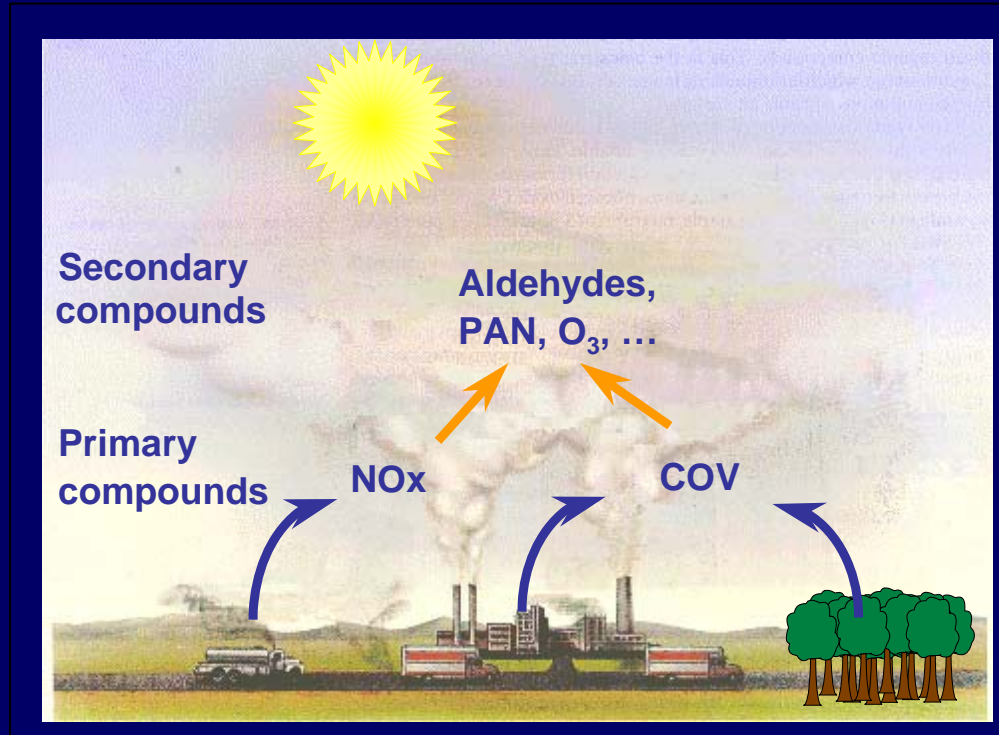


Reactivity of Unsaturated Oxygenated VOC with NO_3 radical

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Tropospheric oxidation of VOC

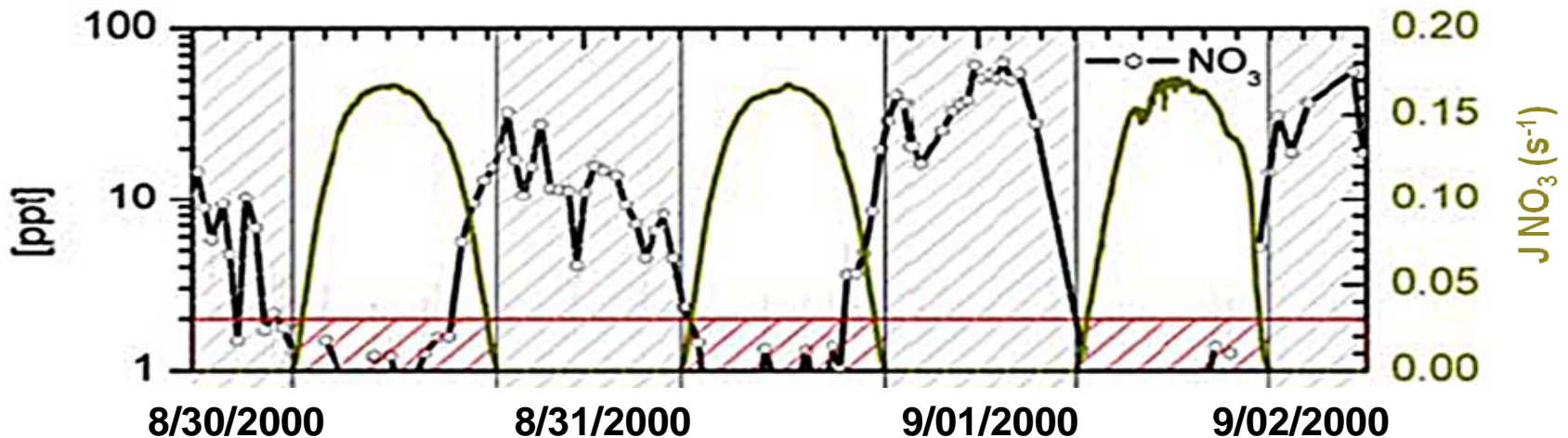


The nitrate radical

NO₃ sources:



NO₃ fates:



Geyer et al, 2003 (Houston, Texas), ground measurement

Reactivity of VOC towards NO₃



Compound	τ_{NO_3} ([NO ₃]= 5.10 ⁶ molecule cm ⁻³)*	τ_{OH} ([OH]= 2.10 ⁶ molecule cm ⁻³)	τ_{O_3} ([NO ₃]= 7.10 ¹¹ molecule cm ⁻³)*
3-methylpentane	3,2 year	1 day	-
Acetaldehyde	2,5 year	10 h	755 years
2-methylbutanal	1,4 days	4h	-
Pentene	152 days	4,5 h	1,7 days
Trans-2-butene	6,3 days	14 min	42 min
6-methyl-5-hepten-2-one	8 h	53 min	1 h
α -pinene	9 h	3 h	5 h
β -pinene	23 h	2 h	1,1 days
2-carene	3 h	2 h	2 h

** : [NO₃]=10.2 ppb, [OH]=330 ppb

(Atkinson et Alvey, 2000)

NO₃ + VOC: state of the art

- Lab studies -

- Many lab studies in the 80's (alkenes, cycloalkenes and haloalkenes)
- since the 90's, kinetic and mechanistic studies on oxygenated VOC:
 - ❖ *alcohols (Canosa-Mas et al, 1999, Noda et al, 2002, Pfrang et al, 2005, ...),*
 - ❖ *carbonyls (D'Anna et al, 2001, Hallquist et al, 1997, Cabanas et al, 2001, ...),*
 - ❖ *ethers (Klotz et al, 2004, ...)*
- ... but reactivity of oxygenated VOC still be poorly understood (compared to their reactivity towards OH)

NO₃ + VOC: state of the art

- previsions by SARs -

- SARs development requires a large database of kinetic data
- SARs for NO₃-oxidation kinetics based on both experimental data and theoretical calculations (HOMO energy) (*King et al, 1999, Pfrang et al, 2006, Grammatica et al, 2003*)
- Moreover, great sensitivity of reactivity with NO₃ to the chemical structure

⇒ **predictions for NO₃-oxidation are less reliable**

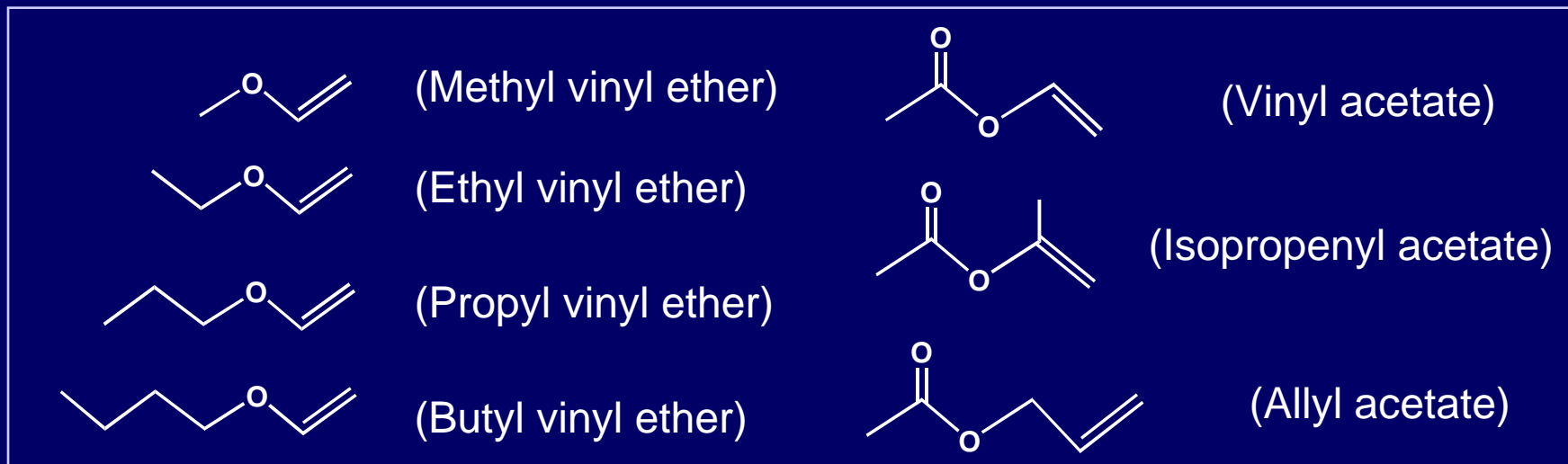
- Oxygenates + NO₃ : unsaturated esters and ketones (*Pfrang et al, 2007*)

$$0.05 < k_{\text{measured}}/k_{\text{predicted}} < 30$$

⇒ **Larger kinetic database is absolutely needed !**

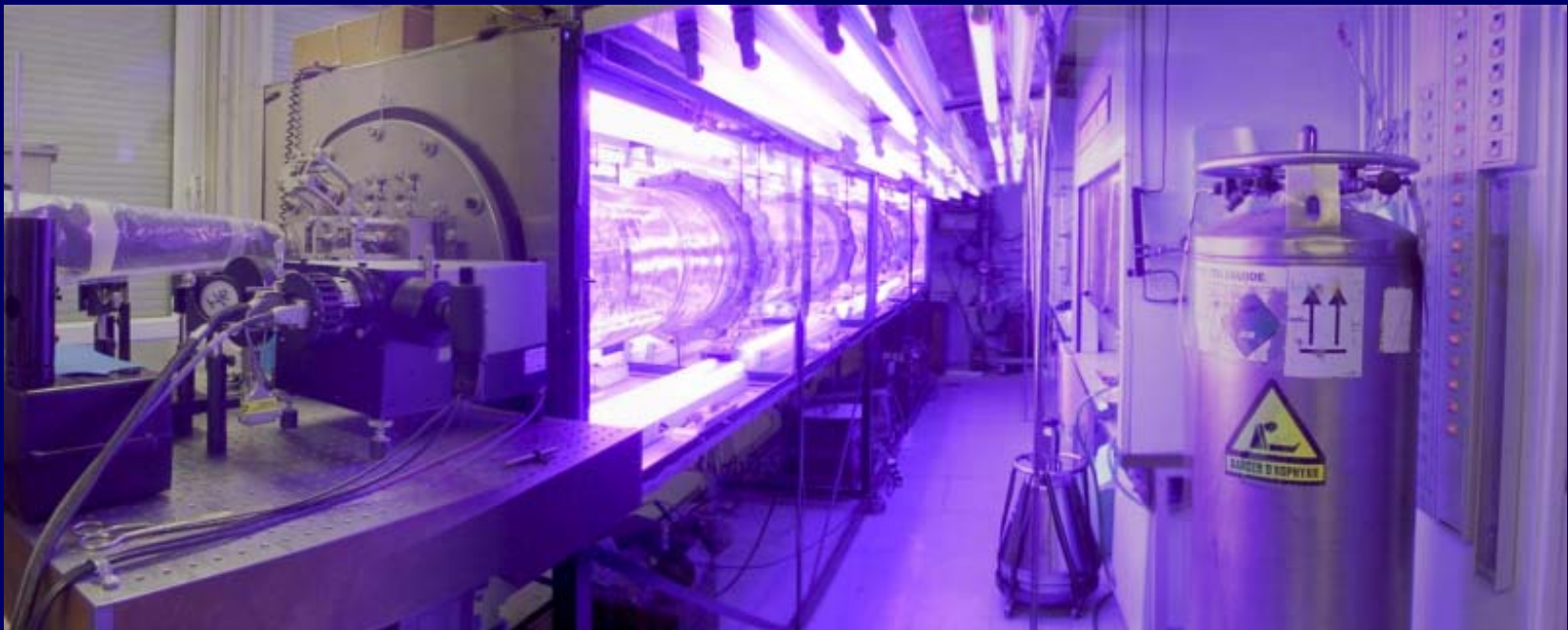
Aim of this study

- **New experiments on NO_3 -oxidation of unsaturated oxygenates** : vinyl ethers and esters emitted by anthropogenic sources (solvents, fuel combustion)
- **Influence of oxygenated functions and alkyl chain ?**
“Systematic approach” - Useful for SARs parametrisation

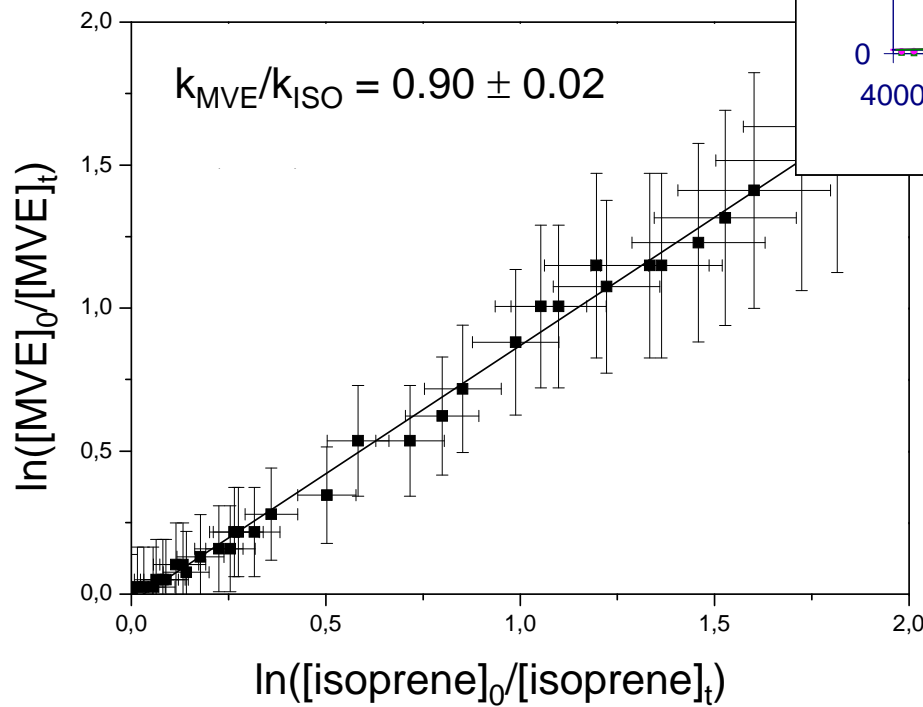
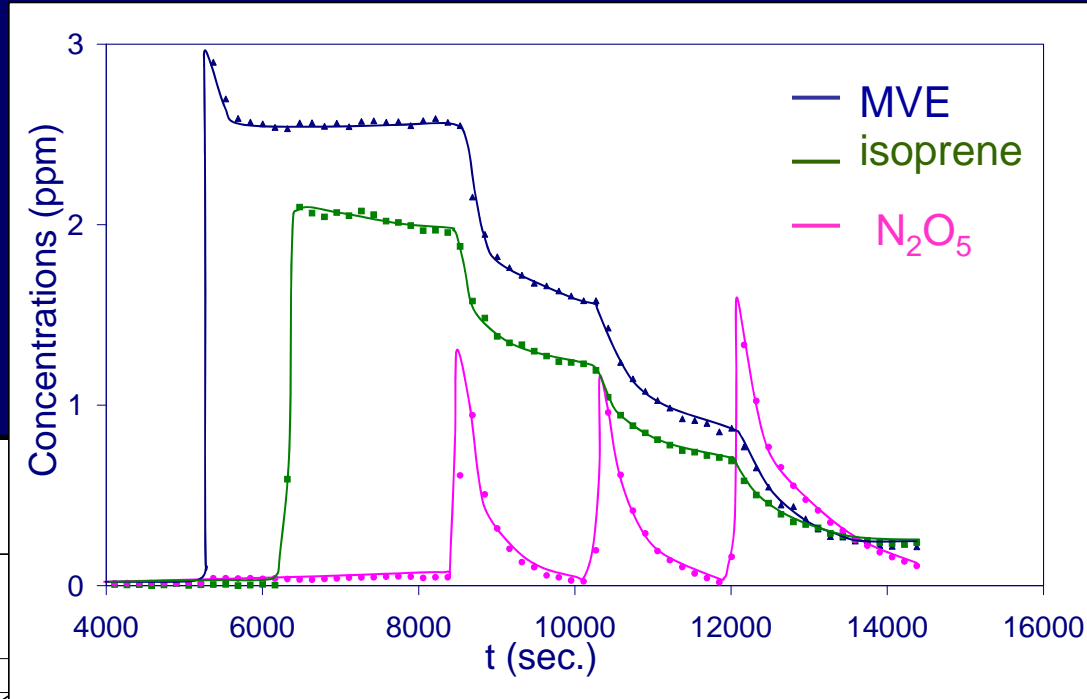


Kinetics and mechanisms investigations

- Use of a 1 m³ Pyrex photoreactor
- Use of *in-situ* long path FTIR (156 m) and *in situ* long-path UV-visible spectrometer (72 m) as analytical techniques
- Use of N₂O₅ (synthesized in the cold trap of a vacuum ramp) as NO₃ radicals source
- Relative and absolute kinetics



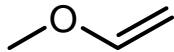
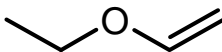
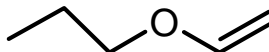
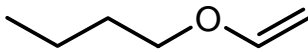
Example of relative rate experiment



$$\ln \frac{[MVE]_0}{[MVE]_t} = \frac{k_{\text{MVE}}}{k_{\text{ISO}}} \times \ln \frac{[ISO]_0}{[ISO]_t}$$

$k_{\text{ISO}} = 6.86 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$
(Berndt et al, 1996)

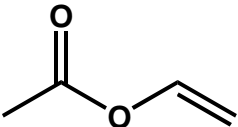
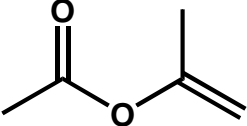
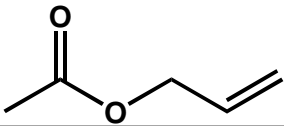
Kinetic results - ethers

Compound	$10^{13} \times k$ (*)	$10^{13} \times k_{\text{aver.}}$ (*)	Litterature (*)
MVE 	7.6 ± 0.4	7.2 ± 2.9	4.68 <i>(Grosjean et al., 1992)</i> <i>(SAR)</i>
	6.1 ± 1.1		
	6.3 ± 0.5		
EVE 	15.1 ± 3.3	13.1 ± 5.3	17 ± 13 <i>(Pfrang et al., 2006)</i> 14.0 ± 3.5 <i>(Zhou et al., 2006)</i>
	13.8 ± 1.5		
	14.5 ± 2.5		
PVE 	13.3 ± 1.8	13.3 ± 5.9	18.5 ± 5.3 <i>(Zhou et al., 2006)</i>
	12.8 ± 1.6		
	12.4 ± 2.0		
	15.1 ± 1.7		
BVE 	15.8 ± 1.8	17.0 ± 7.3	21.0 ± 5.4 <i>(Zhou et al. 2006)</i>
	18.9 ± 1.6		
	16.5 ± 1.4		

(*) : in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 (Reference compound : isoprene)

Scarfogliero et al, 2006
Journal of Physical Chemistry A

Kinetic results - esters

Compound	$10^{15} \times k$ (relative rate) ^(*)	$10^{15} \times k$ (absolute rate) ^(*)	Litterature ^(*)
Vinyl acetate 	7.5 ± 0.5 (ref: propene)	7.1 ± 1.9	141 (Grosjean et al., 1992) (SAR)
Isopropenyl acetate 	110 ± 10 (ref: isoprene)	-	-
Allyl acetate 	1.0 ± 0.3 (ref: methacrolein)	0.7 ± 0.6	-

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

- First experimental determination
- Large difference of reactivity between these three esters !

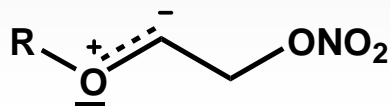
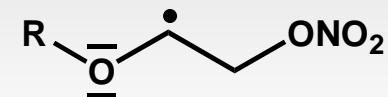
Influence of the oxygenated function ?

Alkyl group	Alkenes (R-CH=CH ₂)	Ethers (R-O-CH=CH ₂)	Esters (RC(O)O-CH=CH ₂)
CH ₃ ⁻	(6.4 ± 0.8).10 ⁻¹⁵	(7.2 ± 1.5).10 ⁻¹³	(7.6 ± 1.0)10 ⁻¹⁵
C ₂ H ₅ ⁻	(13.5 ± 4.1).10 ⁻¹⁵	(13.1 ± 2.7).10 ⁻¹³	-
C ₃ H ₇ ⁻	(15 ± 5).10 ⁻¹⁵	(13.3 ± 3.0).10 ⁻¹³	-
C ₄ H ₉ ⁻	(18 ± 7).10 ⁻¹⁵	(17.0 ± 3.7).10 ⁻¹³	-

X 100

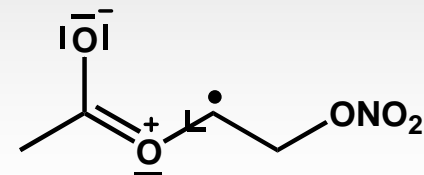
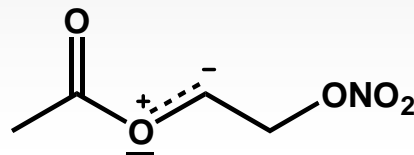
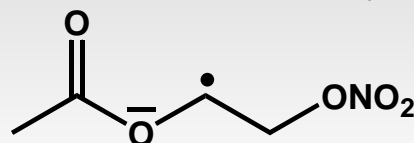
- Ether -

stabilisation by resonance
donating effect



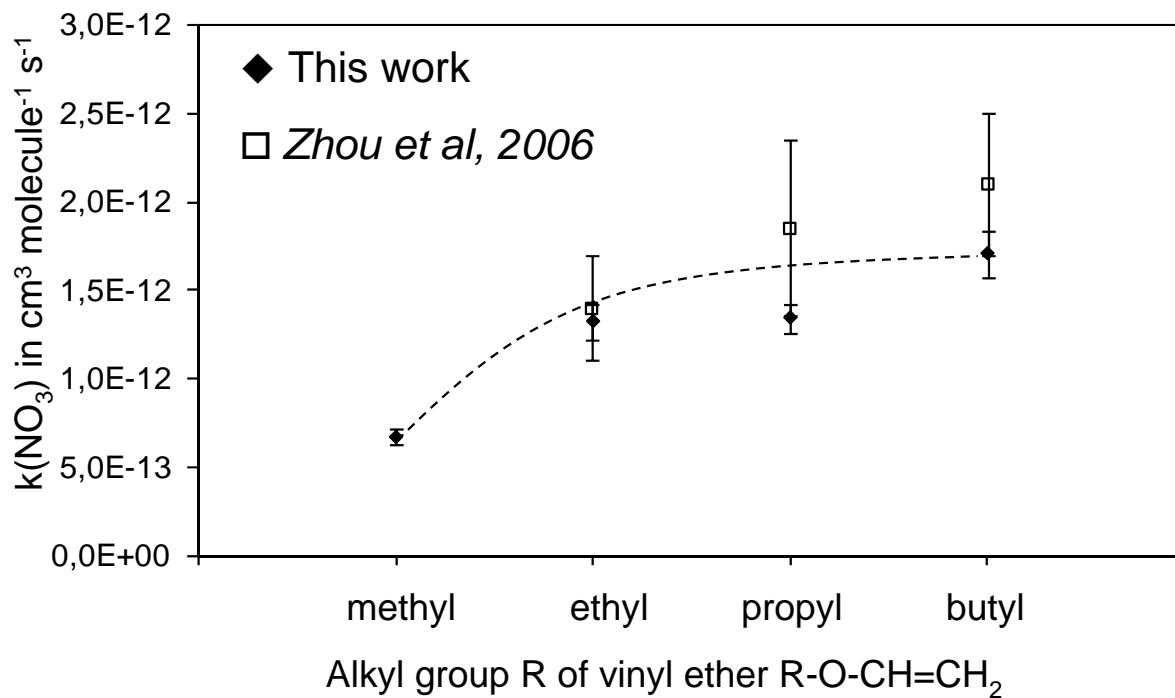
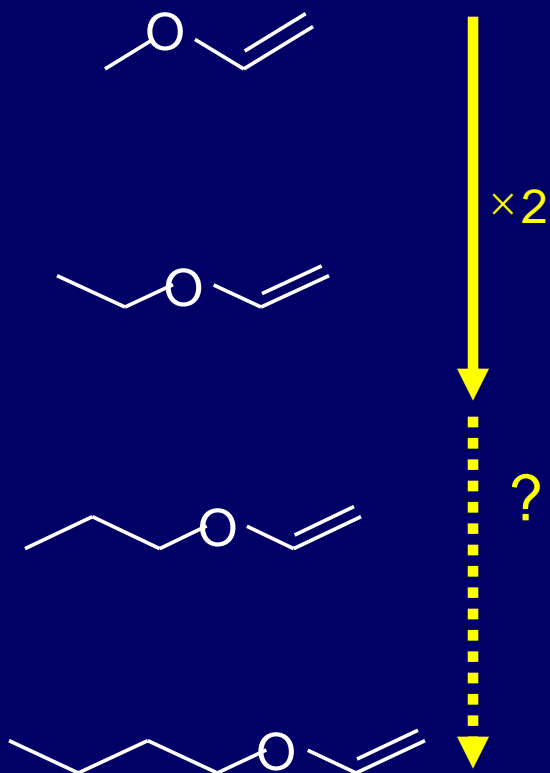
- Ester -

stabilisation by resonance donating effect +
destabilisation by withdrawing inductive effect



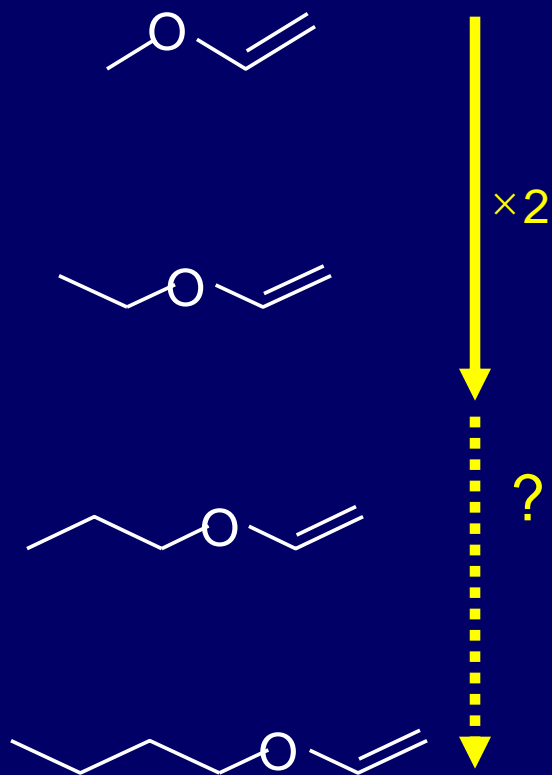
Influence of the alkyl chain ?

Ethers

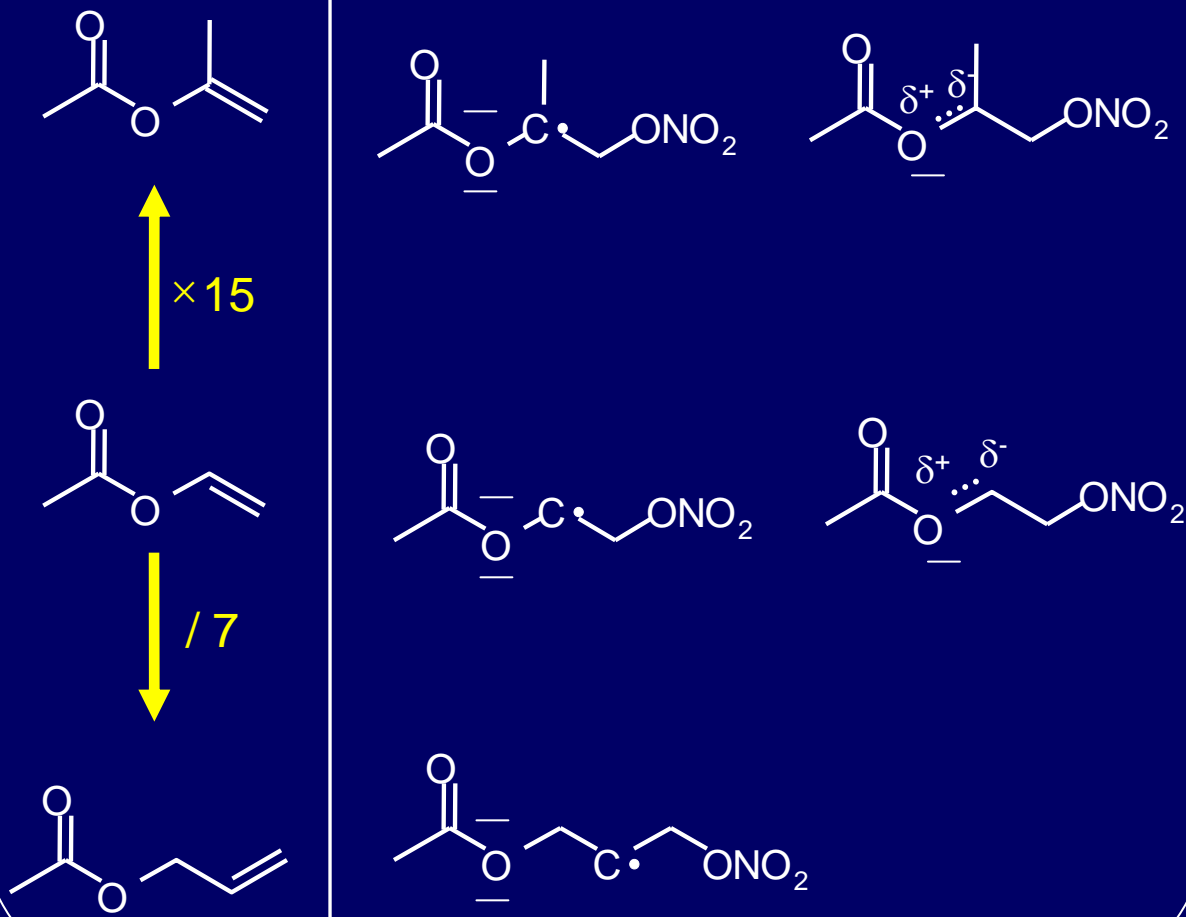


Influence of the alkyl chain ?




Ethers



Esters



Atmospheric implications (lifetimes)

Compound	 $\tau_{\text{NO}_3}^a$ ([NO ₃] = 50 ppt) (night time polluted area)	 $\tau_{\text{NO}_3}^a$ ([NO ₃] = 1 ppt) (daytime polluted area)	 $\tau_{\text{OH}}^{b,c,d}$ ([OH] = 2×10 ⁶ molecule cm ⁻³)
Methyl vinyl ether	20 min	16 h	3 h
Ethyl vinyl ether	10 min	8 h	2 h
Propyl vinyl ether	10 min	8 h	1.5 h
Butyl vinyl ether	8 min	6 h	1.5 h
Vinyl acetate	30 h	60 days	2.8 h
Isopropenyl acetate	2 h	4 days	2 h
Allyl acetate	9 days	460 days	5 h

a : This work; *b* : Thiault, 2002; *c* : Ferrari, 1996; *d* : Grosjean et al.1992

⇒ Nighttime NO₃-oxidation is a significant loss process for vinyl ethers and isopropenyl acetate

⇒ Daytime NO₃-oxidation is a minor (but not negligible) loss process for vinyl ethers

Atmospheric implications (products)

Compound	NO ₃ -oxidation products (<i>This work</i>)	OH-oxidation products (<i>Thiault et al, 2002;</i> <i>Scarfogliero, 2007; this work</i>)
Vinyl ethers	Formaldehyde (~50%) Alkyl formates (~50%) Organic nitrates (~50%)	Formaldehyde (65-95%) Alkyl formates (70-90%)
Vinyl acetate	Formaldehyde (~80%) Acetic anhydride (~80%) Organic nitrates (~20%)	Formaldehyde (detected) Acetic anhydride (~80%)
Isopropenyl acetate	Formaldehyde (~45%) Formic acetic anhydr. (~45%) Organic nitrates (~55%)	Formaldehyde (~95%) Formic acetic anhydr. (~90%)

NO₃-oxidation of oxygenates produces large amount of organic nitrates

⇒ *Impact on NO_x transport in rural area ?*

Conclusion

- Kinetic and mechanistic results for vinyl ethers in good agreement with those published at the same time (*Zhou et al, 2006, Pfrang et al, 2006*)
- First results for unsaturated esters
- NO₃-oxidation is a major tropospheric loss process of vinyl ethers and isopropenyl acetate
- “Systematic approach” useful to improve parametrisation by SARs
- Strong activation effect of the ether function

Future outlook

- Complete kinetic database for oxygenates to improve predictions by SARs
- Impact of NO_3 -oxidation for very reactive VOC (oxygenated biogenics and aromatics) on diurnal chemistry ?
 - ❖ intensively emitted
 - ❖ reactions with NO_3 poorly studied
 - ❖ high reactivity suspected (unsaturation(s) + oxygenated functions)
 - ❖ suspected to play a key role even during the day (*as monoterpenes whom NO_3 -oxidation is estimated to be equal to 10-40% of their diurnal oxidation*)
- Need of further mechanistic studies – identification and quantification of functionalised organic nitrates in VOC + NO_3 reactions
- + reactivity of functionalised organic nitrates ?
 - ❖ impact on NO_x transport ?
 - ❖ impact on SOA formation ?

Acknowledgments

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