

**Cl-ATOM AND OH-RADICAL INITIATED OXIDATION OF
UNSATURATED ESTERS:
TEMPERATURE DEPENDENT STUDIES UNDER ATMOSPHERIC CONDITIONS**



Ian Barnes
University of Wuppertal, Germany

Scientific co-operation between:

University Wuppertal, Germany and University of Cordoba, Argentina

(DAAD and SECyT) : PROALAR

Ian Barnes, Iustinian Bejan, Stefan Kirschbaum and Peter Wiesen
*University of Wuppertal, FB-C - Physikalische Chemie, Gauß Straße 20, 42119
Wuppertal, Germany.*

María B. Blanco and Mariano A. Teruel
*Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de
Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba.
Ciudad Universitaria, 5000 Córdoba, Argentina.*

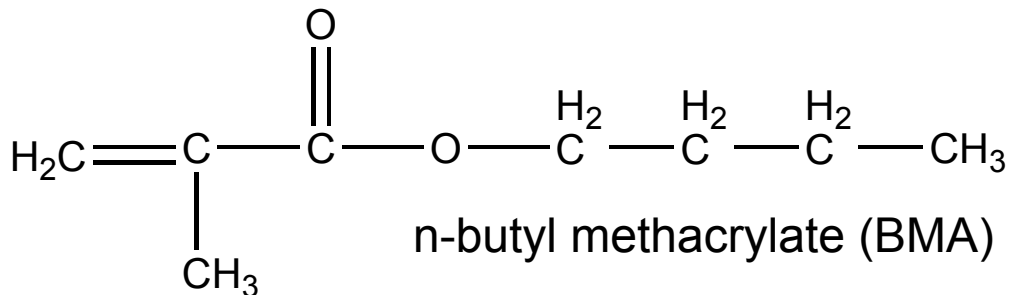
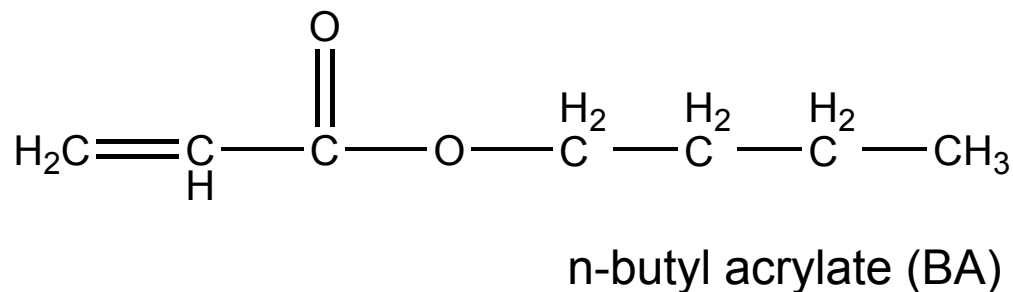
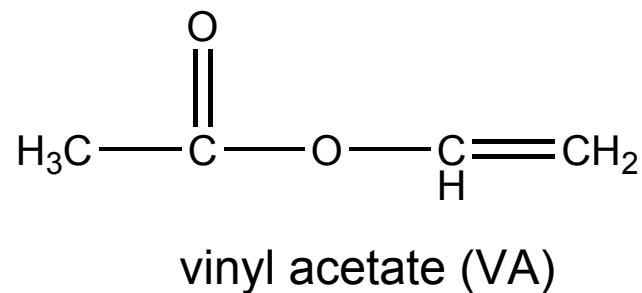
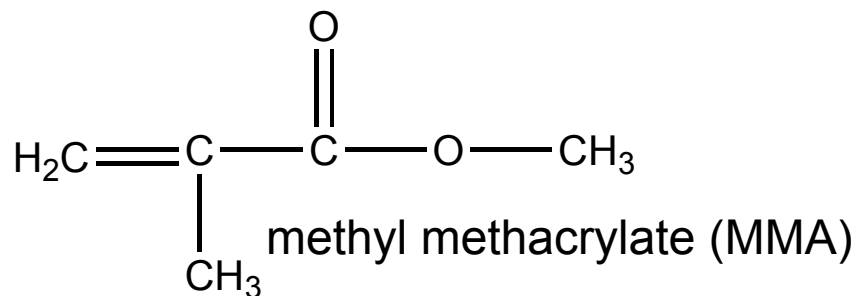
New French-German project examining mainly alkyl esters:
Wuppertal (I. Barnes) / Orleans (W. Mellouki)

Unsaturated esters: Uses and atmospheric sources

- Acrylates and methacrylates are employed as intermediates in the manufacture of polymers and plastics.
- The most important polymer types are cast acrylic sheets and molding/extrusion compounds in addition to emulsions, dispersions and solvent based polymers.
- The unsaturated esters studied are all listed as high (H) production (P) volume (V) chemicals in the OECD integrated HPV database.
- Releases of the unsaturated esters to the atmosphere are expected to be mainly during their production, processing, storage and disposal. Fugitive and stack emissions will be additional atmospheric sources.

Despite large potential releases of the unsaturated esters to the atmosphere there have been surprisingly few measurements of their ambient concentration levels and most of the measurements are relatively old.

Unsaturated esters investigated



Journal Physical Chemistry A : online ASAP

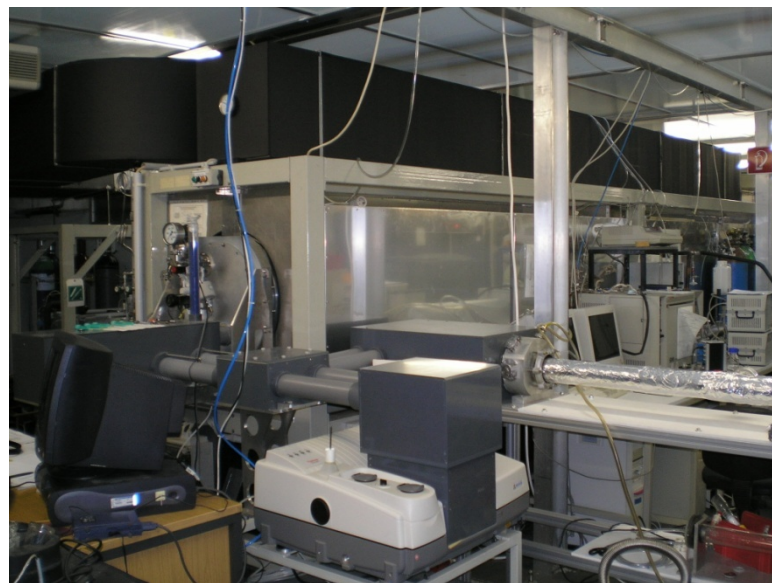
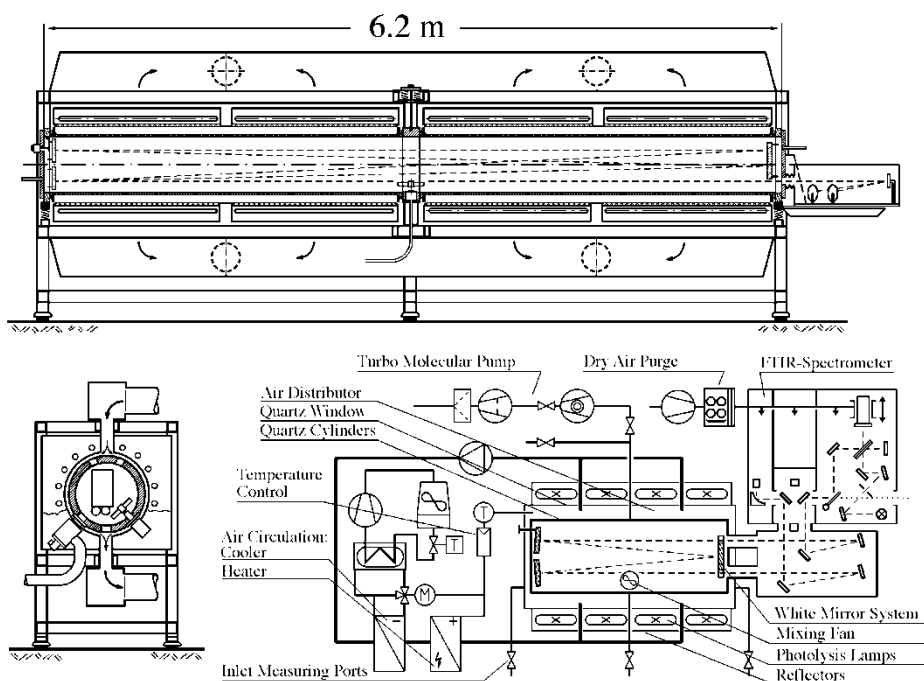
[OH-Initiated Degradation of Unsaturated Esters in the Atmosphere: Kinetics in the Temperature Range of 287–313 K](#)

M. B. Blanco, I. Bejan, I. Barnes, P. Wiesen and M. A. Teruel

Publication Date (Web): April 30, 2009 (Article)

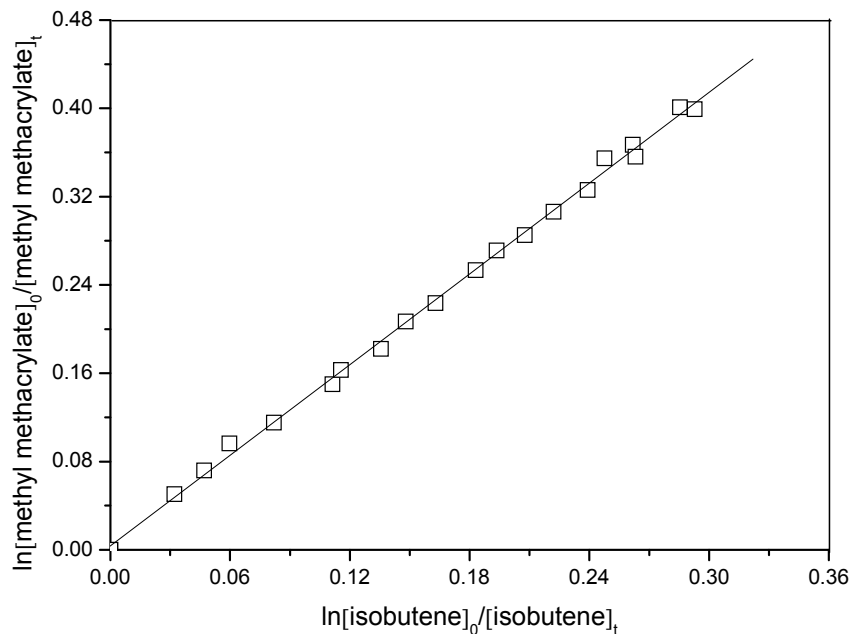
DOI: 10.1021/jp901755x

1080 L Photoreactor Wuppertal



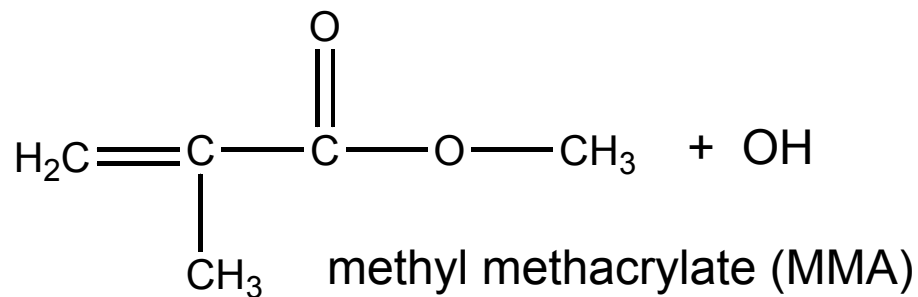
6 Meter or 1080 l reactor (~ 1990)
In situ FITR, GC and DMA
Base path 6 meter, total path 484,7 m

Kinetic Studies on OH with Unsaturated Esters

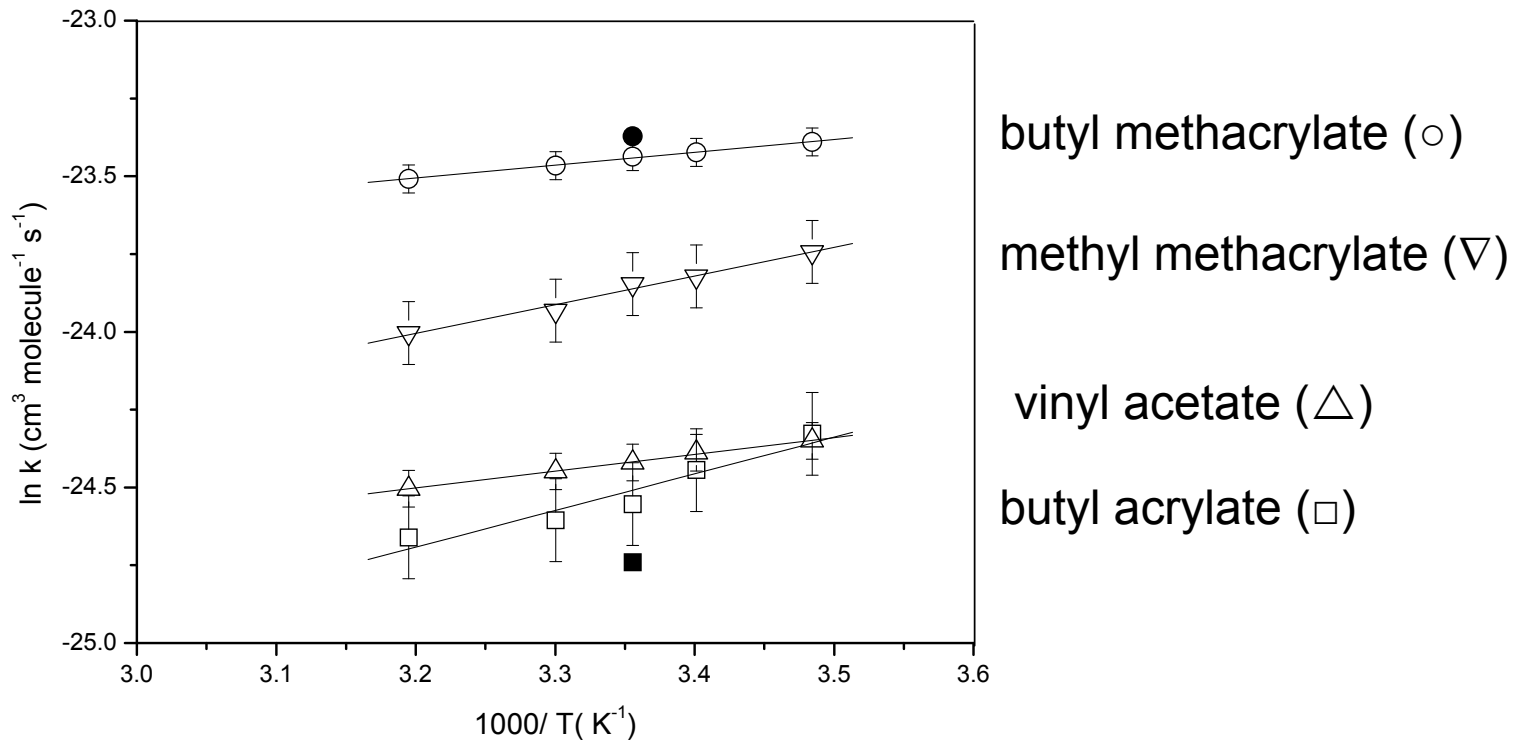


Relative kinetic technique

$$\ln \left\{ \frac{[\text{Ester}]_0}{[\text{Ester}]_t} \right\} = \frac{k_{\text{Ester}}}{k_{\text{ref}}} \ln \left\{ \frac{[\text{Ref}]_0}{[\text{Ref}]_t} \right\}$$



Arrhenius plots of the kinetic data obtained in this study between 287 and 313 K for the reactions of OH with unsaturated esters.



The 298 K single values from Blanco et al. (2006) (\bullet) and Blanco et al. (2008) (\blacksquare)

The following Arrhenius expressions adequately describe the data in the temperature range 287-313K with k in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$:

$$k_1 (\text{OH}+\text{MMA}) = (1.97 \pm 0.95) \times 10^{-12} \times e^{(921 \pm 52)/T}$$

$$k_2 (\text{OH}+\text{BMA}) = (16.5 \pm 10.5) \times 10^{-12} \times e^{(413 \pm 34)/T}$$

$$k_3 (\text{OH}+\text{BA}) = (0.44 \pm 0.25) \times 10^{-12} \times e^{(1177 \pm 56)/T}$$

$$k_4 (\text{OH}+\text{VA}) = (4.06 \pm 2.02) \times 10^{-12} \times e^{(540 \pm 49)/T}$$

Values of rate coefficients: are consistent with the available literature data for the reactions of OH radicals with other unsaturated oxygenated compounds.

Activation energies: are consistent with E_a/R for other unsaturated esters (-300 to -1000 K), unsaturated aldehydes (-333 to -510 K), and alkenes (~ -500 K)

Room Temperature Rate Coefficients: OH + unsat. esters

Ester	$k \times 10^{11}$ ($\text{cm}^3\text{molec}^{-1}\text{s}^{-1}$)	Technique	Reference	SAR ^b $k \times 10^{11}$ ($\text{cm}^3\text{molec}^{-1}\text{s}^{-1}$)
Methyl methacrylate	(3.9 ± 0.4)	PLP-LIF	Teruel et al. (2006)	
	(4.2 ± 1.1)	RR-GC	Teruel et al. (2006)	
	(4.15 ± 0.32)	RR-GC	Blanco et al. (2006)	
	(2.6 ± 0.5)	DF-LIF	Saunders et al. (1994)	
	(4.30 ± 0.98)	RR-FTIR	This work	1.83
Butyl methacrylate	(7.08 ± 0.75)	RR-GC	Blanco et al. (2006)	
	(6.63 ± 1.42)	RR-FTIR	This work	2.27
Butyl acrylate	(1.80 ± 0.26)	RR-GC	Blanco et al. (2008)	
	(2.17 ± 0.48)	RR-FTIR	This work	1.38
Vinyl acetate	(2.5 ± 0.4)	DF-LIF	Saunders et al. (1994)	
	(2.48 ± 0.61)	RR-FTIR	This work	2.63

double bond on the alkoxy oxygen side



more receptive toward OH radical than a double bond on the acyl side



e.g. the rate coefficient for vinyl acetate of

$$2.48 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

almost two times higher than that for methyl acrylate

$$1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (Teruel et al. (2006))}$$

^b Structure activity relationship (SAR): Kwok and Atkinson (1995)

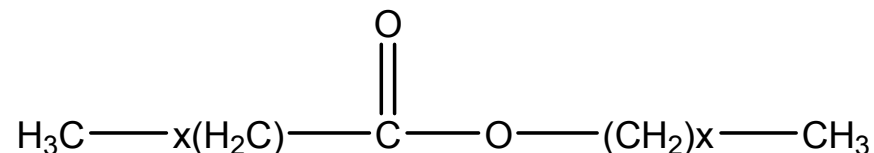
Group Rate Coefficients Estimation (GRC)

Mellouki, A.; Le Bras G. ; Sidebottom, H.

[Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase.](#)

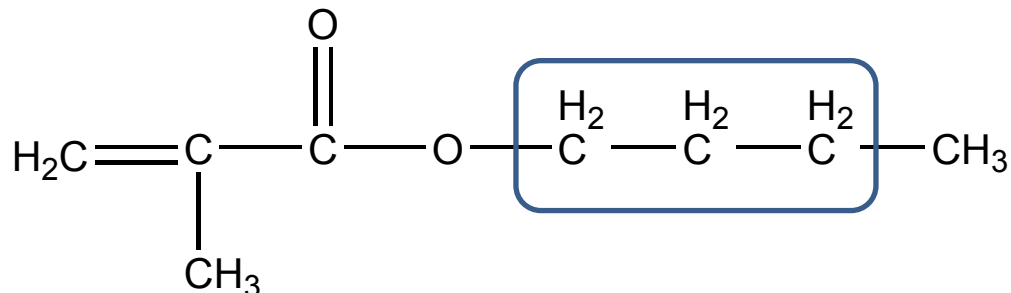
Chem. Rev. **2003**, 103(12), 5077- 5096.

- Mellouki et al. have calculated group rate coefficients for the CH_x ($x = 1, 2$ or 3) groups in alkyl esters (RC(O)OR) as a function of their position in the alkyl group chain relative to the functional group.
- calculations were based on the assumption that the reactivities of the groups on either side of the ether and carbonyl groups of the ester functionality are reasonably independent and additive.



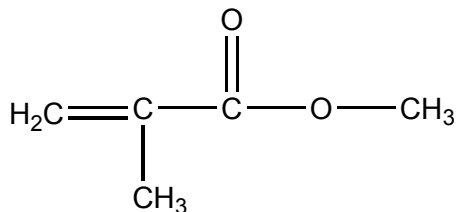
- It is interesting to test if these CH_x group rate coefficients derived for the alkyl esters are consistent with the rate coefficients reported here and in other studies for the unsaturated esters.

butyl methacrylate

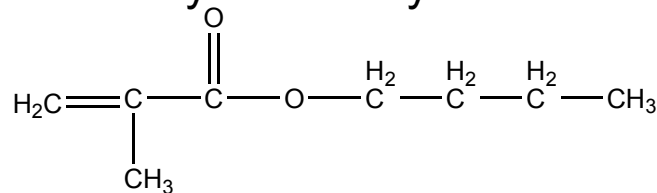


Using the group CH_x rate coefficients given in Mellouki et al. (2003) results in a value of $4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for OH with the $-\text{CH}_2\text{CH}_2\text{CH}_2-$ unit.

methyl methacrylate



butyl methacrylate

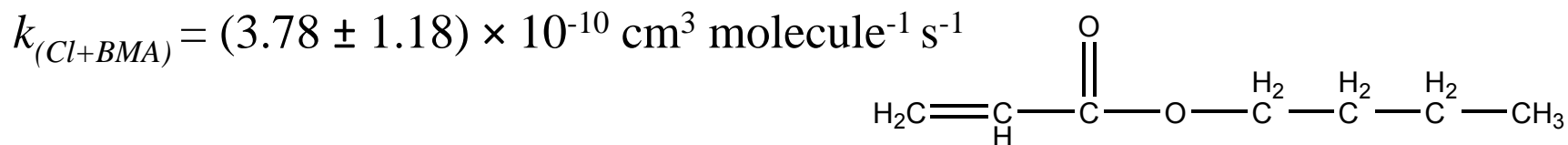
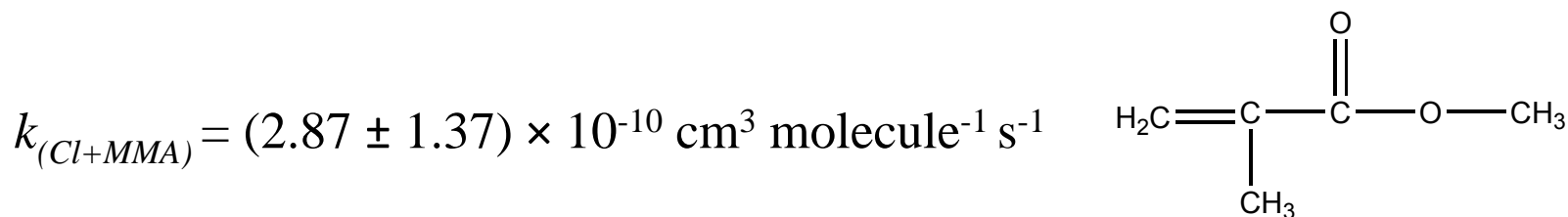
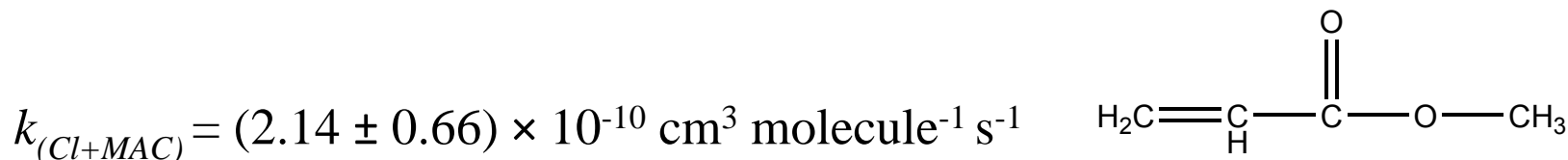


$$k_{\text{OH}} = 4.30 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad k_{\text{OH}} = 6.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Adding the $-\text{CH}_2\text{CH}_2\text{CH}_2-$ unit results in a Δk of $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Cl + Unsaturated Esters

Rate coefficients obtained at room temperature (298 K) in nitrogen and air as bath gases using propene, isobutene and 1,3-butadiene as reference hydrocarbons were as follows:



Cl + Unsaturated Esters

Studied over the temperature range 287-313 K relative to Cl + propene

Only available temperature dependent study for Cl + propene is:

Coquet S. and Ariya P. A. Int. J. Chem. Kinet. 32 (2000) 478-484

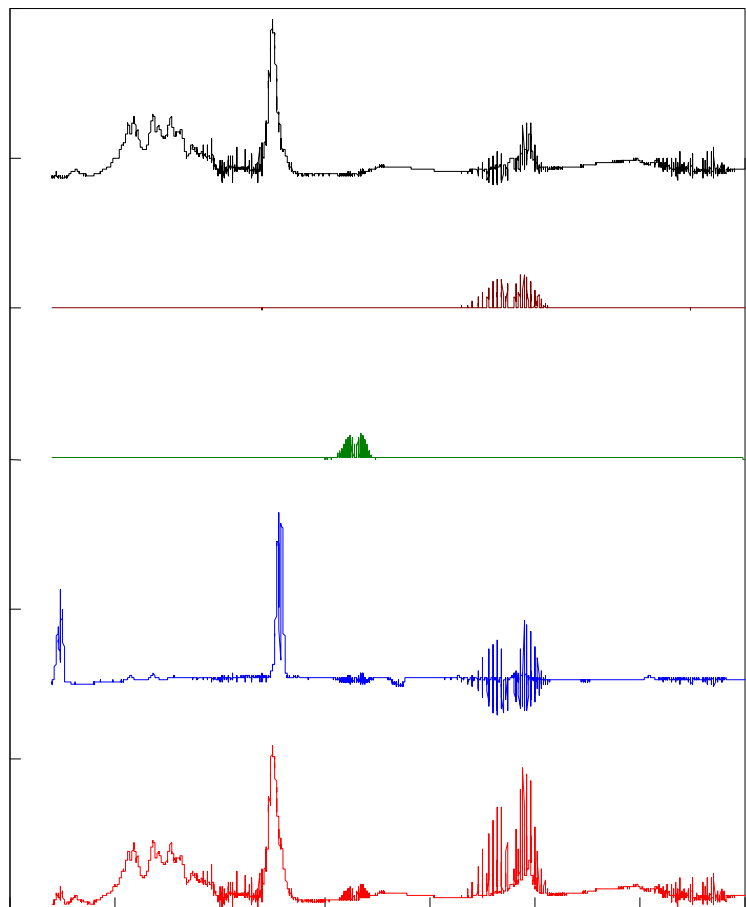
Warning: Arrhenius expressions in Coquet and Ariya (2000) for Cl + alkenes are erroneous

We have recently measured Cl + propene and Cl + butene as a function of temperature

$$\text{Cl + propene: } k = (1.59) \times 10^{-14} \exp\left(\frac{5.69}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Ea is in kcal /mol (preliminary)

Product Study Cl + methyl methacrylate



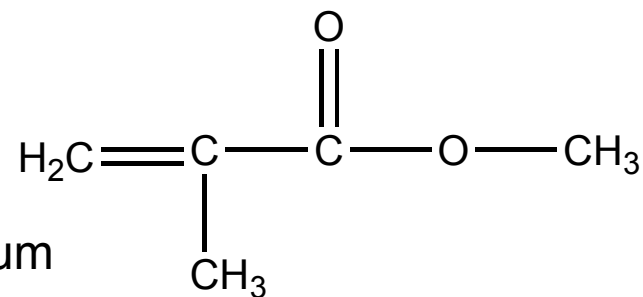
Residual spectrum

HCl

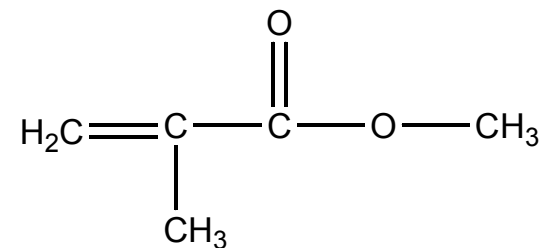
CO

Formyl chloride (HC(O)Cl)

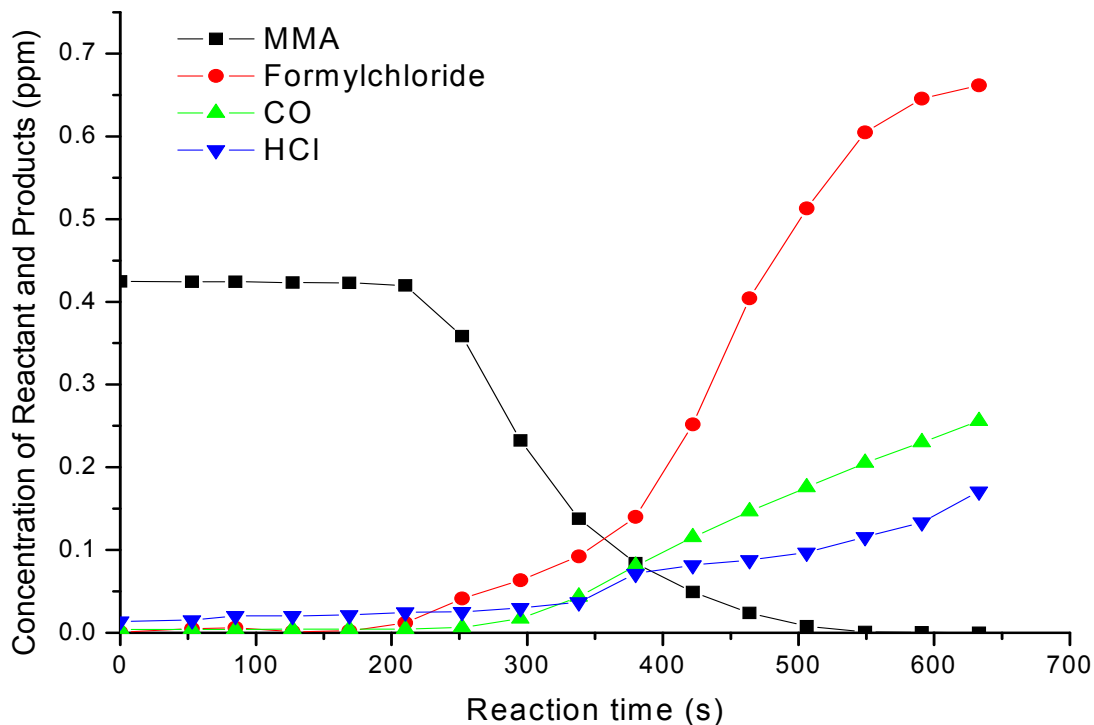
Product spectrum



Product Study Cl + methyl methacrylate



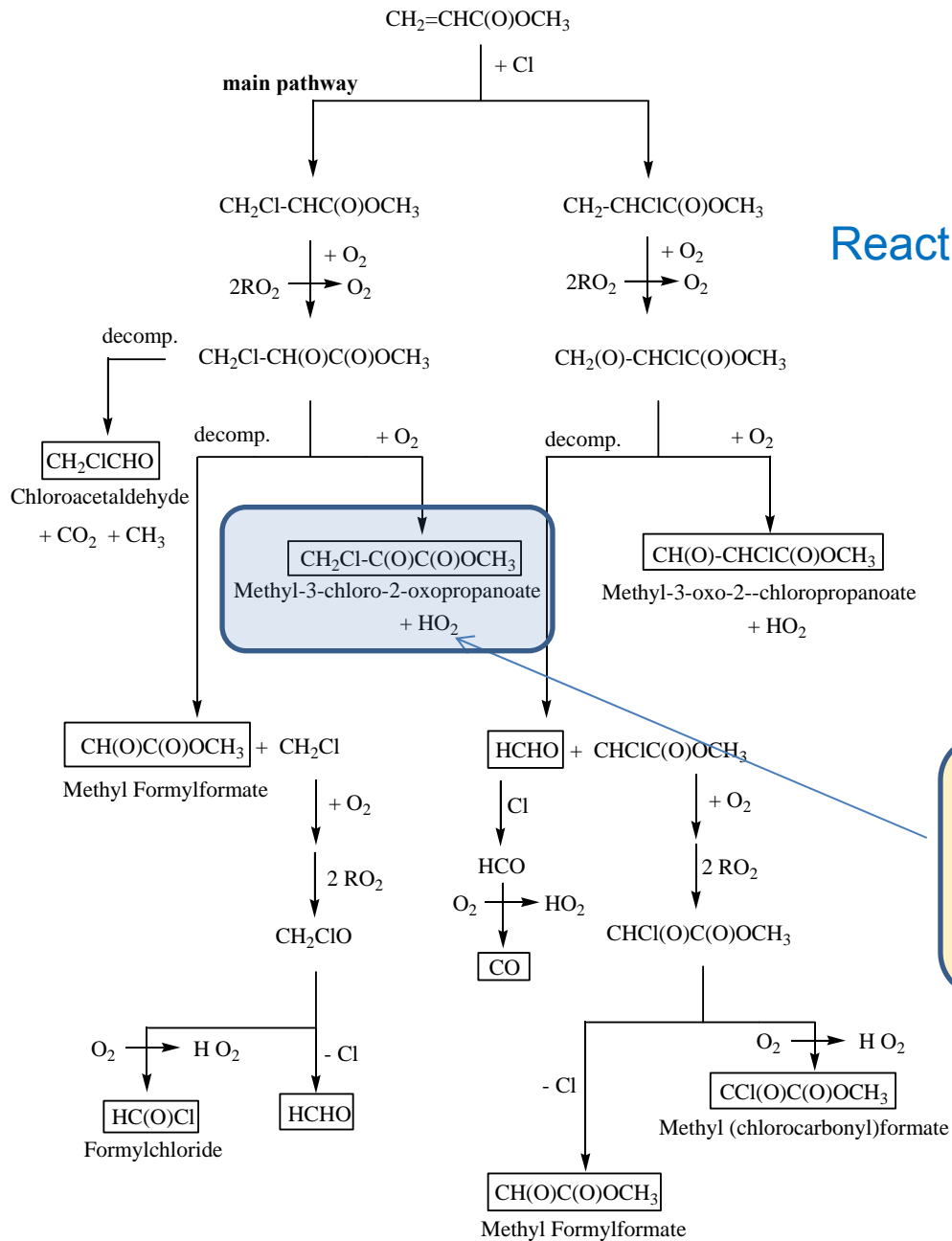
Typical concentration-time profile for the system methyl methacrylate/Cl₂/air.



HCl and CO are secondary products

Formyl chloride is both a primary and secondary product.

Primary yield ~ 25%



Reaction scheme for Cl + methacrylate

Here formyl chloride is a pure secondary product

Major primary product appears to be **methyl-3-chloro-2-oxopropanoate**

THANKS

for EUROCHAMP



see you next time in

EUROCHAMP-2



Also studied: Cl + four fluoroacetates (FACETs)

relative kinetic method, 298 ± 2 K, atmospheric pressure (760 ± 10 Torr)
1080 l quartz-glass photoreactor.

The following rate constants (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were derived:

$$k(\text{Cl} + \text{CF}_3\text{C}(\text{O})\text{OCH}_3) = (0.90 \pm 0.30) \times 10^{-13},$$

$$k(\text{Cl} + \text{CF}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_3) = (1.78 \pm 0.57) \times 10^{-12},$$

$$k(\text{Cl} + \text{CF}_2\text{HC}(\text{O})\text{OCH}_3) = (2.03 \pm 0.65) \times 10^{-13}$$

$$k(\text{Cl} + \text{CF}_3\text{C}(\text{O})\text{OCH}_2\text{CF}_3) = (1.18 \pm 0.43) \times 10^{-15}.$$

Results published:

M. B. Blanco, I. Bejan, I. Barnes, P. Wiesen, M. A. Teruel

Kinetics of the reactions of chlorine atoms with selected fluoroacetates at atmospheric pressure and 298 K

Chemical Physics Letters 453 (2008) 18–23