

**Overhead Slides for**  
**Chapter 12, Part 2**

**of**

**Fundamentals of**  
**Atmospheric**  
**Modeling**

**by**

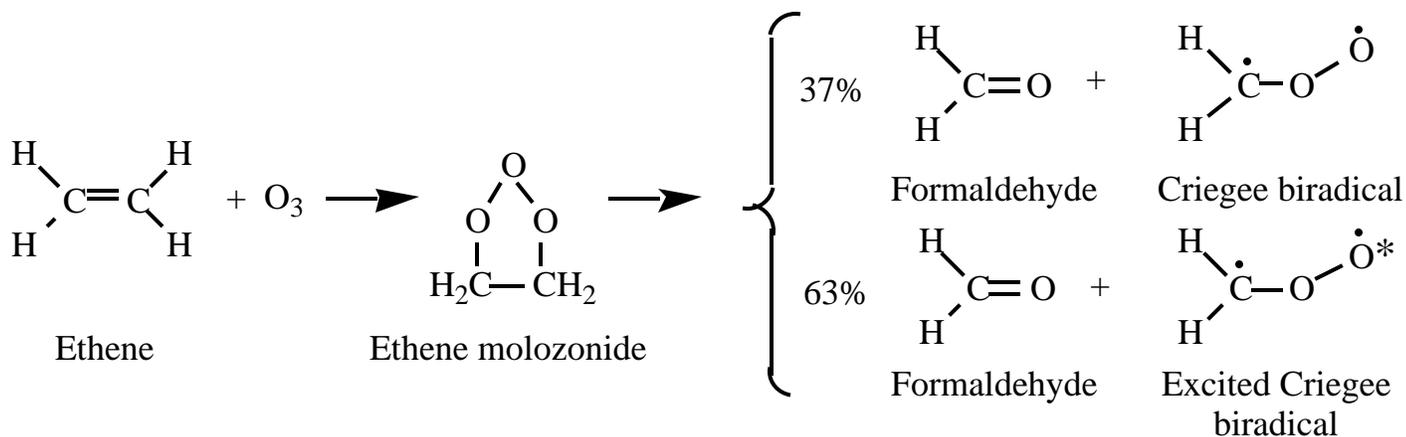
**Mark Z. Jacobson**

**Department of**  
**Civil & Environmental Engineering**  
**Stanford University**  
**Stanford, CA 94305-4020**

**January 30, 2002**

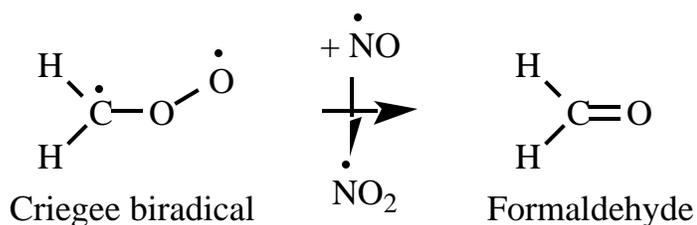
# Alkene Reaction With Ozone

## Ethene



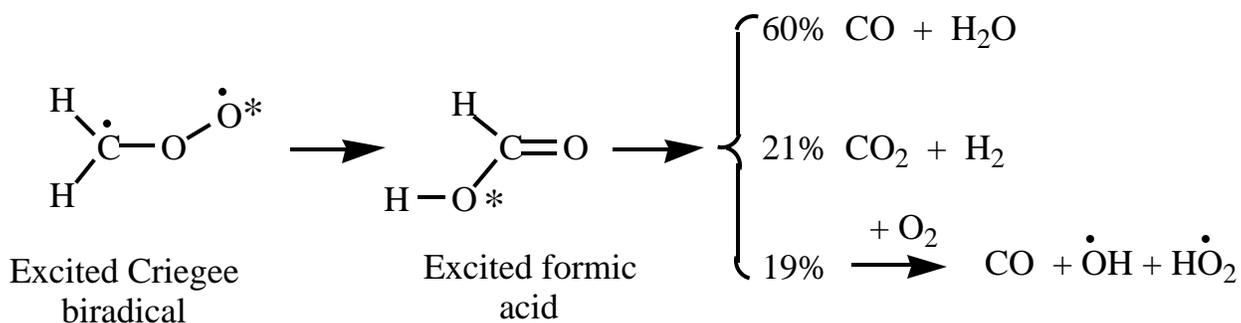
(12.89)

## Criegee biradical reaction



(12.90)

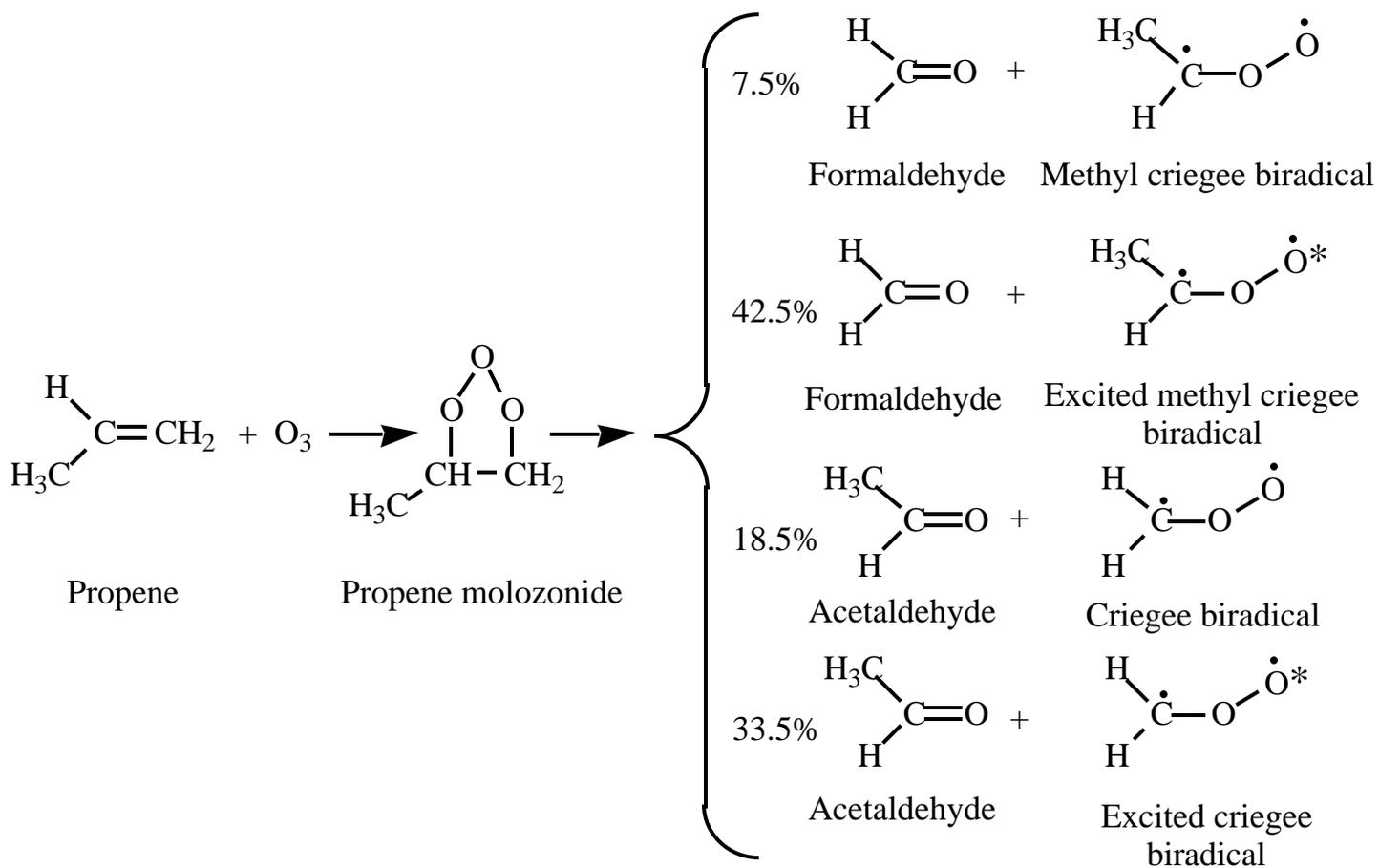
## Excited criegee biradical decomposition



(12.91)

# Alkene Reaction With Ozone

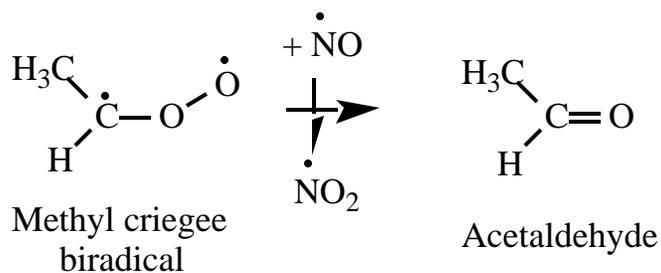
## Propene



(12.92)

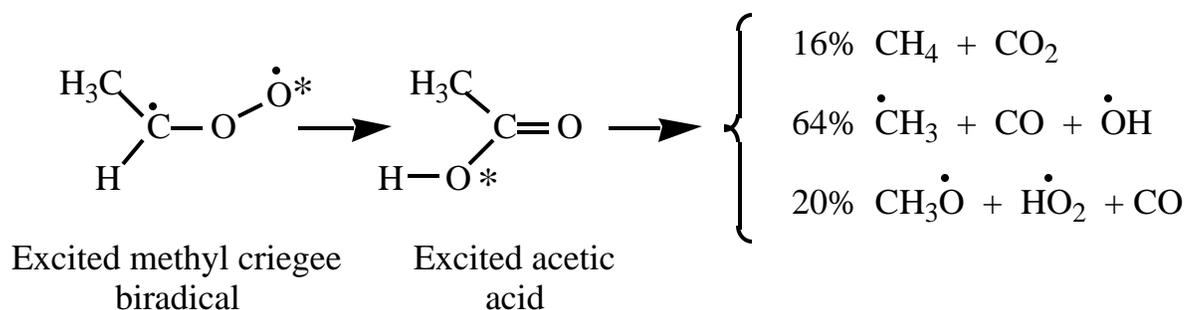
# Alkene Reaction With Ozone

## Methylcriegee biradical reaction



(12.93)

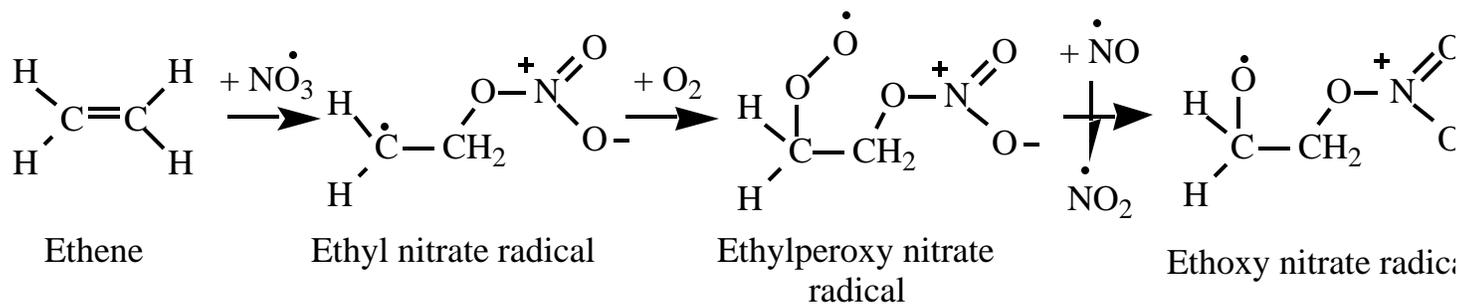
## Excited methylcriegee biradical decomposition



(12.94)

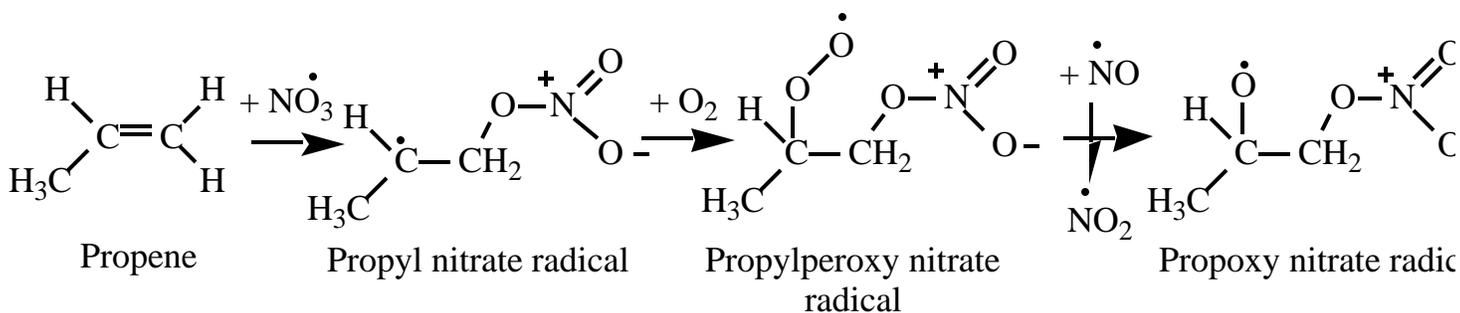
## Alkene Reaction With Nitrate

Ethene --> nitrated organic radicals



(12.95)

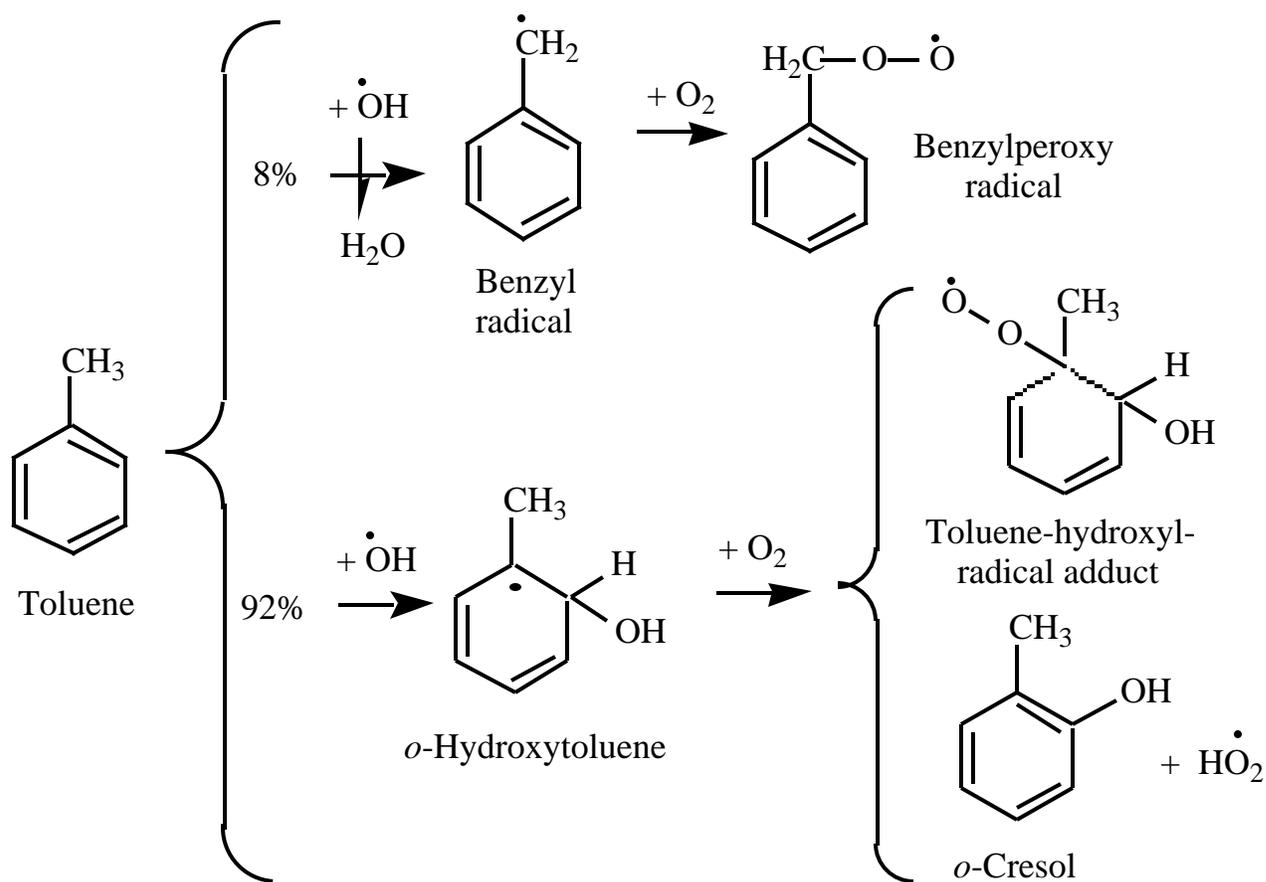
Propene --> nitrated organic radicals



(12.96)

# Aromatic Reaction With Hydroxyl Radical

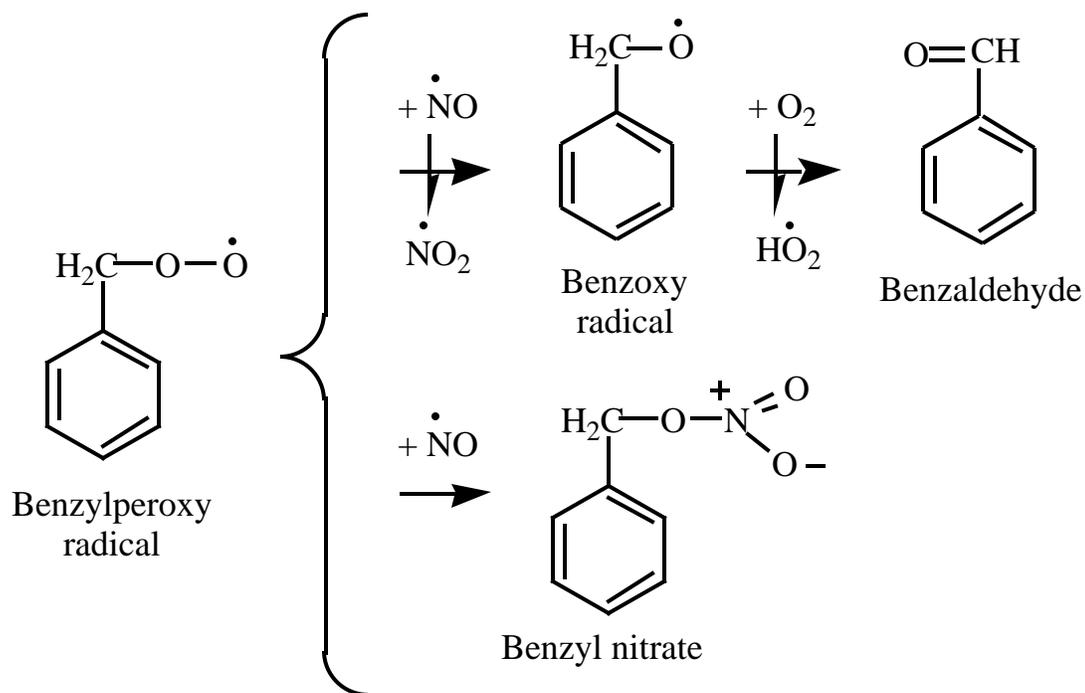
## Toluene oxidation



(12.97)

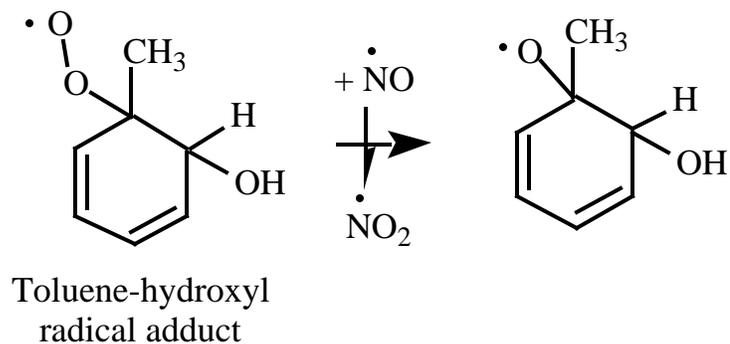
# Aromatic Reaction With Hydroxyl Radical

## Benzylperoxy radical reaction with NO



(12.98)

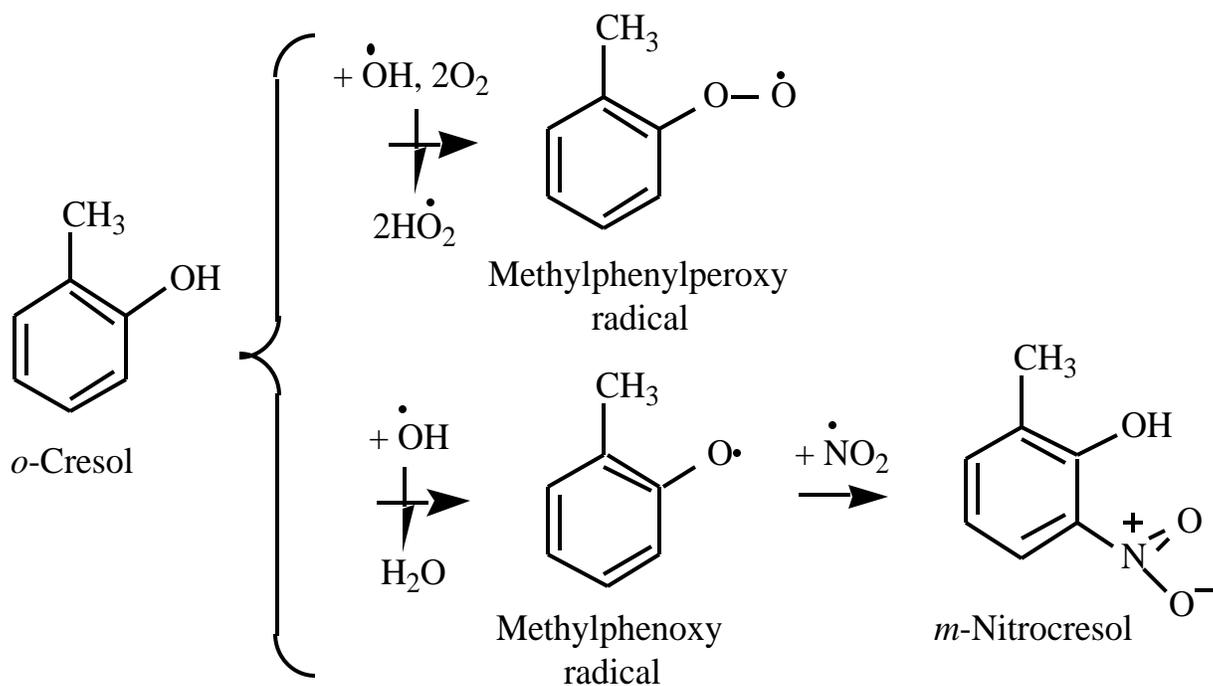
## Toluene-hydroxyl radical adduct reaction



(12.99)

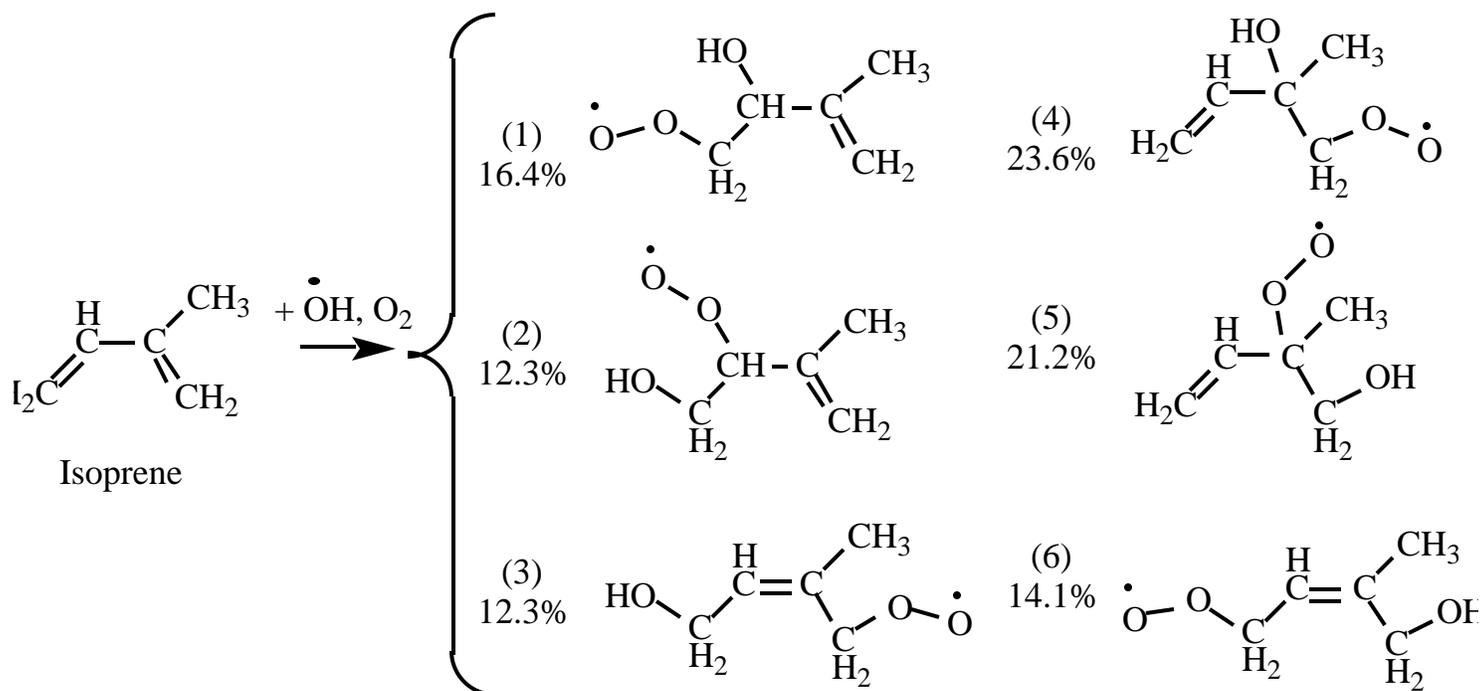
## Fate of Cresol

Cresol --> methylphenylperoxy radical and nitrocresol



(12.100)

## Terpene Reaction With OH



Isoprene peroxy radicals

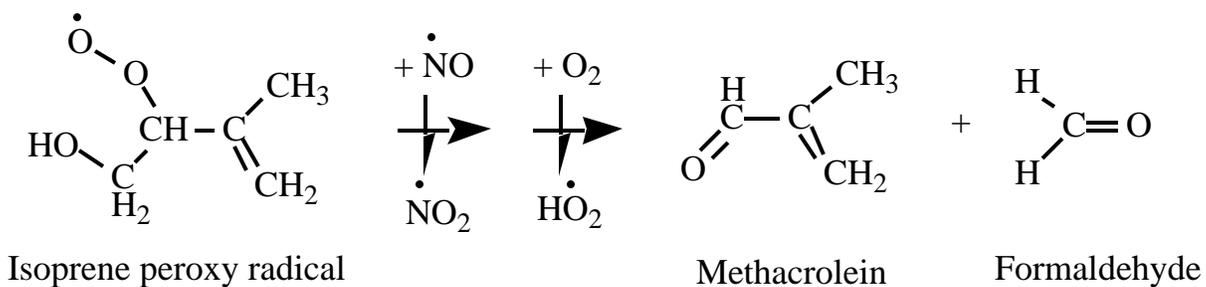
(12.101)

All six products convert NO to NO<sub>2</sub>

# Terpene Reaction With OH

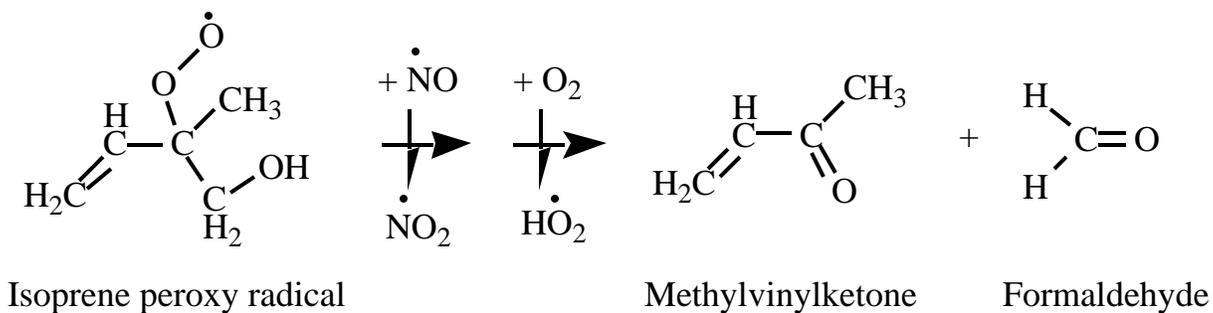
Methacrolein production via second product

(12.102)

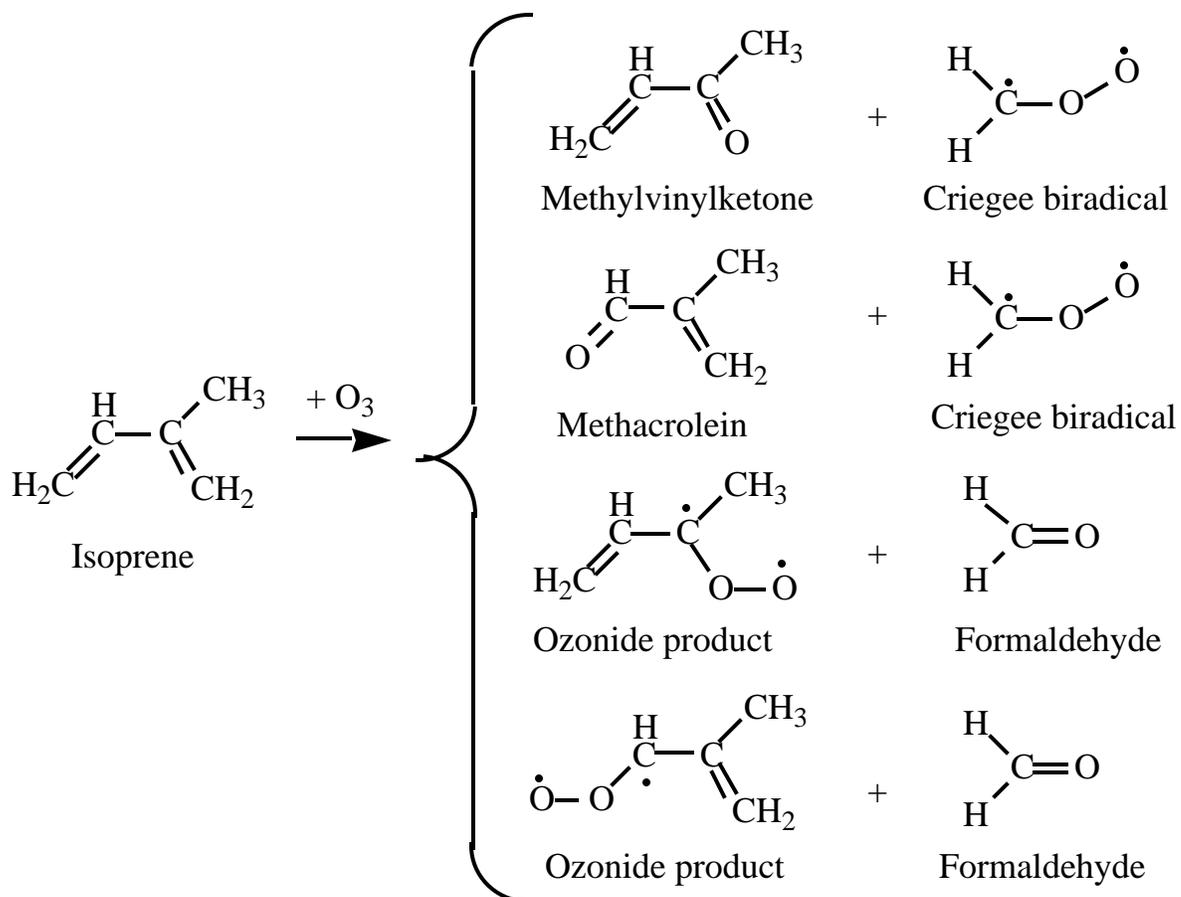


Methylvinylketone production via fifth product

(12.103)



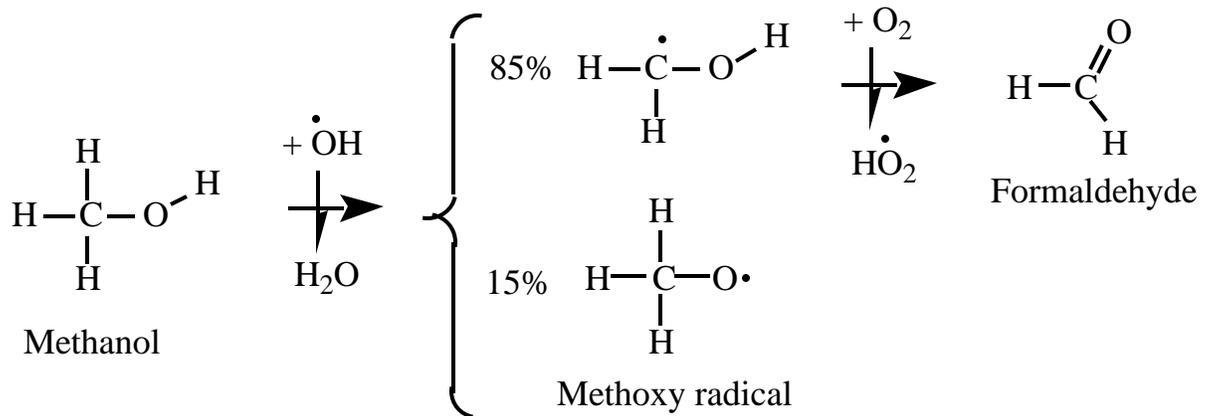
## Terpene Reaction With Ozone



(12.104)

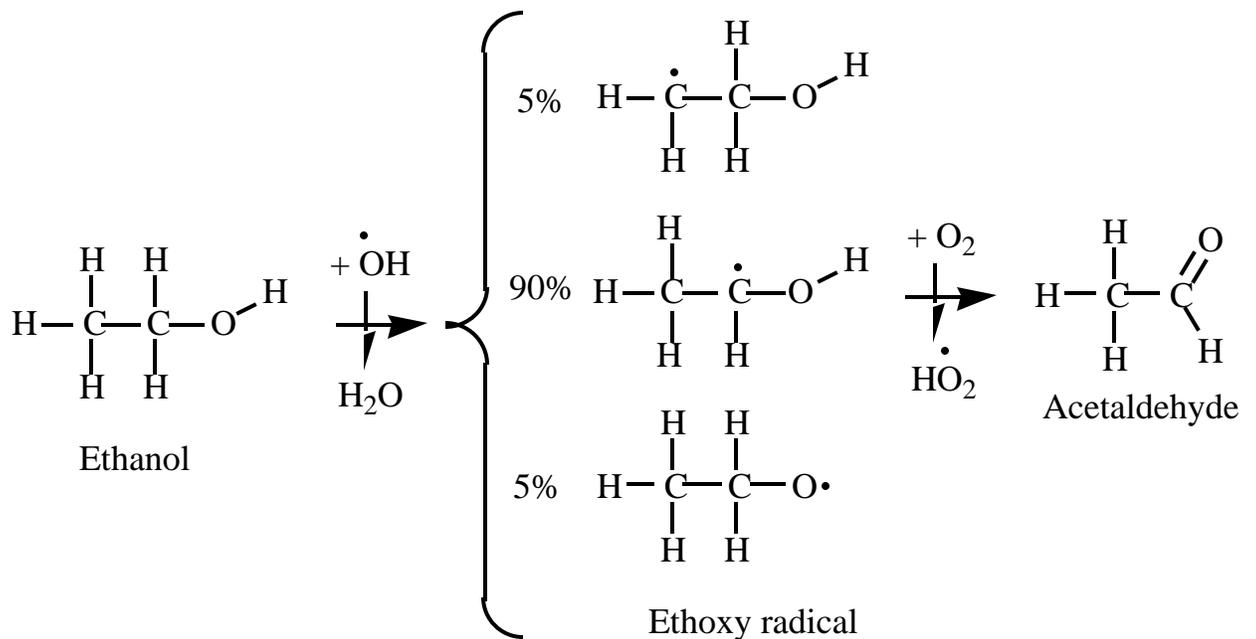
# Alcohol Reactions

Hydroxyl radical scavenges methanol (36-hour lifetime)



(12.105)

Hydroxyl radical scavenges ethanol (10-hour lifetime)



(12.106)

# Carbon Bond Lumping

Organic gases lumped into surrogate groups.

PAR (paraffins) -- Single carbon atoms with a single-bond between them

OLE (olefins) -- Terminal carbon atom pair with a double-bond between the two atoms

ALD2 -- Non-terminal carbon atom pairs with a double bond attached to one of the carbons and terminal two-carbon carbonyl groups [C-C(=O)H]

KET -- Single carbon ketone groups (C=O)

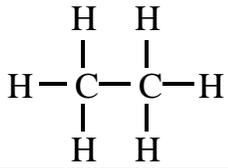
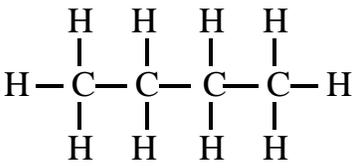
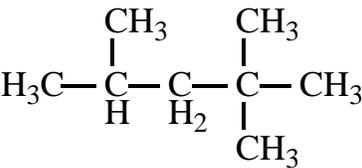
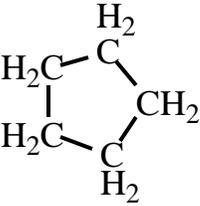
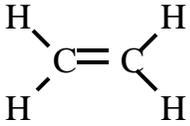
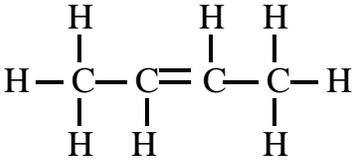
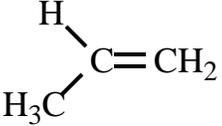
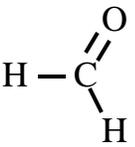
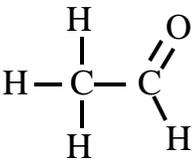
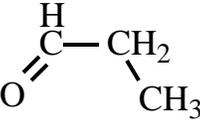
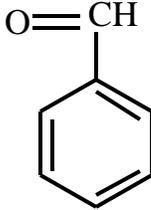
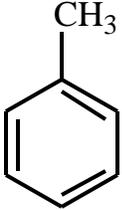
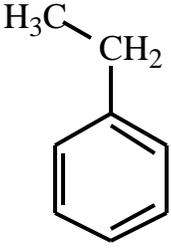
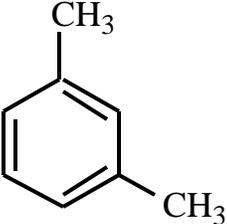
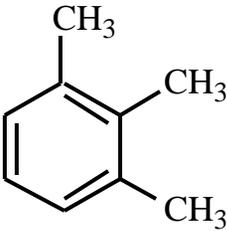
TOL (toluene) -- 7-carbon aromatics

XYL (*m*-xylene) -- 8-carbon aromatics

ISOP (isoprene) -- Terpenes

UNR -- Unreactive

## Carbon Bond Lumping (Table 12.7)

Chemical Name Carbon Bond Group Chemical Structure	Chemical Name Carbon Bond Group Chemical Structure	Chemical Name Carbon Bond Group Chemical Structure	Chemical Name Carbon Bond Group Chemical Structure
<b>Ethane</b> 0.4 PAR + 1.6 UNR 	<b><i>n</i>-Butane</b> 4 PAR 	<b>2,2,4-Trimethylpentane</b> 8 PAR 	<b>Cyclopentane</b> 5 PAR 
<b>Ethene</b> 1 ETH 	<b><i>Trans</i> 2-butene</b> 2 ALD2 	<b>Propene</b> 1 PAR + 1 OLE 	<b>Ethyne</b> 1 PAR + 1 UNR 
<b>Formaldehyde</b> 1 FORM 	<b>Acetaldehyde</b> 1 ALD2 	<b>Propionaldehyde</b> 1 PAR + 1 ALD2 	<b>Benzaldehyde</b> 1 ALD2 + 5 UNR 
<b>Toluene</b> 1 TOL 	<b>Ethylbenzene</b> 1 PAR + 1 TOL 	<b><i>m</i>-Xylene</b> 1 XYL 	<b>1,2,3-Trimethylbenzene</b> 1 PAR + 1 XYL 

# Stratospheric Chemistry

## Ozone mixing ratios

stratosphere

10 ppmv

free troposphere

40 ppbv

urban air

0.1 - 0.3 ppmv

## Ozone production in the stratosphere

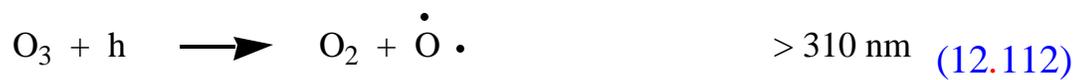
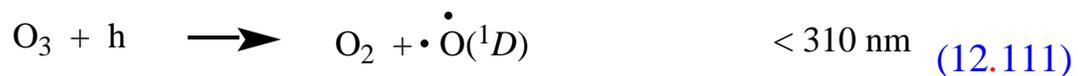
### Oxygen photolysis



### Ozone formation

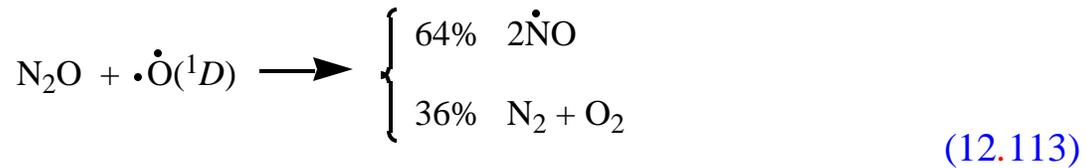


### Ozone photodissociation

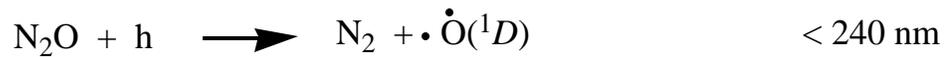


## Ozone Destruction by NO<sub>x</sub>

Nitrous oxide reaction: 10% of N<sub>2</sub>O destruction



Nitrous oxide photolysis: 90% of N<sub>2</sub>O destruction (12.114)

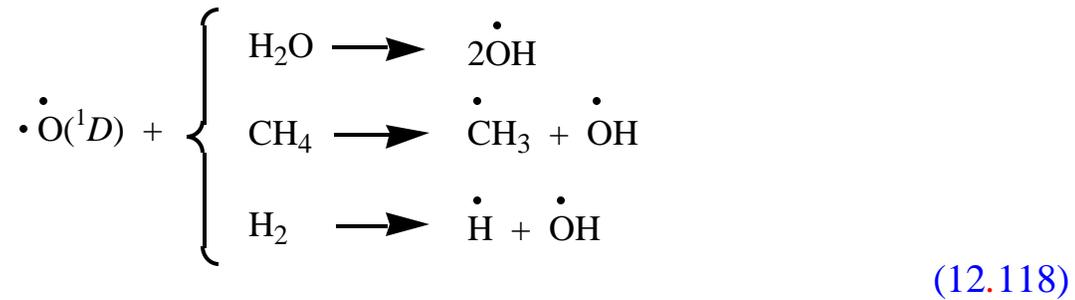


NO catalytically destroys ozone in the upper stratosphere

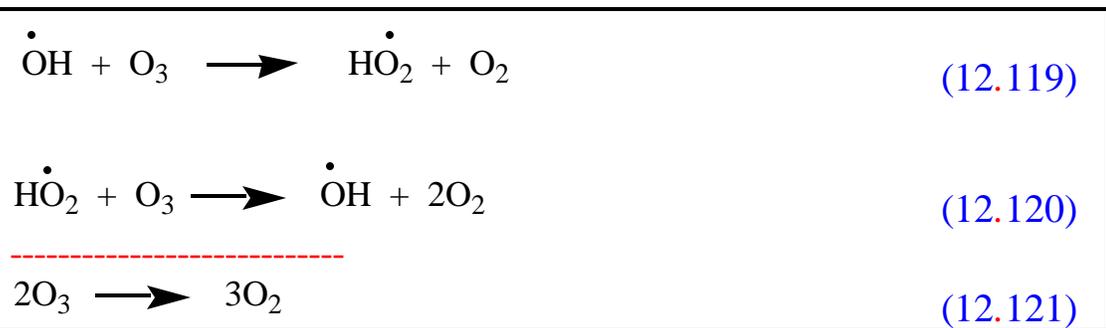


# Ozone Destruction by HOx

Hydroxyl radical formation in stratosphere

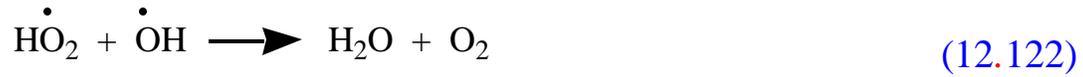


OH catalytically destroys ozone in the lower stratosphere



## Removal of HO<sub>x</sub> and NO<sub>x</sub>

Removal reactions



Nitric acid and peroxyntic acid photodissociation is slow

## Source of Water Vapor



Methane and carbon monoxide reactions in the stratosphere are similar to those in the free troposphere

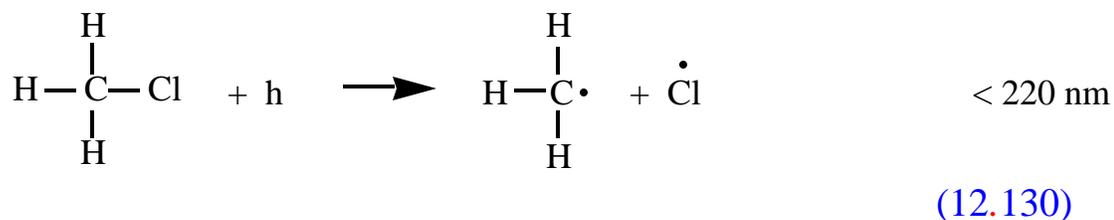
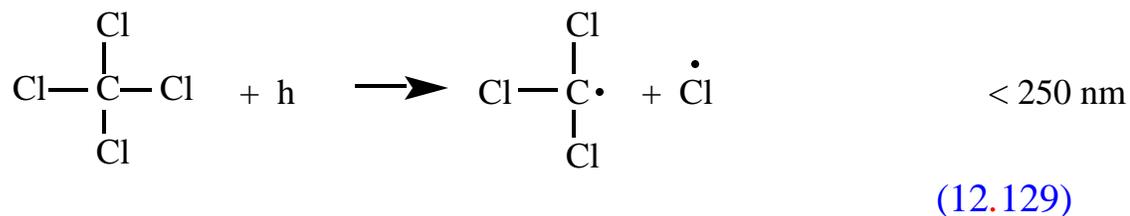
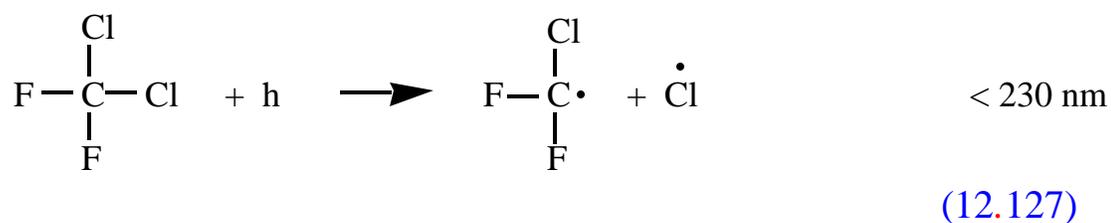
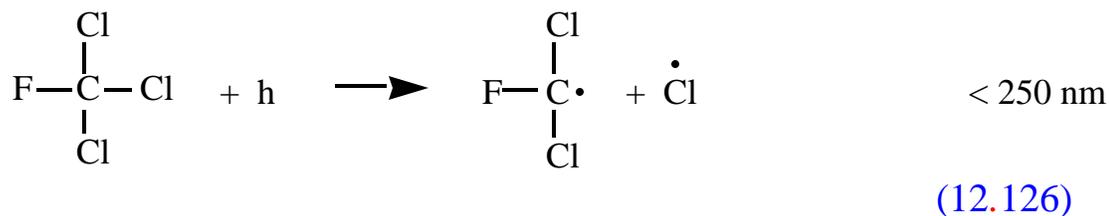
# Chlorine Emissions to Stratosphere

Table 12.8.  
WMO (1994)

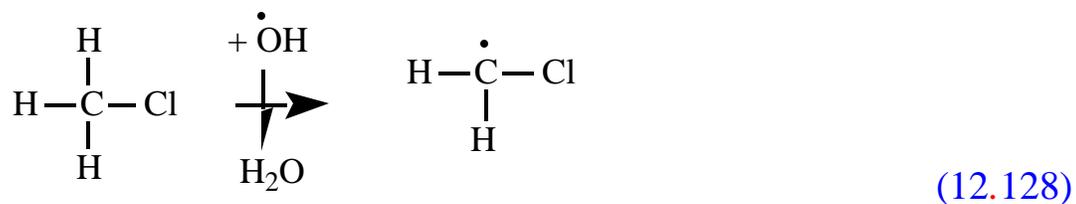
Chemical Formula	Trade Name	Chemical Name	Percent Contribution to Stratospheric Emissions
<b>Anthropogenic Sources</b>			
CF <sub>2</sub> Cl <sub>2</sub>	CFC-12	Dichlorodifluoromethane	28
CFCl <sub>3</sub>	CFC-11	Trichlorofluoromethane	23
CCl <sub>4</sub>		Carbon tetrachloride	12
CH <sub>3</sub> CCl <sub>3</sub>		Methyl chloroform	10
CFCl <sub>2</sub> CF <sub>2</sub> Cl	CFC-113	1-Fluorodichloro,2-difluorochloroethane	6
CF <sub>2</sub> ClH	HCFC-22	Chlorodifluoromethane	3
<b>Natural Sources</b>			
CH <sub>3</sub> Cl	---	Methyl chloride	15
HCl	---	Hydrochloric acid	3
<b>Total</b>			
			100%

# Ozone Destruction by Chlorine

Photolysis of chlorinated compounds above 20 km



Methyl chloride scavenging by hydroxyl radical



# Ozone Destruction by Chlorine

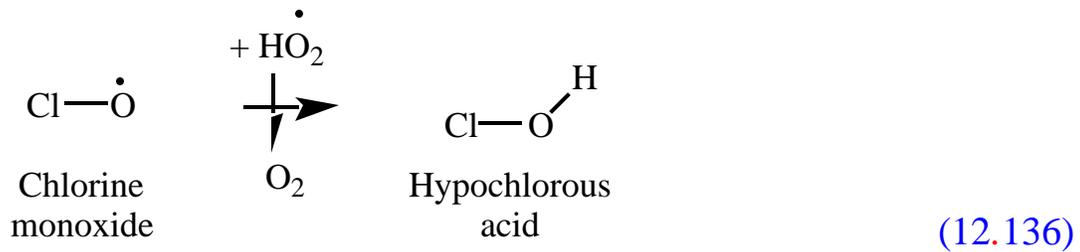
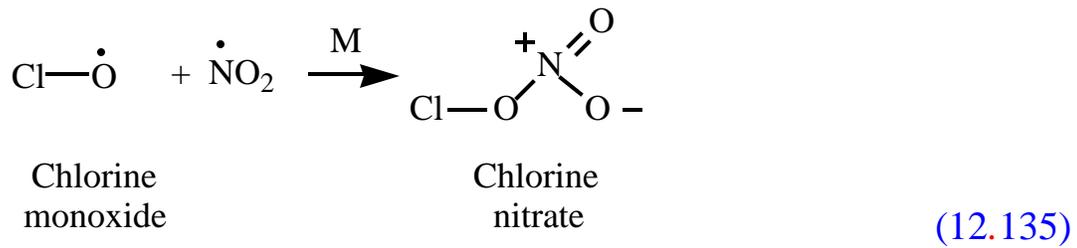
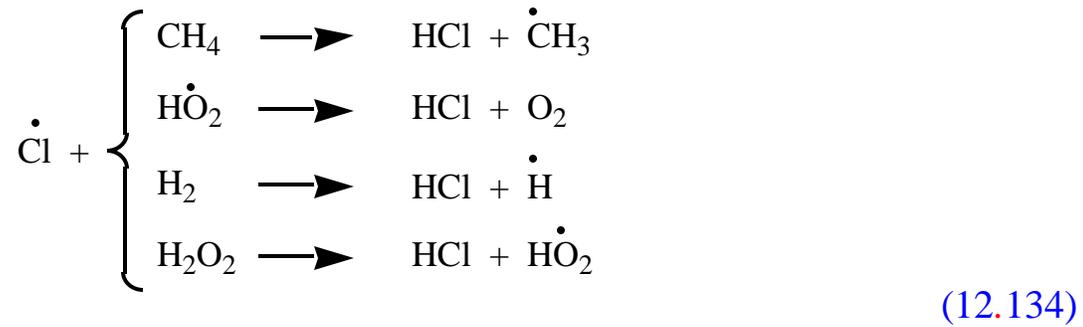
Catalytic ozone destruction by chlorine



Only 1% of chlorine is typically active as Cl or ClO.

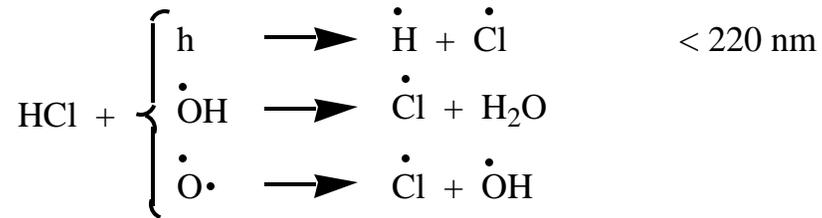
# Removal of Active Chlorine

## Removal of Cl and ClO



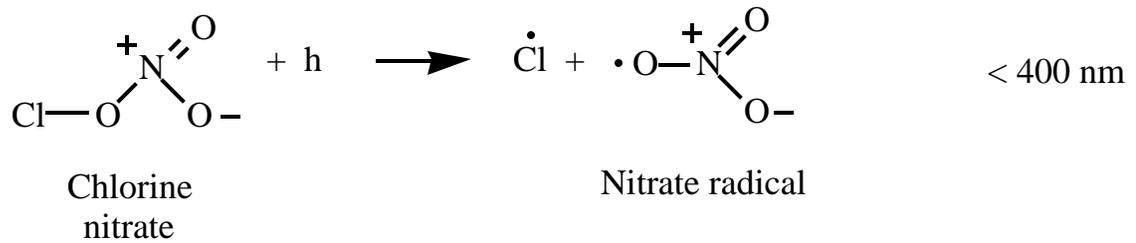
# Removal of Active Chlorine

## HCl reservoir leaks



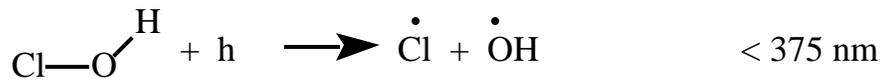
(12.137)

## ClONO<sub>2</sub> reservoir leaks



(12.138)

## HOCl reservoir leaks

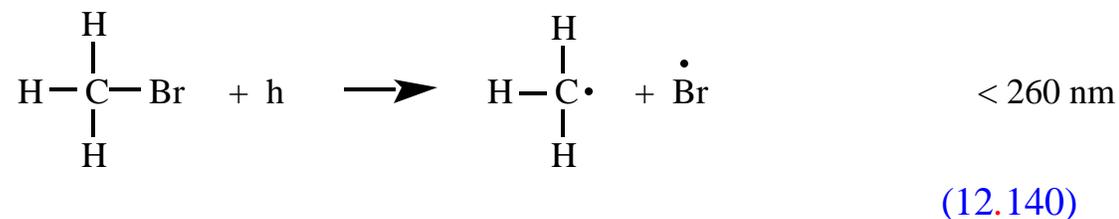


(12.139)

## Ozone Destruction by Bromine

$\text{CH}_3\text{Br}$  = methyl bromide (produced biogenically in the oceans and anthropogenically as soil fumigant)

Photolysis of methyl above 20 km

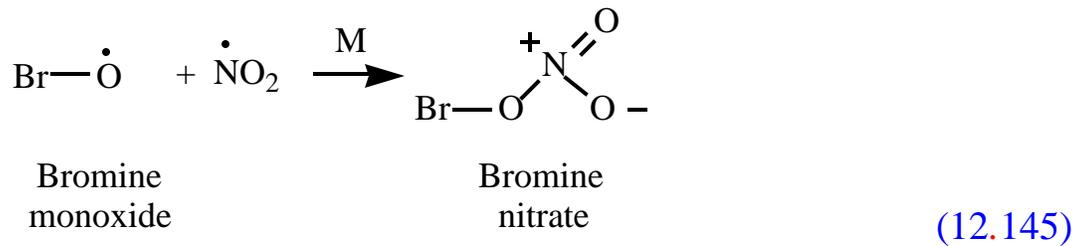
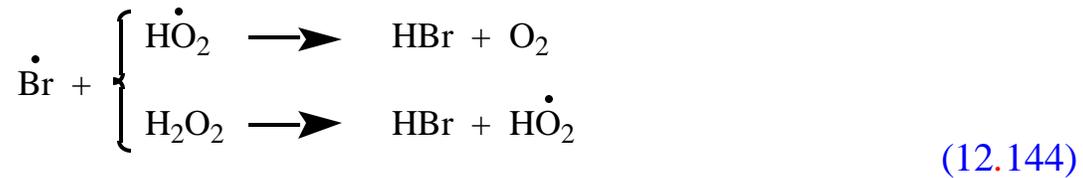


Catalytic ozone destruction by bromine

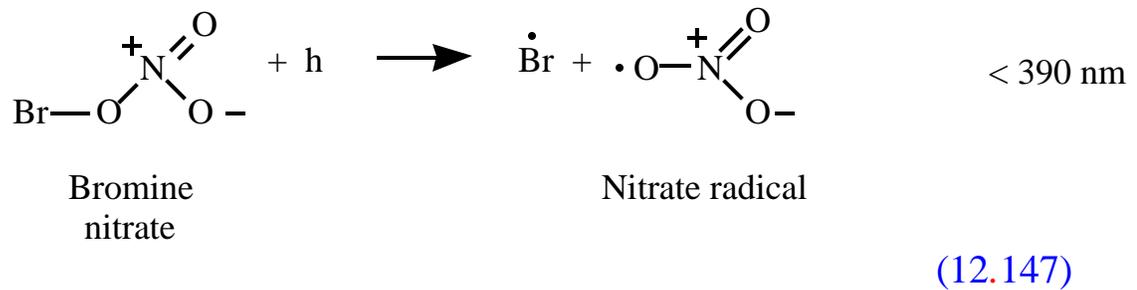


## Removal of Active Bromine

### Removal of Br and BrO

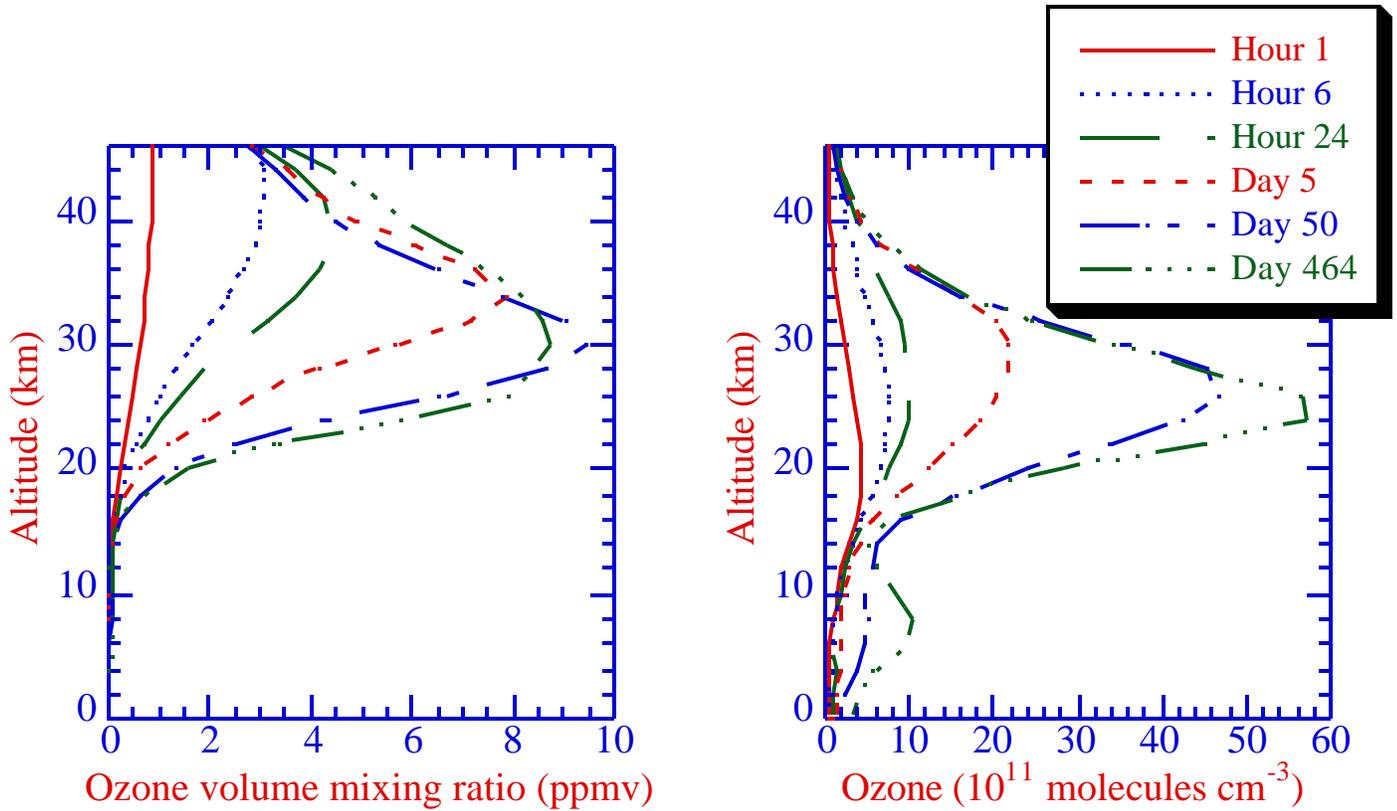


### HBr and BrONO<sub>2</sub> reservoir leaks



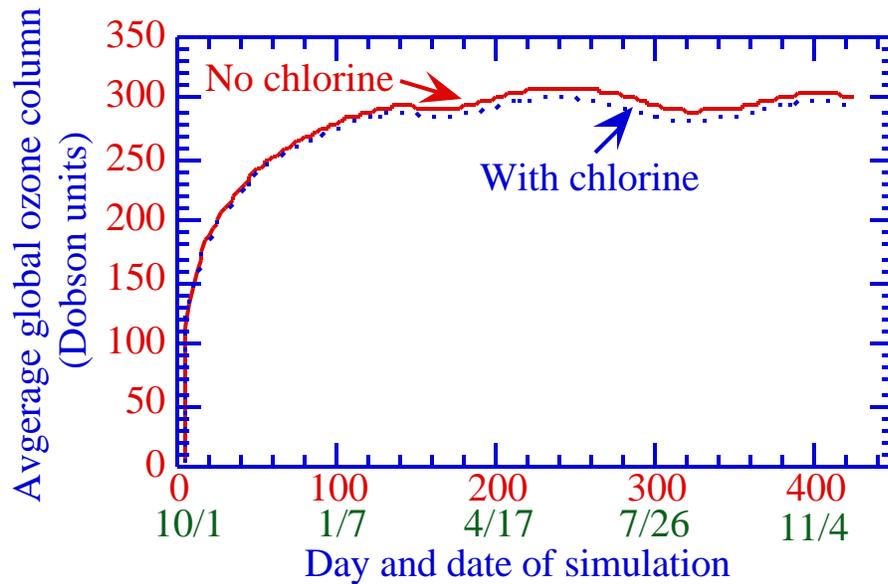
# Ozone Regeneration

Figs. 12.4 a, b. Time-evolution of modeled profile of ozone (a) mixing ratio and (b) number concentration at 34°N latitude, starting with zero ozone.



# Regeneration Rate of the Global Ozone Layer

Fig. 12.2. Change in ozone column abundance, averaged over the globe, during two global model simulations in which chlorine was present and absent, respectively. In both cases, ozone was initially removed from the model atmosphere.



## Ozone Hole Growth

Table 12.9. Minimum measured values of ozone column abundances and areal extent of the ozone hole over Antarctic region from 1979 - 1994. Data from NASA Goddard Space Flight Center. The area of the Antarctic is about 13 million km<sup>2</sup> and the area of North America is about 24 million km<sup>2</sup>.

	Ozone Minimum (DU)	Size (million km <sup>2</sup> )
1979	210	0
1980	195	0.5
1981	206	0
1982	182	3
1983	170	7
1984	154	9
1985	143	13
1986	159	9.5
1987	121	19
1988	179	8
1989	124	18.5
1990	126	17.5
1991	110	18
1992	121	21
1993	86	22
1994	90	23

# Polar Stratospheric Cloud Reactions

## Type I Polar Stratospheric Clouds (PSCs)

nitric acid and water

temperature of formation  $< 195$  K

diameter 0.01 - 3  $\mu\text{m}$

number concentration 1 partic.  $\text{cm}^{-3}$

## Type II Polar Stratospheric Clouds

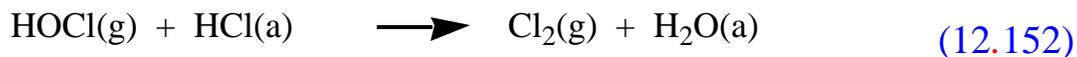
Water ice

temperature of formation  $< 187$  K

diameter 1 - 100  $\mu\text{m}$

number concentration 0.1 partic.  $\text{cm}^{-3}$

## Reactions on Polar Stratospheric Cloud Surfaces



## Surface Reaction Rates

First-order rate coefficient ( $s^{-1}$ )

$$k_{s,q} = \frac{1}{4} \bar{v}_q q a \quad (12.153)$$

Thermal velocity of impinging gas ( $cm\ s^{-1}$ )

$$\bar{v}_q = \frac{8k_B T}{M_q}^{1/2} \quad (12.154)$$

Table 12.10. Estimated reaction probabilities for the gases in reactions (12.147) - (12.151) on Type I and II PSC surfaces. Data from DeMore et al. (1997) and references therein.

Reaction	Type I PSCs	Type II PSCs
$ClONO_2(g) + H_2O(a)$	0.001	0.3
$ClONO_2(g) + HCl(a)$	0.1	0.3
$N_2O_5(g) + H_2O(a)$	0.0003	0.01
$N_2O_5(g) + HCl(a)$	0.003	0.03
$HOCl(g) + HCl(a)$	0.1	0.3

# Polar Ozone Destruction

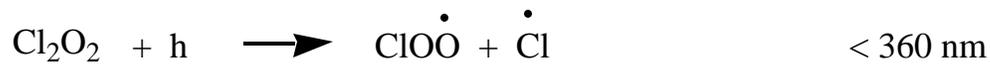
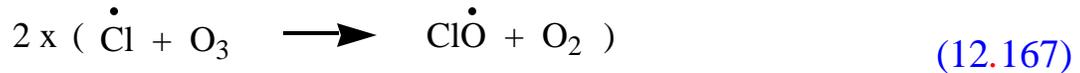
Cl<sub>2</sub> and HOCl photolysis in early spring



Chlorine nitrite photolysis in early spring

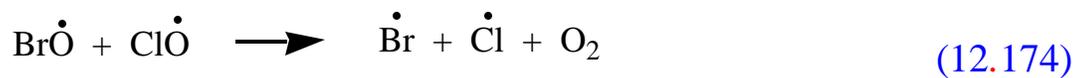


Catalytic ozone destruction by dimer mechanism



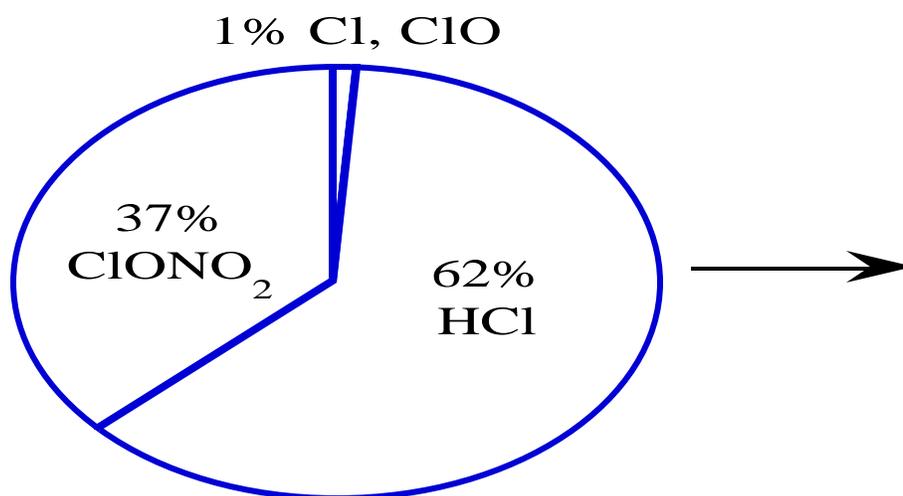
## Polar Ozone Destruction

A second catalytic cycle that involves bromine

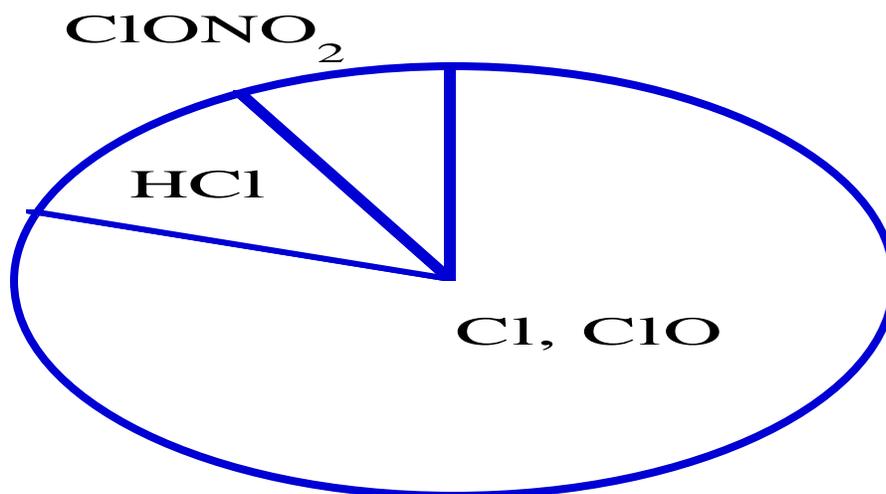


# Conversion of Chlorine Reservoirs to Active Chlorine

Fig. 12.5.



Before PSC and photolysis reactions



After PSC and photolysis reactions