

Atmospheric Gas- and Liquid Phases Chemistry

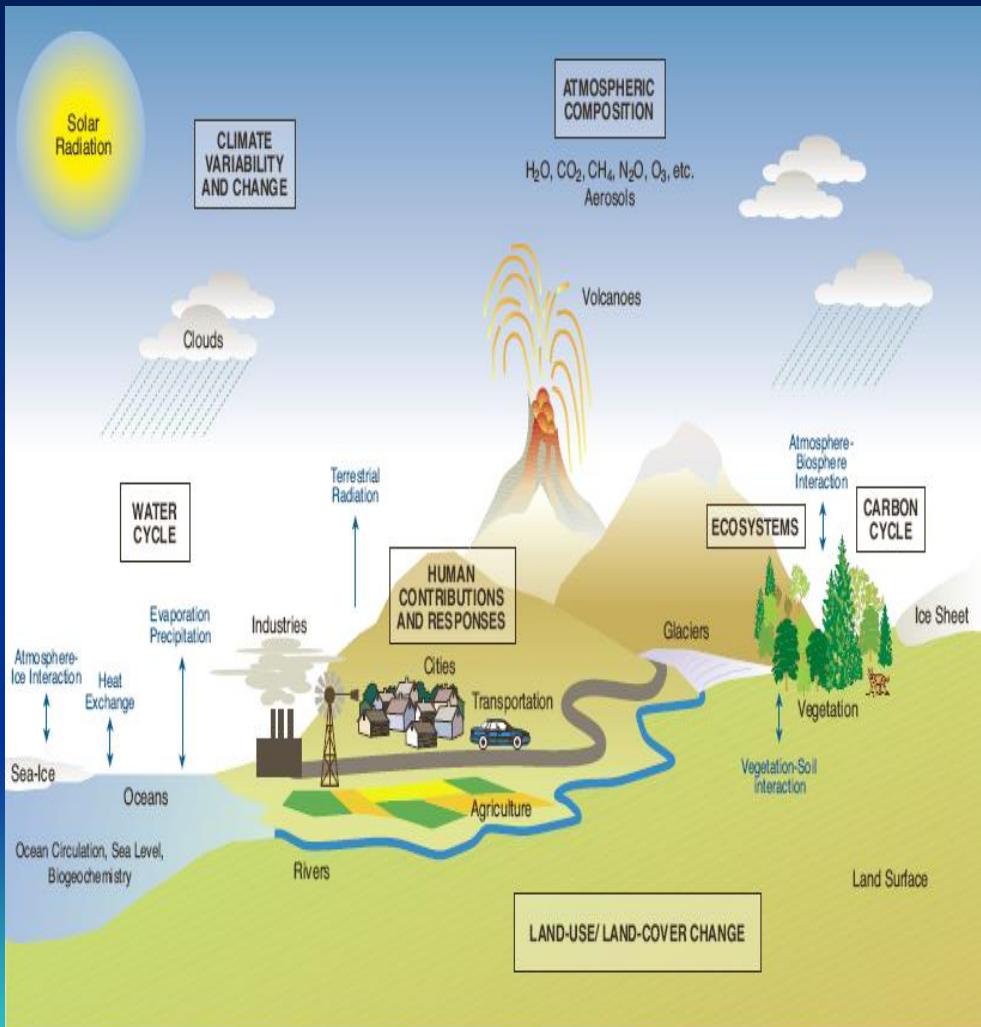
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Atmospheric chemistry and global change

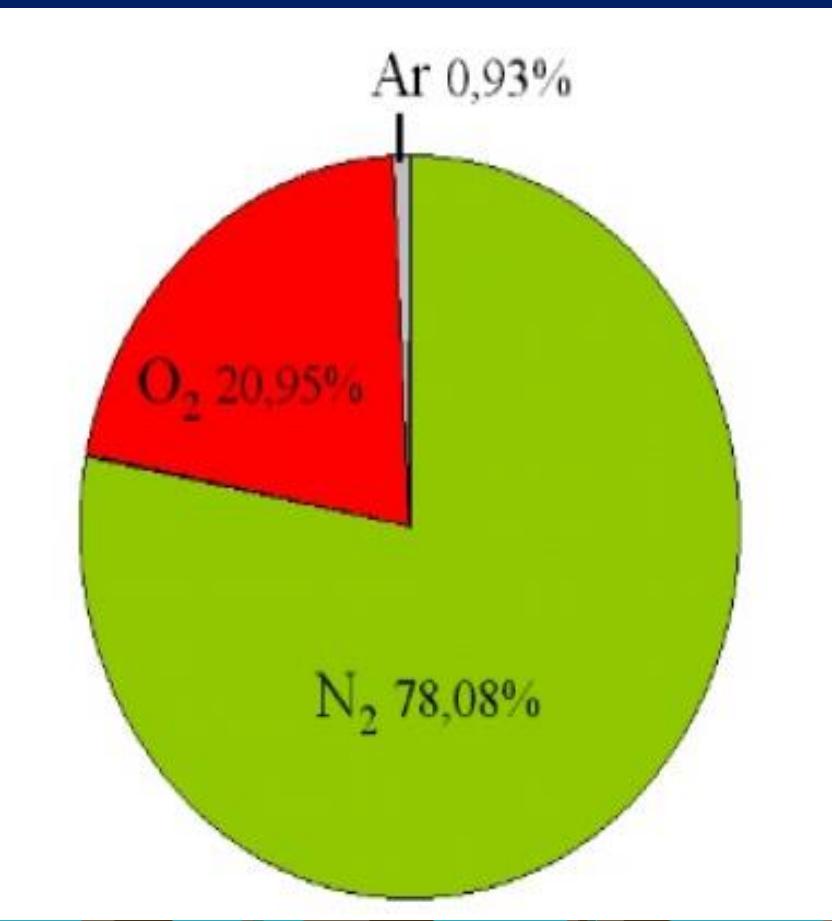


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Many of the global environmental changes forced by human activities are mediated through the chemistry of the atmosphere:

- Degradation of **air quality**: Global pollution resulting from industrial combustion and biomass burning
- Increase in the abundance of **tropospheric oxidants** including ozone and related impacts on the biosphere and human health
- Changes in the **self-cleaning capability** of the atmosphere and in the residence time of anthropogenic trace gases
- Climatic and environmental impact of changes in **land use** including deforestation, wetland destruction, etc.
- Perturbations of **biogeochemical cycles** of carbon, nitrogen, phosphorus, and sulfur
- Acidic precipitation
- Climatic changes (**global warming**) resulting from increasing emissions of CO_2 and other greenhouse gases
- Climatic impacts (regional cooling) of **sulfate aerosols** resulting from anthropogenic SO_2 emissions
- Depletion of **stratospheric ozone**, related increase in the level of UV-B solar radiation at the surface, and impacts on the biosphere and human health

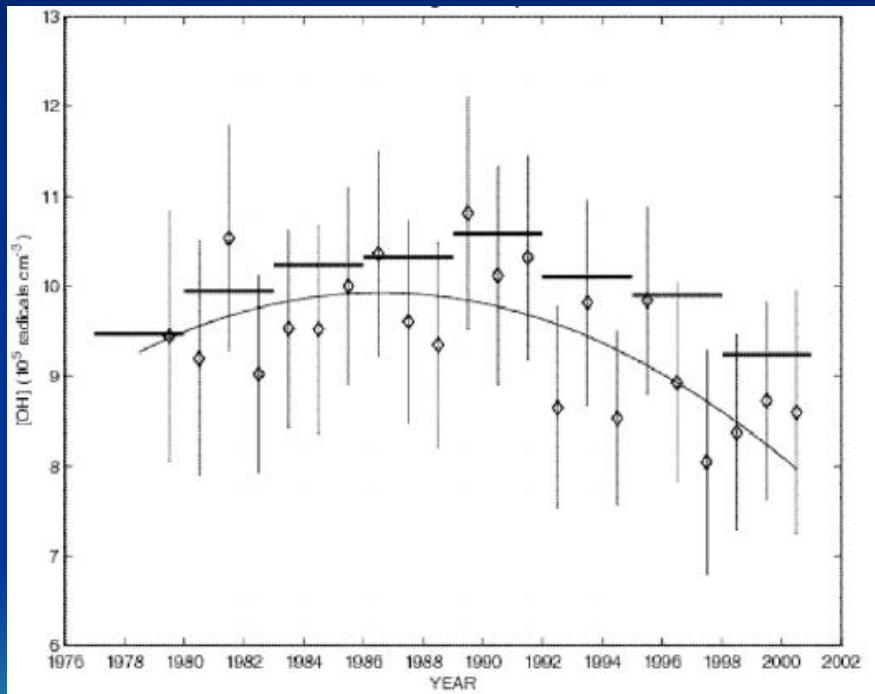
Trace Gases



- There are thousands of gases in the atmosphere.
- Some of the gases are evenly spread all over the world, whereas the concentrations of others depends strongly on sources, local conditions and on the time of day.
- A gas in the atmosphere can be:
 - a major component of the air (oxygen, nitrogen, argon) – 99.96 %
 - a major trace gas (water vapor, carbon dioxide, methane, ozone, nitrogen dioxide)
 - a minor trace gas (organic gases such as butane, ethanol, CFCs)
- Trace gases are gases which make up only a tiny fraction of the air. Levels of these trace gases can be as low as one molecule in one million (ppm), billion (ppb) or even one trillion (ppt) air molecules.

OH Radical is a Strong Oxidant in the Troposphere

OBSERVED TRENDS IN TROPOSPHERIC OH



- OH reacts rapidly with most reduced non-radical species, and is particularly reactive toward H-containing molecules due to H-abstraction reactions converting OH to H₂O.
- Its role in stratospheric oxidation is well known
- Tropospheric OH concentrations of the order of 10⁶ molecules cm⁻³, resulting in a tropospheric lifetime for CO of only a few months and allaying concerns that CO could accumulate to toxic levels.

OH Production in the Atmosphere



- Critical to the generation of OH is the production of O(1D) atoms by (R1).
- Until 1970 it was assumed that production of O(1D) would be negligible in the troposphere because of near-total absorption of UV radiation by the O₃ column overhead.
- It was thought that oxidation of species emitted from the Earth's surface, such as CO and CH₄, required transport to the stratosphere followed by reaction with OH in the stratosphere



O(1D) Production in the Atmosphere



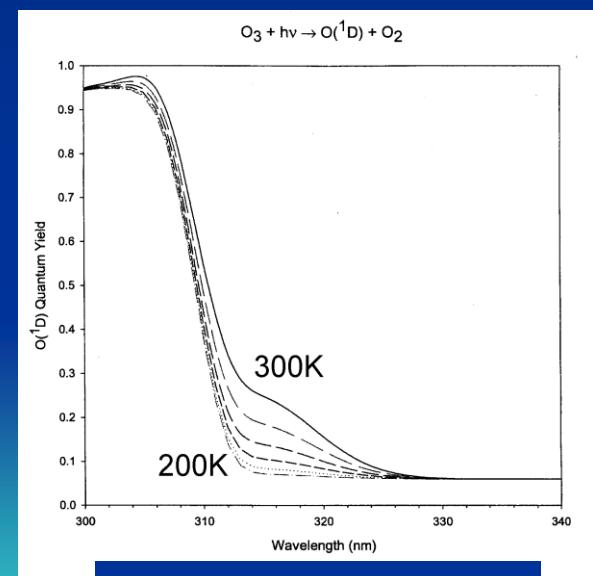
O(¹D) formation is important for the formation of OH, which is the cleansing agent of the atmosphere:



Only a fraction of the O(¹D) radicals react with water vapour, because:

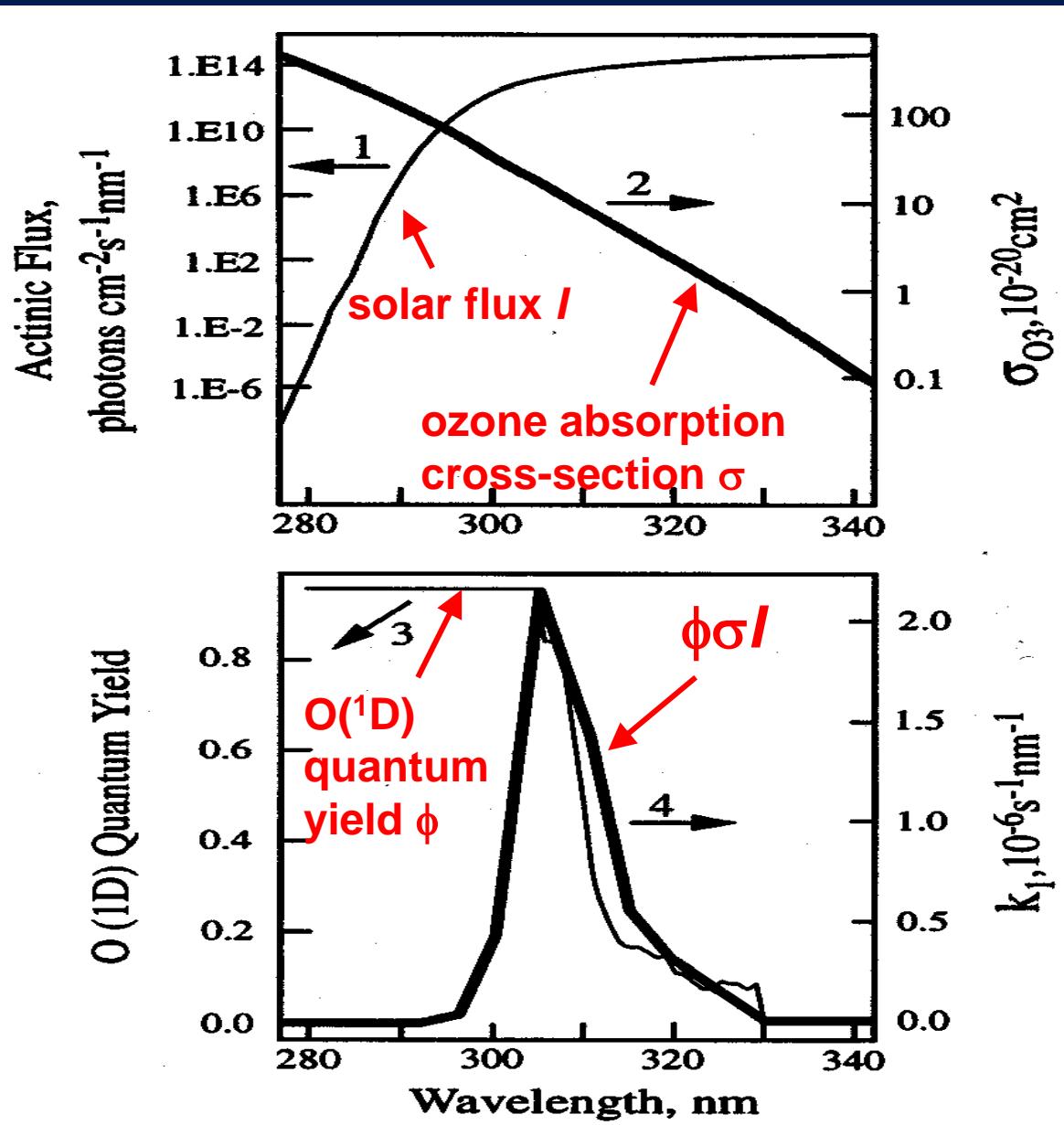


and $\text{O}({}^3\text{P}) + \text{O}_2 \rightarrow \text{O}_3$

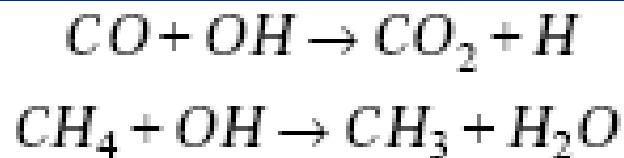


O(¹D) quantum yield

O(¹D) Production in the Troposphere



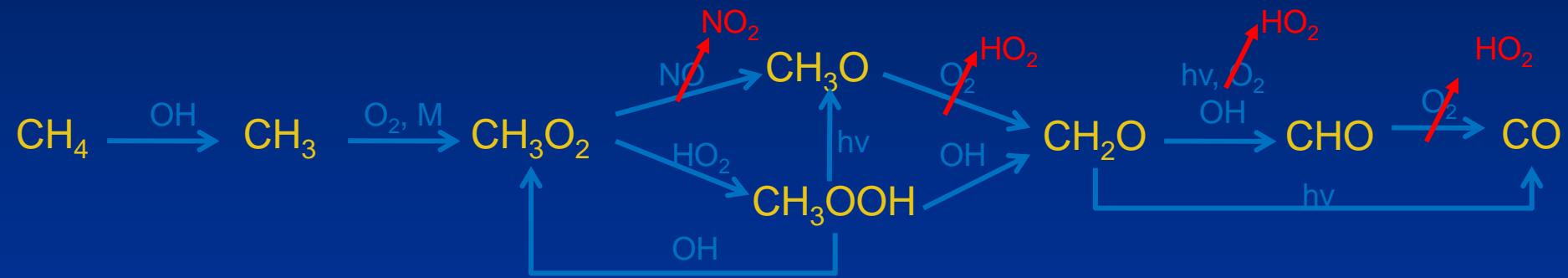
OH Tropospheric Sinks



- Carbon monoxide and methane are the principal sinks for OH in most of the troposphere.
- These two gases play therefore a critical role in controlling OH concentrations;
- and more generally in driving radical chemistry in the troposphere.

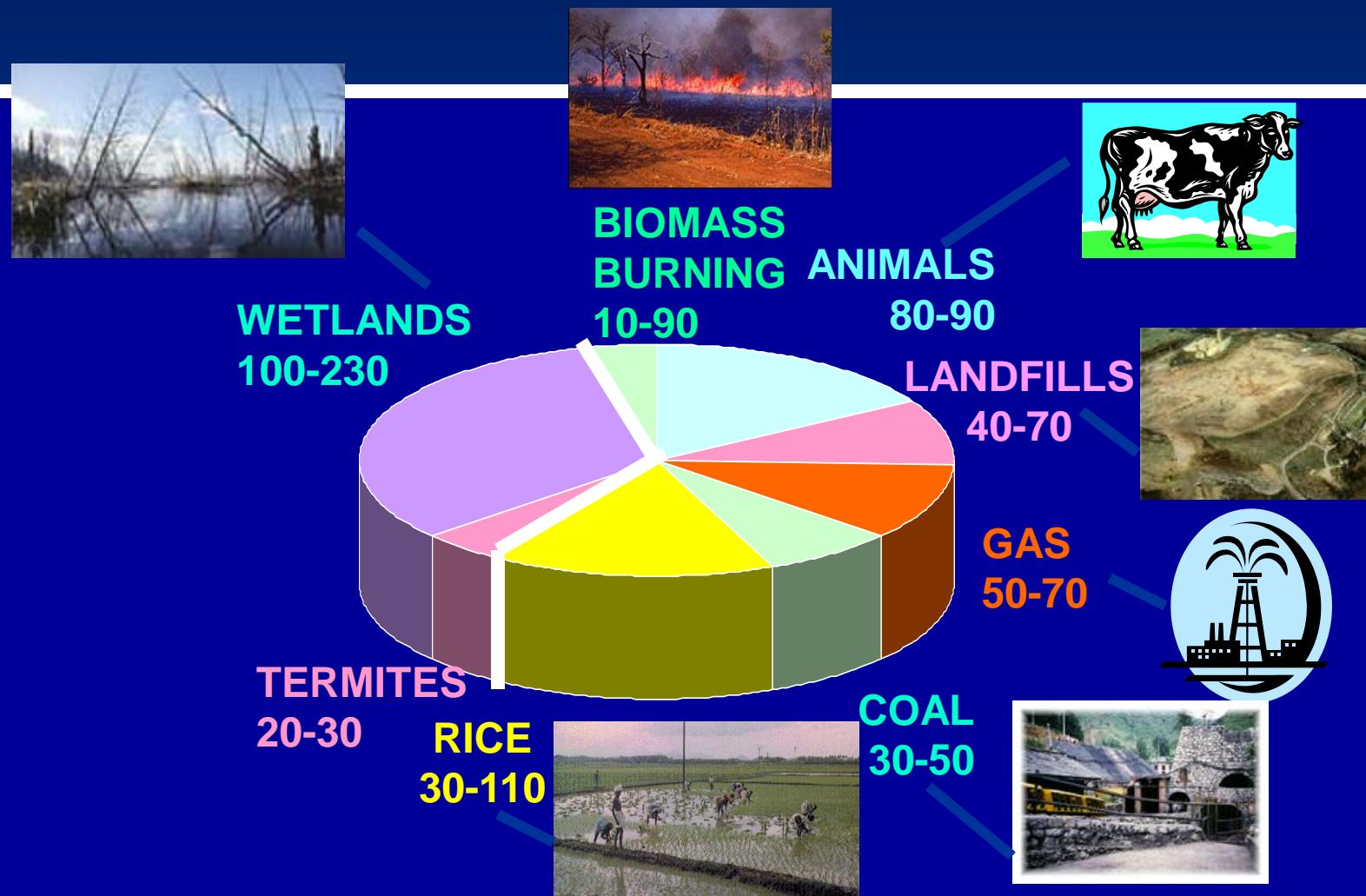


METHANE OXIDATION SCHEME



In clean troposphere, ~70% of OH reacts with CO, 30% with CH_4

GLOBAL METHANE SOURCES, Tg a⁻¹ [IPCC, 2007]

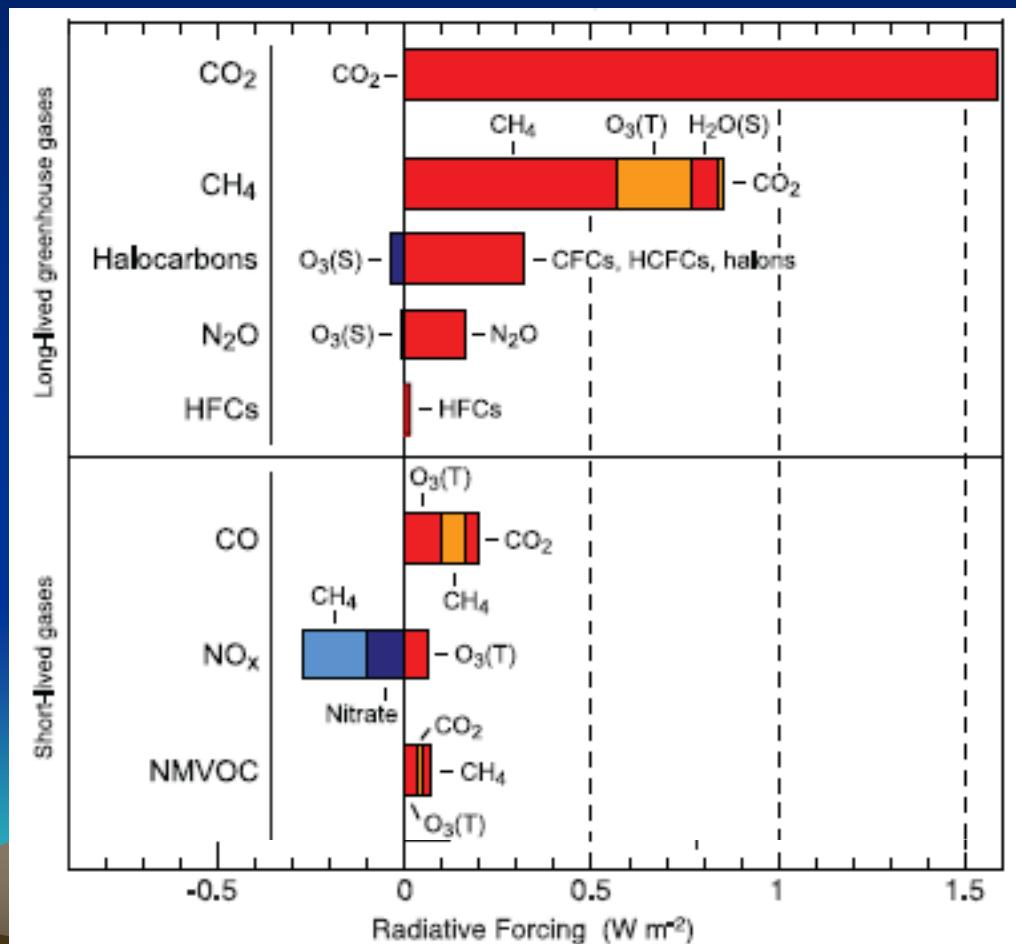
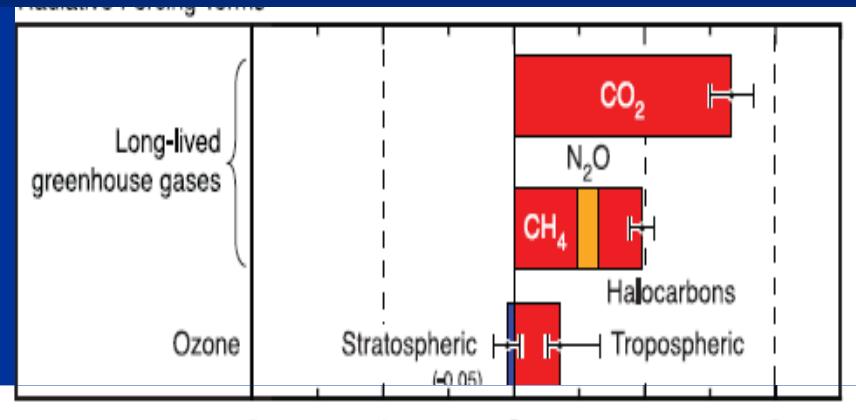


CHEMICAL GREENHOUSE GASES

Greenhouse radiative forcing of climate between 1750 and 2005 [IPCC, 2007]

Referenced to emission

Referenced to concentration



OZONE: “GOOD UP HIGH, BAD NEARBY”

Good
(UV shield)



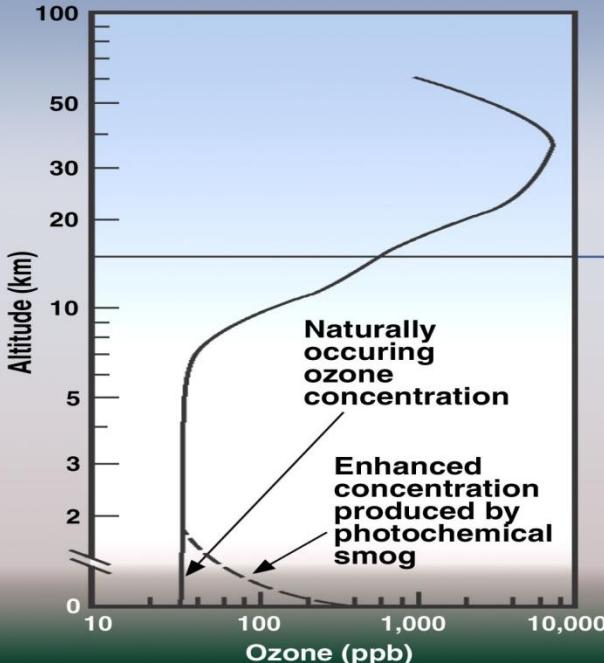
Bad
(greenhouse gas)



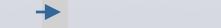
Good
(OH source)



Bad
(smog)



Stratosphere
Troposphere



VOC



Tropospheric
ozone
precursors

Sources: combustion, soils, lightning

Volatile organic compounds (VOCs)

Methane

Sources: wetlands, livestock, natural gas...

Non-methane VOCs (NMVOCs)

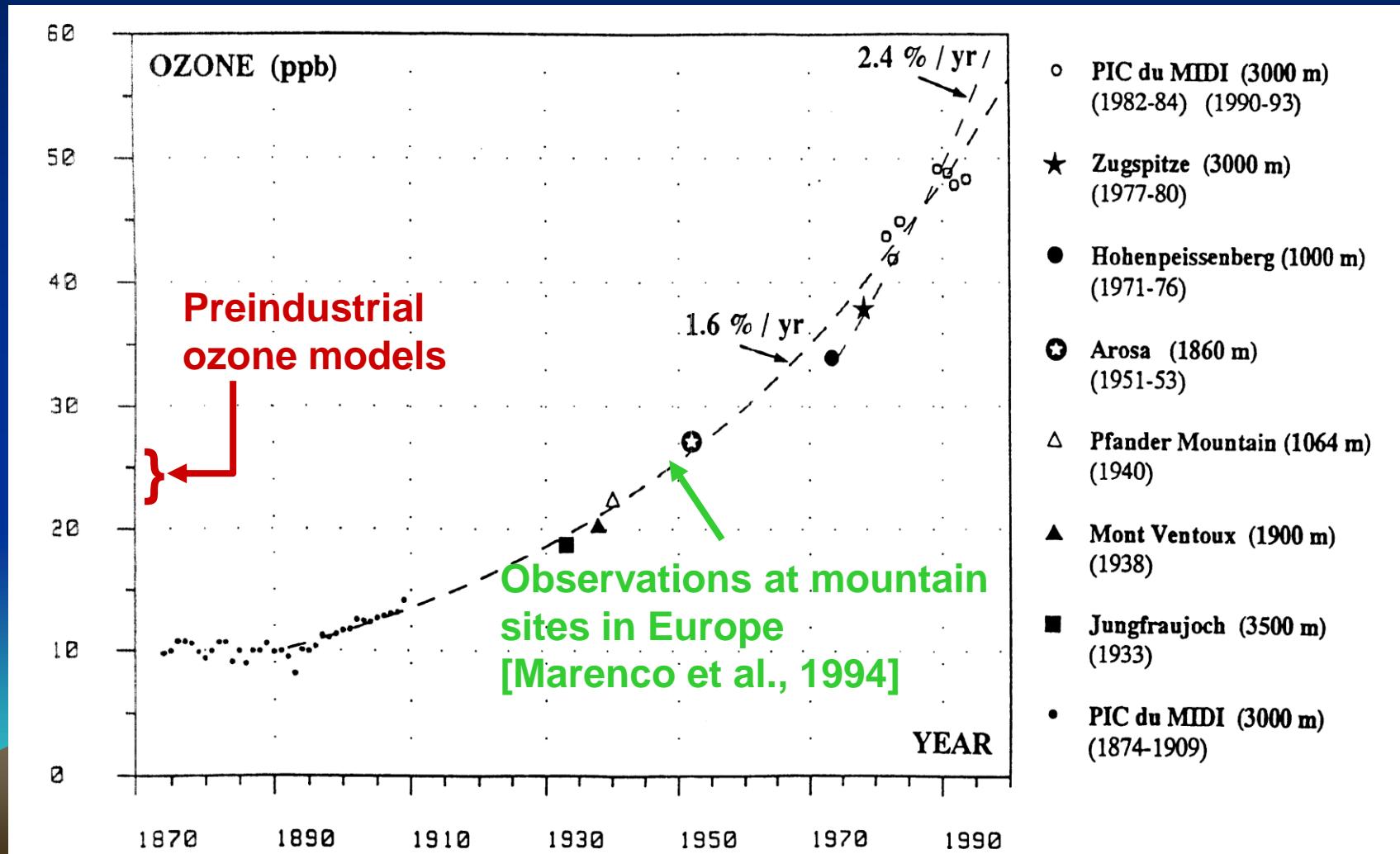
Sources: vegetation, combustion

Carbon monoxide (CO)

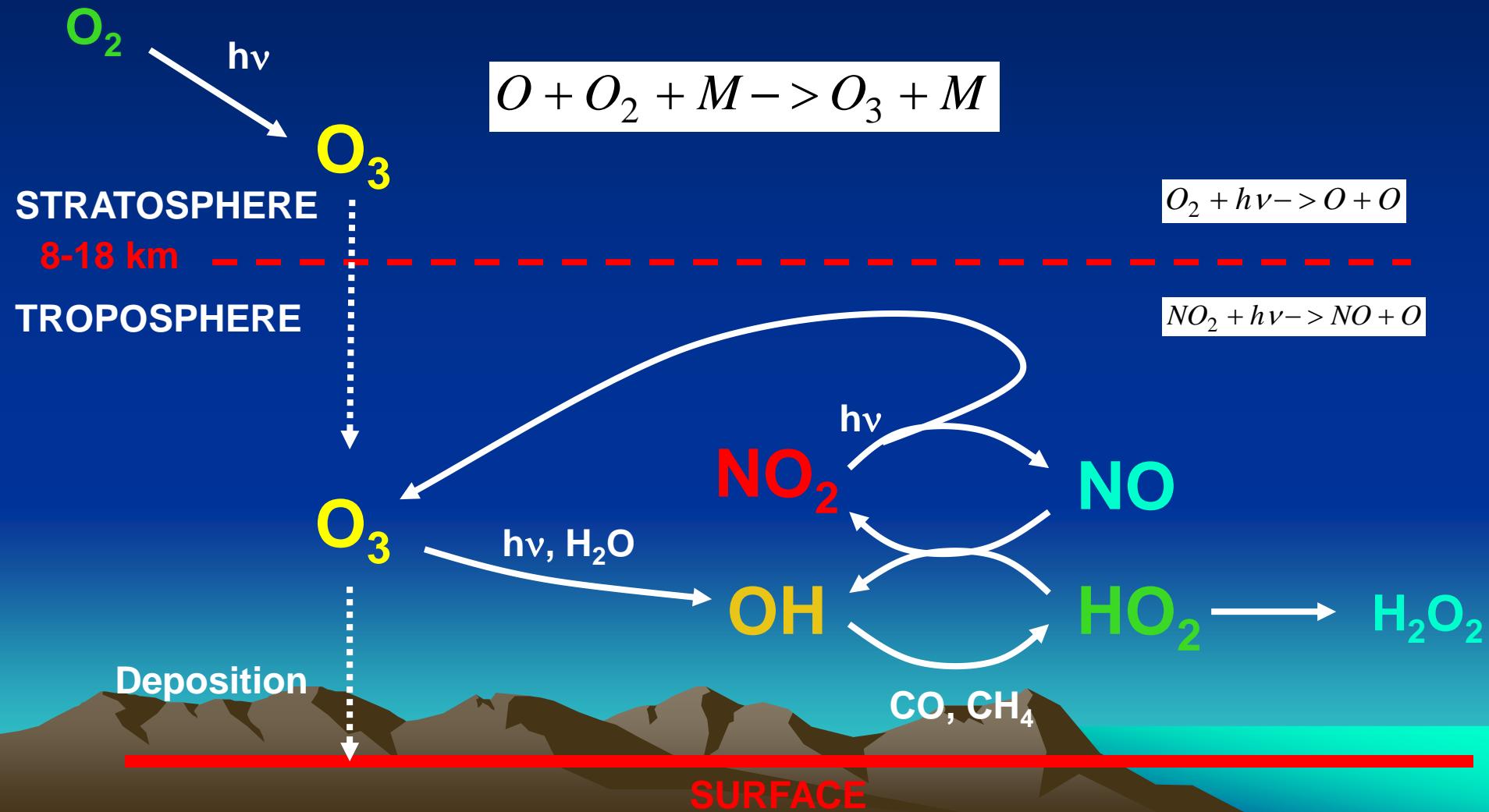
Sources: combustion, VOC oxidation

IPCC RADIATIVE FORCING ESTIMATE FOR TROPOSPHERIC OZONE (0.35 W m^{-2})

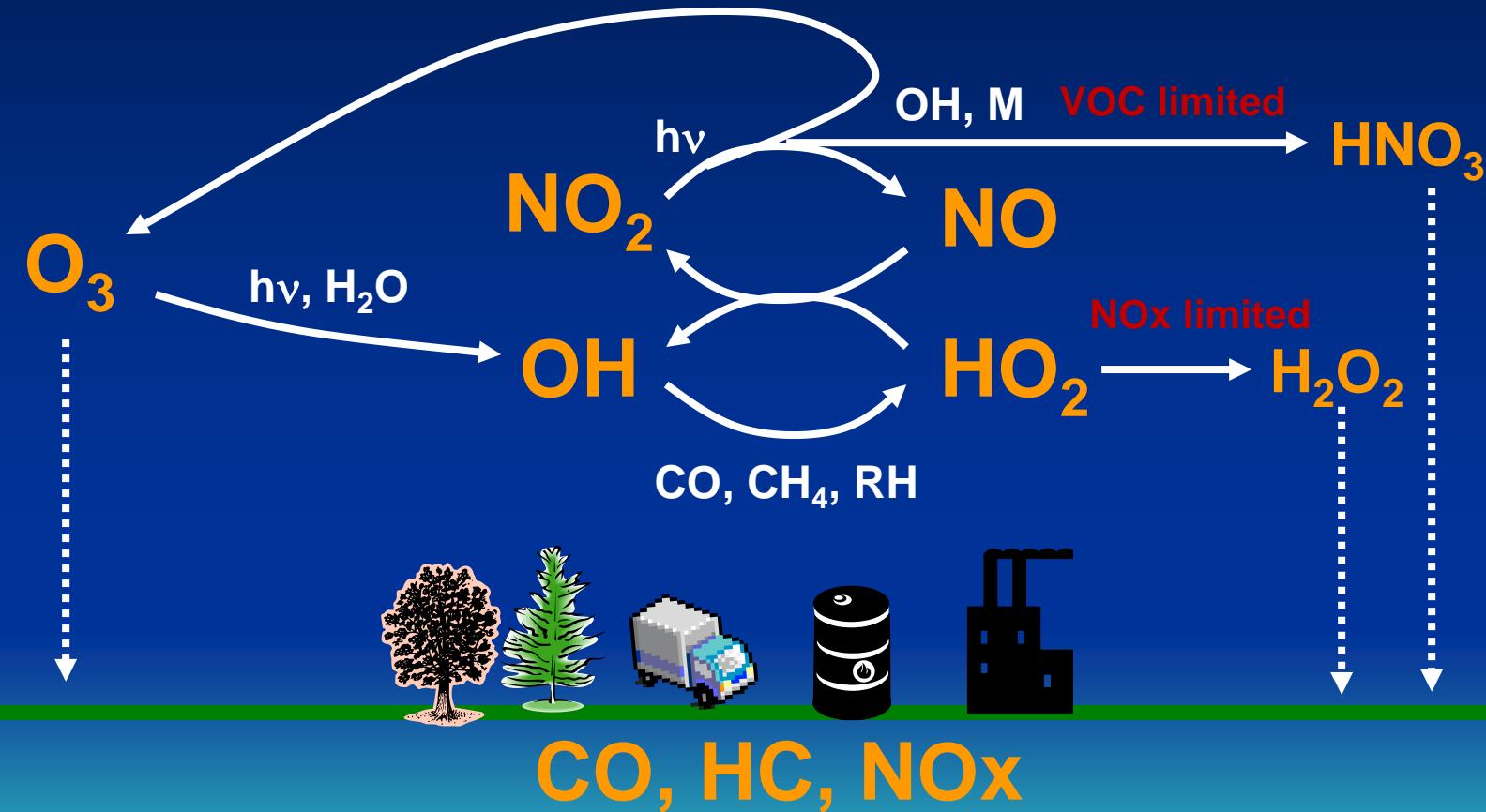
...but these underestimate the observed rise in ozone over the 20th century
Fitting to observations would imply a radiative forcing of 0.8 W m^{-2}



RADICAL CYCLE CONTROLLING TROPOSPHERIC OH AND OZONE CONCENTRATIONS



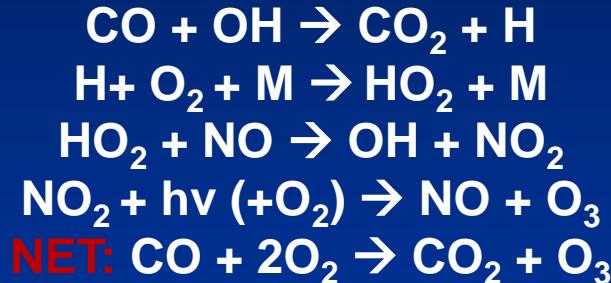
OZONE PRODUCTION: BASIC CHAIN MECHANISM



CHAIN MECHANISM FOR O₃ PRODUCTION: CO OXIDATION

Initiation: source of HOx (OH production)

Propagation:



Termination: by loss of HOx (self reaction of HO₂)

→ Propagation efficiency of the chain determined by the abundance of NOx

NOTE: HOx and NOx catalyze O₃ production in the troposphere, and O₃ destruction in the stratosphere! The key difference is that [O₃] and [O] are much lower in the troposphere, thus NO₂ does not react with O, and OH is far more likely to react with CO, HC, etc. than with O₃

CHAIN MECHANISM FOR O₃ PRODUCTION: CH₄ OXIDATION

Initiation: source of HOx (OH production)

Propagation:



(...then CO oxidation...)

Oxidation from
C(-IV) in CH₄
through to
C(+IV) in CO₂

Ozone production from NO₂ photolysis following peroxy+NO rxns (where peroxy radicals generated by reactions above)

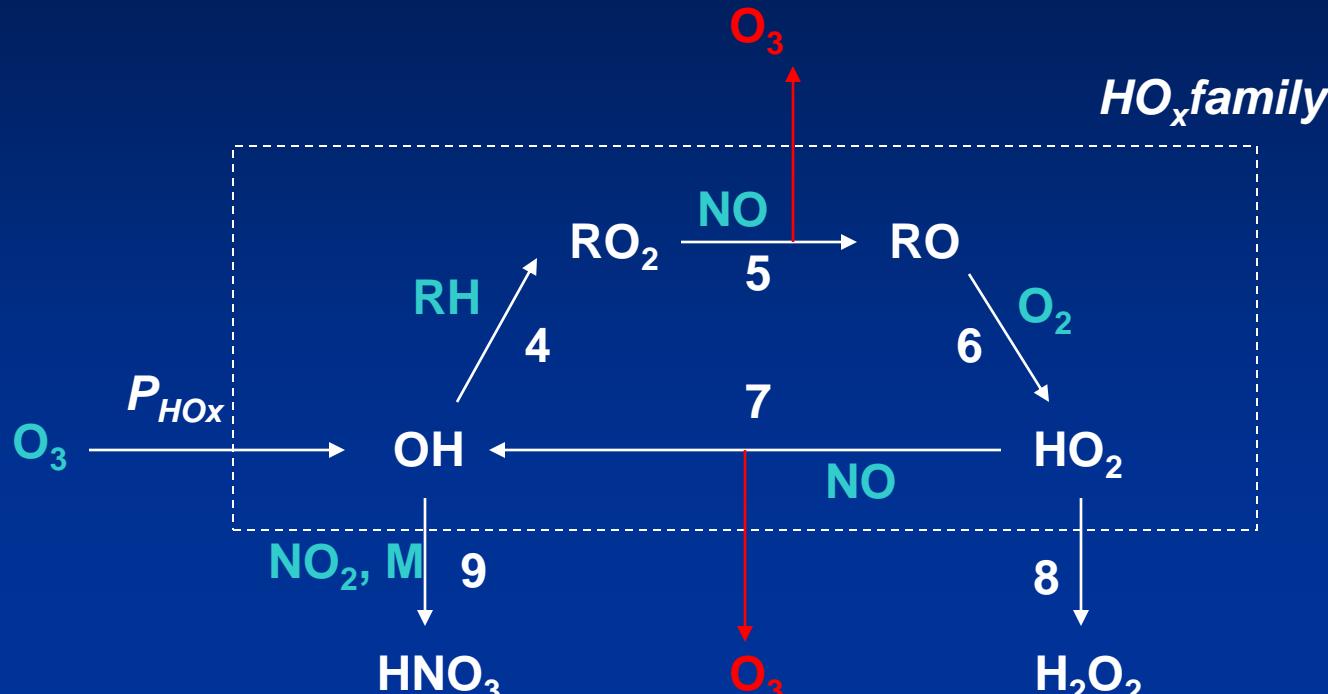
High NO_x: CH₃O₂ and HO₂ react only with NO, and CH₂O removed only by photolysis



Low NO_x: CH₃O₂ reacts with HO₂, CH₃OOH reacts with OH and CH₂O reacts with OH



DEPENDENCE OF OZONE PRODUCTION ON NO_x AND HYDROCARBONS



“NO_x-saturated” or
“hydrocarbon-limited” regime

“NO_x-limited” regime

NON-METHANE VOC EMISSIONS

Isoprene, terpenes,
oxygenates...

Alkenes, aromatics,
oxygenates...

Alkanes, alkenes,
aromatics...

↑
~ 600 Tg C yr⁻¹

↑
~ 50 Tg C yr⁻¹

↑
~ 200 Tg C yr⁻¹



Vegetation

Biomass burning

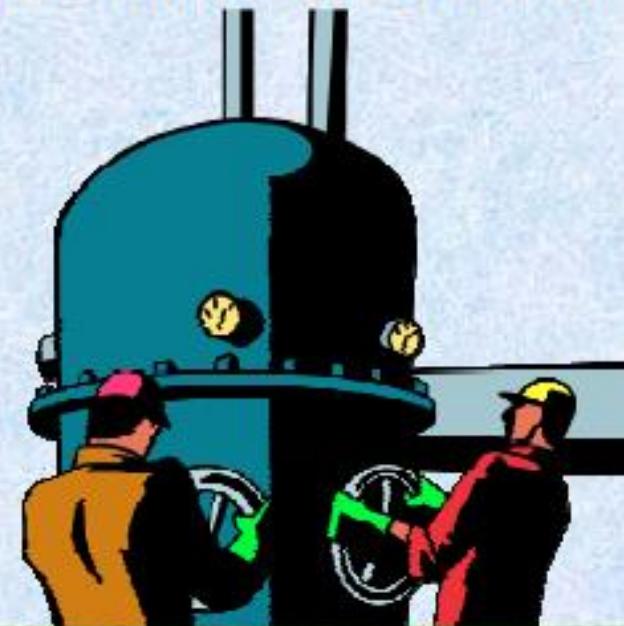
Industry

Largest global flux is from isoprene (300-500 Tg C yr⁻¹)

Sources of Volatile Organic Compound (VOC) Emissions



Refinery Operations
and Chemical Production



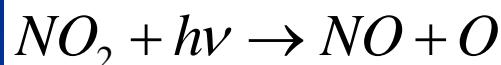
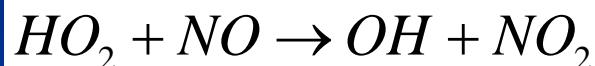
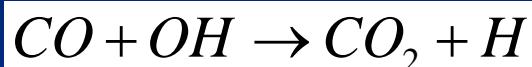
Transportation

Biogenic Emissions

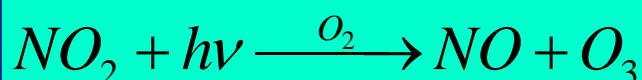
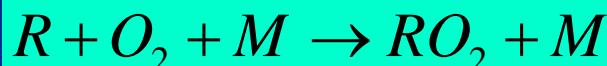
**Photochemical oxidation of CO and volatile organic compounds (VOCs)
catalyzed by hydrogen oxide radicals (HO_x)
in the presence of nitrogen oxide radicals (NO_x)**



Oxidation of CO:



Oxidation of VOC:



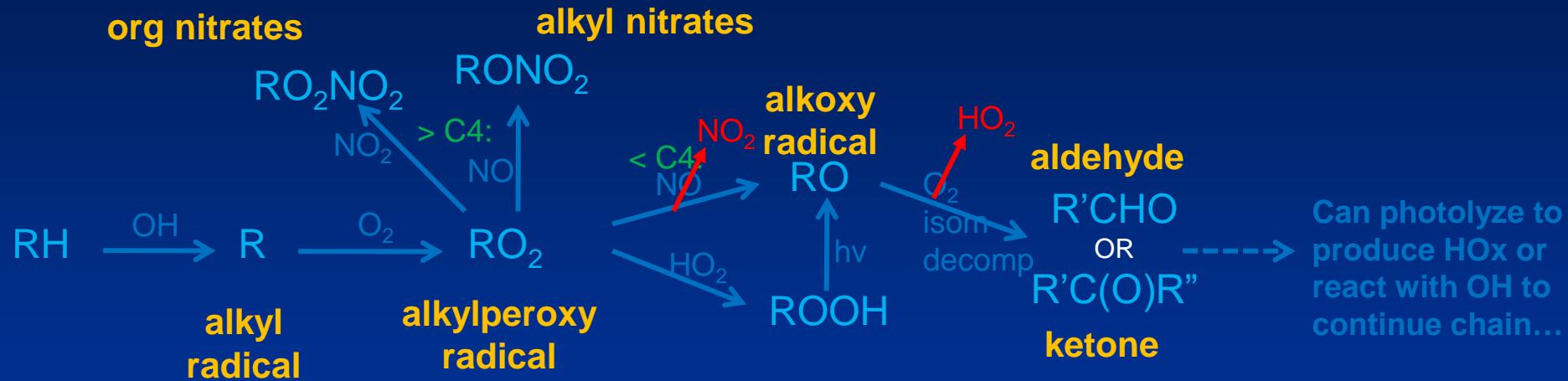
OH can also add to double bonds of unsaturated VOCs

RO can also decompose or isomerize; range of carbonyl products

Carbonyl products can react with OH to produce additional ozone, or photolyze to generate more HO_x radicals (branching reaction)

OXIDATION OF HYDROCARBONS CONTRIBUTE TO OZONE FORMATION IN POLLUTED AIR

Generic Alkane OH Oxidation Scheme (no longer just CO and CH₄!)



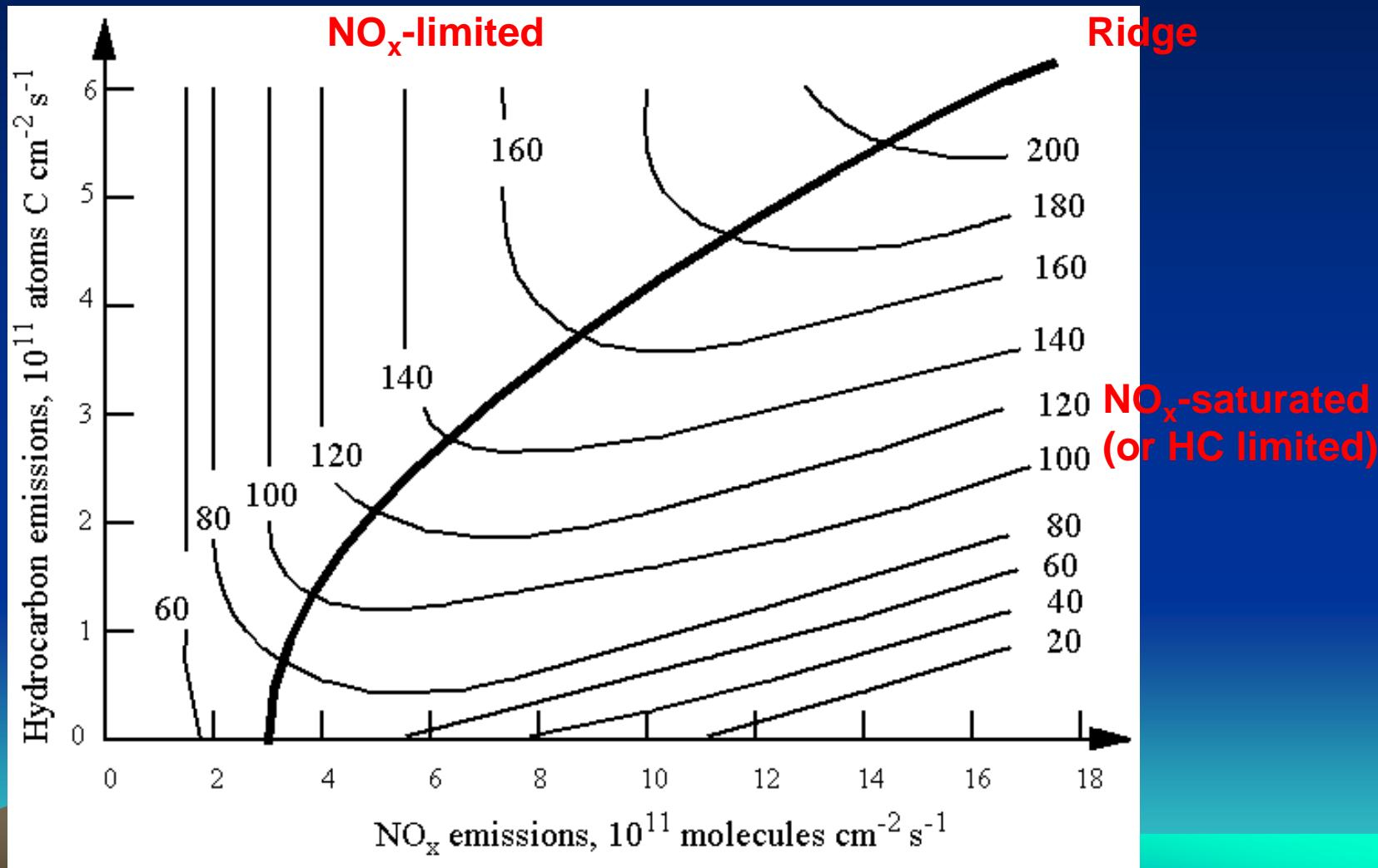
Additional oxidation by NO₃ (but only at night!)

Alkenes: OH oxidation adds to double bond (does not abstract H as with alkanes).

With double bond, alkenes can also be oxidized by ozone

Aromatics (with benzene rings): reactive with OH, via either addition or abstraction
 → source of secondary organic aerosol (SOA)

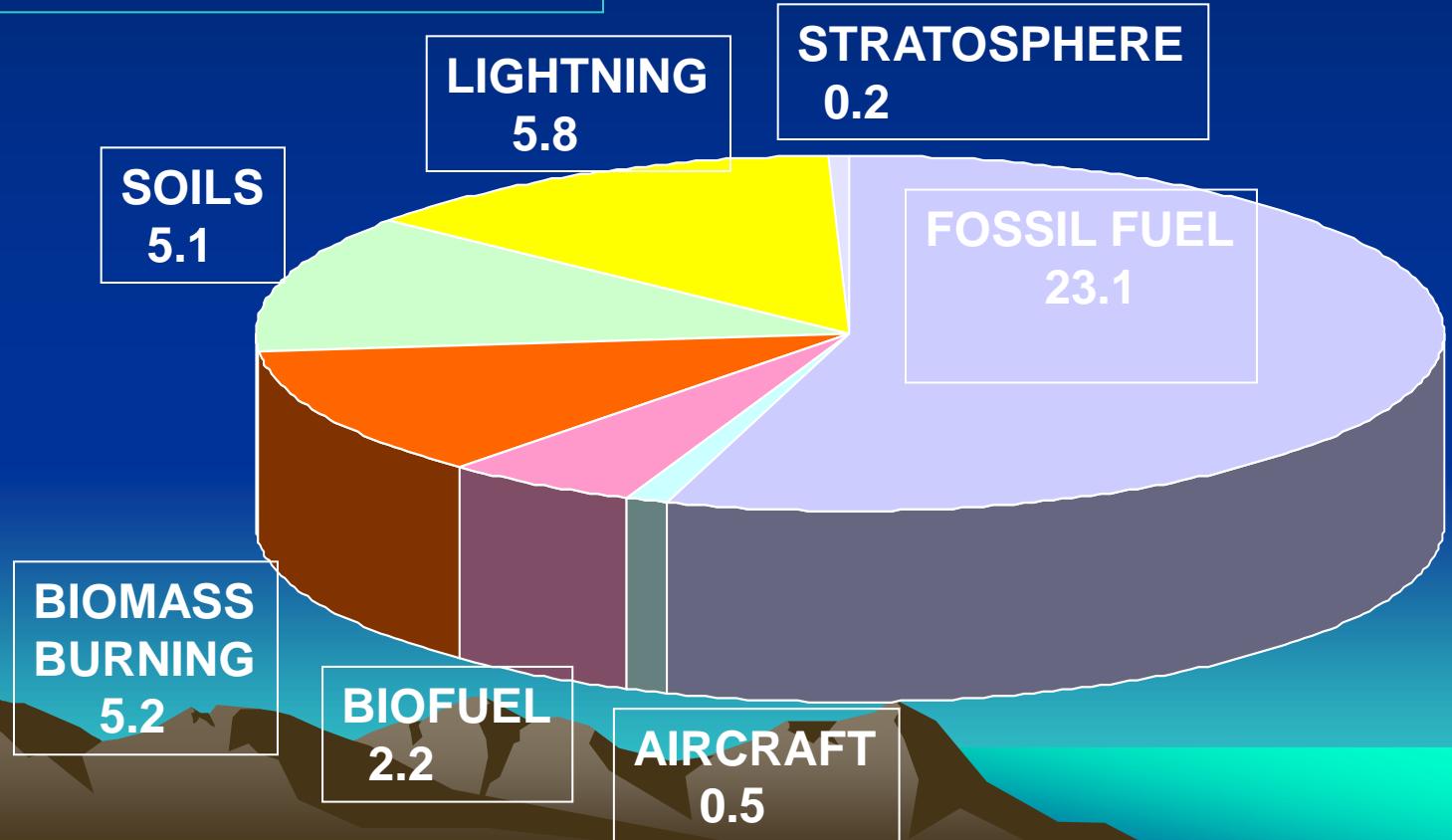
OZONE CONCENTRATIONS vs. NO_x AND VOC EMISSIONS



NO_x EMISSIONS (Tg N yr⁻¹) TO TROPOSPHERE

Zeldovich Mechanism: combustion and lightning

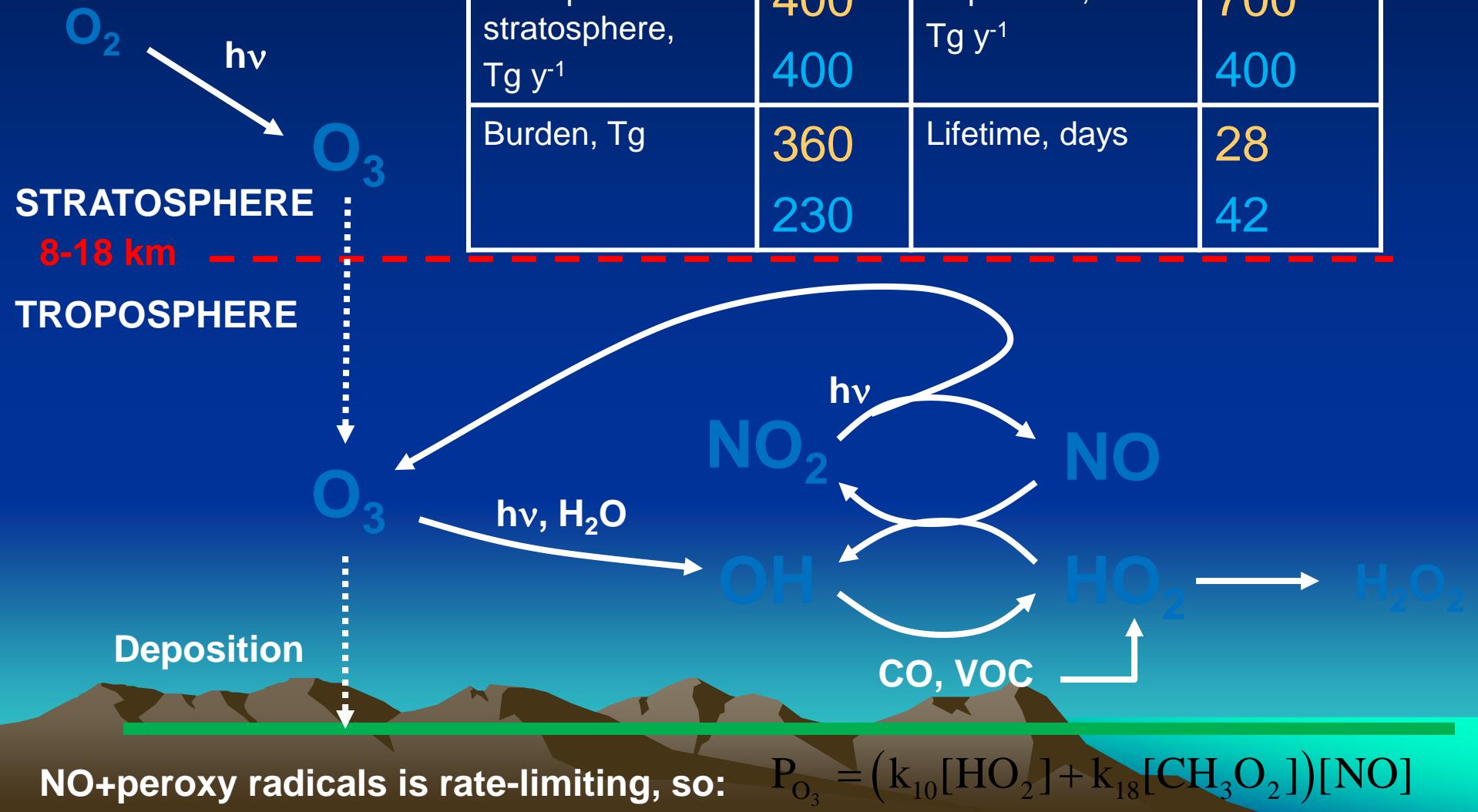
At high T (~2000K) oxygen thermolyzes:



GLOBAL BUDGET OF TROPOSPHERIC OZONE

**Present-day
Preindustrial**

Chem prod in troposphere, Tg y ⁻¹	4300 1600	Chem loss in troposphere, Tg y ⁻¹	4000 1600
Transport from stratosphere, Tg y ⁻¹	400 400	Deposition, Tg y ⁻¹	700 400
Burden, Tg	360 230	Lifetime, days	28 42



General rules for atmospheric oxidation of hydrocarbons

- Attack by OH is by H abstraction for saturated HCs (alkanes), by addition for unsaturated HCs (alkenes)
- Reactivity increases with number of C-H bonds, number of unsaturated bonds
- Organic radicals other than peroxy react with O₂ (if they are small) or decompose (if they are large); O₂ addition produces peroxy radicals.
- Organic peroxy radicals (RO₂) react with NO and HO₂ (dominant), other RO₂ (minor); they also react with NO₂ but the products decompose rapidly (except in the case of peroxyacetyl radicals which produce peroxyacetyl nitrates or PANs)
- RO₂+HO₂ produces organic hydroperoxides ROOH, RO₂+NO produces carbonyls (aldehydes RCHO and ketones RC(O)R')
- Carbonyls and hydroperoxides can photolyze (radical source) as well as react with OH
- Unsaturated HCs can also react with ozone, producing carbonyls and carboxylic acids
- RO₂+R'O₂ reactions produce a range of oxygenated organic compounds including carbonyls, carboxylic acids, alcohols, esters...



Problems of Atmospheric Chemistry Modeling

- While in the air, a substance can be chemically altered in one of **two ways**.
- First, the sunlight itself may contain sufficient energy to break the molecule apart, a so-called **photolysis reaction**.
- The more frequently occurring chemical alteration, however, takes place when two molecules interact and undergo a **chemical reaction** to produce new species.
- Atmospheric chemical transformations can occur **homogeneously** or **heterogeneously**.
- **Homogeneous** reactions occur entirely in one phase;
- **Heterogeneous** reactions involve more than one phase, such as a **gas** interacting with a **liquid** or with a **solid** surface.
- How to estimate the rate of chemical **destruction** or **production** of the gaseous species?
- How to solve chemical **equations** and estimate gases evolution?



Physical Principles

- The fundamental **physical** principle governing the behavior of a chemical in the atmosphere is **conservation of mass**.
- In any imaginary volume of air the following balance must hold:

$$\text{Rate of the species flowing in} - \text{rate of species flowing out} + \text{rate of introduction (emission) of species} = \text{rate of removal of species} = \text{rate of accumulation of species in imaginary volume}$$

- This balance must hold from the smallest volume of air all the way up to the entire atmosphere.



Model Equation of Mass Conservation

$$\frac{dQ}{dt} = (F_{in} - F_{out}) + (P - R)$$

- If we let Q denote the total mass of the substance in the volume of air;
- F_{in} and F_{out} the mass flow rates of the substance in and out of the air volume, respectively;
- P the **rate** of production of the species from chemical sources;
- and R the **rate** of chemical removal of the species



REACTION RATES

- A **reaction rate** is the time rate of change of **concentration** of any **reactant** in a reaction.
- The rate of an elementary chemical reaction equals a **rate coefficient** multiplied by the concentration of each **reactant**.
- If reactant concentrations are expressed in units of molecules of gas per cubic centimeter of air, the rate of reaction is in units of molec $\text{cm}^{-3} \text{ s}^{-1}$, regardless of whether the reaction has a first-, second-, or third-order rate coefficient;
- A **rate coefficient** relates concentrations to a reaction rate and depends on the reaction order.



ORDER OF REACTION

Three types of chemical reaction are important:



First-order reaction rate



$$\frac{d[A]}{dt} = -k_1 [A]$$

$$\frac{dB}{dt} = \frac{dC}{dt} = k_1 A$$

- The rate of a first-order reaction is expressed in molecules cm⁻³ s⁻¹
- the first-order rate coefficient k_1 has units of s⁻¹ (reciprocal seconds)

True first-order reactions



- Few reactions are truly first-order, in that they involve decomposition of a molecule without intervention of a second molecule.
- The classic example of a true first-order reaction is radioactive decay

Photodissociation Reactions



$$\frac{dB}{dt} = \frac{dC}{dt} = -\frac{dA}{dt} = J_A A$$

- In the atmosphere, by far the most important class of first-order reactions is photodissociation reactions in which absorption of a photon of light ($h\nu$) by the molecule induces chemical change;
- $h\nu$ represents a photon of light of frequency ν .
- In the photolysis of species A, the rate coefficient is customarily denoted by the symbol j_A

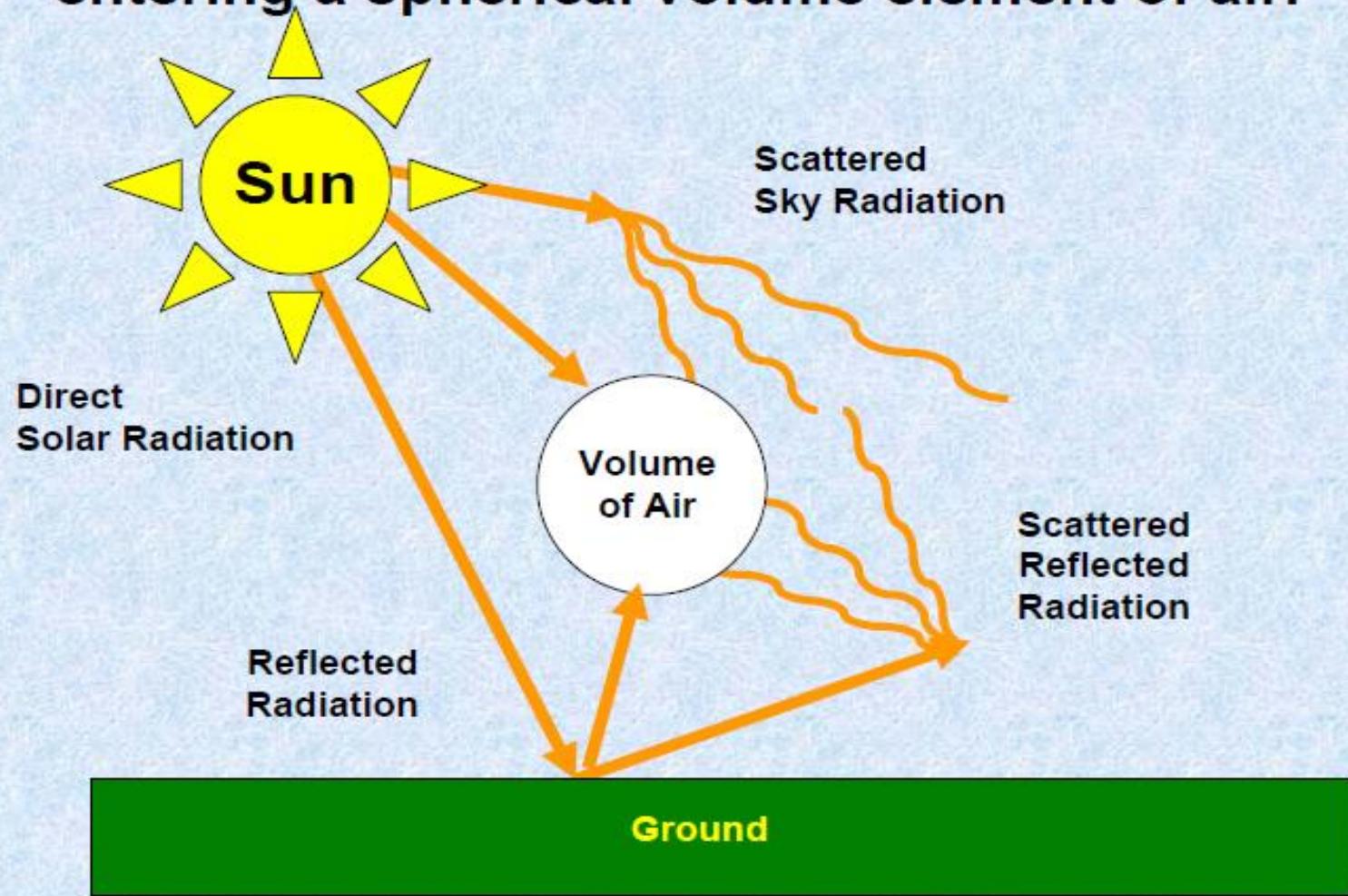
Photodissociation rate parameters depend on spectrally resolved actinic flux.

Photolysis Rate Parameter

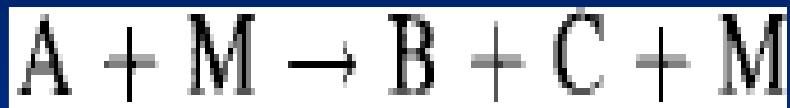
$$J = \int I(\lambda) \times \sigma(\lambda) \times \varphi(\lambda) d\lambda$$

Actinic Flux Absorption Cross-Section Quantum Yield Wavelength

**Actinic Flux is total flux
entering a spherical volume element of air.**



Thermal decomposition

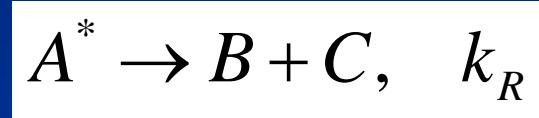
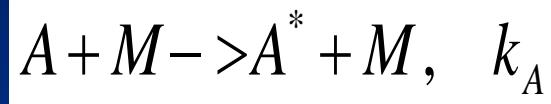


$$\frac{dB}{dt} = \frac{dC}{dt} = -\frac{dA}{dt} = k_T \cdot A \cdot M$$

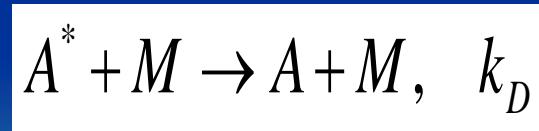
$$k_1 = k_T \cdot M$$

- Thermal decomposition of a molecule is often represented as first-order, but the energy required for decomposition is usually supplied through collision with another molecule.
- If the other molecule is an air molecule, it is denoted as M

Two Stages of Thermal Decomposition



OR



- Apparently unimolecular reaction is really the result of the processes of activation, reaction and deactivation



Rate of two stage reaction

$$-\left(\frac{d(A)}{dt}\right) = k_r(A^*)$$

$$\frac{d(A^*)}{dt} = 0 = k_{act}(A)(M) - [k_d(M) + k_r](A^*)$$

$$(A^*) = \frac{k_{act}(A)(M)}{k_r + k_d(M)}$$

$$\frac{d(A)}{dt} = -\left(k_r \frac{k_{act}(A)(M)}{k_r + k_d(M)}\right)$$

$$k_u = k_{act}(M) \frac{k_r}{k_r + k_d(M)}$$

- The rate of decomposition of A (which is equal to the rate of formation of B or C);
- The steady state concentration of A* is derived;
- and the effective first order reaction rate k_u (sec^{-1})

Second-order reactions



$$\frac{d[A]}{dt} = -k_2[A][B]$$

- The rate of a second-order, or bimolecular, reaction is
- where the second-order rate coefficient k_2 has units of $\text{cm}^3 \text{molecule}^{-1} \text{ s}^{-1}$.



Collision Theory



$$R_{AB} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \pi d^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} n_A n_B$$

$$R_{AB} = \pi d^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \exp\left(-\frac{E}{RT}\right) n_A n_B$$

$$k = \underbrace{\pi d^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2}}_A \exp\left(-\frac{E}{RT}\right)$$

- Consider the bimolecular reaction
- If reaction occurred with every collision, then the rate of reaction between A and B would be just
- Not every collision will result in reaction; only those collisions that have sufficient kinetic energy to surmount the energy barrier for reaction will lead to reaction. For a Maxwell distribution the fraction of encounters that have energy greater than a barrier E (kJ mol⁻¹) is $\exp(-E/RT)$.
- The rate of reaction is then



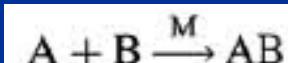
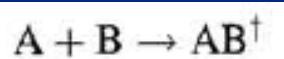
Arrhenius form

$$k = A \exp\left(-\frac{E}{RT}\right)$$

- As indicated, the terms multiplying the exponential are customarily denoted by A , the *collision frequency factor*, or simply the *preexponential factor*.
- Thus, the reaction rate coefficient consists of two components, the frequency with which the reactants collide and the fraction of collisions that have enough energy to overcome the barrier to reaction.
- In many cases the preexponential factor can be considered to be independent of temperature, and the rate coefficient is written as



Termolecular reactions



- The termolecular reaction actually does not take place as the result of the simultaneous collision of all three molecules A, B, and M.
- The probability of such an event happening is practically zero.
- Rather, what actually occurs is that molecules A and B collide to produce an energetic intermediate AB^\dagger (the dagger representing vibrational excitation)
- In order for AB^\dagger to proceed to the product AB, its excess energy must be removed through collision with another molecule denoted by M, to which the excess energy is transferred

SETS OF REACTIONS



- Atmospheric chemical problems require the determination of gas concentrations when many reactions occur at the same time.
- A difficulty arises because a species is usually produced and/or destroyed by several reactions.



$$\begin{aligned}
 \frac{d[NO]}{dt} &= P_c - L_c = Rate_3 + Rate_4 - Rate_1 \\
 &= J[NO_2] + k_3[NO_2][O] - k_1[NO][O_3]
 \end{aligned}$$

$$\begin{aligned}
 \frac{d[NO_2]}{dt} &= P_c - L_c = Rate_1 - Rate_3 - Rate_4 \\
 &= k_1[NO][O_3] - J[NO_2] - k_3[NO_2][O]
 \end{aligned}$$

$$\begin{aligned}
 \frac{d[O]}{dt} &= P_c - L_c = Rate_3 - Rate_2 - Rate_4 \\
 &= J[NO_2] - k_2[O][O_2][M] - k_3[NO_2][O]
 \end{aligned}$$

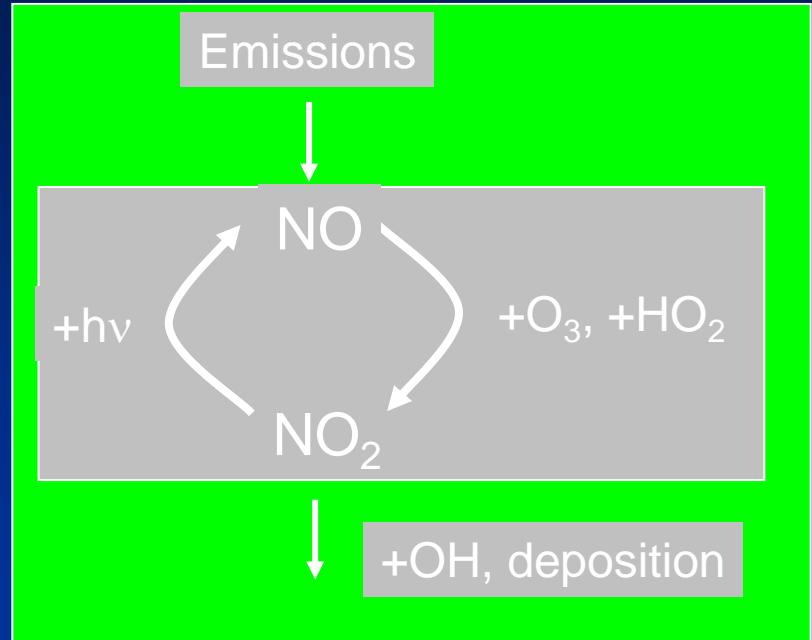
$$\frac{d[O_3]}{dt} = P_c - L_c = Rate_2 - Rate_1 = k_2[O][O_2][M] - k_1[NO][O_3]$$

Chemical Families

Species are grouped together so that the fast reactions don't change the group concentration.

Example:

$$\text{NO}_x = \text{NO} + \text{NO}_2$$



$$\frac{d\text{NO}}{dt} = \text{Emissions} + j_{\text{NO}_2} \cdot \text{NO}_2 - \text{NO}(k_1 \cdot \text{O}_3 + k_2 \cdot \text{HO}_3)$$

$$\frac{d\text{NO}_2}{dt} = \text{NO} \cdot (k_1 \cdot \text{O}_3 + k_2 \cdot \text{HO}_3) - j_{\text{NO}_2} \cdot \text{NO}_2 - k_3 \cdot \text{NO}_2 \cdot \text{OH} - \text{deposition}$$

$$\frac{d\text{NO}_x}{dt} = \frac{d\text{NO}}{dt} + \frac{d\text{NO}_2}{dt} = \text{Emissions} - k_3 \cdot \text{NO}_2 \cdot \text{OH} - \text{deposition}$$

Condensed mechanisms for organic chemistry

- The number of chemical reactions involving organic gases in urban air is large.
- Explicit chemical mechanisms with thousands of organic reactions have been developed (Madronich and Calvert 1989; Jenkin *et al.* 2003; Saunders *et al.* 2003).
- Although such mechanisms can now be solved in a three-dimensional atmospheric model for a period of a few days (e.g., Liang and Jacobson 2000),
- The computational demand for long-term and most practical simulations requires that the number of species and reactions be reduced.



Methods of reducing the number of organic reactions

- Three methods of reducing the number of organic reactions in a model are the **carbon-bond lumping method** (e.g., Whitten *et al.* 1980; Gery *et al.* 1989),
- The **surrogate-species method** (e.g., Atkinson *et al.* 1982; Lurmann *et al.* 1987; Griffin *et al.* 2002), and
- The **lumped-species method** (e.g., Stockwell 1986; Carter 1990, 2000).



Carbon-Bond Lumping Method

- With the **carbon-bond lumping method**, individual organic gases are segregated into one or more bond groups that have similar chemical reactivity.
- For example, a butane molecule, which has four carbons connected by single bonds, is divided into four single carbon atoms, each represented by the **paraffin (PAR)** bond group.



Surrogate-Species Method

- With the **surrogate-species method**, all species of similar reactivity are grouped together.
- Propane and pentane are assumed to have the same reactivity as *n*-butane,
- And all three species are grouped as one surrogate species.



Lumped-Species Method

- With the **lumped-species method**, species of similar reactivity are lumped together, just as with the surrogate species method.
- The difference is that with the surrogate-species method the reaction rate coefficient for each surrogate species is set equal to that of a particular gas.
- The reaction rate coefficient of a lumped species is determined before a model simulation by taking a mole-fraction-weighted average of the reaction rates of each species in the lumped group



SUMMARY OF URBAN CHEMISTRY

- Photochemical smog production is governed by emission of oxides of nitrogen and reactive organic gases.
- Emitted gases, called primary pollutants, react in the presence of sunlight to produce secondary pollutants, such as ozone and peroxyacetyl nitrate.
- The radicals that break down emitted reactive organic gases are OH, HO₂, O₃, NO₃ , and O.
- Photolysis also breaks down certain organics.
- Because reactive organic gas radicals compete with O₃ to produce NO₂ from NO, the photostationary-state relationship does not usually hold in urban air.
- Because gasphase organic chemistry involves reactions among thousands of species, **condensed reaction mechanisms** have been developed to simplify the simulation of organic chemistry in numerical models.



Further reading

- This lecture is based on the materials of the following books that are recommended for further reading
- J.H.Seinfeld and S.N.Pandis. ATMOSPHERIC CHEMISTRY AND PHYSICS: From Air Pollution to Climate Change. JOHN WILEY & SONS, INC. 2006.
- MARK Z. JACOBSON. Fundamentals of Atmospheric Modeling. Cambridge University Press 2005.
- Daniel J. Jacob. INTRODUCTION TO ATMOSPHERIC CHEMISTRY. Princeton University Press. 1999.



**THANKS
FOR
YOUR ATTENTION !!!**

