Overhead Slides for

Chapter 12, Part 1

of

Fundamentals of Atmospheric Modeling

by

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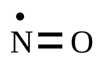
Types of Gases

Inorganic gases

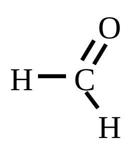
Contain O, N, S, Cl, Br, and maybe H or C, but not both.

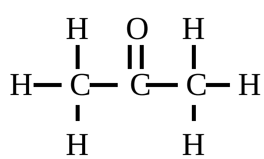
Nitric oxide -- 

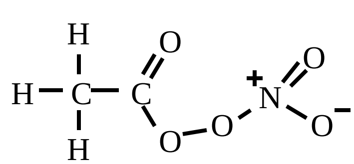
Carbon dioxide -- 

Organic gases

Contain both H and C, but may also contain other atoms.

Formaldehyde -- 

Acetone -- 

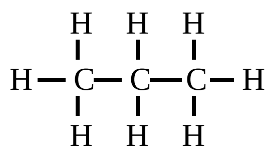
Peroxyacetylnitrate -- 

Hydrocarbons

Organic gases that ontain only hydrogen and carbon

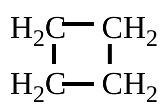
Alkanes - Carbons bonded by a single bond

Propane --



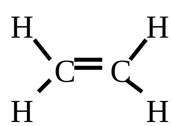
Cycloalkanes - A ring of alkanes

Cyclobutane --



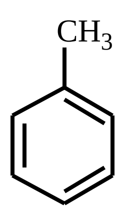
Alkenes - Carbons bonded by a double bond

Ethene (ethylene) --



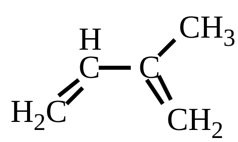
Aromatics - Carbons that form a benzene ring

Toluene --



Terpenes - Biogenic hydrocarbons

Isoprene --



Definitions

Non-methane hydrocarbons (NMHC)

Hydrocarbons, except for methane

Oxygenated hydrocarbons

Hydrocarbons with oxygenated functional groups, such as aldehydes, ketones, alcohols, acids, and nitrates, added to them

Reactive organic gas (ROG)

The sum of oxygenated and NMHC

Total organic gas (TOG)

The sum of ROG and methane

Photostationary State Relationship

$$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2 \qquad (12.1)$$

$$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\cdot \qquad \lambda < 420 \text{ nm} \qquad (12.2)$$

$$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M \qquad (12.3)$$

Time rate of change of nitrogen dioxide

$$\frac{d[NO_2]}{dt} = k_1[NO][O_3] - J[NO_2] \qquad (12.4)$$

Steady state --> photostationary state relationship

$$[O_3] = \frac{J[NO_2]}{k_1[NO]} \qquad (12.5)$$

Example 12.1.

Estimate ozone mixing ratio when

p_d	= 1013 mb	T	= 298 K
χ_{NO}	= 5 pptv	χ_{NO_2}	= 10 pptv
k_1	≈ 1.8×10^{-14} cm^3 molec.$^{-1}$ s^{-1}	J	≈ 0.01 s^{-1}

Solution

$[O_3]$ = 1.1×10^{12} molec. cm^{-3}

N_d = 2.46×10^{19} molec. cm^{-3}

χ_{O_3} = 44.7 ppbv

Other Reactions Affecting Ozone

Photodissociation of ozone

$$O_3 + h\nu \longrightarrow O_2 + \cdot\dot{O}(^1D) \qquad \lambda < 310 \text{ nm} \qquad (12.6)$$

$$O_3 + h\nu \longrightarrow O_2 + \dot{O}\cdot \qquad \lambda > 310 \text{ nm} \qquad (12.7)$$

Conversion of excited to ground-state atomic oxygen

$$\cdot\dot{O}(^1D) \xrightarrow{M} \dot{O}\cdot \qquad (12.8)$$

Hydroxyl Radical Production

$$^{\bullet}\dot{O}(^{1}D) + H_2O \longrightarrow 2\dot{O}H \quad (12.9)$$

Scavenging by Hydroxyl Radical

$$\dot{O}H + O_3 \longrightarrow H\dot{O}_2 + O_2 \quad (12.10)$$

$$\dot{O}H + H\dot{O}_2 \longrightarrow H_2O + O_2 \quad (12.11)$$

$$\dot{O}H + H_2O_2 \longrightarrow H\dot{O}_2 + H_2O \quad (12.12)$$

$$\dot{O}H + \dot{N}O_2 \xrightarrow{M} HNO_3 \quad (12.14)$$

$$\dot{O}H + \dot{N}O_3 \longrightarrow H\dot{O}_2 + \dot{N}O_2 \quad (12.15)$$

$$\dot{O}H + SO_2 \xrightarrow{M} HS\dot{O}_3 \quad (12.17)$$

$$\dot{O}H + CO \longrightarrow \dot{H} + CO_2 \quad (12.18)$$

$$\dot{O}H + CH_4 \longrightarrow H_2O + \dot{C}H_3 \quad (12.19)$$

Hydroperoxy Radical Production

$$\dot{H} + O_2 \xrightarrow{M} H\dot{O}_2 \qquad (12.23)$$

Hydroperoxy Radical Reactions

Hyrdoxyl radical reactions in presence of NO

$$\left.\begin{aligned} H\dot{O}_2 + \dot{N}O &\longrightarrow \dot{O}H + \dot{N}O_2 \\ H\dot{O}_2 + \dot{N}O_2 &\xrightarrow{M} HO_2NO_2 \end{aligned}\right\} \quad (NO > 10\ pptv) \qquad (12.24)$$

$$H\dot{O}_2 + O_3 \longrightarrow \dot{O}H + 2O_2 \quad (NO\ 3\text{-}10\ pptv) \qquad (12.25)$$

$$H\dot{O}_2 + H\dot{O}_2 \longrightarrow H_2O_2 + O_2 \quad (NO < 3\ pptv) \qquad (12.26)$$

Recycling of Hydroxyl Radical

Nitrous acid photodissociates quickly in the early morning

$$HONO + h\nu \longrightarrow \dot{O}H + \dot{N}O \qquad (12.27)$$

Nitric acid photodissociates with 15-21 day lifetime

$$HNO_3 + h\nu \longrightarrow \dot{O}H + \dot{N}O_2 \qquad (12.28)$$

Peroxynitric acid decomposes at high temperatures

$$HO_2NO_2 \xrightarrow{M} H\dot{O}_2 + \dot{N}O_2 \qquad (12.29)$$

Hydrogen peroxide photolyzes with 1-2 day lifetime

$$H_2O_2 + h\nu \longrightarrow 2\dot{O}H \qquad (12.31)$$

Nighttime Nitrogen Photochemistry

Production of nitrate radical

$$\dot{N}O_2 + O_3 \longrightarrow \dot{N}O_3 + O_2 \qquad (12.32)$$

Dinitrogen pentoxide formation / decomposition

$$\dot{N}O_2 + \dot{N}O_3 \overset{M}{\rightleftharpoons} N_2O_5 \qquad (12.33)$$

Dinitrogen pentoxide reaction, photolysis

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \qquad (12.34)$$

$$N_2O_5 + h\nu \longrightarrow \dot{N}O_2 + \dot{N}O_3 \qquad (12.36)$$

Nitrate radical photolysis (lifetime of minutes)

$$\dot{N}O_3 + h\nu \longrightarrow \begin{cases} \dot{N}O_2 + \dot{O}\cdot & 410\text{ nm} < \lambda < 670\text{ nm} \\ \dot{N}O + O_2 & 590\text{ nm} < \lambda < 630\text{ nm} \end{cases} \qquad (12.35)$$

Ozone Formation From Carbon Monoxide

$$CO + \dot{O}H \longrightarrow CO_2 + \dot{H} \qquad (12.37)$$

$$\dot{H} + O_2 \xrightarrow{M} H\dot{O}_2 \qquad (12.38)$$

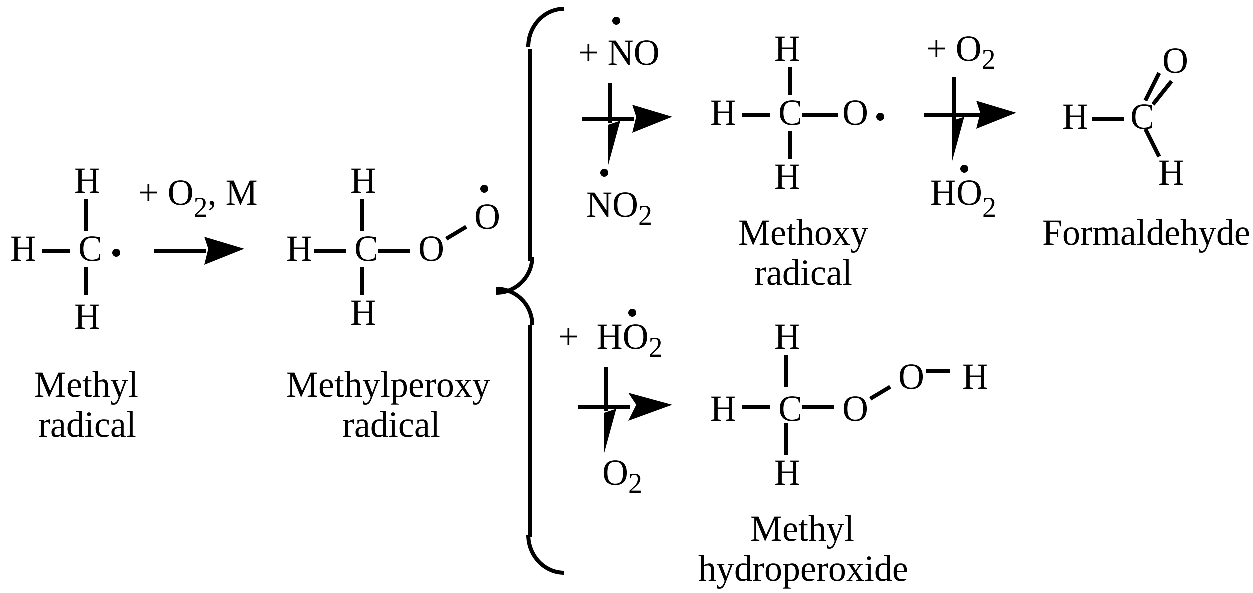
$$\dot{N}O + H\dot{O}_2 \longrightarrow \dot{N}O_2 + \dot{O}H \qquad (12.39)$$

$$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\bullet \qquad \lambda < 420 \text{ nm} \qquad (12.40)$$

$$\dot{O}\bullet + O_2 + M \longrightarrow O_3 + M \qquad (12.41)$$

Ozone Formation From Methane

$$CH_4 + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_3 + H_2O \qquad (12.42)$$

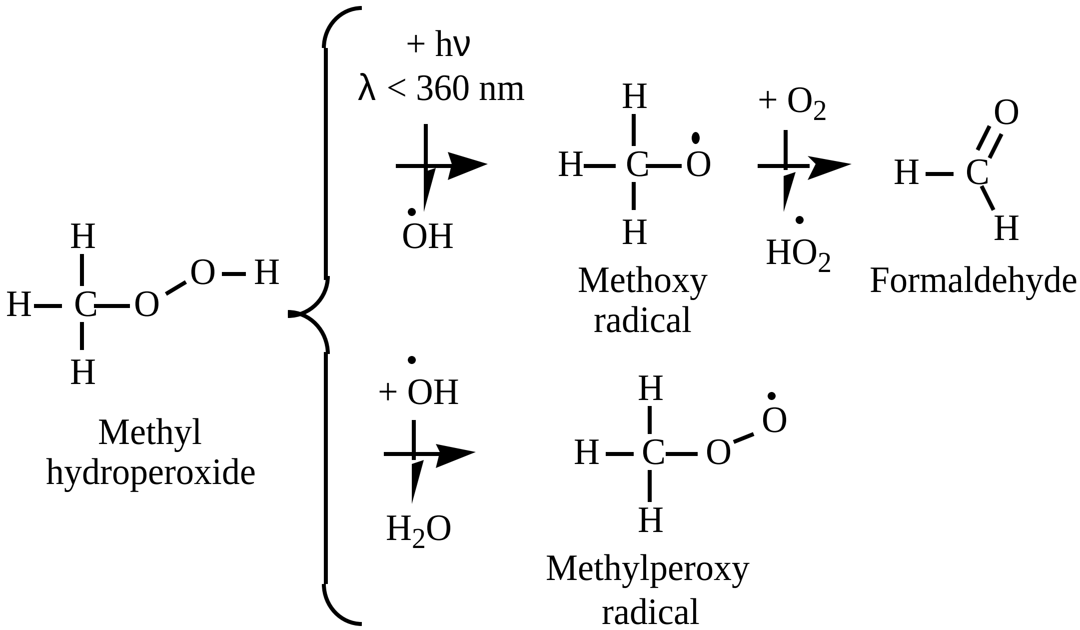


(12.43)

$$ {}^{\bullet}NO_2 + h\nu \longrightarrow {}^{\bullet}NO + {}^{\bullet}O^{\bullet} \qquad \lambda < 420 \text{ nm} \qquad (12.40)$$

$$ {}^{\bullet}O^{\bullet} + O_2 + M \longrightarrow O_3 + M \qquad (12.41)$$

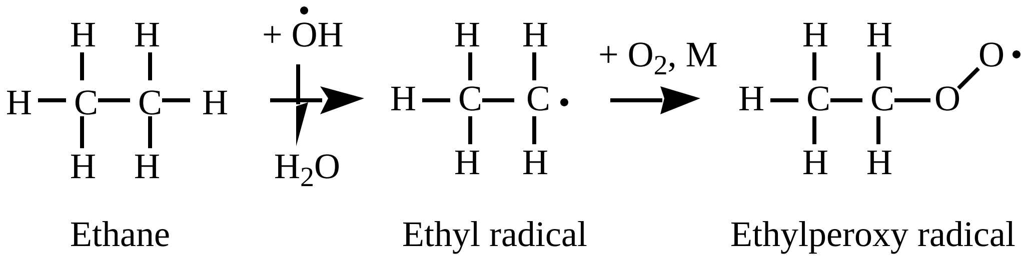
Methyl Hydroperoxide Decomposition



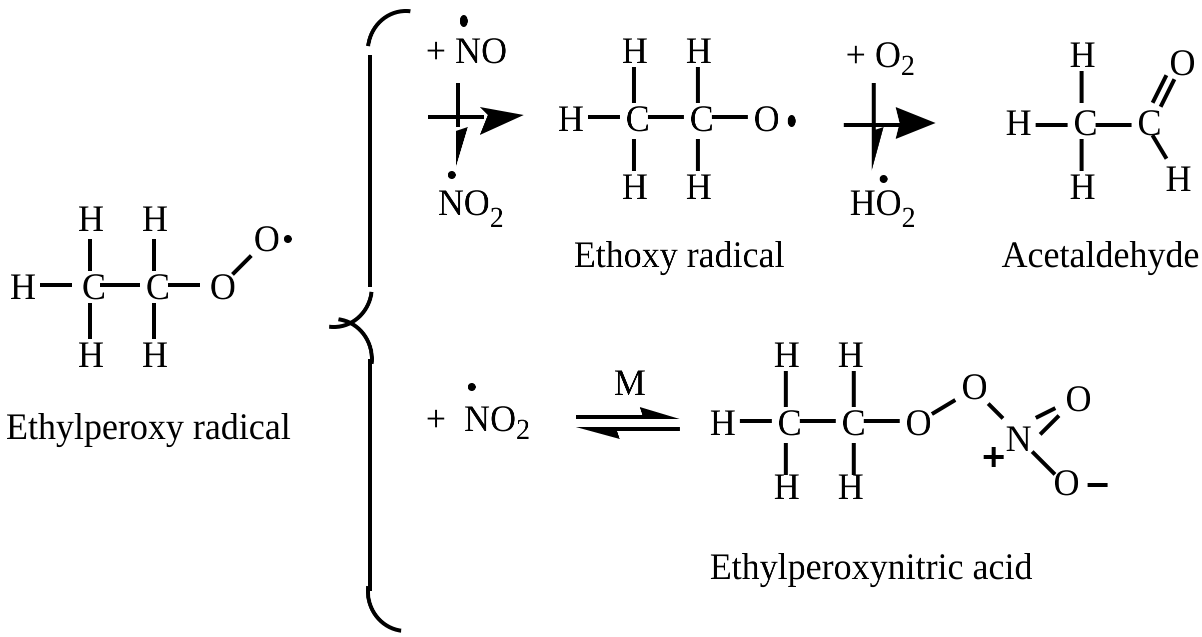
(12.44)

Ethane Oxidation

Methylperoxy radical production and loss



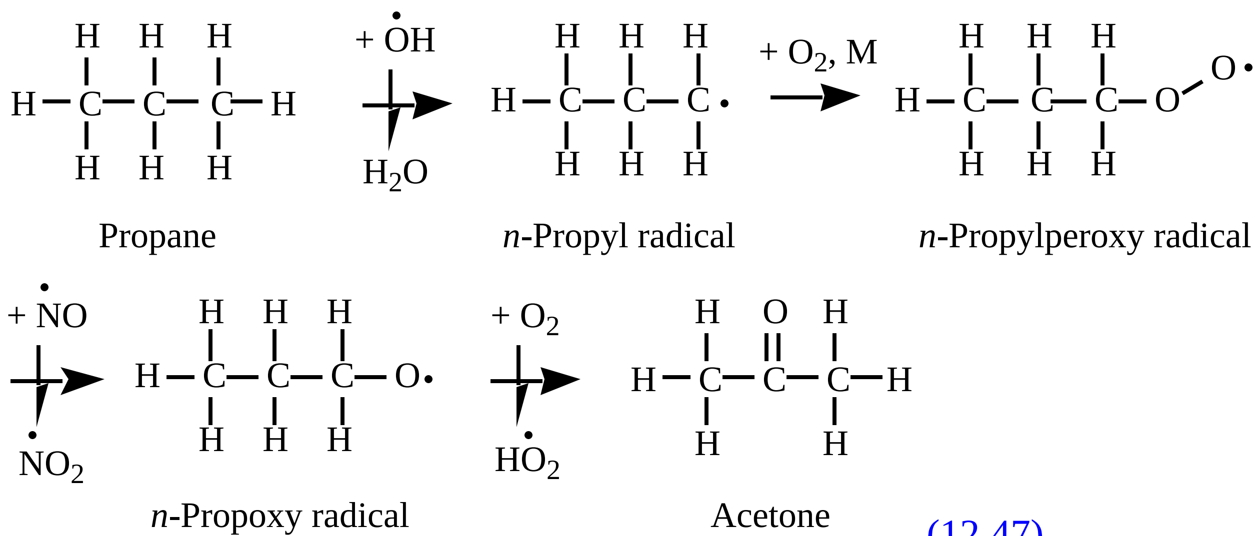
(12.45)



(12.46)

Propane Oxidation

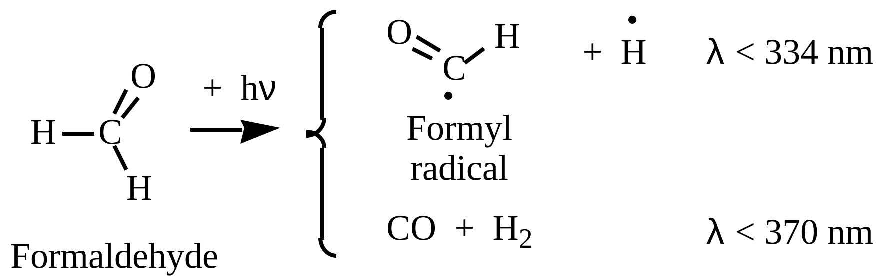
Methylperoxy radical production and loss



(12.47)

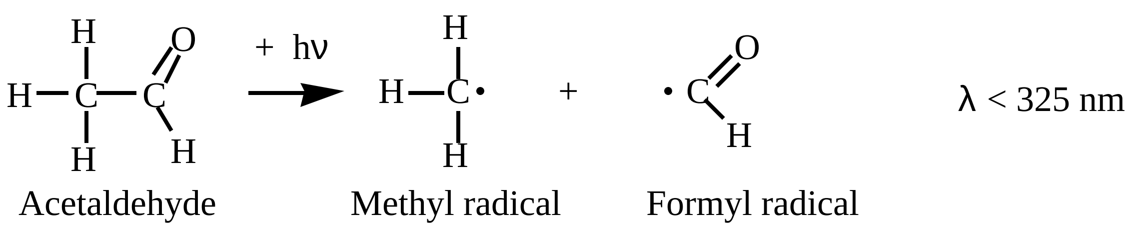
Formaldehyde and Acetaldehyde Photolysis

Formaldehyde



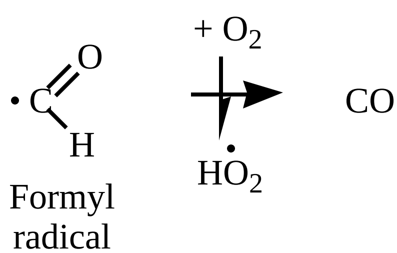
(12.48)

Acetaldehyde



(12.49)

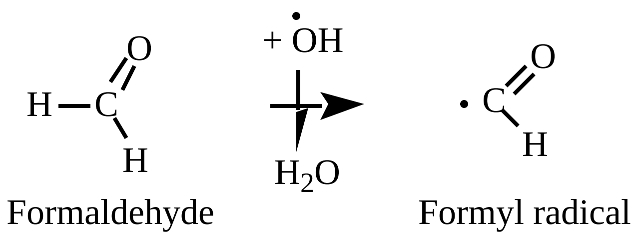
Formyl radical



(12.50)

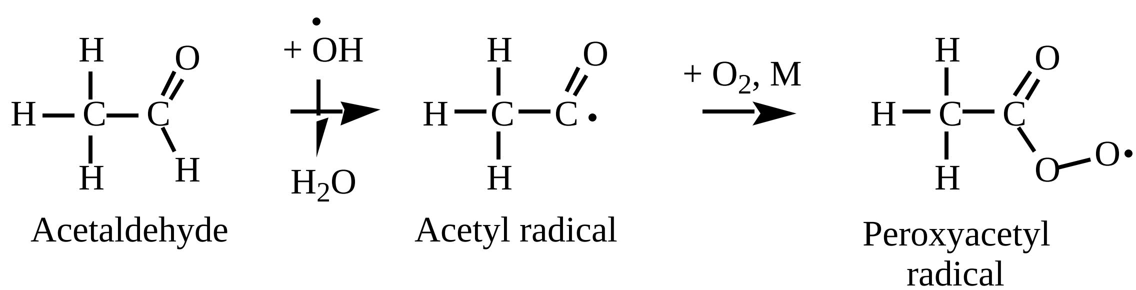
Formaldehyde and Acetaldehyde Reaction

Formaldehyde



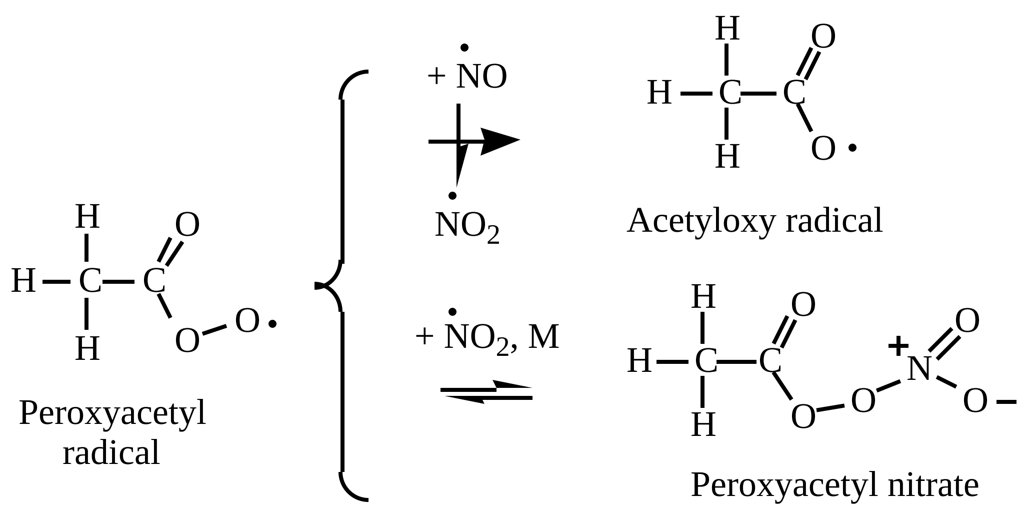
(12.51)

Acetaldehyde



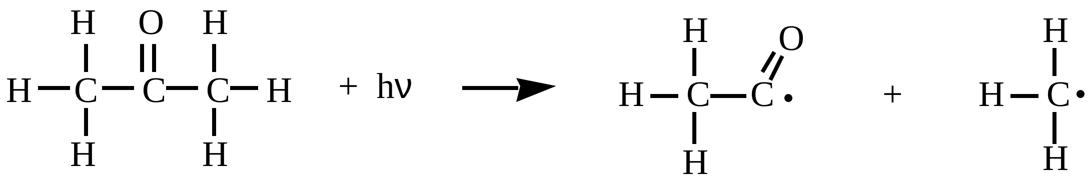
(12.52)

PAN formation



(12.53)

Acetone Photolysis



Acetone　　Acetyl radical　　Methyl radical

(12.55)

Sulfur Photochemistry

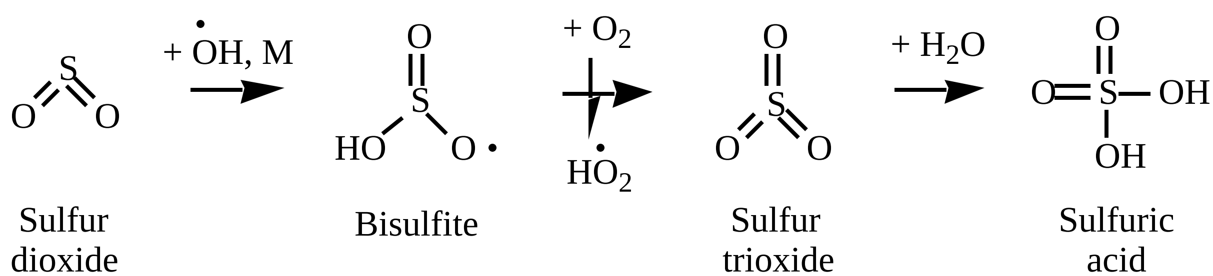
Biogenic sulfur

H_2S	-- hydrogen sulfide
CH_3SH	-- methyl sulfide
CH_3SCH_3	-- dimethyl sulfide (DMS)
CH_3SSCH_3	-- methyl disulfide

Volcanic sulfur

CS_2	-- carbon disulfide
OCS	-- carbonyl sulfide
SO_2	-- sulfur dioxide
H_2S	-- hydrogen sulfide

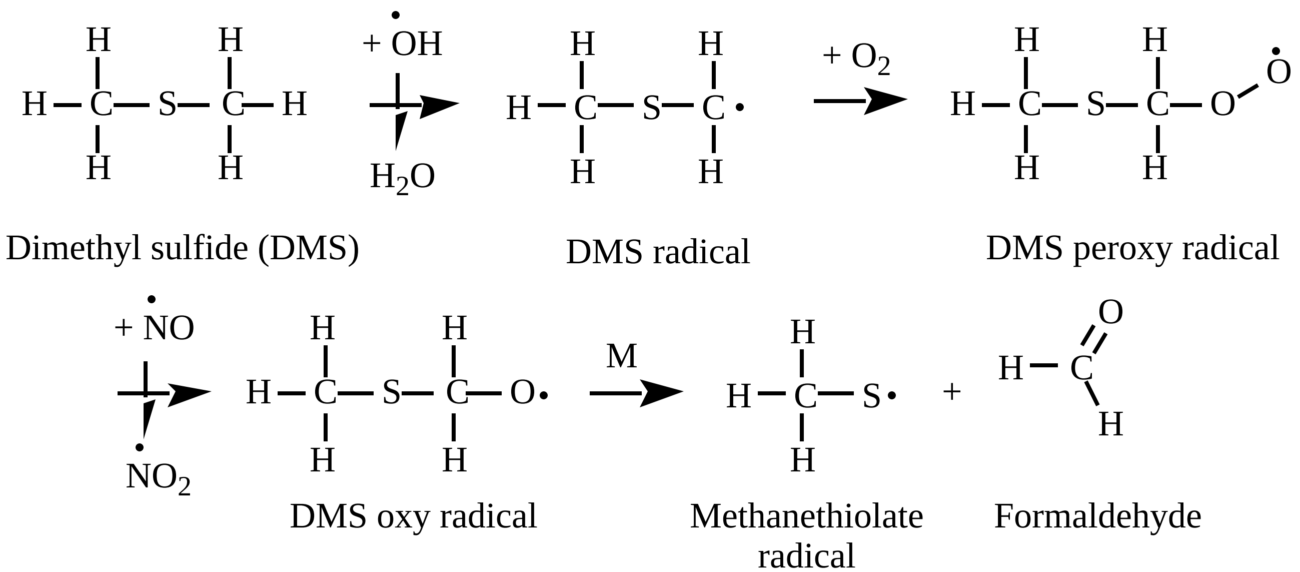
Sulfuric acid formation from sulfur dioxide



(12.74)

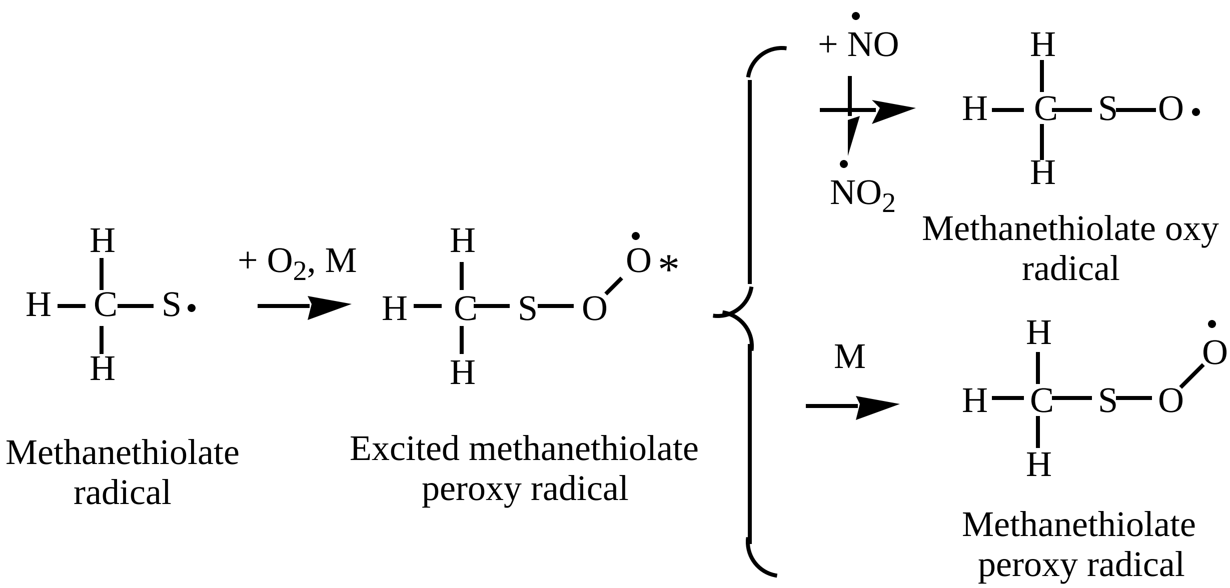
DMS Abstraction Pathway

Sulfur dioxide production from dimethyl sulfide (DMS)



(12.56)

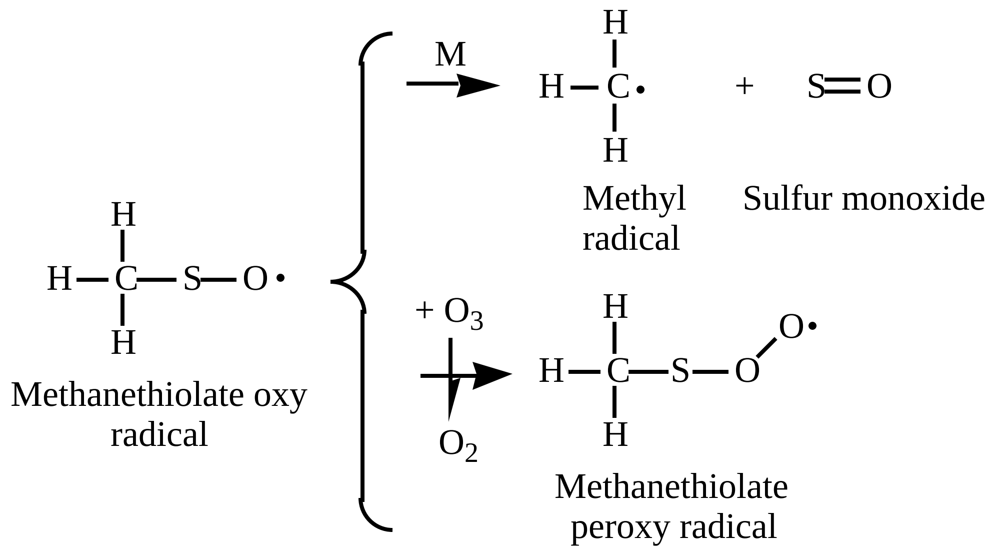
Methanethiolate radical reaction



(12.57)

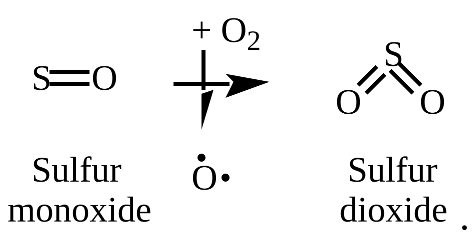
DMS Abstraction Pathway

Methanethiolate oxy radical reaction



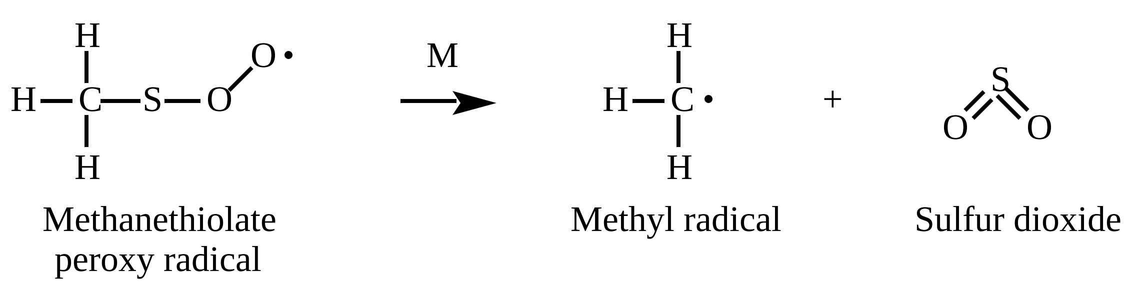
(12.58)

Sulfur dioxide production from sulfur oxide



(12.59)

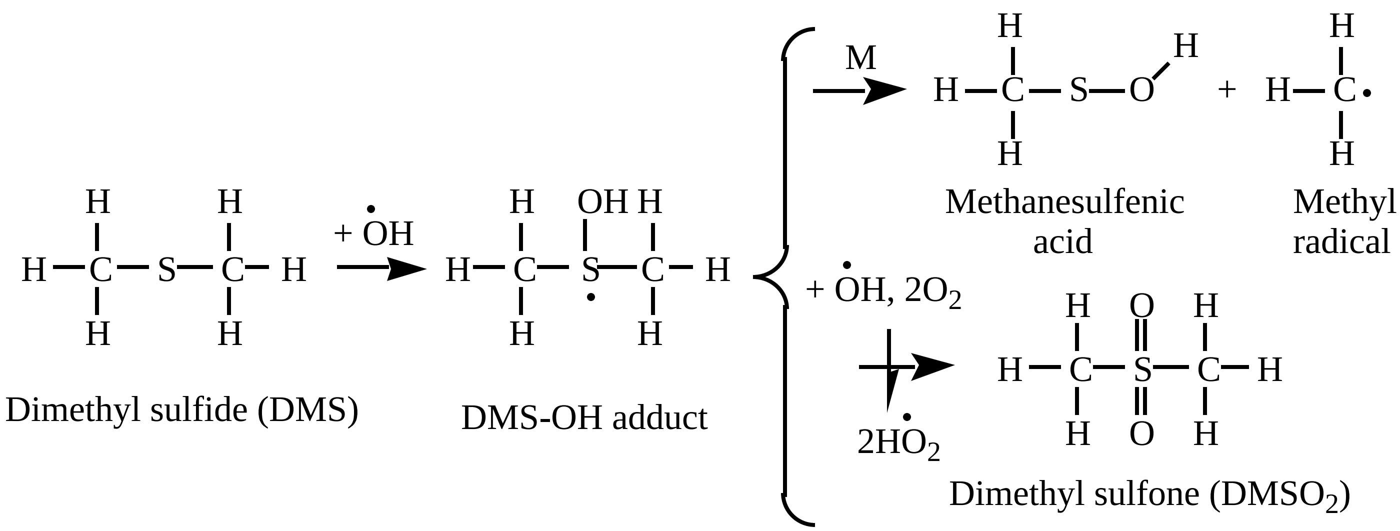
Sulfur dioxide production from methanethiolate peroxy radical



(12.60)

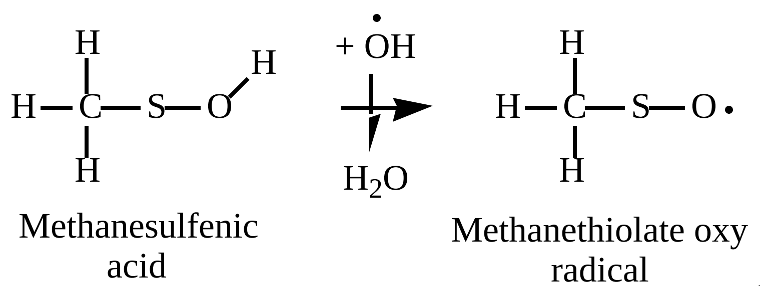
DMS Addition Pathway

Methanethiolate oxy radical reaction



(12.61)

Methanesulfenic acid oxidation

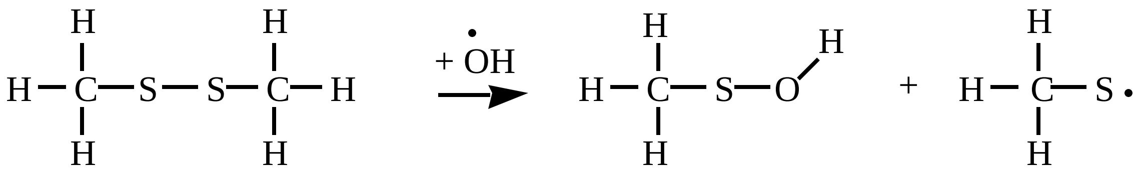


(12.60)

(12.62)

DMDS Reaction

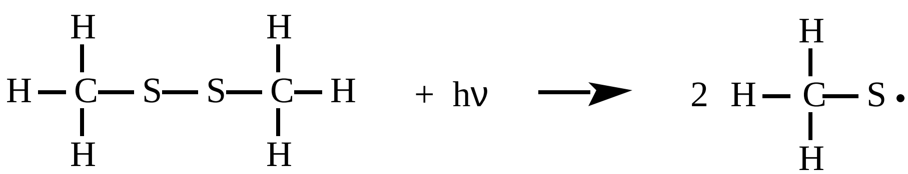
OH addition



Dimethyl disulfide (DMDS) — Methanesulfenic acid — Methanethiolate radical

(12.63)

Photolysis

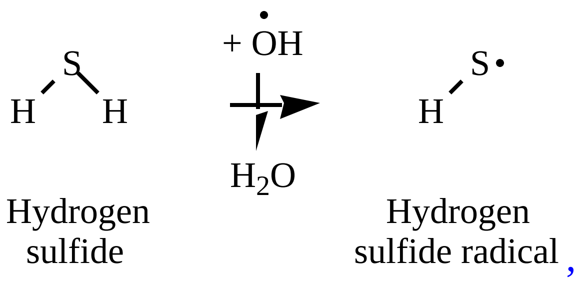


Dimethyl disulfide (DMDS) — Methanethiolate radical

(12.64)

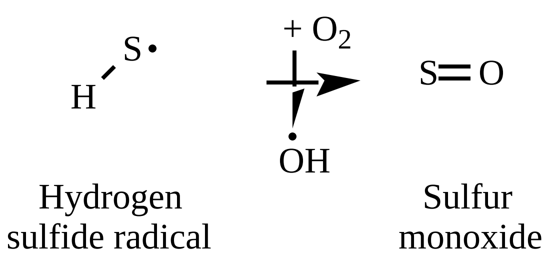
Biogenic Sulfur

Hydrogen sulfide oxidation



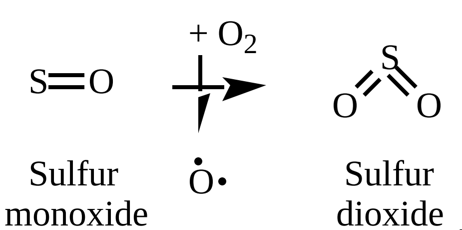
(12.65)

Hydrogen sulfide radical reaction



(12.66)

Sulfur dioxide production from sulfur oxide



(12.59)

Volcanic Sulfur

Sulfur monoxide production from carbonyl sulfide

$$\underset{\text{Carbonyl sulfide}}{O{=}C{=}S} + \dot{O}H \longrightarrow \underset{\text{Hydrogen sulfide radical}}{H{-}S\bullet} + CO_2 , \qquad (12.68)$$

$$\underset{\text{Carbonyl sulfide}}{O{=}C{=}S} + h\nu \longrightarrow \underset{\text{Carbon monoxide}}{CO} + \underset{\text{Atomic sulfur}}{\dot{S}\bullet} \qquad \lambda < 260\ \text{nm} \qquad (12.69)$$

$$\underset{\text{Atomic sulfur}}{\dot{S}\bullet} \xrightarrow[\ \dot{O}\bullet\ ]{+\ O_2} \underset{\text{Sulfur monoxide}}{S{=}O} , \qquad (12.70)$$

Sulfur oxide production from carbon disulfide

$$\underset{\text{Carbon disulfide}}{S{=}C{=}S} + \dot{O}H \longrightarrow \underset{\text{Hydrogen sulfide radical}}{H{-}S\bullet} + \underset{\text{Carbonyl sulfide}}{O{=}C{=}S} , \qquad (12.71)$$

$$\underset{\text{Carbon disulfide}}{S{=}C{=}S} + h\nu \longrightarrow \underset{\text{Carbon monosulfide}}{{}^{-}C{\equiv}S^{+}} + \underset{\text{Atomic sulfur}}{\dot{S}\bullet} \qquad \lambda < 340\ \text{nm} \qquad (12.72)$$

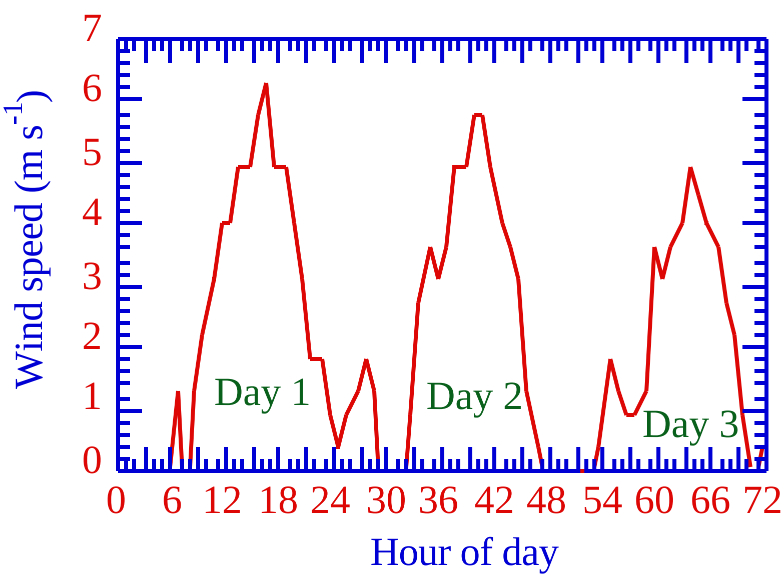
$$\underset{\text{Carbon monosulfide}}{{}^{-}C{\equiv}S^{+}} + O_2 \longrightarrow \underset{\text{Carbonyl sulfide}}{O{=}C{=}S} + \dot{O}\bullet , \qquad (12.73)$$

Urban Photochemistry

Ozone production in smog

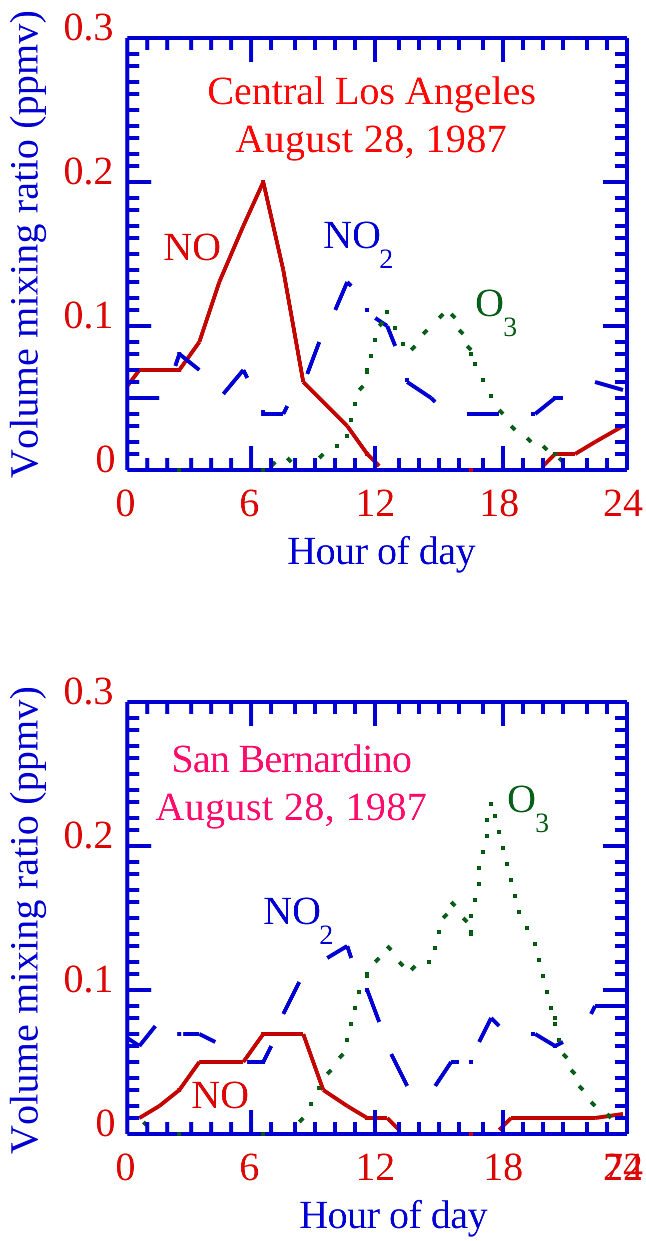
$\dot{N}O + ROG^* \longrightarrow \dot{N}O_2 + ROG^{**}$	(12.75)
$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2$	(12.76)
$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\cdot \quad \lambda < 420$ nm	(12.77)
$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M$	(12.78)

Fig. 12.1 c. Sea Breeze at Hawthorne



Source / Receptor Regions in Los Angeles

Figs. 12.1 a and b



Urban Emissions

Nitric oxide from combustion

$$N\equiv N \;+\; O=O \;+\; \text{heat} \longrightarrow 2\;\dot{N}=O \qquad (12.79)$$

Table 12.2. Emissions for Aug. 27th, 1987 in a 400 x 150 km region of the Los Angeles basin.

Inorganics (tons day^{-1})	Non-Stack	Stack	Total
Carbon monoxide (CO)	9773	23	9796
Nitric oxide (NO)	700	54	754
Nitrogen dioxide (NO_2)	120	9	129
Nitrous acid (HONO)	6	0.5	6.5
Sulfur dioxide (SO_2)	96	13	109
Sulfur trioxide (SO_3)	4	0.5	4.5
Organics (10^6 moles day^{-1})	Non-Stack	Stack	Total
Methane (CH_4)	56	0.3	56.3
Paraffins (PAR)	88	0.3	88.3
Ethene (ETH)	5.2	«1	5.2
Olefins (OLE)	3.5	«1	3.5
Formaldehyde (HCHO)	1.2	«1	1.2
C_2+ aldehydes (ALD2)	1.4	«1	1.4
Methanol (MEOH)	0.2	«1	0.2
Ethanol (ETOH)	0.6	«1	0.6
Acetone (AONE)	0.4	«1	0.4
Other ketones (KET)	0.1	«1	0.1
Toluene (TOL)	2.6	«1	2.6
Xylene (XYL)	1.9	«1	1.9
Isoprene (ISOP)	0.8	0	0.8
Other unreactive	15	<1	15

Percent Emissions by Source

Table 12.3.

(Chang *et al.*, 1991)

	CO	NO_x	SO_x	ROG
Stationary Sources*				
Fuel combustion	1.56	22.1	17.28	1.22
Waste burning	0.06	0.14	0.34	0.08
Solvent use	0.00	0.02	0.00	33.72
Petrol. procs / storage.	0.13	0.75	14.40	7.75
Industrial processes	0.14	0.96	5.66	2.99
Misc. processes	0.11	0.06	0.06	4.19
	--------	--------	--------	--------
Total stationary sources	2.00	24.03	37.74	49.95
Mobile Sources*				
On road vehicles	87.47	54.97	23.53	43.96
Other mobile	10.53	21.00	38.73	6.09
	--------	--------	--------	--------
Total mobile sources	98.00	75.97	62.26	50.05
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Total stat. / mobile	100	100	100	100

Organics Emitted in Greatest Abundance in Los Angeles

Table 12.4.

(SCAQMD / Pilinis and Seinfeld, 1988)

1. Methane	10. Propylene
2. Toluene	11. Chloroethylene
3. Pentane	12. Acetylene
4. Butane	13. Hexane
5. Ethane	14. Propane
6. Ethylene	15. Benzene
7. Octane	16. Methyl chloroform
8. Xylene	17. Pentene
9. Heptane	18. *n*-Butyl acetate

19. Acetone	28. Methylcyclohexane
20. *n*-Pentadecane	29. Nonane
21. Cyclohexane	30. Methyl alcohol
22. Methylethylketone	31. 1-Hexane
23. Acetaldehyde	32. Methylcyclopentane
24. Trimethylbenzene	33. Methylpentane
25. Ethylbenzene	34. Dimethylhexane
26. Methylvinylketone	35. Cyclopentene
27. Naphta	

Lifetime of Reactive Organic Gases in Urban Air (Table 12.5)

ROG Species		Oxidizing species and concentration (molec. cm^{-3})				
	Photol.	$OH\cdot$	$HO_2\cdot$	$O(^3P)$	$NO_3\cdot$	O_3
		$5x10^6$	$2x10^9$	$8x10^4$	$1x10^{10}$	$5x10^{12}$
n-Butane	---	22 h	1000 y	18 y	29 d	650 y
trans-2-Butene	---	52 m	4 y	6.3 d	4 m	17 m
Acetylene	---	3.0 d	---	2.5 y	---	200 d
Toluene	---	9.0 h	---	6 y	33 d	200 d
Isoprene	---	34 m	---	4 d	5 m	4.6 h
Formaldehyde	7 h	6.0 h	1.8 h	2.5 y	2.0 d	3200 y
Acetone	23 d	9.6	---	---	---	---

Lifetime of Reactive Organic Gases in Free-Tropospheric Air (Table 12.5)

ROG Species		Oxidizing species and concentration (molec. cm^{-3})				
	Photol.	$OH\cdot$	$HO_2\cdot$	$O(^3P)$	$NO_3\cdot$	O_3
		$5x10^5$	$3x10^8$	$3x10^3$	$5x10^8$	$1x10^{12}$
n-Butane	---	9.2 d	6700 y	480 y	1.6 y	3250 y
trans-2-Butene	---	8.7 h	27 y	168 d	1.3 h	1.4 h
Acetylene	---	30 d	---	67 y	---	2.7 y
Toluene	---	3.8 d	---	160 y	1.8 y	2.7 y
Isoprene	---	5.7 h	---	106 d	1.7 h	23 d
Formaldehyde	7 h	2.5 d	11.7 h	67 y	40 d	16,000 y
Acetone	23 d	96 d	---	---	---	---

Most Abundant Species in Terms of Ozone Production Reactivity

Table 12.6.

(Carter, 1991)

1. *m*- and *p*-Xylene	8. *o*-Xylene
2. Ethene	9. Butane
3. Acetaldehyde	10. Methylcyclopentane
4. Toluene	11. 2-Methylpentane
5. Formaldehyde	12. Pentane
6. *i*-Pentane	13. 1,2,4-Trimethylbenzene
7. Propene	14. Benzene

15. *m*-Ethyltoluene	22. *p*-Ethyltoluene
16. Pentanal	23. C_4 Olefin
17. Propane	24. 3-Methylpentane
18. Propanal	25. *o*-Ethyltoluene
19. *i*-Butane	
20. C_6 Carbonyl	
21. Ethylbenzene	

Hydroxyl Radical Sources in Polluted Air

Early morning source

$$HONO + h\nu \longrightarrow \dot{O}H + \dot{N}O$$, (12.80)

Mid-morning source

$$HCHO + h\nu \longrightarrow \dot{H} + H\dot{C}O$$,

$$\dot{H} + O_2 \xrightarrow{M} H\dot{O}_2$$, (12.82)

$$H\dot{C}O + O_2 \longrightarrow H\dot{O}_2 + CO$$, (12.83)

$$\dot{N}O + H\dot{O}_2 \longrightarrow \dot{N}O_2 + \dot{O}H$$, (12.84)

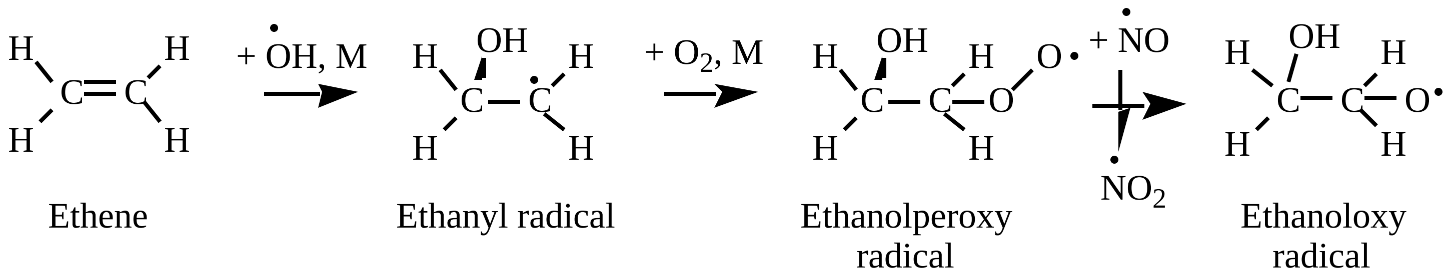
Afternoon source

$$O_3 + h\nu \longrightarrow O_2 + \cdot\dot{O}(^1D)$$, (12.85)

$$\cdot\dot{O}(^1D) + H_2O \longrightarrow 2\,\dot{O}H$$, (12.86)

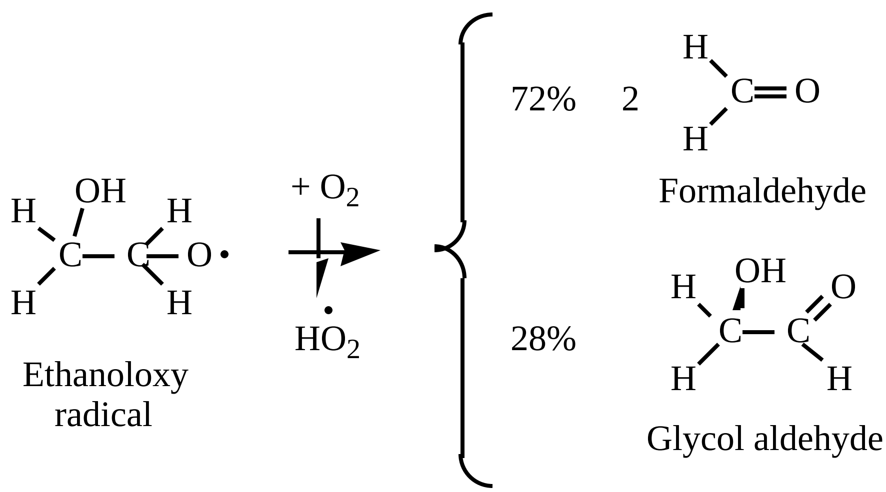
Alkene Reaction With Hydroxyl Radical

Ethene --> ethanyl radical --> ethanol peroxy radical



(12.87)

Ethanoloxy radical oxidation --> glycol aldehyde etc.



(12.88)