Part 1. The Earth's Atmosphere

Chapter 3. Stratospheric Chemistry : Ozone

Chapter 3. Stratospheric chemistry

3.0 Generals

- Gas molecules in stratosphere, mainly dioxygen and dinitrogen

  - act as absorbing centers, moderating the transmission of solar radiation to the Earth.

  - can be significantly altered by human activity processes

  - by high solar energy radiation, dioxygen turns to ozone or vice versa

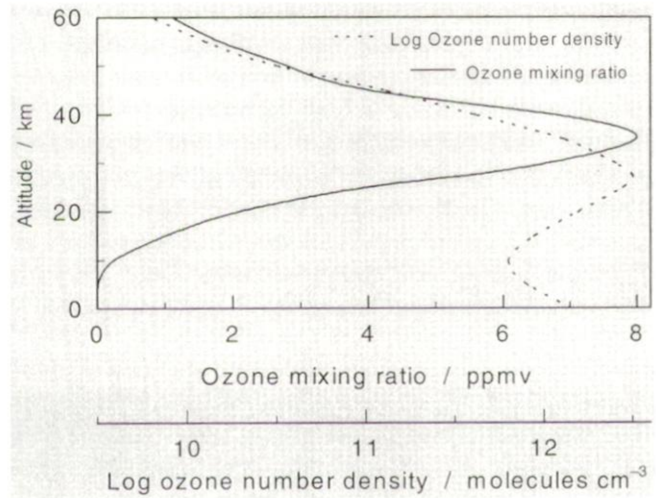


Fig. 3.1 Concentration profile of ozone in the lower atmosphere, shown both as the mixing ratio (solid line) and as the log of number density (broken line). (Data from Wayne, R. P., *Chemistry of Atmospheres*, Clarenden Press; Oxford; 1991. Reprinted with permission.)

Chapter 3. Stratospheric chemistry

3.0 Generals

- Classification of UV radiation
- UV-A: λ= 315~400 nm,
- UV-B: λ= 280~315 nm,
- UV-C: λ<280 nm.

Ozone in the stratosphere is an effective filter capable of absorbing UV with λ=200~315 nm

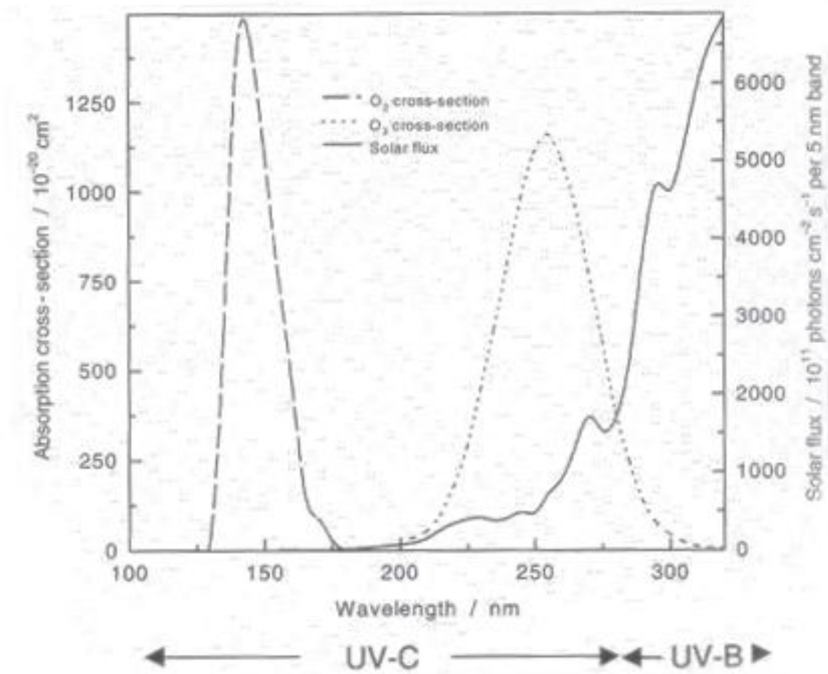


Fig. 3.2 Absorption cross-section of oxygen (broken line) and ozone (dotted line) compared to the solar flux density (solid line) over the region of biologically harmful ultraviolet radiation (Data from Chamberlain, J. W. and D. M. Hunten, *Theory of Planetary Atmospheres*, Academic Press; 1987. Reprinted with permission.)

Chapter 3. Stratospheric chemistry

3.1 Formation and turnover of ozone

- Four fundamental reactions

- Synthesis:

$O_2 + h\nu\ (\lambda < 240\ nm) \rightarrow O + O$	slow	$\Delta H° = -E(h\nu) + 498.4$ kJ	(3.1)
$O + O_2 + M \rightarrow O_3 + M\ (N_2 \text{ or } O_2)$	fast	$\Delta H° = -106.5$ kJ	(3.2)

- Decomposition

$O_3 + h\nu\ (\lambda \approx 230\text{-}320\ nm) \rightarrow O_2^* + O^*$	fast	$\Delta H° = -E(h\nu) + 386.5$ kJ	(3.3)
$O + O_3 \rightarrow O_2 + O_2$	slow	$\Delta H° = -391.9$ kJ	(3.4)

Chapter 3. Stratospheric chemistry

3.2 Catalytic decomposition processes of ozone

- Additional decomposition reactions

$X + O_2 \rightarrow XO + O_2$ (3.6)

$XO + O \rightarrow X + O_2$ (3.7)

net rxn. $O + O_3 \rightarrow 2O_2$ (3.8)

Here, X = HO_x (·H, ·OH, HOO·), No_x (·NO, $\cdot NO_2$), ClO_x (·Cl, ClO·)

- HO_x cycle

Radical formation $O(^1D) + H_2O \rightarrow 2\ \cdot OH$ (3.9)

$H_2O + h\nu \rightarrow \cdot H + \cdot OH$ (3.10)

Ozone consumption $\cdot OH + O_3 \rightarrow HOO\cdot + O_2$ (3.11)

$HOO\cdot + O \rightarrow HO\cdot + O_2$ (3.12)

net reaction $O + O_3 \rightarrow 2\ O_2$ (3.13)

$\cdot H + O_3 \rightarrow HO\cdot + O_2$ (3.14)

$\cdot OH + O \rightarrow H\cdot + O_2$ (3.15)

net reaction $O + O_3 \rightarrow 2\ O_2$ (3.16)

Chapter 3. Stratospheric chemistry

3.2 Catalytic decomposition processes of ozone

- NO_x cycle

Ozone consumption

$NO + O_3 \rightarrow NO_2 + O_2$ (3.17)

$NO_2 + O \rightarrow NO + O_2$ (3.18)

net reaction $O + O_3 \rightarrow 2\ O_2$ (3.19)

in the lower part of strato

$N_2 + h\nu(\lambda<126\ nm) \rightarrow N(^4S) + N(^2D)$ (3.20)

$N(^4S) + O_2 \rightarrow NO + O$ (3.21) altitude>30 km

$NO_2 + O(^1D) \rightarrow 2NO$ (3.22) altitude<30 km

Depletion of NO radical $\cdot NO + \cdot OH + M \rightarrow HNO_2 + M$ (3.23)

Chapter 3. Stratospheric chemistry

3.2 Catalytic decomposition processes of ozone

ClO_x cycle-mainly by chlorofluorocarbons(CFCs)

Radial formation

$CH_3Cl + h\nu \rightarrow \cdot CH_3 + \cdot Cl$ (3.24)

$CH_3Cl + \cdot OH \rightarrow \cdot CH_2Cl + H_2O$ (3.25)

Ozone consumption

$\cdot Cl + O_3 \rightarrow ClO\cdot + O_2$ (3.26)

$ClO\cdot + O \rightarrow Cl\cdot + O_2$ (3.27)

net reaction $O + O_3 \rightarrow 2\ O_2$ (3.28)

$\cdot OOH + ClO\cdot \rightarrow HOCl + O_2$ (3.29)

$HOCl + h\nu \rightarrow \cdot OH + Cl\cdot$ (3.30)

$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$ (3.31)

$\cdot OH + O_3 \rightarrow HOO\cdot + O_2$ (3.32)

net reaction $2O_3 \rightarrow 3\ O_2$ (3.33)

Chapter 3. Stratospheric chemistry

3.2 Catalytic decomposition processes of ozone

- Anthropogenic sources of chlorine
  > mainly CFCs

Table 3.1 Properties of common CFCs

	Formula	Atmospheric lifetime/y	ODP[a]	Release rate/ 10^6 kg y^{-1}	Concentration/pptv 1977	Concentration/pptv 1993	Contribution to O_3 loss[b] /%
CFC-11	$CFCl_3$	60	1.0	281	140	272	31
CFC-12	CF_2Cl_2	195	1.0	370	255	519	36
CFC-113	$CF_2ClCFCl_2$	101	0.8	138	–	–	14
CFC-114	CF_2ClCF_2Cl	236	1.0	–	–	–	–
CFC-115	CF_2ClCF_3	522	0.6	–	–	–	–

[a]Ozone depletion potential (ODP).
[b]The percentage contribution to ozone depletion is based on the major halogen-containing species only.
ODP values were obtained from the US EPA's Stratospheric Protection Division; CFC concentrations and from Environment Canada (SOE Bulletin No 94–6, Fall 1994); and the remaining values are from Wayne, R. P., *Chemistry of Atmospheres*, Clarendon Press, Oxford; 1991.

Table 3.2 CFC alternatives, applications, and regulations

Substance	Formula	ODP[a]	Major uses	Regulatory outlook
HCFC-22	$CHClF_2$	0.055	Foams, air-conditioning, refrigeration, aerosols	Clean Air Act bans aerosol use in new equipment after 2005
HCFC-142b	CH_3CClF_2	0.065	Foams, refrigerants	EPA likely to ban use in new equipment after 2005
HCFC-141b	CH_3CCl_2F	0.11	Foams, solvents	EPA likely to approve for foams use only and ban use in new equipment after 2005
HCFC-123	$CHCl_2CF_3$	0.02	Foams, air-conditioning, fire fighting	EPA likely to approve only air-conditioning use; Clean Air Act bans use in new equipment after 2015
HFC-134a	CH_2FCF_3	0.0	Refrigeration, air-conditioning	No restrictions anticipated
HCFC-124	$CHClFCF_3$	0.022	Refrigeration, sterilant	Clean Air Act bans use in new equipment after 2005
HFC-125	CHF_2CF_3	0.0	Refrigeration	No restrictions anticipated
HFC-22	CH_2F_2	0.0	Refrigeration, air-conditioning	No restrictions anticipated

[a]Estimates from United Nations Environment Program's 'Scientific Assessment of Ozone Depletion: 1991'. Estimates depend on chlorine content and atmospheric lifetime. Potentials are set relative to CFC-11, which is assigned a value of 1.0.
Reproduced with permission from Zurer, P. S., *Industry*, consumers prepare for compliance with pending CRC ban, *Chem. Eng. News*, **70** (1992), 7–13.

Chapter 3. Stratospheric chemistry

3.2 Catalytic decomposition processes of ozone

- Kinetic calculations-refer to the text pp54-55.

E.g. at an altitude of 20 km (T~220 K), for reactions 3.17~3.19

reaction rate = $k_{17}[NO][O_3]$, rate = $k_{18}[NO_2][O]$

Which rxn is rate determining?

the Arrhenius expression, $k = Ae^{-E_a/RT}$

	E_a/kJ mol^{-1}	A/cm^3 molecule^{-1}s^{-1}	k/cm^3 molecules^{-1}s^{-1}
• rxn 3.17	11.4	1.8×10^{-12}	3.5×10^{-15}
• rxn 3.18	0	9.3×10^{-12}	9.3×10^{-12}

- At an altitude of 20 km,
- $[O]=2.0 \times 10^7$ molecules/cm^3 $[O_3]=3.0 \times 10^{12}$ molecules/cm^3
- $[NO]=2.0 \times 10^9$ molecules/cm^3 $[NO_2]=8.0 \times 10^9$ molecules/cm^3
- Then, $rate_{3.17} = 2.1 \times 10^7$ molecules/cm^3/s,
- $rate_{3.18} = 1.5 \times 10^6$ molecules/cm^3/s :
- CF: at an altitude of 40 km (T~220 K), rxn 3.17 becomes rate determining

Chapter 3. Stratospheric chemistry

3.3 Null and holding cycles

- Null cycles involving NOs – see rxns from 3.39-3.50

$NO + O_3 \rightarrow NO_2 + O_2$ (3.39)

$NO_2 + h\nu \rightarrow NO + O$ (3.40)

net rxn $O_3 + h\nu \rightarrow O_2 + O$ (3.41)

- Another type of Null cycles involving NOs

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (3.42)

$NO_3 + h\nu \rightarrow NO_2 + O$ (3.43)

net rxn $O_3 + h\nu \rightarrow O_2 + O$ (3.44)

$NO_3 + NO_2 \leftrightarrow N_2O_5 + M$ (3.45)

this is holding cycle that temporarily limiting the availability of NOx for catalyzing ozone decomposition in the stratosphere.

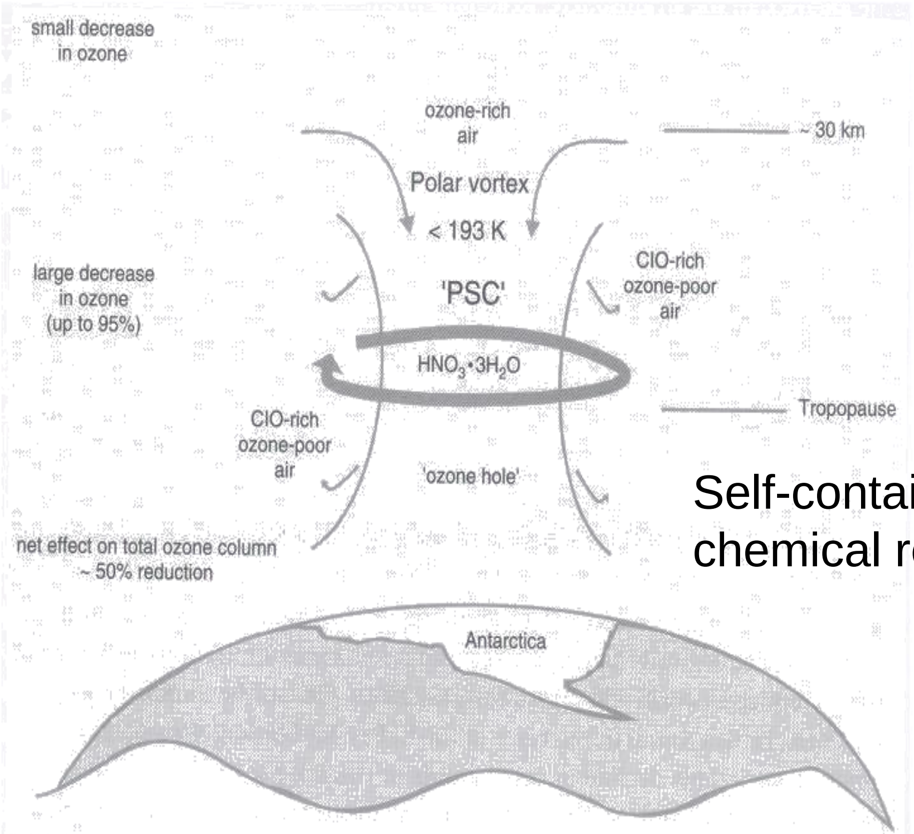
$\cdot NO_2 + \cdot OH + M \rightarrow HNO_3 + M$ (3.46)

$\cdot Cl + CH_4 \rightarrow HCl + \cdot CH_3$ (3.47)

Chapter 3. Stratospheric chemistry

3.4 Antarctic and Arctic ‘ozone hole’ formation

- Ozone holes –thinned ozone layer



Self-contained chemical reactor

Fig. 3.3. The Antarctic ‘ozone hole’ illustrating the polar vortex and the location and relative amounts of ozone loss during the polar sunrise. (Redrawn with permission from R. P. Wayne, *Chemistry of Atmospheres*, Clarendon Press, Oxford; 1991.)

Chapter 3. Stratospheric chemistry

3.4 Antarctic and Arctic ‘ozone hole’ formation

- Ozone holes –thinned ozone layer

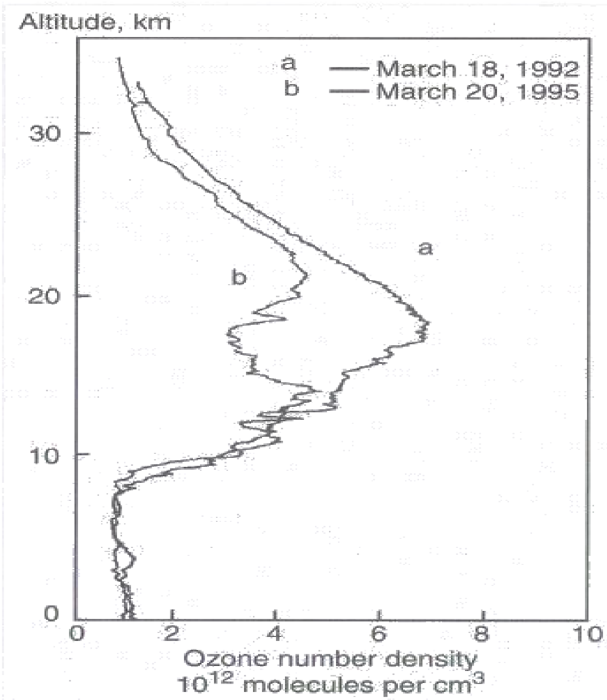


Fig. 3.4 Ozone vertical profiles determined by balloon-borne sensors above Spitsbergen, Norway (79° N). (Reprinted with permission from von der Gathen, P., Complexities of ozone loss continue to challenge scientists, *Chem. Eng. News*, 73 (1995), 24.)

Stratospheric sulfate in the form of an aerosol acts as a catalyst for the removal of N_2O_5 gas

$$N_2O_5 + H_2O \rightarrow \rightarrow \rightarrow \rightarrow 2HNO_3 \quad (3.60)$$

sulfate aerosol

Part 1. The Earth's Atmosphere

Chapter 4. Troposhperic Chemistry: Smog

Chapter 4. Tropospheric chemistry : smog

4.1 Smog

- **Smog:** a general term referring to forms of air pollutions in which atmospheric visibility is partially obscured by a haze consisting of solid particulates and/or liquid aerosols.
- \- classical (London) smog

: associated with the use of the traditional fuel, coal

: contains high conc. of unburned carbon soot (serves as nuclei for condensing of water droplets, forming an irritating fog) and elevated level of SO_2 (a mild reducing agent and weak acid precursor)

- \- photochemical (Los Angeles) smog

: based on emissions from petroleum combustion, followed by a sequence of chemical and photochemical reactions under specific conditions

: contains high level of oxidants and carbon-containing reaction products.

Chapter 4. Tropospheric chemistry : smog

4.1 Photochemical smog – HO· production chemistry

- $N_2 + O_2 \leftrightarrow 2NO$ (4.1)
- $2NO + O_2 \rightarrow 2NO_2$ (4.2)
- $NO + O_3 \rightarrow NO_2 + O_2$ (4.3)
- $ROO\cdot + NO \rightarrow RO\cdot + NO_2$ (4.4)
- $NO_2 + h\nu(\lambda<400\text{ nm}) \rightarrow NO + O$ (4.5)
- $O + O_2 + M \rightarrow O_3 + M$ (4.6)
- $O_3 + h\nu(\lambda<315\text{ nm}) \rightarrow O_2^* + O^*$ (4.7)
- $O^* + H_2O \rightarrow 2\cdot OH$ (4.8)
- Net rxns from 4.5 to 4.8, $NO_2 + H_2O \rightarrow NO + 2\cdot OH$ (4.9)

2nd mechanism

- $NO + NO_2 + H_2O \rightarrow 2HONO$ (4.10)
- $2HONO + h\nu(\lambda<400\text{ nm}) \rightarrow 2NO + 2\cdot OH$ (4.11)
- Net rxns $NO_2 + H_2O \rightarrow NO + 2\cdot OH$ (4.12)

Chapter 4. Tropospheric chemistry : smog

4.1 Photochemical smog – HO· production chemistry

- $OH + RCH_3 \leftrightarrow RCH_2\bullet + H_2O$ (4.13)
- $RCH_2\bullet + O_2 + M \rightarrow RCH_2OO\bullet + M$ (4.14)
- $RCH_2OO\bullet + NO \rightarrow RCH_2O\bullet + NO_2$ (4.15)
- $RCH_2O\bullet + O_2 \rightarrow RCHO + HOO\bullet$ (4.16)
- $HOO\bullet + NO \rightarrow NO_2 + \bullet OH$ (4.17)

Net rxns from 4.13 to 4.17,

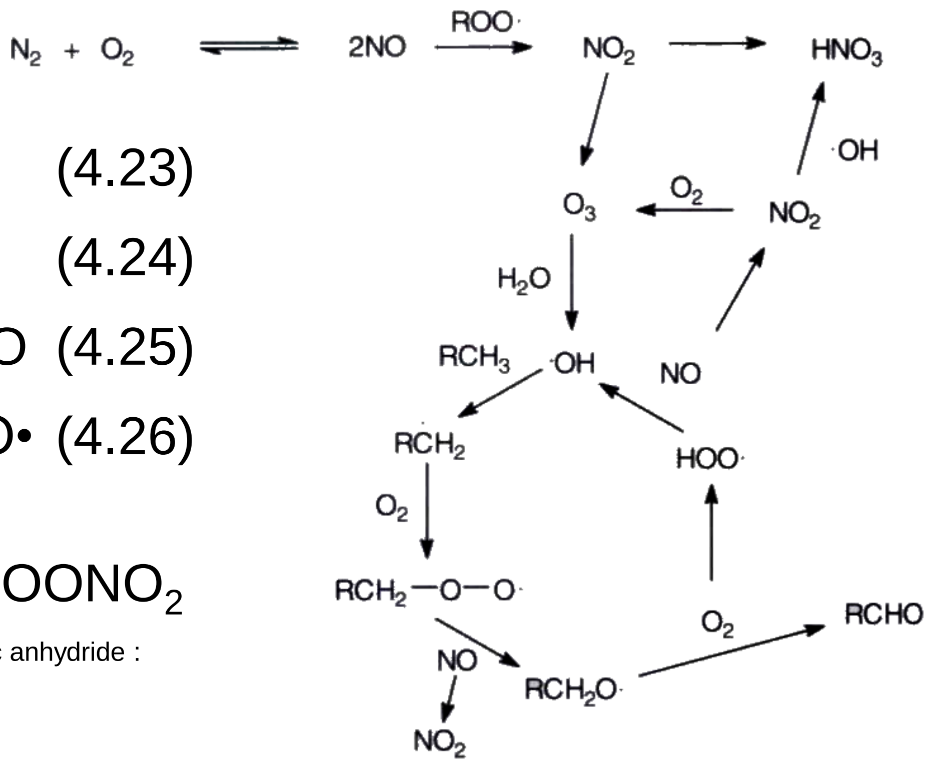
- $RCH_3 + 2O_2 + 2NO \rightarrow RCHO + 2NO_2 + H_2O$ (4.18)
- $RCH_3 + 2O_2 + H_2O \rightarrow 4\bullet OH$ (4.19) (rxn 4.9 + rxn 4.18)

HO• termination reactions

- $HO\bullet + \bullet NO_2 + M \rightarrow HNO_3 + M$ (4.20)
- $2HOO\bullet \rightarrow 2H_2O_2$ (4.21)
- $HO\bullet + HOO\bullet \rightarrow H_2O + O_2$ (4.22)

Chapter 4. Tropospheric chemistry : smog

4.2 Photochemical smog – secondary reactions



- $NO_2 + h\nu(\lambda<400\text{ nm}) \rightarrow NO + O$ (4.23)
- $O + O_2 + M \rightarrow O_3 + M$ (4.24)
- $CH_3CHO + \bullet OH \rightarrow CH_3CO\bullet + H_2O$ (4.25)
- $CH_3CO\bullet + O_2 + M \rightarrow CH_3C(O)OO\bullet$ (4.26)

acetylperoxy

- $CH_3C(O)OO\bullet + \bullet NO_2 \leftrightarrow CH_3C(O)OONO_2$

(4.27)

peroxyacetic nitric anhydride :
eye irritants

Fig. 4.3

Chapter 4. Tropospheric chemistry : smog

4.2 Photochemical smog – Volatile organic compounds (VOCs)

Table 4.2

Compound	Atmospheric concentration/$\mu g\ m^{-3}$
Toluene	980
m,*p*-xylene	910
o-xylene	510
Benzene	370
Ethylbenzene	310
1,3,5-trimethylbenzene	230
1-ethyl,4-methylbenzene	200
Hexane	150
Heptane	130
1-ethyl,2-methylbenzene	120

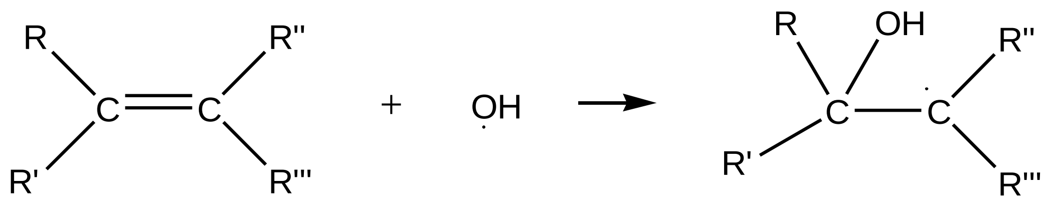
From Chan, C.-C., S.-H. Lin, and G.-R. Her, Student's exposure to volatile organic compounds while commuting by motorcycle and bus in Taipei city. *Air and Waste*, **43** (1993), 1231–8.
Measurements were made in the breathing zone of cyclists and pedestrians in three parts of the city frequented by commuters.

Chapter 4. Tropospheric chemistry : smog

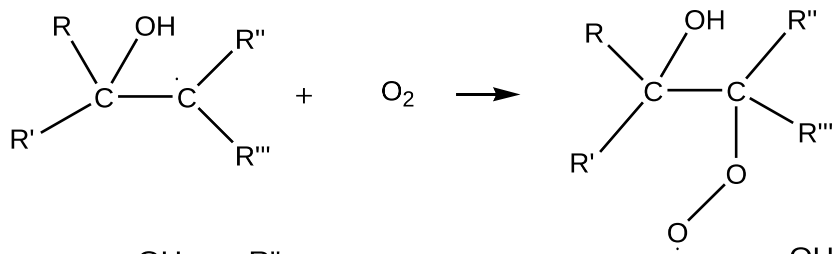
4.2 Photochemical smog – Alkenes and alkynes

Rxn

4.28-4.32



(4.28)



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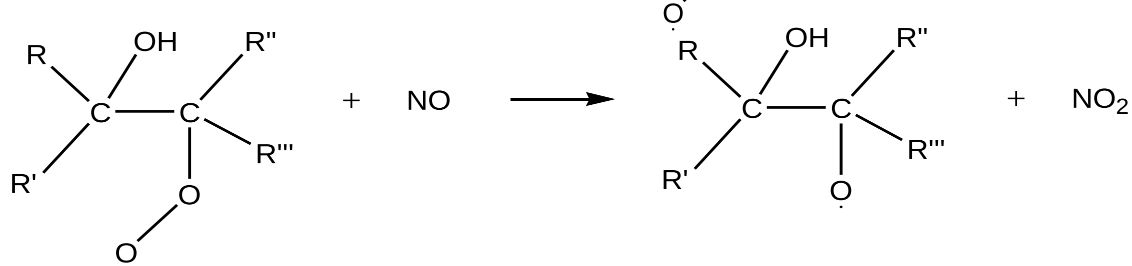

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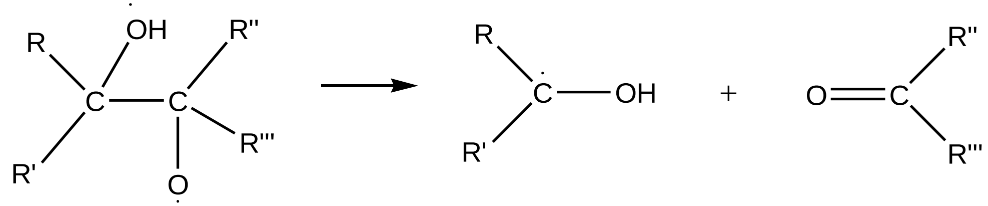
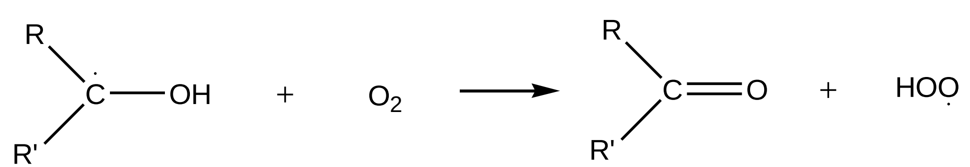


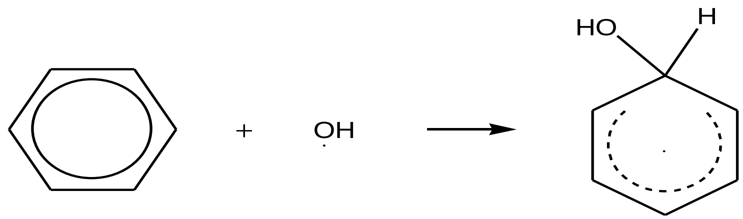
(4.31)



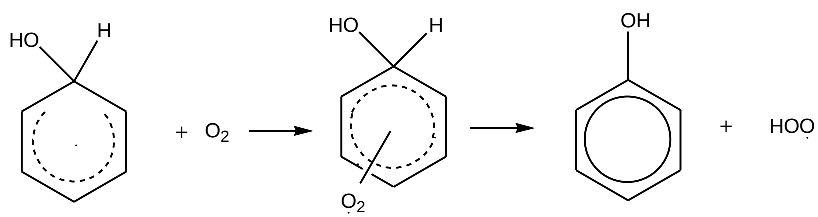
(4.32)

Chapter 4. Tropospheric chemistry : smog

4.2 Photochemical smog – Aromatics, aldehydes, and ketones



(4.33)



(4.34)

$$CH_3C(O)OO^{\bullet} + NO \longrightarrow CH_3C(O)O^{\bullet} + NO_2 \qquad (4.35)$$

$$CH_3C(O)O^{\bullet} \longrightarrow {}^{\bullet}CH_3 + CO_2 \qquad (4.36)$$

$$H_3C\text{—}CHO \xrightarrow{h\nu, (\lambda \cong 290\ \mathrm{nm})} {}^{\bullet}CH_3 + H\dot{C}O \qquad (4.37)$$

$$H_3C\text{—}CHO \xrightarrow{h\nu, (\lambda \cong 290\ \mathrm{nm})} CH_4 + CO \qquad (4.38)$$

Chapter 4. Tropospheric chemistry : smog

4.2 Photochemical smog – Methane

$$CH_4 + \cdot OH \longrightarrow \cdot CH_3 + H_2O \quad (4.39)$$

$$\cdot CH_3 + O_2 \longrightarrow CH_3OO\cdot \quad (4.40)$$

$$CH_3OOH + NO \longrightarrow CH_3O\cdot + NO_2 \quad (4.41)$$

$$CH_3O\cdot + O_2 \longrightarrow CH_2O + HOO\cdot \quad (4.42)$$

$$CH_4 + \cdot OH + 2O_2 + NO \longrightarrow CH_2O + H_2O + HOO\cdot + NO_2 \quad (4.43)$$

$$CH_2O \xrightarrow{h\nu, (\lambda < 330\ nm)} H\dot{C}OH + \cdot H \quad (4.44)$$

$$H\dot{C}O + O_2 \longrightarrow HOO + CO \quad (4.45)$$

$$CO + \cdot OH \longrightarrow CO_2 + \cdot H \quad (4.46)$$

$$2\left(\cdot H + O_2 \longrightarrow HOO\cdot\right) \quad (4.47)$$

$$2\left(HOO\cdot + NO \longrightarrow \cdot OH + NO_2\right) \quad (4.48)$$

$$CH_4 + 5O_2 + 2H_2O \longrightarrow 2HOO\cdot + 6\cdot OH + CO_2 \quad (4.49)$$

Chapter 4. Tropospheric chemistry : smog

4.2 Photochemical smog – General principles of VOCs oxidation

1. Initiation begins with dehydrogenation or hydroxyl addition
2. Radical from step 1 adds O_2, forming peroxyl radicals, or in the case of aromatics, the dioxygen abstracts a hydrogen
3. The peroxy species transfers O atom to NO
4. The product molecule loses H atom to another O_2 molecule, or it splits into two smaller species. In either case, aldehydes (or, less commonly, ketones) are formed. OH radical is another product.
5. The aldehydes react with NO_2 to form PANs(peracetic nitric anhydrides), undergo further hydroxyl initiated oxidation, or photochemically decompose.
6. The decomposition products are again subject to oxidation and the ultimate stable products are CO_2 and H_2O

Chapter 4. Tropospheric chemistry : smog

4.3 Exhaust gases from the internal combustion engine –

Gasoline-powered four-stroke engines

- Efficiency of the Otto engine (see fig. 4-4)

- To increase the efficiency, the compression ratio should be high, but high compression ratio leads to engine knocking.

- Two ways to overcome engine knocking:

  – increase octane number (binary mixing ratio of 2,2,4-trimethylpentane ('isooctane') to n-heptane). E.g. octane number 87 means 87:13

  – addition of tetraethyl lead ($(C_2H_5)4Pb$) by 1g/L gasoline. The added lead reacts with halogenated compounds in the fuel to produce a variety of volatile lead halides (condense in the ambient atmosphere and form aerosol which is deposited on the surrounding vegetation, soil, water.

Chapter 4. Tropospheric chemistry : smog

4.3 Exhaust gases from the internal combustion engine –

Gasoline-powered four-stroke engines

- The complete combustion of octane

$$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$$

- With insufficient oxygen, incomplete combustion occurs and the reaction products include CO and insufficiently reacted HCs. CO should be typically in range of 10 to 30 ppmv in the atmosphere.

- With excess of air supply, increase combustion T and compression ratio and maximize fuel efficiency. But, with the increase supply of N_2 and O_2 in the combustion mixture, increase the formation and release of NO.

- Reactions of unreacted HCs, H_2 gas, and CO

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (4.53)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \qquad (4.54)$$

- Reactions of unreacted HCs, H_2 gas, and CO

$$RH + O_2 \rightarrow CO_2 + H_2O \quad (4.55) \qquad CO + \tfrac{1}{2} O_2 \rightarrow CO_2 \qquad (4.56)$$

$$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \qquad (4.57)$$

Chapter 4. Tropospheric chemistry : smog

4.3 Exhaust gases from the internal combustion engine –

Gasoline-powered four-stroke engines

- Table 4.3

	Output/10^{-8}g J^{-1}		
	CO	NO_x	Hydrocarbons
Two-stroke engine	165	0.3	89
Four-stroke engine	127	0.7	7

- Table 4-4

	Output/g km^{-1}		
	CO	NO_x	Hydrocarbons
Production engine	21.7	0.01	16.9
Optimized engine	1.7	0.03	10.4
Engine with catalyst	0.8	0.02	1.9
Swiss standards	8	0.1	3

Chapter 4. Tropospheric chemistry : smog

4.3 Exhaust gases from the internal combustion engine – Diesel-powered engines

- Exhaust gas contains:
- 1) particules consisting of unburned carbon particles (soot) and a soluble organic fraction (SOF),
- 2) inorganic sulfates in the aerosol,
- 3) nitric oxide
- Think how to minimize the impacts of the abovementioned materials!