



The Atmospheric Oxidation of Unsaturated Oxygenated Compounds



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Sources of Oxygenated Organic Compounds

- Biogenic

mainly vegetative emissions eg 2-methyl-3-buten-2-ol, acetone, methanol, cis-3-hexen-1-ol, cis-3-hexenyl acetate and camphor

- Anthropogenic

vehicle emissions

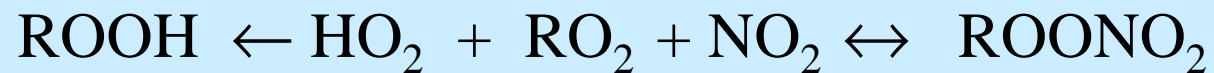
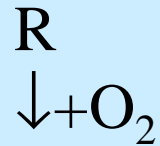
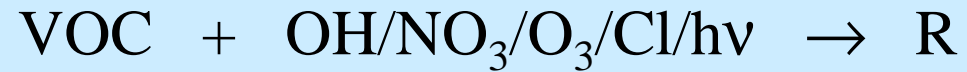
fuel additives

polymer manufacturing
and degradation

solvent usage

VOC oxidation

Atmospheric Oxidation of Unsaturated Oxygenated Compounds



Products

Atmospheric Fate of Unsaturated Oxygenated Compounds

- Lifetimes
- Oxidation products

Atmospheric Lifetimes

(i) Substrate + OH or O₃ → Products

$$\tau_{\text{OH}} = 1/k_{\text{OH}}[\text{OH}] \quad [\text{OH}] \sim 1 \times 10^6 \text{ molecules cm}^{-3}$$

$$\tau_{\text{O}_3} = 1/k_{\text{O}_3}[\text{O}_3] \quad [\text{O}_3] \sim 7.4 \times 10^{11} \text{ molecules cm}^{-3}$$

(ii) Substrate + hν → Products

$$\tau_{\text{phot}} = 1/k_{\text{phot}}$$

(iii) Substrate + water droplets → Products

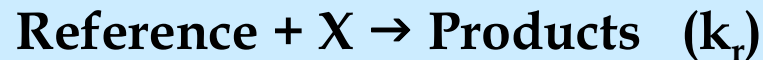
$$\tau \sim 10\text{--}15 \text{ days}$$

Kinetic Measurements

- Complementary techniques used
- Relative rate technique
- Absolute rate technique

Relative Rate Technique

- Reference compound required
- Rate coefficient of reference compound well established
- Simultaneous measurements of



where $X = \text{OH}$ or O_3

provide their relative degree of reaction

Rate coefficient determined from

$$\ln \frac{[\text{Substrate}]_0}{[\text{Substrate}]_t} = \frac{k_s}{k_r} \ln \frac{[\text{Reference}]_0}{[\text{Reference}]_t}$$

- Detection by GC and long-path FTIR

Absolute Rate Technique

Substrate + X \rightarrow Products where X = OH/O₃

$$[S]_0 \gg \gg [X]_0$$

$$\frac{-d[X]}{dt} = k[S][X]$$

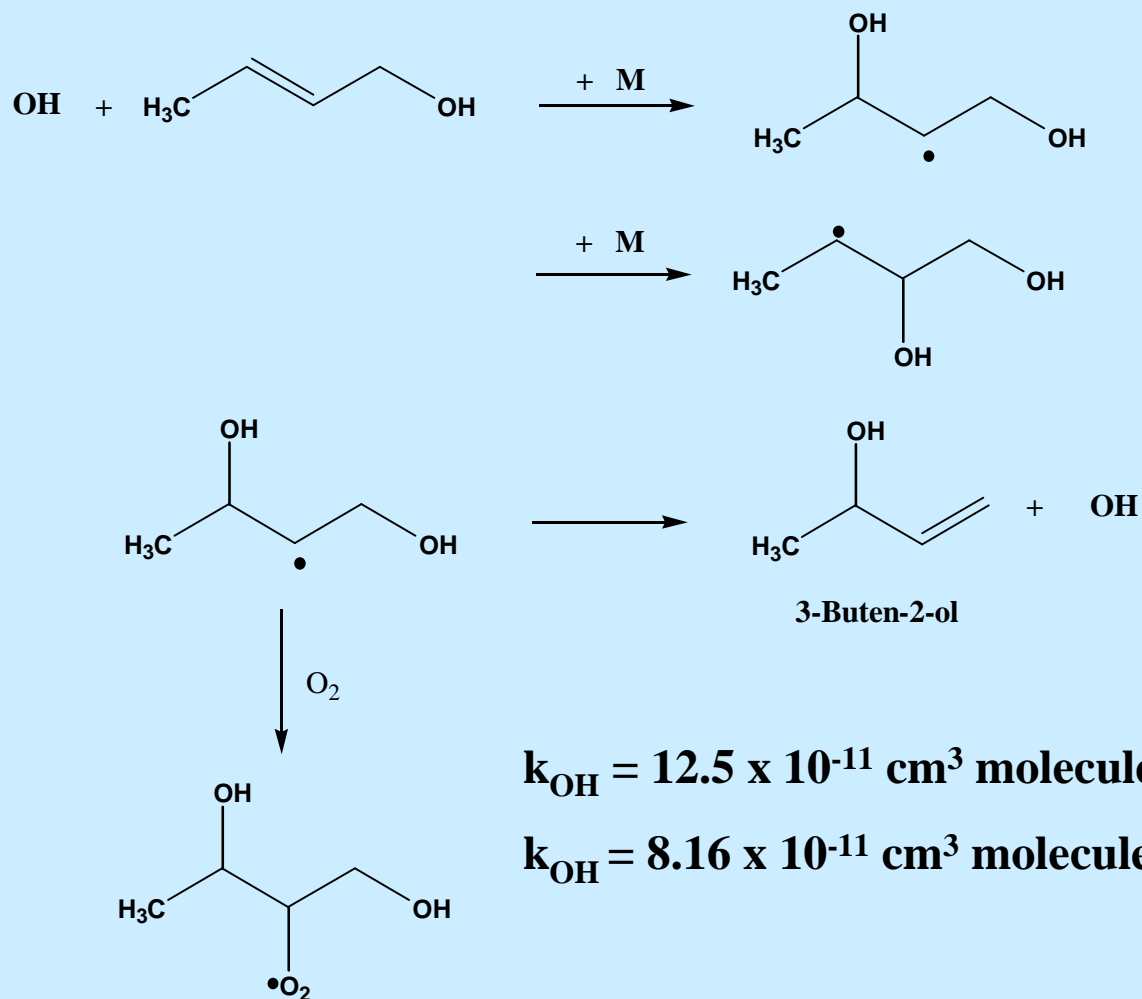
$$\frac{-d[X]}{dt} = k'[X] \quad \text{where } k' = k[S]_0$$

$$\text{Hence } [X]_t = [X]_0 e^{-k't}$$

$$\ln[X]_0/[X]_t = k't$$

Reaction of OH Radicals with Crotyl Alcohol

- $\text{OH} + \text{CH}_3\text{CH}=\text{CHCH}_2\text{OH} \rightarrow \text{Products}$

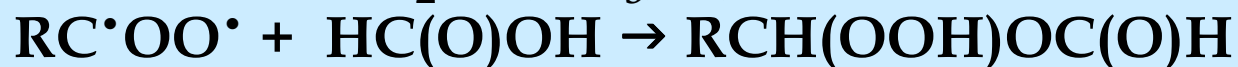
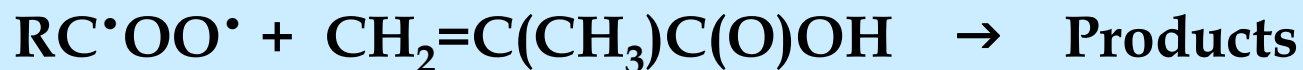
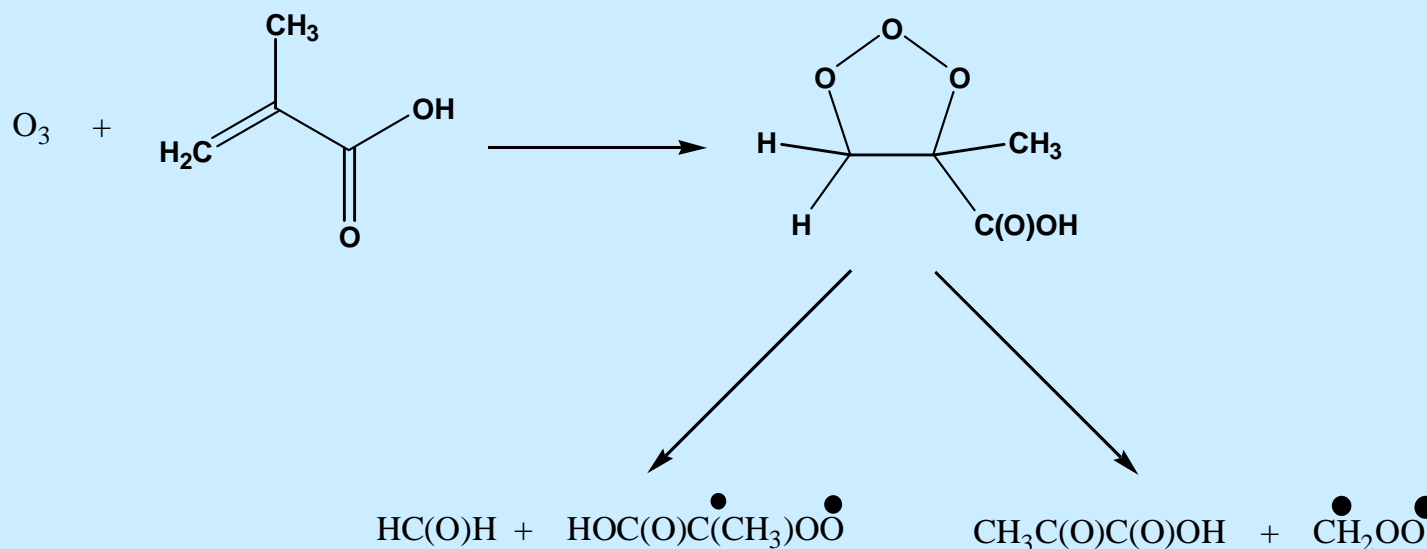


Reaction of O₃ with Methacrylic Acid

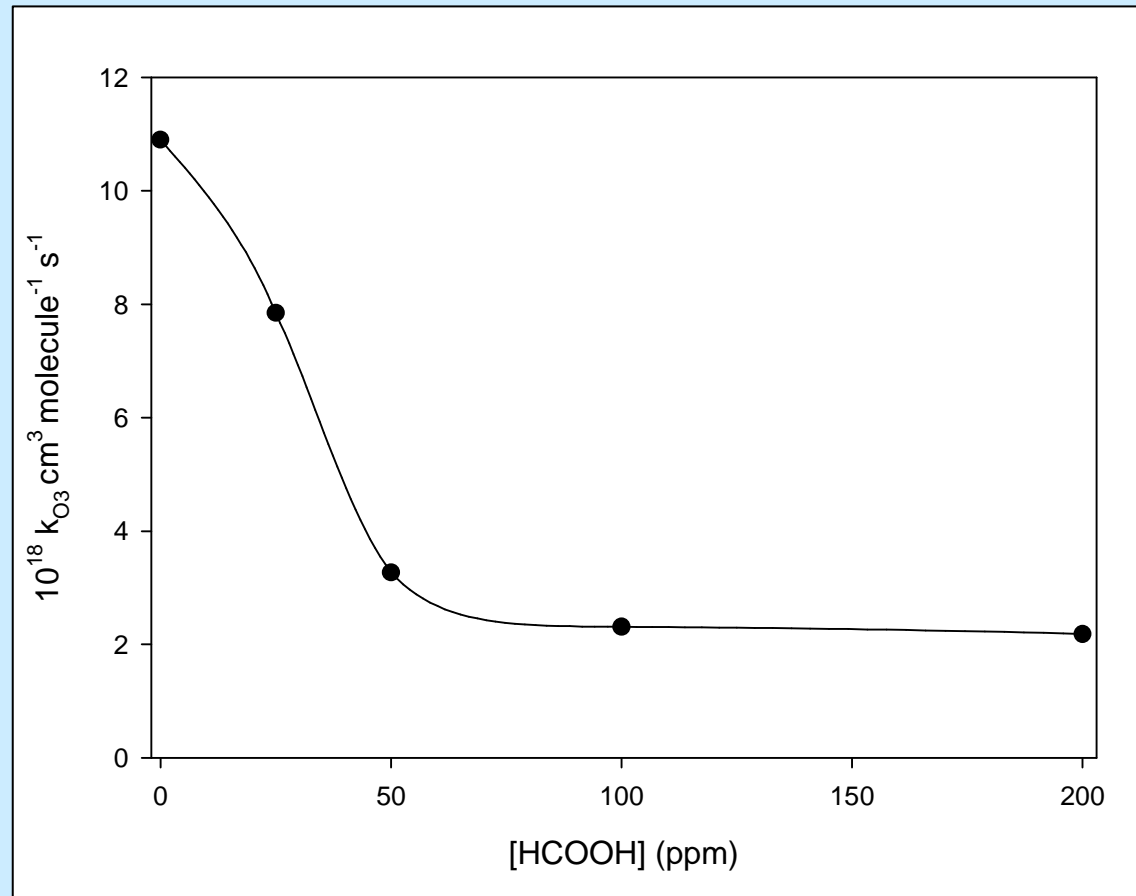


$k_{O_3} = 11 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ Relative Rate

$k_{O_3} = 2.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ Absolute Rate



Criegee Scavenger Effect



Kinetics and Mechanisms for the Reactions of OH and O₃ with Unsaturated Oxygenated Compounds

Propene	$\text{CH}_2=\text{CHCH}_3$
Vinyl alcohols	$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CH}_2\text{OH}$ (n=0-3)
Ethyl vinyl ether	$\text{CH}_2=\text{CHOC}_2\text{H}_5$
Acrolein	$\text{CH}_2=\text{CHC}(\text{O})\text{H}$
Methyl vinyl ketone	$\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$
Acrylic acid	$\text{CH}_2=\text{CHC}(\text{O})\text{OH}$
Methyl acrylate	$\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$
Vinyl acetate	$\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_3$

Rate Coefficient Data for the Reactions of OH Radicals with a Series of Unsaturated Oxygenated Compounds at 298 K

Compound	$10^{11}k_{\text{OH}}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Tech.	Ref.
CH ₂ =CHCH ₂ OH	5.5±0.4	RR	Papagni <i>et al.</i> (2001)
	4.5±0.6	RR	Orlando <i>et al.</i> (2001)
	3.7±0.5	PLP-LIF	Upadhyaya <i>et al.</i> (2001)
	5.0±0.5	PLP-LIF	Le Person <i>et al.</i> (2009)
	5.1±0.4	RR	Le Person <i>et al.</i> (2009)
	5.3±0.2	RR	This work
CH ₂ =CHOC ₂ H ₅	7.3±0.9	RR	Thiault <i>et al.</i> (2002)
	6.8±0.7	PLP-LIF	Thiault <i>et al.</i> (2002)
	5.5±0.2	RR	This work
CH ₂ =CHC(O)H	1.9±0.2	RR	Kerr & Shepard (1981)
	1.8±0.1	RR	Atkinson <i>et al.</i> (1983)
	2.0±0.1	RR	Edney <i>et al.</i> (1986)
	2.0±0.2	PLP-LIF	Magneron <i>et al.</i> (2002)
	1.9±0.2	RR	This work
CH ₂ =CHC(O)CH ₃	1.8±0.3	FP-RF	Kleindlenst <i>et al.</i> (1982)
	1.9±0.1	RR	Atkinson <i>et al.</i> (1983)
	2.0±0.2	PLP-LIF	Gierezak <i>et al.</i> (1997)
	2.3±0.2	RR	This work

Rate Coefficient Data for the Reactions of OH Radicals with a Series of Unsaturated Oxygenated Compounds at 298 K (cont.)

Compound	$10^{11}k_{\text{OH}}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Tech.	Ref.
CH ₂ =CHC(O)OH	1.8±0.5	RR	Teruel <i>et al.</i> (2007)
	1.4±0.1	RR	This work
CH ₂ =CHC(O)OCH ₃	2.5±0.4	DF-LIF	Saunders <i>et al.</i> (1994)
	1.3±0.2	RR	Teruel <i>et al.</i> (2007)
	1.3±0.1	PLP-LIF	Teruel <i>et al.</i> (2007)
	1.1±0.1	RR	This work
CH ₂ =CHOC(O)CH ₃	2.0±0.2	RR	This work

Rate Coefficient Data for the Reactions of O₃ with a Series of Unsaturated Oxygenated Compounds at 298 K

Compound	10 ¹⁸ k _{O₃} cm ³ molecule ⁻¹ s ⁻¹	Tech.	Ref.
CH ₂ =CHCH ₂ OH	14±2	S-UV	Grosjean <i>et al.</i> (1993)
	18±2	S-UV	Le Person <i>et al.</i> (2009)
	17±2	RR	This work
	19±2	S-CL	This work
CH ₂ =CHOC ₂ H ₅	154±30	S-UV	Grosjean & Grosjean (1998)
	200±20	S-UV/IR	Thiault <i>et al.</i> (2002)
	125±20	RR	This work
	143±10	S-CL	This work
CH ₂ =CHC(O)H	0.28±0.01	S-CL	Atkinson <i>et al.</i> (1981)
	0.30±0.01	S-CL	Treacy <i>et al.</i> (1992)
	0.26±0.01	S-UV	Grosjean <i>et al.</i> (1993)
	0.34±0.06	RR	This work
	0.36±0.01	S-CL	This work

Rate Coefficient Data for the Reactions of O₃ with a series of Unsaturated Oxygenated Compounds at 298 K (cont.)

Compound	10 ¹⁸ k _{O₃} cm ³ molecule ⁻¹ s ⁻¹	Tech.	Ref.
CH ₂ =CHC(O)CH ₃	4.8±0.2	S-CL	Atkinson <i>et al.</i> (1981)
	4.3±0.4	S-CL	Treacy <i>et al.</i> (1992)
	5.8±0.4	S-UV	Grosjean & Grosjean (1998)
	3.7±0.3	RR	This work
	5.3±0.2	S-CL	This work
CH ₂ =CHC(O)OH	0.65±0.13	S-IR	Neeb <i>et al.</i> (1998)
	0.71±0.03	RR	This work
	0.79±0.13	S-CL	This work
CH ₂ =CHC(O)OCH ₃	1.1±0.2	S-UV	Grosjean & Grosjean (1998)
	1.2±0.1	RR	This work
	1.0±0.1	S-CL	This work
CH ₂ =CHOC(O)CH ₃	3.2±0.5	S-UV	Grosjean & Grosjean (1998)
	2.1±0.2	RR	This work
	2.8±0.4	S-CL	This work

Kinetic Data for the Reactions of OH Radicals and O₃ with Unsaturated Compounds

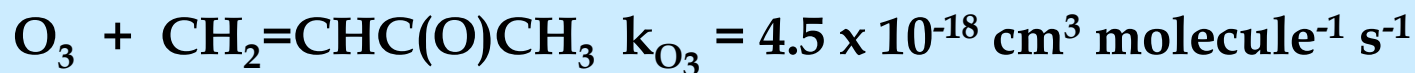
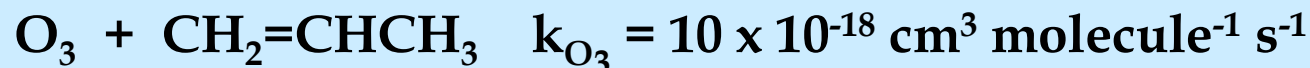
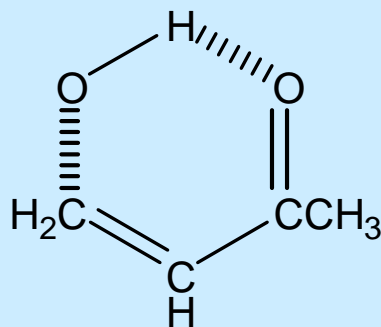
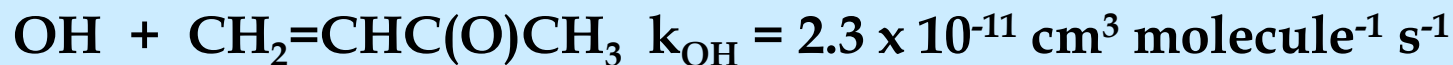
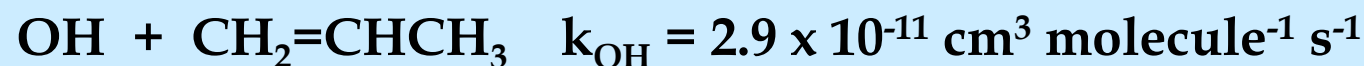
Compound	10 ¹¹ k _{OH} ^a	τ _{OH} ^b (hours)	10 ¹⁸ k _{O₃} ^a	τ _{O₃} ^c (days)
CH ₂ =CH ₂	0.85	33	1.6	10
CH ₂ =CHCH ₃	2.9	9.6	10	1.6
CH ₂ =CHCF ₃	0.15	185	0.033	470
CH ₂ =CHCH ₂ OH	5.3	5.2	18	0.87
CH ₂ =CHOC ₂ H ₅	5.5	5.1	134	0.12
CH ₂ =CHC(O)H	1.9	15	3.5	4.5
CH ₂ =CHC(O)CH ₃	2.3	12	4.5	3.5
CH ₂ =CHC(O)OH	1.4	20	0.75	21
CH ₂ =CHC(O)OCH ₃	1.1	25	1.1	14
CH ₂ =CHOC(O)CH ₃	2.0	14	2.5	6.3

^a In units of cm³ molecule⁻¹ s⁻¹

^b τ_{OH} = 1/k_{OH}[OH] [OH] = 1 x 10⁶ molecules cm⁻³

^c τ_{O₃} = 1/k_{O₃}[O₃] [O₃] = 7.4 x 10¹¹ molecules cm⁻³

Hydrogen Bond Formation in the Reaction of OH Radicals with Unsaturated Oxygenates



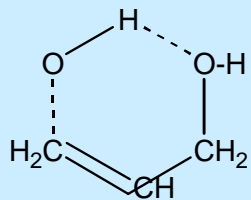
Rate Coefficient Data for the Reactions of OH Radicals with a series of Vinyl Alcohols and Ethers at 298 K

Compound	$10^{11}k_{\text{OH}}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Tech.	Ref.
$\text{CH}_2=\text{CHCH}_3$	2.9	Eval.	
$\text{CH}_2=\text{CHCH}_2\text{OH}$	5.5 ± 0.4	RR	Papagni <i>et al.</i> (2001)
	4.5 ± 0.6	RR	Orlando <i>et al.</i> (2001)
	3.7 ± 0.5	PLP-LIF	Upadhyaya <i>et al.</i> (2001)
	5.0 ± 0.5	PLP-LIF	Le Person <i>et al.</i> (2009)
	5.1 ± 0.4	RR	Le Person <i>et al.</i> (2009)
	5.3 ± 0.2	RR	This work
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$	5.5 ± 0.2	RR	Papagni <i>et al.</i> (2001)
	5.6 ± 0.2	RR	This work
	5.5 ± 0.3	PLP-LIF	This work
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_2\text{OH}$	4.1 ± 0.2	RR	This work
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2\text{OH}$	4.0 ± 0.5	RR	This work
<i>c</i> - $\text{C}_6\text{H}_9\text{OH}$	6.6 ± 0.4	RR	This work
$\text{CH}_2=\text{CHOCH}_2\text{CH}_3$	7.3 ± 0.9	RR	Thiault <i>et al.</i> (2002)
	6.8 ± 0.7	PLP-LIF	Thiault <i>et al.</i> (2002)
	5.5 ± 0.2	RR	This work
$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_3$	5.7 ± 0.5	RR	This work
	5.7 ± 0.1	PLP-LIF	This work

Comparison of the Rate Coefficients for the Reactions of OH Radicals with Unsaturated Alcohols and Ethers with the Rate Coefficients for the Reaction with the Corresponding Alkenes

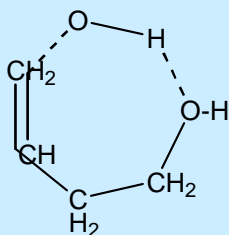
Compound	$10^{11}k_{\text{OH}}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$k(\text{OH}+\text{substituted compound})/$ $k(\text{OH}+\text{unsubstituted compound})$
$\text{CH}_2=\text{CHCH}_3$	2.9	—
$\text{CH}_2=\text{CHCH}_2\text{OH}$	5.3	1.8
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	3.1	—
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$	5.6	1.8
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3$	3.3	—
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_2\text{OH}$	4.1	1.2
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$	3.7	—
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2\text{OH}$	4.0	1.1
c-C ₆ H ₁₀	6.6	—
c-C ₆ H ₉ OH	6.6	1.0
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	3.1	—
$\text{CH}_2=\text{CHOCH}_2\text{CH}_3$	5.5	1.8
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$	3.3	—
$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_3$	5.7	1.7

Hydrogen Bonding in the Transition States for the Reactions of OH Radicals with Unsaturated Alcohols



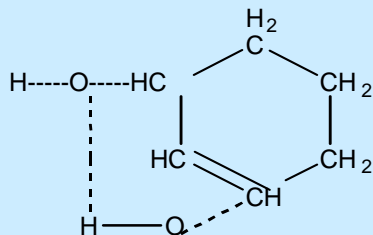
six-membered ring

allyl alcohol



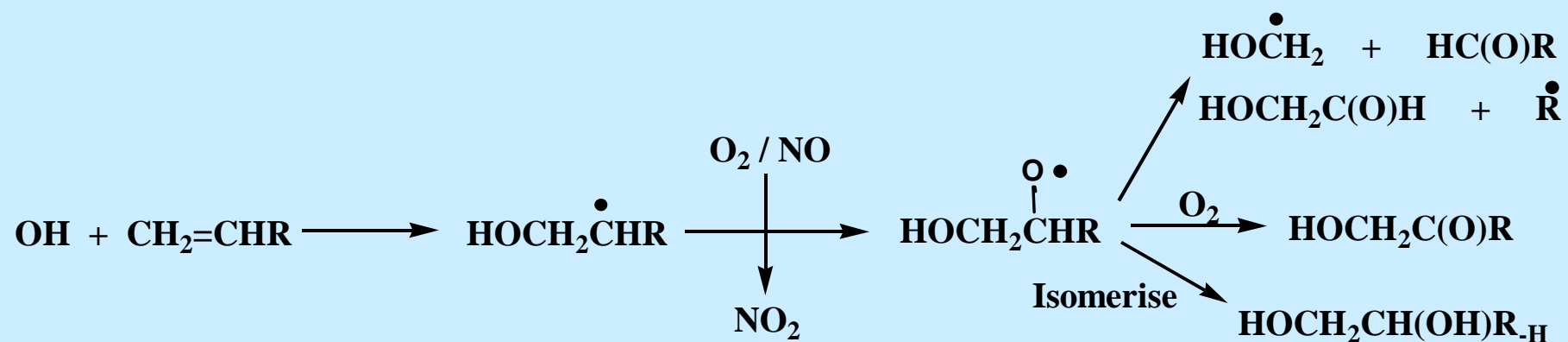
seven-membered ring

3-buten-1-ol



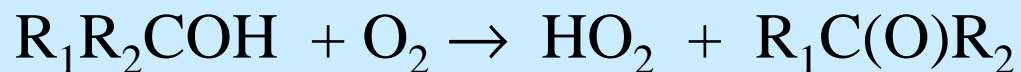
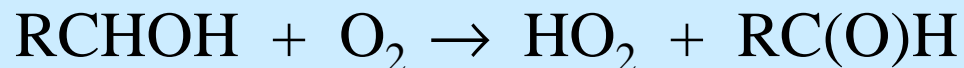
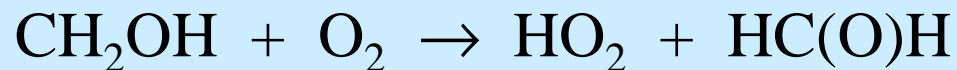
2-cyclohexen-1-ol

Products from the Reactions of OH Radicals with a Series of Unsaturated Organic Compounds

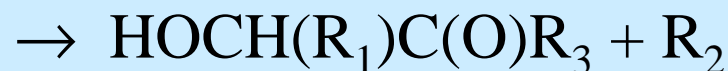
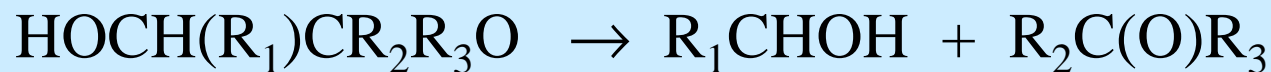
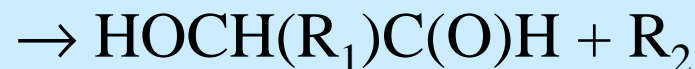
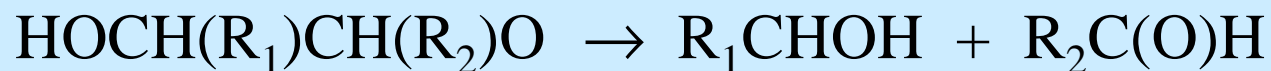
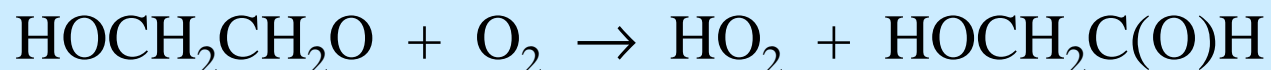


Degradation of Hydroxy Alkoxy Radicals

- α -hydroxy alkyl radicals

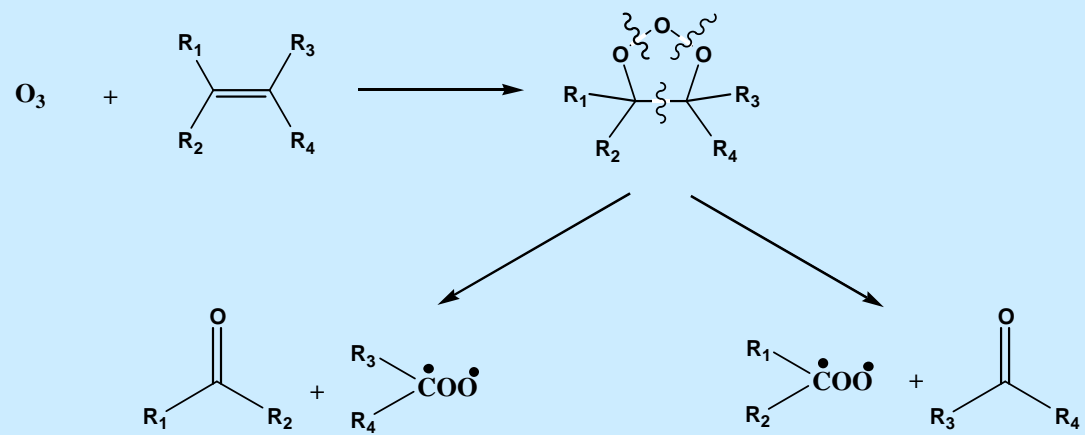


- β -hydroxy alkoxy radicals



Compound	Alkoxy Radicals	Major Products
$\text{CH}_2=\text{CHCH}_3$	$\text{HOCH}_2\text{---CH(O)-CH}_3$ (65%) $\text{OCH}_2\text{---CH(OH)-CH}_3$ (35%)	$\text{HC(O)H} + \text{CH}_3\text{C(O)H}$ $\text{HC(O)H} + \text{CH}_3\text{C(O)H}$
$\text{CH}_2=\text{CHCF}_3$	$\text{HOCH}_2\text{---CH(O)-CF}_3$	$\text{HC(O)H} + \text{CF}_3\text{C(O)H}$
$\text{CH}_2=\text{CHCH}_2\text{OH}$	$\text{HOCH}_2\text{---CH(O)-CH}_2\text{OH}$	$\text{HC(O)H} + \text{HOCH}_2\text{C(O)H}$
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	$\text{HOCH}_2\text{---CH(O)-OC}_2\text{H}_5$	$\text{HC(O)H} + \text{C}_2\text{H}_5\text{C(O)H}$
$\text{CH}_2=\text{CHC(O)H}$	$\text{HOCH}_2\text{-CH(O)---C(O)H}$ (>85%) $\text{OCH}_2\text{---CH(OH)-C(O)H}$ (<15%)	$\text{HOCH}_2\text{C(O)H} + \text{HC(O)}$ $\text{HC(O)H} + \text{HC(O)C(O)H}$
$\text{CH}_2=\text{CHC(O)CH}_3$	$\text{HOCH}_2\text{-CH(O)---C(O)CH}_3$ (70%) $\text{OCH}_2\text{---CH(OH)-C(O)CH}_3$ (30%)	$\text{HOCH}_2\text{C(O)H} + \text{CH}_3\text{C(O)}$ $\text{HC(O)H} + \text{CH}_3\text{C(O)C(O)H}$
$\text{CH}_2=\text{CHC(O)OH}$	$\text{HOCH}_2\text{---CH(O)-C(O)OH}$	$\text{HC(O)H} + \text{HOC(O)C(O)H}$
$\text{CH}_2=\text{CHC(O)OCH}_3$	$\text{HOCH}_2\text{---CH(O)-C(O)OCH}_3$	$\text{HC(O)H} + \text{CH}_3\text{OC(O)C(O)H}$
$\text{CH}_2=\text{CHOC(O)CH}_3$	$\text{HOCH}_2\text{---CH(O)-OC(O)CH}_3$	$\text{HC(O)H} + \text{CH}_3\text{C(O)OC(O)H}$

Ozonolysis of Unsaturated Organic Compounds



Compound	Stable Products/ approx. % Yields	
$\text{CH}_2=\text{CHCH}_3$	HC(O)H (65)	$\text{CH}_3\text{C(O)H}$ (45)
$\text{CH}_2=\text{CHCF}_3$	HC(O)H (4)	$\text{CF}_3\text{C(O)H}$ (96)
$\text{CH}_2=\text{CHCH}_2\text{OH}$	HC(O)H (45)	$\text{HOCH}_2\text{C(O)H}$ (55)
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	HC(O)H (27)	$\text{C}_2\text{H}_5\text{OC(O)H}$ (84)
$\text{CH}_2=\text{CHC(O)H}$	HC(O)H (55)	HC(O)C(O)H (50)
$\text{CH}_2=\text{CHC(O)CH}_3$	HC(O)H (55)	$\text{CH}_3\text{C(O)C(O)H}$ (50)
$\text{CH}_2=\text{CHC(O)OH}$	HC(O)H (145)	HOC(O)C(O)H (12)
$\text{CH}_2=\text{CHC(O)OCH}_3$	HC(O)H (54)	$\text{CH}_3\text{OC(O)H}$ (43)
$\text{CH}_2=\text{CHOC(O)CH}_3$	HC(O)H (35)	$\text{CH}_3\text{C(O)OC(O)H}$ (70)

Atmospheric Consequences of the Degradation of Unsaturated Oxygenated Compounds

- Rate coefficient data show that the tropospheric lifetimes with respect to reaction with OH radicals are less than 1 day. Reactions with O₃ and NO₃ are slower and correspond to lifetimes of several days. Hence these compounds will be removed close to their emission sources.
- Product distribution studies on the reactions of O₃ and OH radicals show that unsaturated alcohols and ketones generate hydroxy aldehydes and ketones, which will further react to give PANs. The reactions of ethers produce esters, which form anhydrides and acids on further reaction. Oxidation of unsaturated acids and esters give dicarbonyls and anhydrides providing additional sources of PANs.
- The fate of long-chain and polyfunctionalized oxygenated alkoxy radicals may lead to isomerization reactions resulting in the production of low vapour pressure products. Formation of products having relatively low reactivity and low vapour pressures suggests that uptake into cloud droplets and formation of secondary organic aerosols is likely to be important in the atmospheric chemistry of long-chain oxygenated organic compounds.