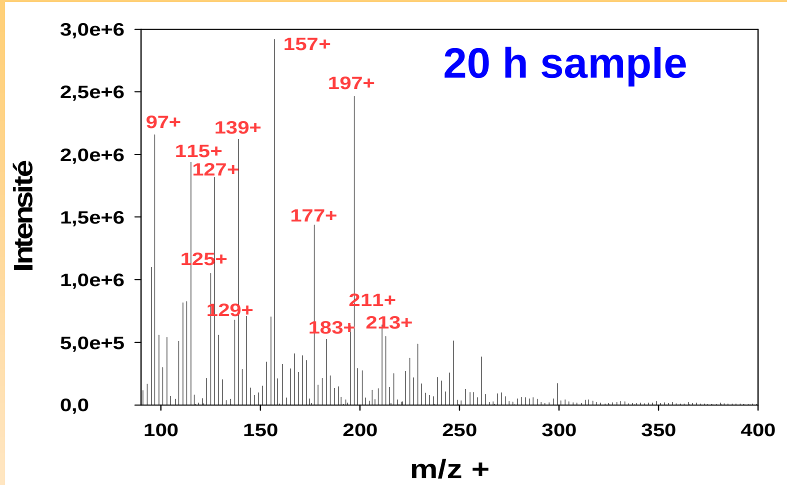


Photooxidation of methacrolein

Comparison with synthetic mixtures

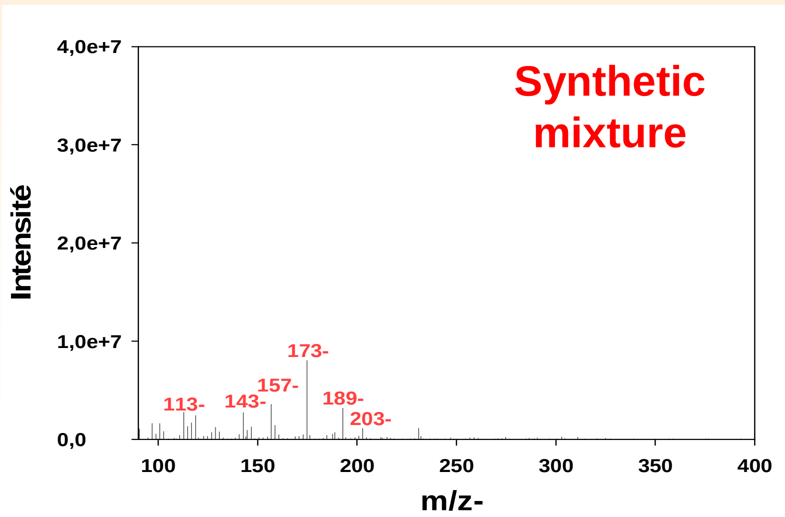
Mode +

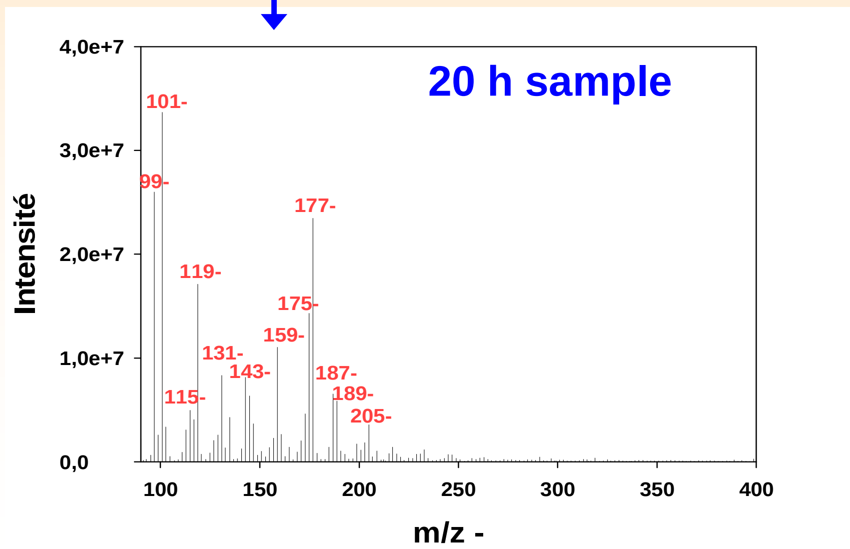




$3x10^{-3}$ M : MACR
$6x10^{-4}$ M : formaldehyde, methylglyoxal, AcOH
formic, acetic acids
$3x10^{-5}$ M : pyruvic, oxalic, glyoxylic, methacrylic

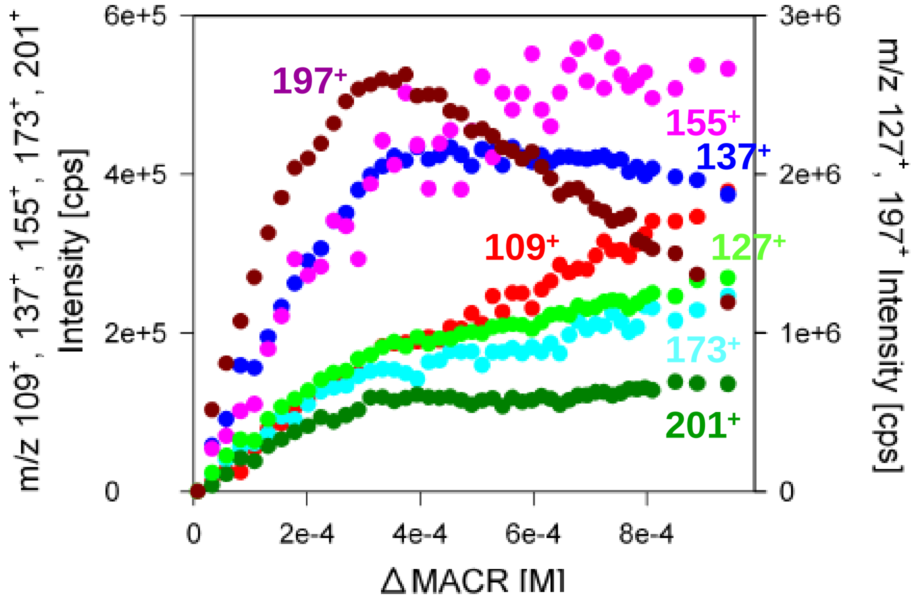
Mode -

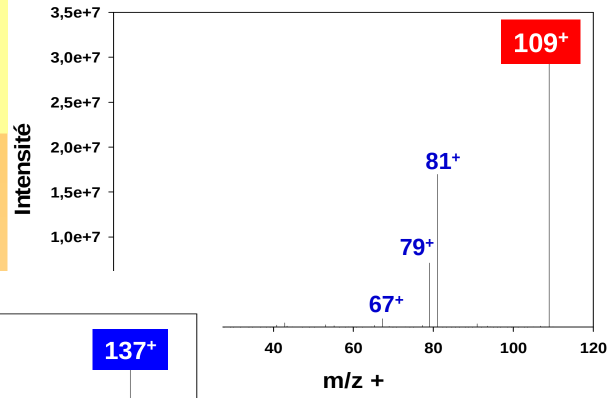


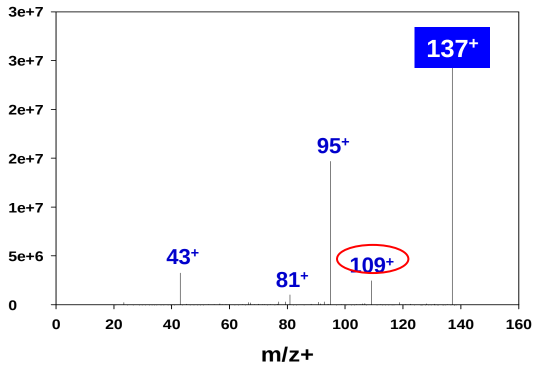


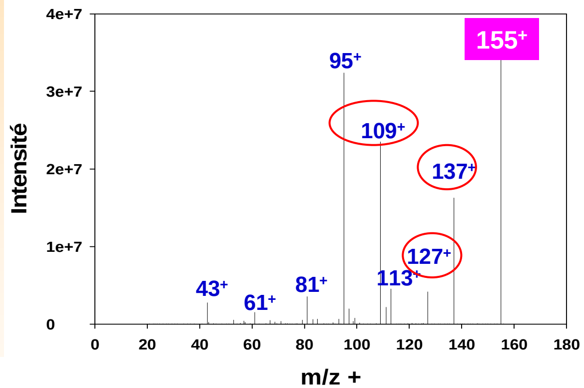
Photooxidation of methacrolein

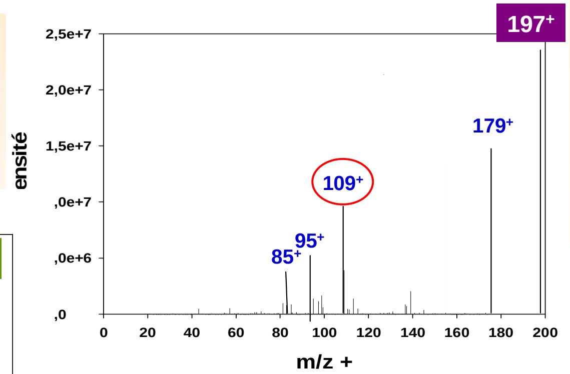
Oligomer series

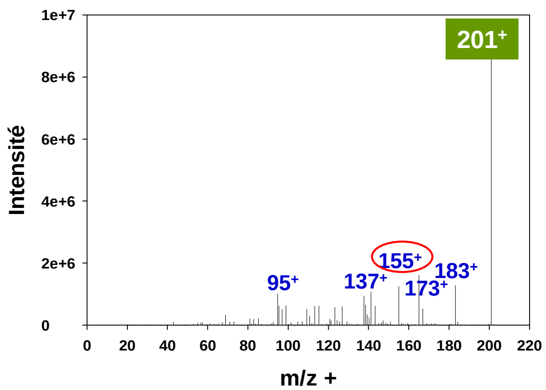


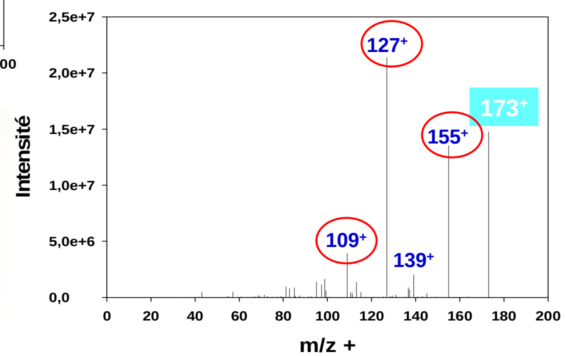












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