

0. Basics

0.1 Chemical conversion in the atmosphere - conceptually



The air / environment (geosphere): Is it a reactor ?

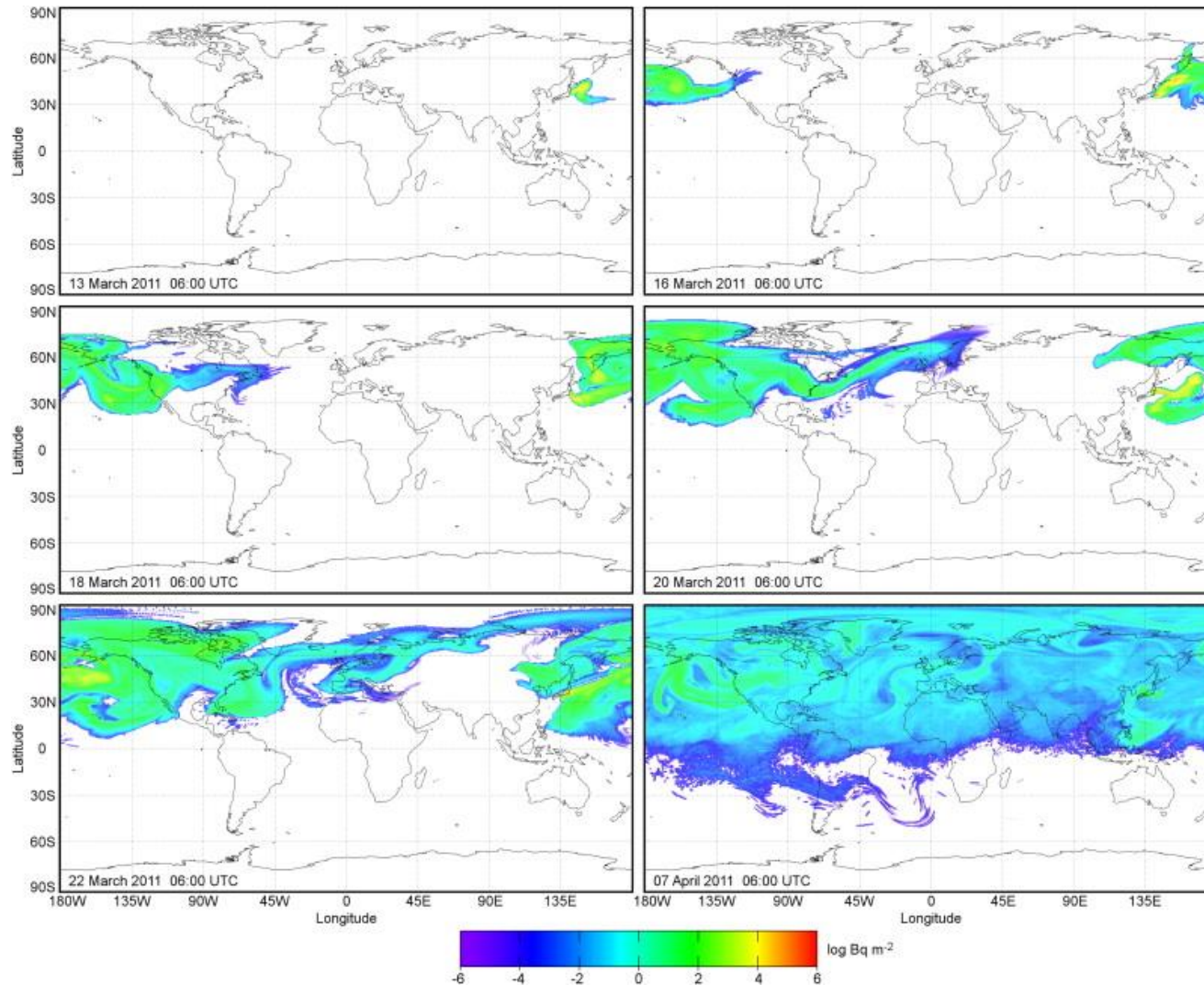
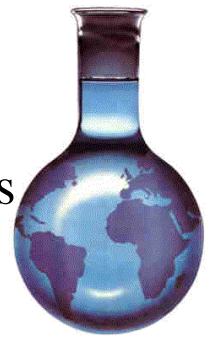
It's a matter of reactions and transports and mixing !

mixing times:

- vertically lower few kilometers (boundary layer) 1h-1d, mixing with free troposphere 2-10 days
- around the globe on the same latitude (zonal transport) within 1-4 weeks

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Atmospheric transport after the Fukushima Dai-ichi accident (Marzo, 2014)

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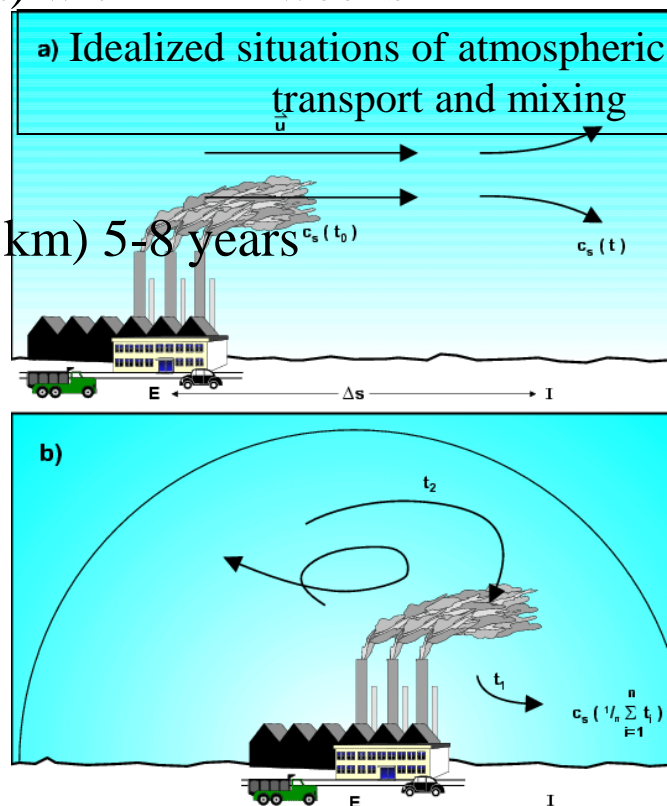
- vertically lower few kilometers (boundary layer) 1h-1d, mixing with free troposphere 2-10 days
- around the globe on the same latitude (zonal transport) within 1-4 weeks
- from mid latitudes to the pole (meridional transport) within days to weeks, hemispheric mixing 2-6 months
- between hemispheres ≈ 1 year
- troposphere-stratosphere 1-3 years, mesosphere (>50 km) 5-8 years

Substance concentration changes result from:

- (chemical) reactions
- (meteorological) transports and mixing

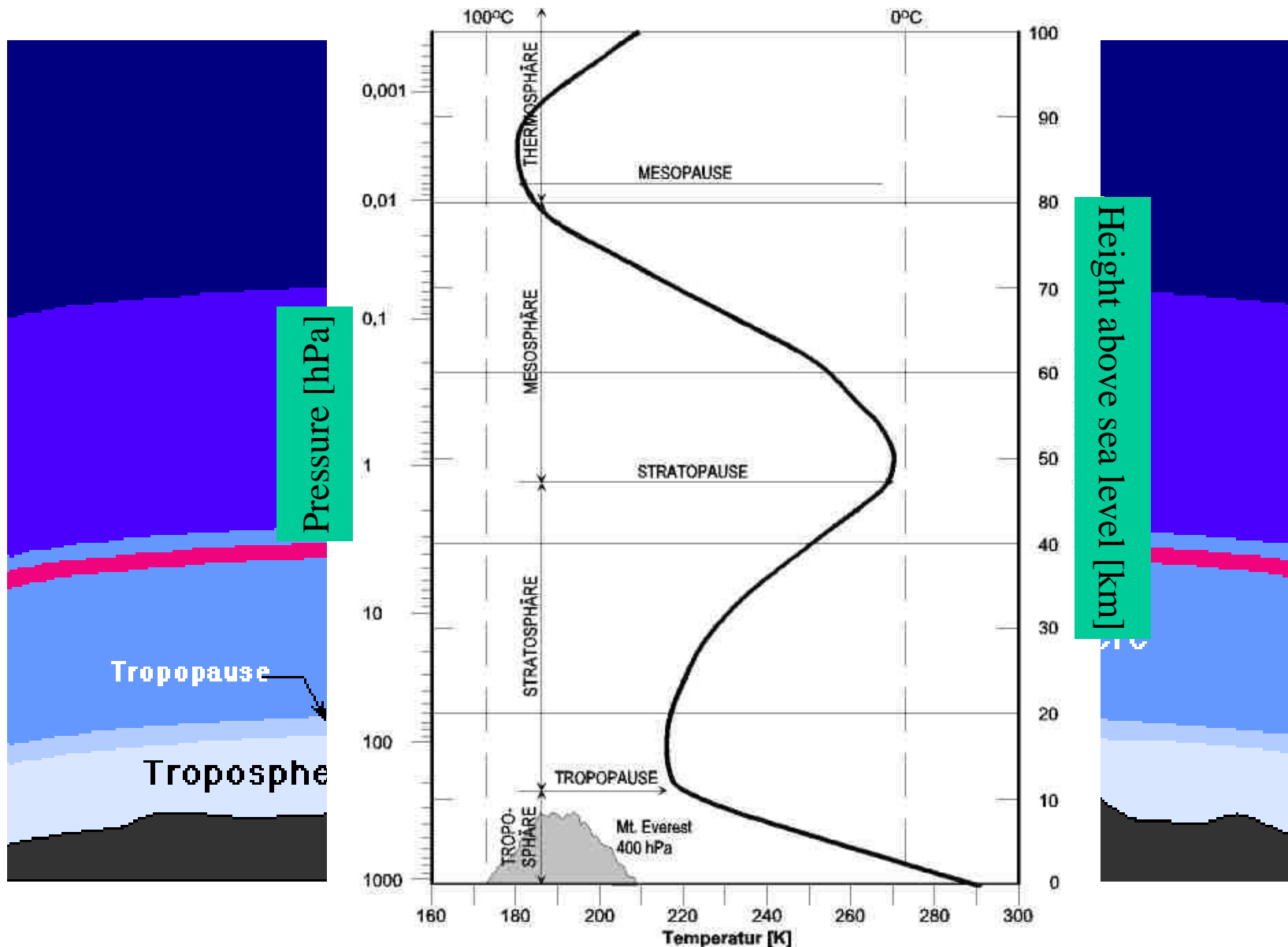
Tools to understand:

- 3D transport models
- model parameters isolated in laboratory experiments
- significant 'ingredients' identified in the 'field'



Atmospheric pressure and composition

Pressure and temperature profiles in the atmosphere



Pressure decline with altitude

$$\rho = 1.225 \text{ mg/cm}, g = 981 \text{ cm/s}^2, R = 8.206 \text{ Pa cm}^3/\text{mol/K}$$

$$\rightarrow \Delta z/\Delta p = 8 \text{ m/hPa at ground}$$

16 m/hPa in 6km altitude

„barometric step“

$$p(z) = p_0 e^{-zg/RT} \quad (\Delta T/\Delta z = 0) \rightarrow p(z, T) \approx p_0 e^{-zg/RT}$$

, Standard ` atmosphere (US Std 1962)

km	T [°C]	p [hPa]	M _g [g/mol]	N _{Lu} /V [molec/cm ³]
0	0	1013	28.964	2.69x10 ¹⁹
0	15	1013	28.964	2.55x10 ¹⁹
0	25	1013	28.964	2.46x10 ¹⁹
3	-4.4	700	28.964	1.76x10 ¹⁹
10	-49.9	265	28.964	6.67x10 ¹⁸
20	-56.5	55	28.964	1.38x10 ¹⁸
30	-46.6	12	28.964	0.30x10 ¹⁸
100	-63	0.00021	28.5	5.29x10 ¹²

Units for quantification of atmospheric trace substances

Ideal gas law: $pV = nRT = mRT/M_g$

Universal gas constant $R = 0.082 \text{ at L}/(\text{mol K}) = 8.314 \text{ J}/(\text{mol K}) = N_A k_B$

Avogadro's number $N_A = 6.023 \times 10^{23} \text{ molec/mol}$

Boltzmann constant $k_B = 1.38 \times 10^{-23} \text{ J/K}$

1 at = 1013 hPa, 1 Pa = 1 N/m² = 1 J/m³

,Molar' volume at $T_0 = 273 \text{ K}$ and $p_0 = 101325 \text{ Pa}$: $V = 22.414 \text{ L/mol}$

→ ,Molar' mass $M_{g \text{ air}} \approx 28.9 \text{ g/mol}$

Concentration $c_i = m_i/V$ [$\mu\text{g}/\text{m}^3$] (for gases: = density)

Mass mixing ratio $\mu_{m i} = c_i/c$ [, %, ppmm, ppbm]

Partial pressure $p_i = n_i RT/V_i$ [Pa]

Volume mixing ratio $\mu_{V i} = p_i/p = V_i/V$ [, %, ppmV, ppbV]

billion = 10^9 (Am., not Brit.)

Concentration $n_i/V = p_i/RT$ [mol/m^3]

Number density $N_i/V = n_i N_A/V = p_i N_A/RT$ [molec/cm^3]

More details: Schwartz & Warneck (1995): Units for use in atmospheric chemistry, Pure Appl. Chem. 67, 1377-1406

Chemical Composition of the Atmosphere

<i>Constituent</i>	<i>Chemical Formula (sum)</i>	<i>Volume Mixing Ratio in Dry Air</i> 10^{-13} - 1!	<i>Major Sources and Remarks</i>
Nitrogen	N ₂	78.084%	Biological
Oxygen	O ₂	20.948%	Biological
Argon	Ar	0.934%	Inert
Carbon dioxide	CO ₂	360 ppmv	Combustion, ocean, biosphere
Neon	Ne	18.18 ppmv	Inert
Helium	He	5.24 ppmv	Inert
Methane	CH ₄	1.7 ppmv	Biogenic and anthropogenic
Hydrogen	H ₂	0.55 ppmv	Biogenic, anthropogenic, and photochemical
Nitrous oxide	N ₂ O	0.31 ppmv	Biogenic and anthropogenic
Carbon monoxide	CO	50-200 ppbv	Photochemical and anthropogenic
Ozone (troposphere)	O ₃	10-500 ppbv	Photochemical
Ozone (stratosphere)	O ₃	0.5-10 ppm	Photochemical
Nonmethane hydrocarbons		5-20 ppbv	Biogenic and anthropogenic
Halocarbons (as chlorine)		3.8 ppbv	85% anthropogenic
Nitrogen species	NO _y	10 ppt-1 ppm	Soils, lightning, anthropogenic
Ammonia	NH ₃	10 ppt-1 ppb	Biogenic
Particulate nitrate	NO ₃ ⁻	1 ppt-10 ppb	Photochemical, anthropogenic
Particulate ammonium	NH ₄ ⁺	10 ppt-10 ppb	Photochemical, anthropogenic
Hydroxyl	OH	0.1 ppt-10 ppt	Photochemical
Peroxyl	HO ₂	0.1 ppt-10 ppt	Photochemical
Hydrogen peroxide	H ₂ O ₂	0.1 ppb-10ppb	Photochemical
Formaldehyde	CH ₂ O	0.1-1 ppb	Photochemical
Sulfur dioxide	SO ₂	10 ppt-1 ppb	Photochemical, volcanic,

Reaction types, kinetics

Quantifying chemical transformations: Law of mass action

Reaction	(1)	$aA + bB \rightarrow$	$cC + dD$
		Reactants	Products
Back reaction	(-1)	$cC + dD \rightarrow$	$aA + bB$
Equilibrium	(1)	$aA + bB \rightleftharpoons$	$cC + dD$
or:	(1, -1)		

Law of mass action (dt.: *Massenwirkungsgesetz*):

The ratio of the product of the concentrations of the products and the product of the concentrations of the reactants (= educts) is constant for a given temperature and pressure in a homogeneous (i.e. single-phase) reaction (*Guldberg & Waage, 1867*):

$$K_1 = c_C^c c_D^d / (c_A^a c_B^b) \quad K_1 = \text{equilibrium constant (dt.: Gleichgewichtskonstante)}$$

implications:

A reaction, $A+B \rightarrow$, will cease, when K_1 is achieved

The rates of formation and decay of the products are equal when equilibrium is established, i.e. $k_1 c_C^c c_D^d = k_{-1} c_A^a c_B^b$ and $K_1 = k_1/k_{-1}$

Reaction types, kinetics

Reaction rate coefficient k

Temperature dependence:

$$-dc_i/dt = k_T c_i$$

$$k_T = A(T) e^{[\Delta E/(RT)]}$$

Universal gas constant $R = k_B N_A = 1.38 \times 10^{-23} \text{ J/K} \times 6.023 \times 10^{23} / \text{mol}$

Providing the energy is sufficiently large, the temperature dependence of A is negligible, and k_T follows the Arrhenius expression:

$$k_T = A e^{[-E_a/(RT)]}$$

with activation energy E_a

Frequently used, too: van t'Hoff expression:

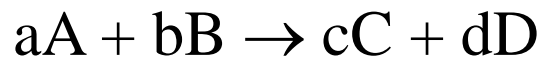
$$k_T = B e^{[-E_a/R (1/T - 1/T_{\text{ref}})]},$$

The two expressions are equal via: $A = B e^{[E_a/(RT_{\text{ref}})]}$

Homogeneous gas-phase reactions

Reactions can be unimolecular, bi- or termolecular.

The rate law of a reaction of the general form



Is defined as

$$\text{Rate (dt.: Rate)} = -dc_A/dt/a = -dc_B/dt/b = dc_C/dt/c = dc_D/dt/d$$

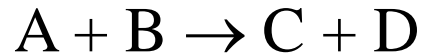
example:



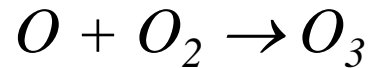
$$\text{Rate} = -dc_{NO}/dt/2 = -dc_{O_2}/dt = dc_{NO_2}/dt/2$$

Second order

Usually: bimolecular



example:



Reaction rate: 2nd order (1+1=2) $dc_C/dt = -dc_A/dt = -dc_B/dt = k c_A^1 c_B^1$

Reaction rate coefficient: $k^{(2)}$

$$k = A \exp [-(E_a/R)T]$$

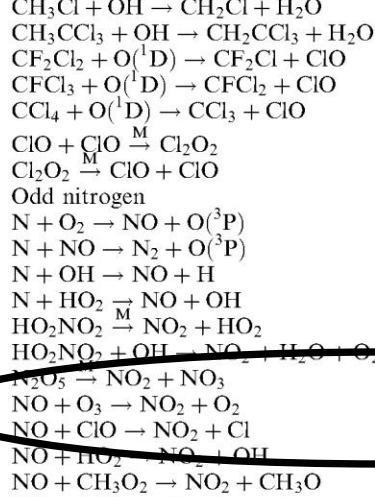
Arrhenius expression, preexponential factor A, activation energy E_a

$k(T^{-1}) \rightarrow$ slope $-E_a/R$, intercept $\ln A$, $E_a/R > 0 \leftrightarrow$ faster at higher T

The reaction order is given by the sum of the exponentials, $n+m+\dots$, of the concentration terms in the rate law of the form $-dc_A/dt = k c_A^n c_B^m$ ($n =$ zero or integer or fraction*)

It is determined empirically.

* ,overall‘ reactions only



$$\begin{aligned}
R_{\text{Cl14}} &= 2.1 \times 10^{-12} \exp(-1150/T) \\
R_{\text{Cl15}} &= 1.8 \times 10^{-12} \exp(-1550/T) \\
R_{\text{Cl16}} &= 1.4 \times 10^{-10} \\
R_{\text{Cl17}} &= 2.3 \times 10^{-10} \\
R_{\text{Cl18}} &= 3.3 \times 10^{-10} \\
R_{\text{Cl19}} &= f(K_0, K_\infty), K_0 = 1.9 \times 10^{-32} [M] (300/T)^{3.9}, K_\infty = 7.0 \times 10^{-32} \\
R_{\text{Cl20}} &= R_{\text{Cl19}} / (3.0 \times 10^{-27} \exp(8450/T)) \\
R_{\text{N1}} &= 1.5 \times 10^{-11} \exp(-3600/T) \\
R_{\text{N2}} &= 3.4 \times 10^{-11} \\
R_{\text{N3}} &= 5.3 \times 10^{-11} \\
R_{\text{N4}} &= 2.0 \times 10^{-10} \\
R_{\text{N5}} &= R_{\text{N16}} / (2.1 \times 10^{-27} \exp(10900/T)) \\
R_{\text{N6}} &= 1.3 \times 10^{-12} \exp(380/T) \\
R_{\text{N7}} &= R_{\text{N18}} / (4.0 \times 10^{-27} \exp(16930/T)) \\
R_{\text{N8}} &= 2.0 \times 10^{-12} \exp(-1400/T) \\
R_{\text{N9}} &= 6.4 \times 10^{-12} \exp(290/T) \\
R_{\text{N10}} &= 3.7 \times 10^{-12} \exp(250/T) \\
R_{\text{N11}} &= 4.2 \times 10^{-12} \exp(180/T)
\end{aligned}$$

k(T)

Example



$$k = A e^{[-(E_a/R)T]}$$

Arrhenius expression, preexponential factor A, activation energy E_a

$k(T^{-1}) \rightarrow$ slope $m = -E_a/R$, intercept $\ln A$, $E_a/R > 0 \leftrightarrow$ faster at higher T

$$A = 2 \times 10^{-12} \text{ cm}^3/\text{molec/s}$$

$$E/R = -1400 \text{ K}$$

\rightarrow

$$k_{298 \text{ K}} = 1.8 \times 10^{-14} \text{ cm}^3/\text{molec/s}$$

$$k_{230 \text{ K}} = 0.45 \times 10^{-14} \text{ cm}^3/\text{molec/s}$$

Quasi steady state approximation

Lindemann-Hinshelwood mechanism:



Here, M stands for any molecule or atom (i.e. N₂, O₂,...), not transformed but required to absorb excess energy, e.g. of an activated intermediate state:



A* in steady state:

$$dc_{A^*}/dt = k_1^{(2)}c_Ac_M - k_{-1}^{(2)}c_{A^*}c_M - k_2^{(1)}c_{A^*} = 0$$

$$c_{A^*} = k_1^{(2)}c_Ac_M / (k_{-1}^{(2)}c_M + k_2^{(1)})$$

$$dc_B/dt = k_2^{(1)} k_1^{(2)}c_Ac_M / (k_{-1}^{(2)}c_M + k_2^{(1)})$$

If (-1) much faster than (2):

$$k_{-1}^{(2)}c_{A^*}c_M \gg k_2^{(1)}c_{A^*}, \text{ then}$$

$$k_{-1}^{(2)}c_M + k_2^{(1)} \approx k_{-1}^{(2)}c_M \text{ and}$$

$$dc_B/dt = k_2^{(1)} k_1^{(2)}c_A / k_{-1}^{(2)}$$

the overall process (1+2) is first order in c_A.

Shifts to second order for c_M → 0 (i.e., low pressure):

$$dc_B/dt = k_2^{(1)} k_1^{(2)}c_Ac_M / k_2^{(1)}$$

First order (but not uni-mo

if c_B >> c_A



$$-dc_B/dt \approx 0$$

Odd nitrogen

N + O ₂ → NO + O(³ P)	R _{N1} = 1.5 × 10 ¹⁰
N + NO → N ₂ + O(³ P)	R _{N2} = 3.4 × 10 ¹⁰
N + OH → NO + H	R _{N3} = 5.3 × 10 ¹⁰
N + HO ₂ → NO + OH	R _{N4} = 2.9 × 10 ¹⁰
HO ₂ NO ₂ \xrightarrow{M} NO ₂ + HO ₂	R _{N5} = R _{N16} / (2.1 × 10 ¹⁰)
HO ₂ NO ₂ \xrightarrow{M} OH + NO ₂ + H ₂ O + O ₂	R _{N6} = 1.3 × 10 ¹⁰
N ₂ O ₅ \xrightarrow{M} NO ₂ + NO ₃	R _{N7} = R _{N18} / (4.0 × 10 ¹⁰)
NO + O ₃ → NO ₂ + O ₂	R _{N8} = 2.0 × 10 ¹⁰
NO + ClO → NO ₂ + Cl	R _{N9} = 6.4 × 10 ¹⁰
NO + HO ₂ → NO ₂ + OH	R _{N10} = 3.7 × 10 ¹⁰
NO + CH ₃ O ₂ → NO ₂ + CH ₃ O	R _{N11} = 4.2 × 10 ¹⁰
NO + NO ₃ → 2NO ₂	R _{N12} = 1.5 × 10 ¹⁰
NO ₂ + O(³ P) → NO + O ₂	R _{N13} = 6.5 × 10 ¹⁰
NO ₂ + ClO → ClONO ₂	R _{N14} = f(K ₀ , K _∞)
NO ₂ + O ₃ → NO ₃ + O ₂	R _{N15} = 1.2 × 10 ¹⁰
NO ₂ + HO ₂ \xrightarrow{M} HO ₂ NO ₂	R _{N16} = f(K ₀ , K _∞)
NO ₂ + OH \xrightarrow{M} HNO ₃	R _{N17} = f(K ₀ , K _∞)
NO ₂ + NO ₃ \xrightarrow{M} N ₂ O ₅	R _{N18} = f(K ₀ , K _∞)
HNO ₃ + OH → H ₂ O + NO ₃	R _{N19} = K ₁ + K ₂
	K ₃ = 4.1
ClONO ₂ + O(³ P) → ClO + NO ₂	R _{N20} = 2.9 × 10 ¹⁰

Example: thermic dissociation

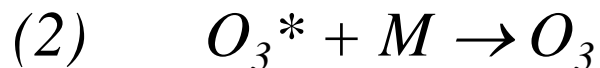


Reaction rate

$$dc_C/dt = -dc_A/dt = k^{(1)}c_A$$

H + O ₃ → OH + O ₂	R _{H9} = 1.4 × 10 ¹⁰
H + HO ₂ → 2OH	R _{H10} = 7.1685 × 10 ¹⁰
HO ₂ + O(³ P) → OH + O ₂	R _{H11} = 3.0 × 10 ¹⁰
HO ₂ + mechanism: Steil et al., 1998	1 × 10 ¹⁰
H + O ₂	f(K ₀ , K _∞)
OH + O ₃ → HO ₂ + O ₂	R _{H14} = 1.6 × 10 ¹⁰

Example



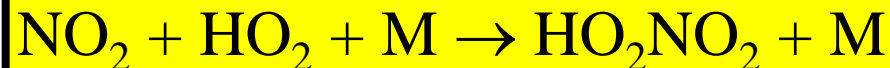
$$c_{O_3^*} = k_1 c_O c_{O_2} / (k_{-1} + k_2 c_M)$$

$$dc_{O_3^*}/dt = k_2 c_{O_3^*} c_M$$

$$dc_{O_3}/dt = k_1 k_2 c_O c_{O_2} c_M / (k_{-1} + k_2 c_M) = \underbrace{[k_1 k_2 c_M / (k_{-1} + k_2 c_M)]}_{k^{(2)}} c_O c_{O_2}$$

$$\text{High pressure limit, } k_\infty^{(2)}: \quad k_{-1} \approx 0 \quad \Rightarrow \quad k_\infty = k_1$$

$$\text{Low pressure limit, } k_0^{(2)}: \quad c_M \rightarrow 0 \quad \Rightarrow \quad k_0 = k_1 k_2 / k_{-1}$$



$$k_{288 \text{ K}/1000 \text{ hPa}} = 1.9 \times 10^{-12} \text{ cm}^3/\text{molec/s}$$

$$k_{288 \text{ K}/500 \text{ hPa}} = 1.5 \times 10^{-12} \text{ cm}^3/\text{molec/s}$$

$$k_{230 \text{ K}/500 \text{ hPa}} = 2.3 \times 10^{-12} \text{ cm}^3/\text{molec/s}$$

$$k_{230 \text{ K}/1000 \text{ hPa}} = 3.0 \times 10^{-12} \text{ cm}^3/\text{molec/s}$$

Reaction orders



is 2nd order or – in case $dc_B/dt \approx 0$ - pseudo-1st order



is 2nd order or – in case $dc_B/dt \approx 0$ - pseudo-1st order or
– if $p \ll 1000$ hPa - between 2nd and 3rd order

The unit of a homogeneous gas-phase rate is [molec/cm³/s].

A 1st or pseudo-1st order rate law reads:

$$-dc_A/dt = dc_C/dt = k^{(1)} c_C, \text{ with } k^{(1)} [1/s].$$

A 2nd order rate law reads:

$$-dc_A/dt = dc_C/dt = k^{(2)} c_C c_D, \text{ with } k^{(2)} [\text{cm}^3/\text{molec}/s].$$

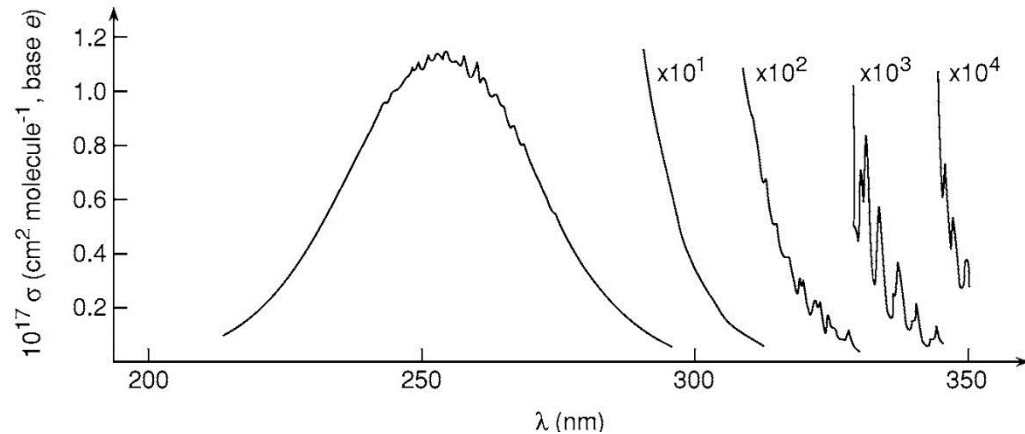
A 3rd order rate law reads e.g.:

$$-dc_A/dt = k^{(3)} c_C^2 c_D, \text{ with } k^{(3)} [\text{cm}^6/\text{molec}^2/s].$$

Photochemical reactions

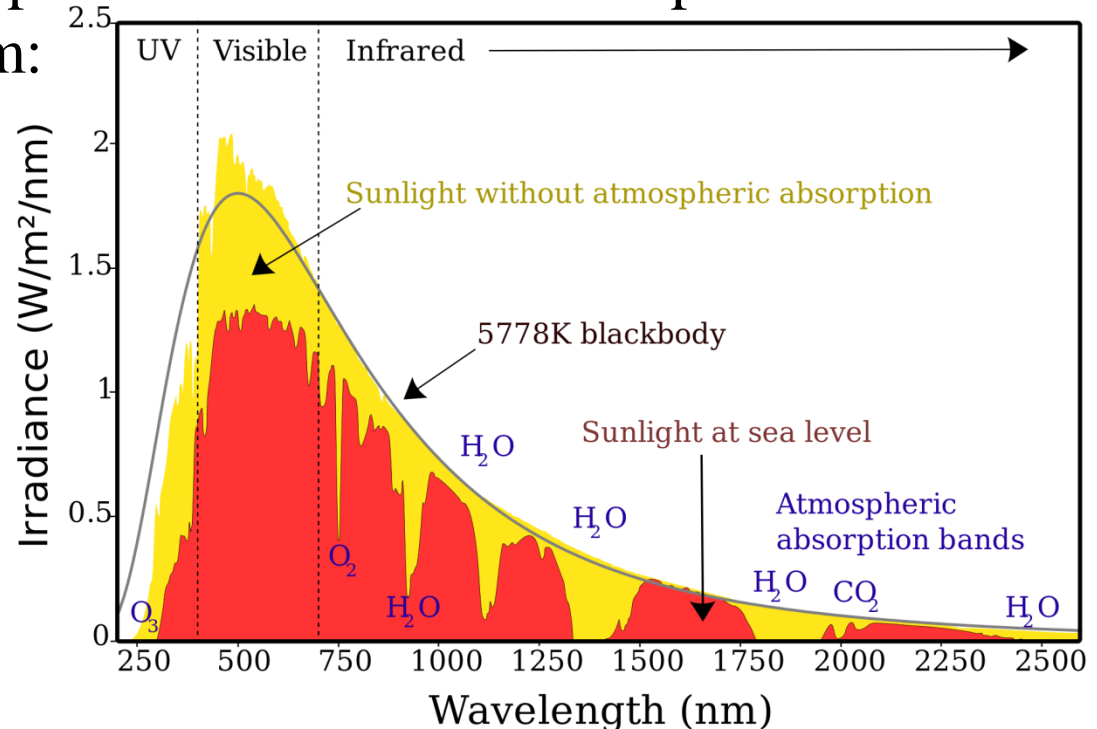
Absorption of radiation by molecules in the atmosphere

Gaseous molecules absorb ultraviolet, visible and infrared light: O_3



Consequences:

- photophysical and photochemical molecular processes
- change of spectrum:



Energy ranges, correspondence between energy and wavelength

$$\lambda = c/\nu$$

with frequency ν

$$\Delta E = hc/\lambda = hc\omega$$

Planck relationship (wavelength λ , wavenumber ω ,

Planck's constant $h = 6.626 \times 10^{-34}$ Js)

Commonly used energy units:

(kJ mol⁻¹)

$$\times 0.2390 = \text{kcal mol}^{-1}$$

$$\times 0.0104 = \text{eV}$$

$$\times 83.59 = \text{cm}^{-1}$$

(kcal mol⁻¹)

$$\times 4.184 = \text{kJ mol}^{-1}$$

$$\times 0.04336 = \text{eV}$$

$$\times 349.8 = \text{cm}^{-1}$$

(cm⁻¹)

$$\times 1.196 \times 10^{-2} = \text{kJ mol}^{-1}$$

$$\times 2.859 \times 10^{-3} = \text{kcal mol}^{-1}$$

$$\times 1.240 \times 10^{-4} = \text{eV}$$

(eV)

$$\times 96.49 = \text{kJ mol}^{-1}$$

$$\times 23.06 = \text{kcal mol}^{-1}$$

$$\times 8.064 \times 10^3 = \text{cm}^{-1}$$

Energy ranges, correspondence between energy and wavelength

$$\lambda = c/\nu$$

$$\Delta E = hc/\lambda = hc\omega$$

Planck relationship

(wavelength λ , wavenumber ω , Planck's constant $h = 6.626 \times 10^{-34}$ Js)

Name	Typical wavelength or range of wavelengths (nm)	Typical range of frequencies ν (s^{-1})	Typical range of wavenumbers ω (cm^{-1})	Typical range of energies (kJ einstein $^{-1}$) ^a
Radiowave	$\sim 10^8$ – 10^{13}	$\sim 3 \times 10^4$ – 3×10^9	10^{-6} – 0.1	$\sim 10^{-3}$ – 10^{-8}
Microwave	$\sim 10^7$ – 10^8	$\sim 3 \times 10^9$ – 3×10^{10}	0.1 – 1	$\sim 10^{-2}$ – 10^{-3}
Far-infrared	$\sim 10^5$ – 10^7	$\sim 3 \times 10^{10}$ – 3×10^{12}	1 – 100	$\sim 10^{-2}$ – 1
Near-infrared	$\sim 10^3$ – 10^5	$\sim 3 \times 10^{12}$ – 3×10^{14}	10^2 – 10^4	~ 1 – 10^2
Visible				
Red	700	4.3×10^{14}	1.4×10^4	1.7×10^2
Orange	620	4.8×10^{14}	1.6×10^4	1.9×10^2
Yellow	580	5.2×10^{14}	1.7×10^4	2.1×10^2
Green	530	5.7×10^{14}	1.9×10^4	2.3×10^2
Blue	470	6.4×10^{14}	2.1×10^4	2.5×10^2
Violet	420	7.1×10^{14}	2.4×10^4	2.8×10^2
Near-ultraviolet	400–200	$(7.5$ – $15.0) \times 10^{14}$	$(2.5$ – $5) \times 10^4$	$(3.0$ – $6.0) \times 10^2$
Vacuum ultraviolet	~ 200 – 50	$(1.5$ – $6.0) \times 10^{15}$	$(5$ – $20) \times 10^4$	$\sim (6.0$ – $24) \times 10^2$
X-Ray	~ 50 – 0.1	$\sim (0.6$ – $300) \times 10^{16}$	$(0.2$ – $100) \times 10^6$	$\sim 10^3$ – 10^6
γ -Ray	≤ 0.1	$\sim 3 \times 10^{18}$	$\geq 10^8$	$> 10^6$

^a For kcal einstein $^{-1}$, divide by 4.184 (1 cal = 4.184 J).

The rate of photochemical reactions

Absorption

$$\ln(I_0/I) = \sigma Nd$$

Beer-Lambert law

$$I/I_0 = e^{(-\sigma Nd)}$$

absorption cross section σ (cm², default: base e)

molecule concentration N (cm⁻³), depth of absorptive layer d (cm)

optical depth $OD = \sigma Nd$

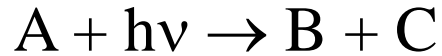
Caution: Most measurements are made to the

base 10 ($\log(I_0/I) = \sigma_{10} Nd$) $\Rightarrow \times 2.303$ to reach base e

Photolysis

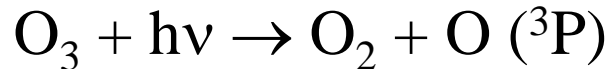
Most important class of photochemical reactions: Photodissociations

Unimolecular



A, B, C, D molecules or radicals

example:



Reaction rate coefficient j (photolysis rate):

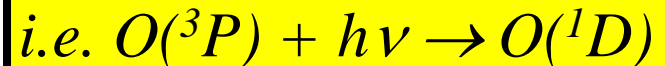
$$dc_C/dt = -dc_A/dt = j c_A$$

Ground state, A

/excitation state, A*:



Example:



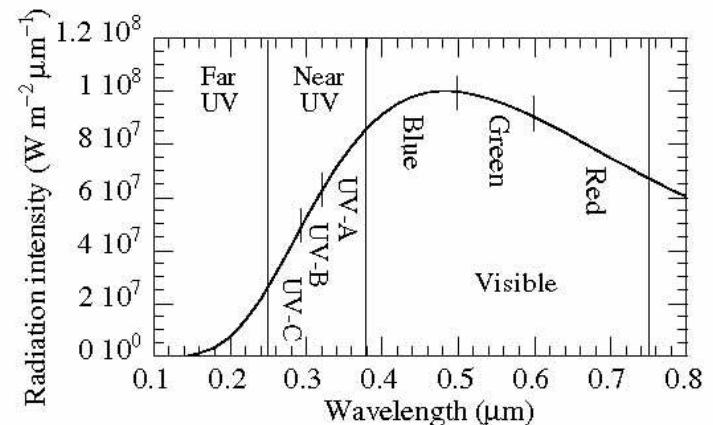
The photolysis rate

The photolysis rate, j (s^{-1}), in $dc_A/dt = j c_A$ is given by:

$$j = \int_{\lambda} \phi(\lambda) \sigma(\lambda) L(\lambda) d\lambda$$

- quantum yield $\phi(\lambda)$ (),
- absorption cross section σ (cm^2),
- actinic flux $L(\lambda)$ ($\text{cm}^{-2} \text{s}^{-1}$)

L is the total intensity of effective light (direct + scattered + reflected, spherically integrated).

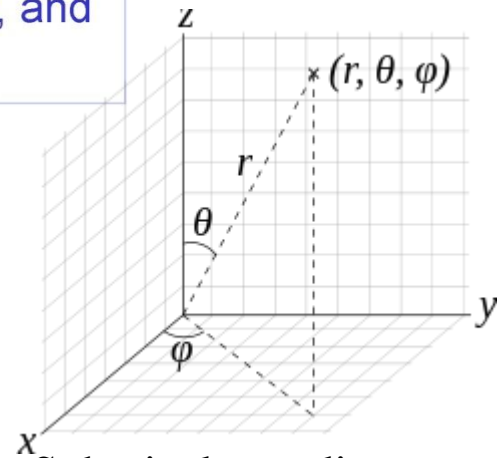


(adopted from: Jacobson, 2005)

The actinic flux $L(\lambda)$ is a function of the solar zenith angle, cloudiness, aerosol concentration, and surface albedo.

$$\frac{dn_A}{dt} = -n_A \underbrace{\int_{\lambda} \phi(\lambda) \sigma(\lambda) \left(\int_0^{2\pi} \int_0^{\pi} L(\lambda, \theta, \varphi) \sin \theta \, d\theta \, d\varphi \right) d\lambda}_{j_A}$$

Typical j -values for midlatitude noontime equinox conditions range from $\sim 1 \cdot 10^{-5} \text{ s}^{-1}$ for $j_{\text{O}(1\text{D})}$ to $\sim 0.2 \text{ s}^{-1}$ for j_{NO_3} . The actinic flux under these conditions is about $2 \cdot 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$ at 315-320 nm, and $7 \cdot 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$ at 360-365 nm.



Spherical coordinate system: Radial distance r , polar angle θ , azimuthal angle φ

L is measured using a (2π) radiometer or by measuring the photolytic decay (so-called chemical actinometry). Its value can be estimated via tabulated values of ϕ and σ for intervals of λ and estimates of $L(\lambda)$ for given conditions.

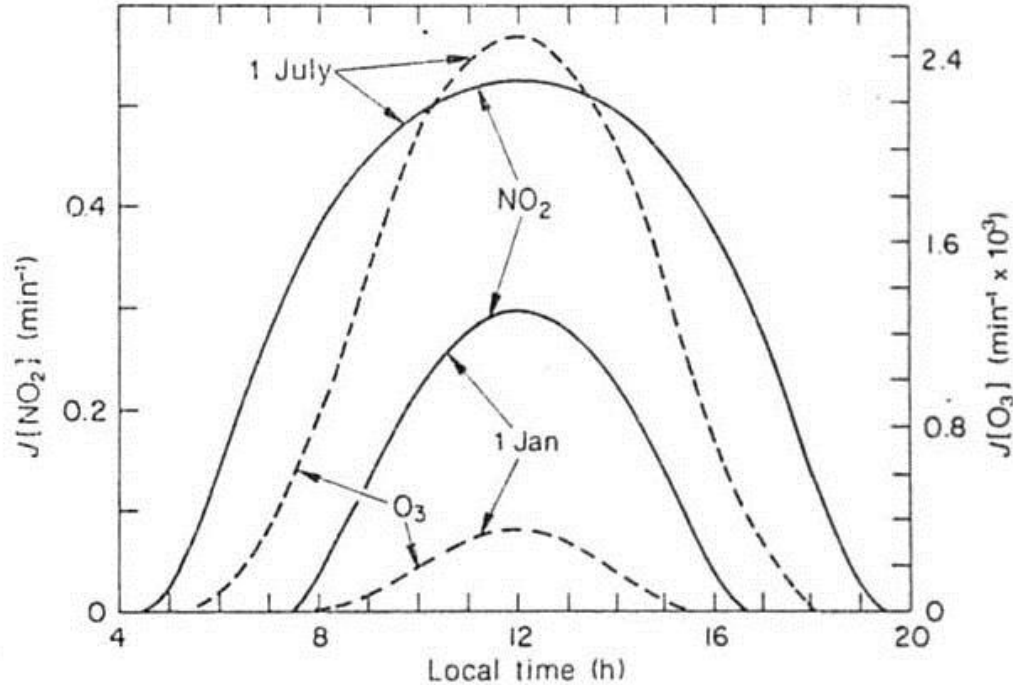


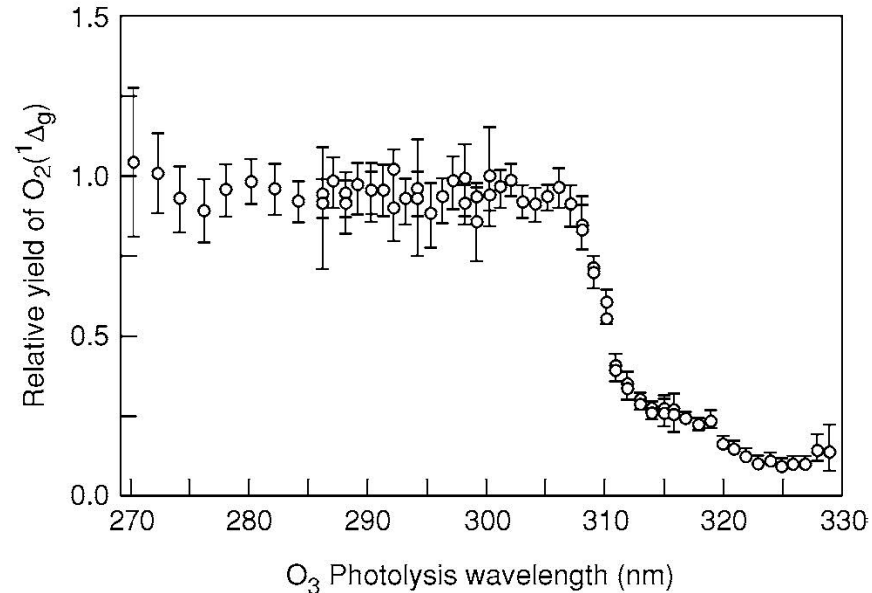
Fig. 3 Theoretical diurnal variation of the $J[\text{NO}_2]$ and $J[\text{O}_3]$ values for midsummer and midwinter at 40°N latitude near sea level. (Calvert, 1985)

Example j_{O_3} : (1) Quantum yield $\phi_i(\lambda)$ for $i = O_3 + h\nu \rightarrow O(^1D) + O_2(^3\Sigma_g^-)$

TABLE 4.6 Parameterization of Quantum Yields for $O(^1D)$ Production from O_3 Photolysis in the 306- to 329-nm Region at Various Temperatures^a

Wavelength (nm)	A	B
306	0.80	9.84
307	0.78	1.44
308	0.87	53.1
309	0.76	73.9
310	1.31	305.5
311	2.37	600
312	5.8	925.9
313	11.4	1191
314	20.1	1423
315	26.4	1514
316	26.8	1512
317	26.8	1542
318	28.33	1604
319	30.6	1604
320	44.4	1866
321	50.2	1931
322	27.8	1882
323	74.1	2329
324	868	3085
325	0.37	689
326	0.24	619
327	0.068	258
328	26.16	2131
329	0.15	470

^a Using the quantum yield expression recommended by Talukdar *et al.*, 1998: $\phi = 0.06 + Ae^{-B/T}$.



$$\phi_{O_3 \rightarrow O(^1D)}(310-320 \text{ nm}) \approx 0.2$$

Example j_{O_3} : (2) Absorption cross section $\sigma(\lambda, T)$ of O_3

TABLE 4.3 Ozone Absorption Cross Sections (Base e)^a

Wavelength (nm)	$10^{20} \sigma$ (cm ² molecule ⁻¹)		Wavelength (nm)
	$T = 226$ K	$T = 298$ K	
185.0	64.37	65.37	262.0
186.0	62.59	61.87	263.0
187.0	59.33	59.41	264.0
188.0	56.55	56.59	265.0
189.0	54.63	54.24	266.0
190.0	51.63	51.14	267.0
191.0	48.42	48.80	268.0
192.0	45.95	46.06	269.0
193.0	43.12	43.36	270.0
194.0	40.88	40.66	271.0
195.0	38.27	38.64	272.0
196.0	36.42	36.73	273.0
197.0	34.63	35.00	274.0
198.0	33.33	33.49	275.0
199.0	32.13	32.09	276.0
200.0	31.45	31.54	277.0
201.0	31.26	31.15	278.0
202.0	31.56	31.79	279.0
203.0	32.55	32.51	280.0
204.0	34.00	33.65	281.0
205.0	36.23	35.85	282.0
206.0	38.87	38.55	283.0
207.0	42.39	42.00	284.0
208.0	46.84	46.40	285.0
209.0	51.88	51.18	286.0
210.0	58.06	57.16	287.0
211.0	65.28	64.02	288.0
212.0	73.12	71.94	289.0
213.0	82.58	81.04	290.0
214.0	92.55	90.96	291.0
215.0	104.1	102.3	292.0
216.0	116.9	114.6	293.0
217.0	131.4	128.7	294.0
218.0	146.4	143.9	295.0
219.0	163.8	160.1	296.0
220.0	179.9	178.5	297.0
221.0	200.0	198.2	298.0
222.0	221.7	220.0	299.0
223.0	244.3	242.9	300.0
224.0	268.8	268.4	301.0
225.0	296.3	294.3	302.0
226.0	323.9	322.6	303.0
227.0	354.2	351.3	304.0
228.0	385.7	382.9	305.0
229.0	416.4	414.1	306.0
230.0	450.6	447.6	307.0
231.0	485.9	481.4	308.0
232.0	523.0	518.1	309.0

TABLE 4.4 Ozone Absorption Cross Sections^{a,b} as a Function of Temperature Averaged over the Spectral Intervals Shown

Wavelength range (nm)	Parameters		
	a	b	c
277.778–281.690	4.0293×10^2	$+4.3819 \times 10^{-2}$	0
281.690–285.714	2.7776×10^2	$+6.3125 \times 10^{-2}$	0
285.714–289.855	1.8417×10^2	-9.6665×10^{-2}	2.1026×10^{-4}
289.855–294.118	1.1300×10^2	-1.0700×10^{-1}	3.2697×10^{-4}
294.118–298.507	6.5087×10	-8.0018×10^{-2}	2.2679×10^{-4}
298.507–303.030	3.6161×10	-6.7156×10^{-2}	3.3314×10^{-4}
303.030–307.692	1.9615×10	-4.4193×10^{-2}	2.0338×10^{-4}
307.692–312.5	1.0459×10	-2.8831×10^{-2}	1.3909×10^{-4}
312.5–317.5	5.4715	-2.0092×10^{-2}	9.8870×10^{-5}
317.5–322.5	2.7569	-1.0067×10^{-2}	2.9515×10^{-5}
322.5–327.5	1.3527	-5.7513×10^{-3}	1.1088×10^{-5}
327.5–332.5	6.9373×10^{-1}	-2.9792×10^{-3}	3.1038×10^{-6}
332.5–337.5	3.2091×10^{-1}	-1.9502×10^{-3}	5.6456×10^{-6}
337.5–342.5	1.4484×10^{-1}	-1.1025×10^{-3}	2.8818×10^{-6}
342.5–347.5	7.5780×10^{-2}	-5.7359×10^{-4}	1.6055×10^{-6}

^a $\sigma(O_3, T) = a + b(T - 230) + C(T - 230)^2$; T is in K; $\sigma(O_3)$ is in units of 10^{-20} cm² molecule⁻¹ (base e).

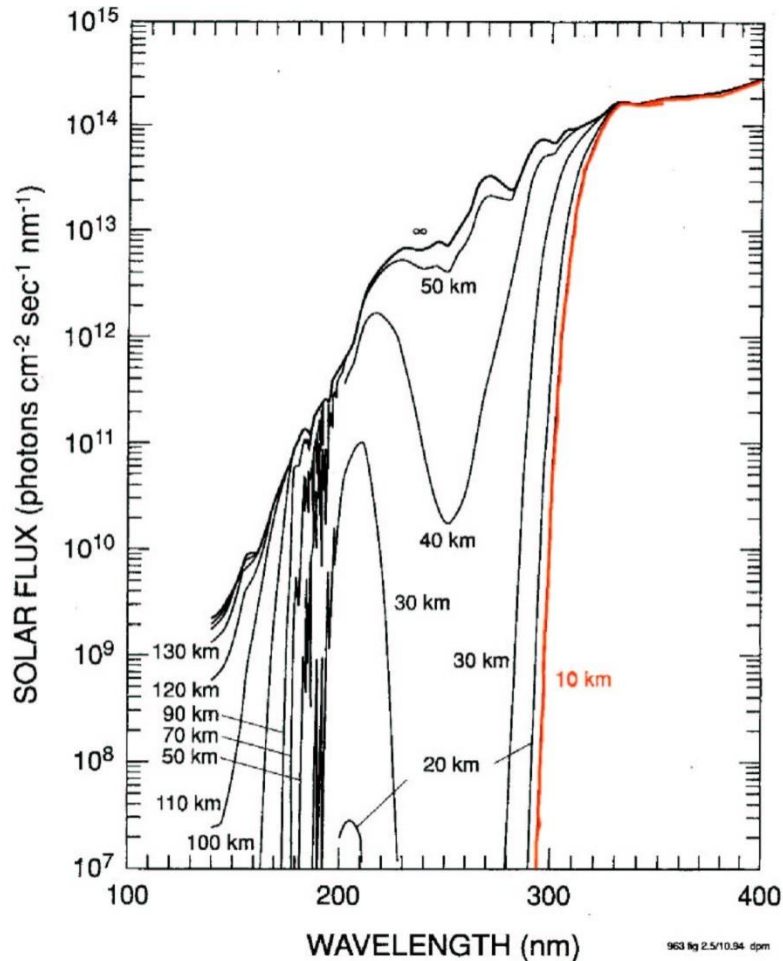
^b From Molina and Molina (1986).

Example:

$$\sigma_{O_3}(310-320 \text{ nm}) \approx 60 \times 10^{-20} \text{ cm}^2/\text{molec for } T = 298 \text{ K}$$

Data src.: Finlayson-Pitts & Pitts, 1998

(3) Actinic flux – determined by radiation absorption in the atmosphere



Actinic flux $L(\lambda)$ - Example:
For $z = 15$ km and solar zenith angle
of 40° :

$$L_{310-320 \text{ nm}} = (1.69 + 2.08 + 2.35 + 2.88 + 2.95) \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1} \\ \approx 12 \times 10^{14} \text{ s}^{-1}$$

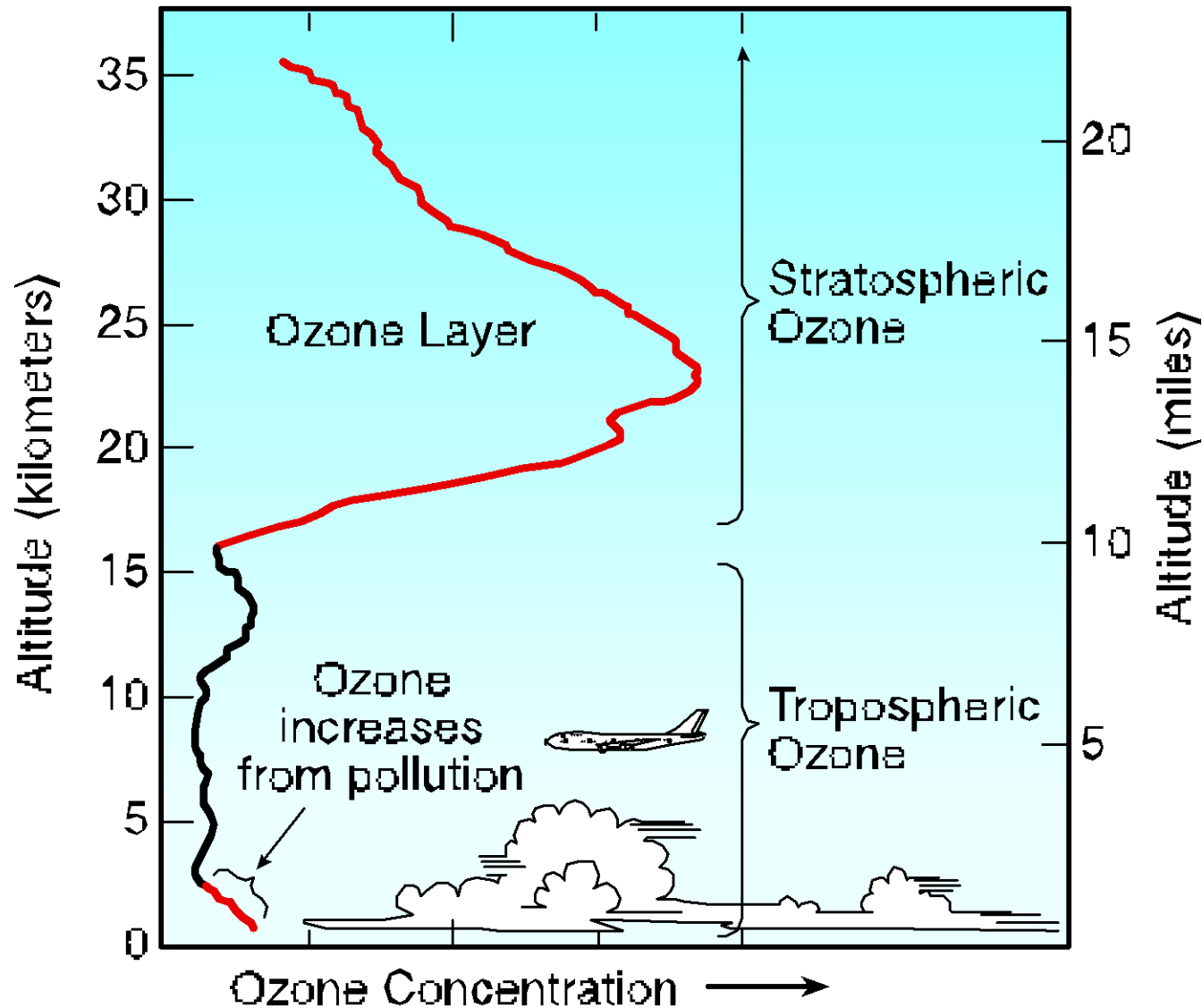
Order of magnitude estimate of
 $\dot{j}_{\text{O}_3 \rightarrow \text{O}^*}$ for a selected wavelength
interval:

$$(1-3) \dot{j}_{\text{O}_3 \rightarrow \text{O}^*}(310-320 \text{ nm}) \approx \\ \approx 0.2 \times 60 \times 10^{-20} \times 12 \times 10^{14} \text{ s}^{-1} \approx \\ \approx 10^{-4} \text{ s}^{-1}$$

Tropospheric chemistry

Tropospheric ozone and hydrocarbon chemistry

Ozone in the Atmosphere



Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

Tropospheric O₃: Significance

Toxicology:

- concentrations $> 120\text{-}150\ \mu\text{g}/\text{m}^3$ are relevant, at least for sensitive persons.
No epidemiological evidences.
- Significant loss of physical performance at higher concentrations, i.e. $\approx 400\ \mu\text{g}/\text{m}^3$ (EU, 1992: $180\ \mu\text{g}/\text{m}^3$ warning, $360\ \mu\text{g}/\text{m}^3$ dangerous)

Climate:

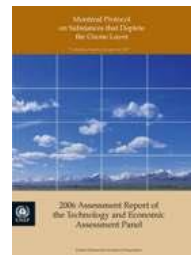
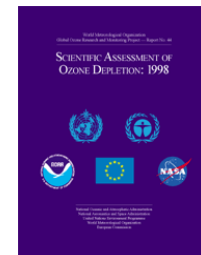
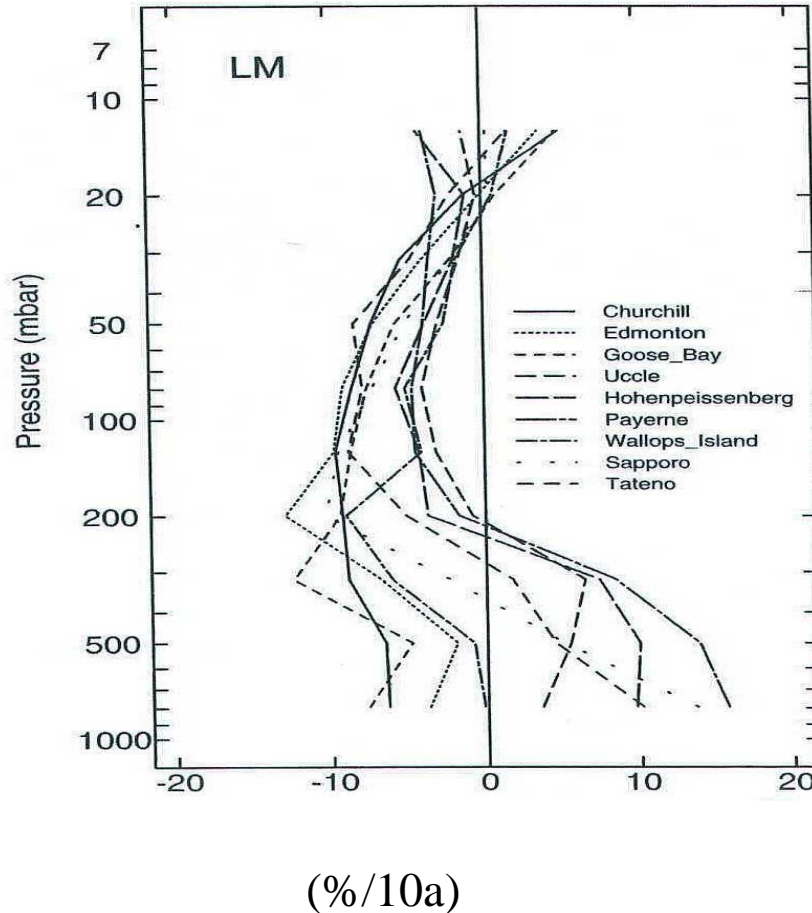
- absorption in the atmospheric 'window' region near $\lambda = 9.6\ \mu\text{m}$ \rightarrow radiative forcing $+0.35 \pm 0.15\ \text{W m}^{-2}$ since 1850

Ecotoxicology:

- toxic to plants (uptake through stomatae prevails, radical formation); sensitive crops (potato, wheat, rye, barley) and trees (larch, pine)
- for same dosis damage is highest under peak concentrations, synergistic effects with NO₂ and SO₂
-

Trends of ozone - stratospheric and tropospheric

36-59°N, 1996 vs. 1970

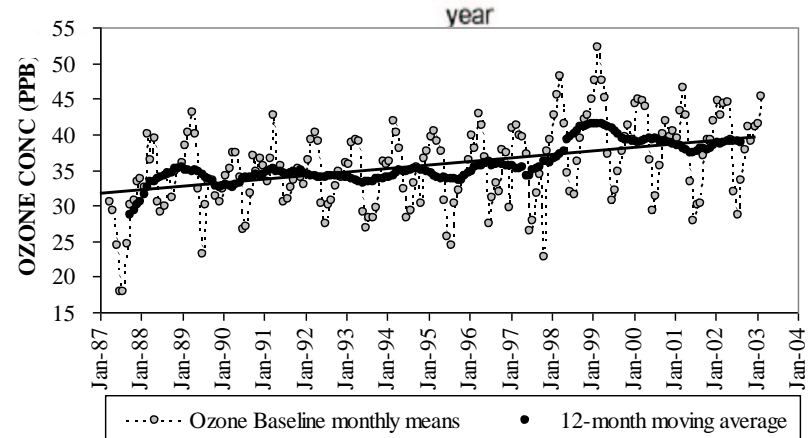
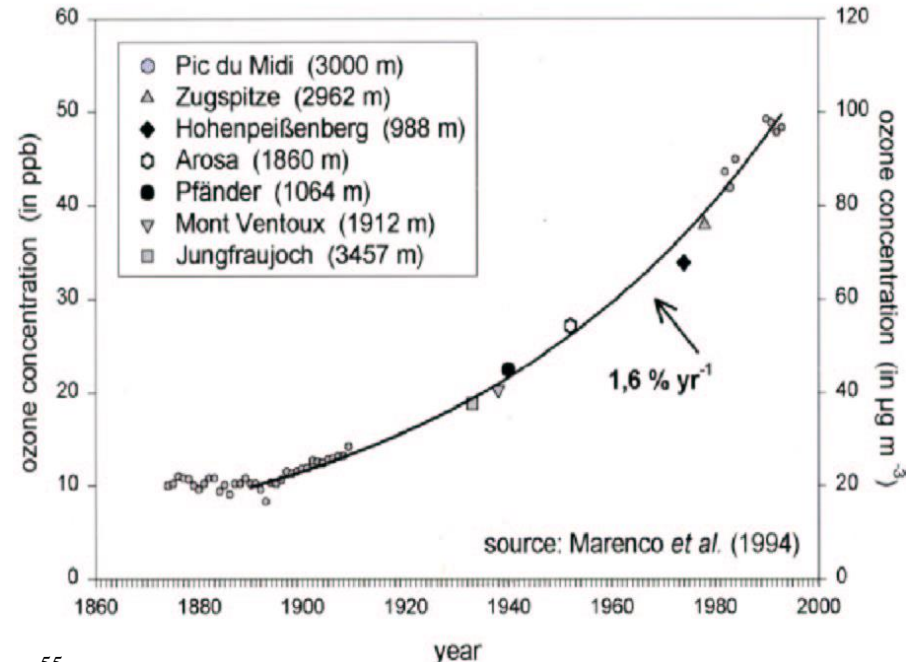


(WMO, 1998, after Logan & Megretskiaia) <http://ozone.unep.org/>

Tropospheric ozone temporal trends

Background stations

Mauna Loa Mace Head

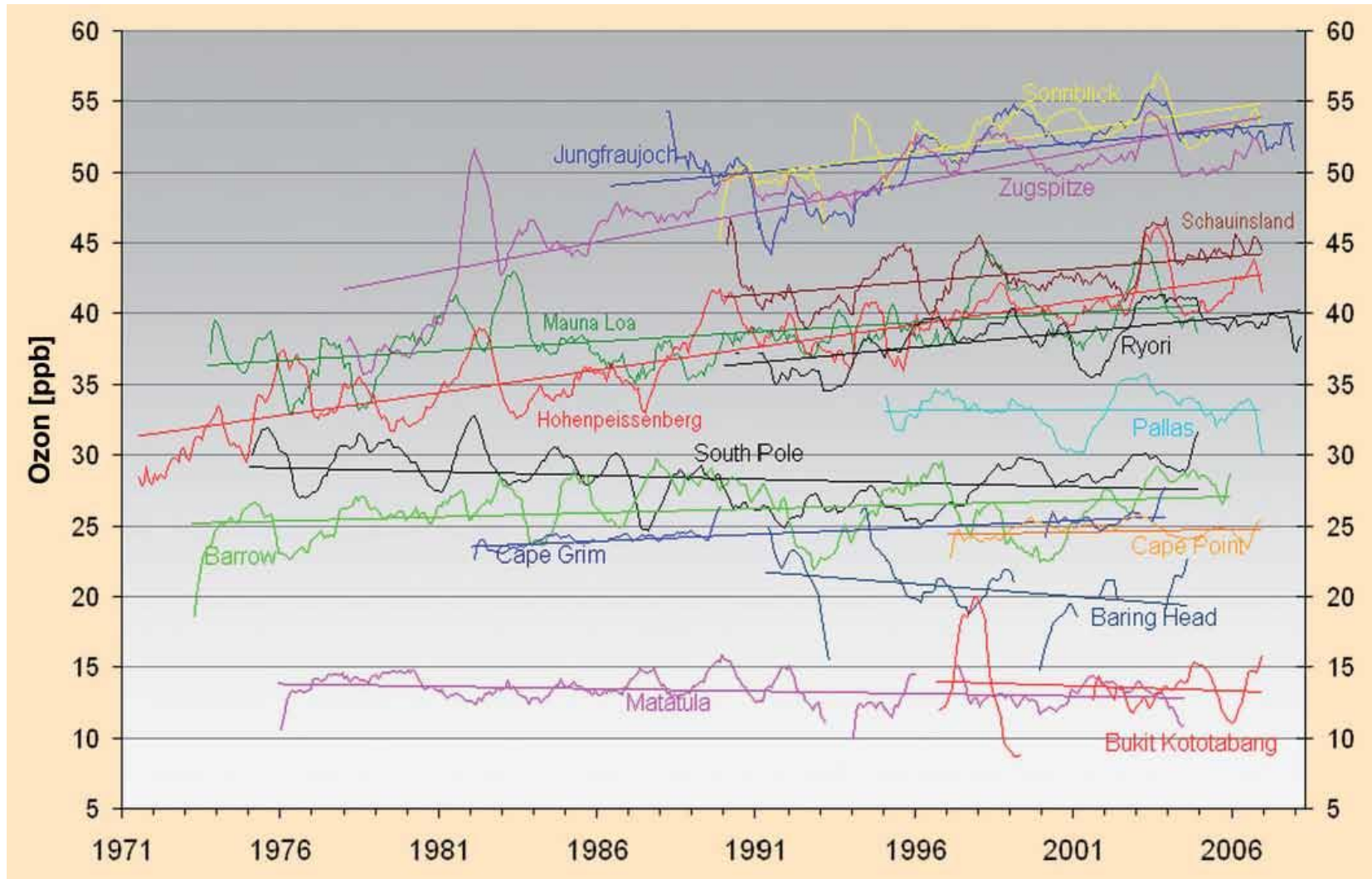


(courtesy of Parrish et al., 2009)

Mace Head, IRL (Derwent, 2004)

Tropospheric ozone temporal trends

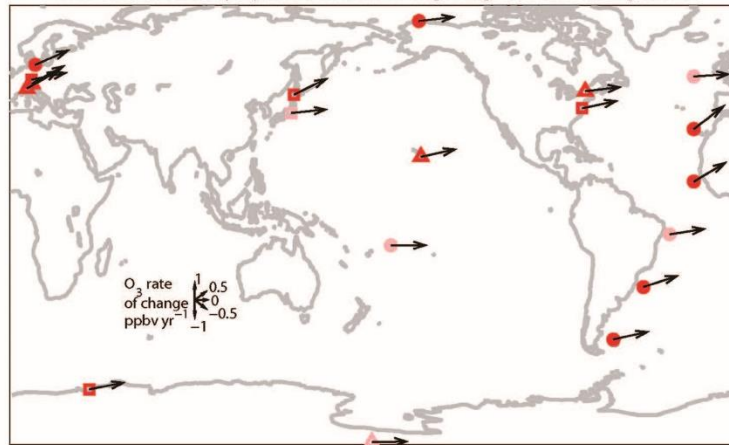
Ground stations



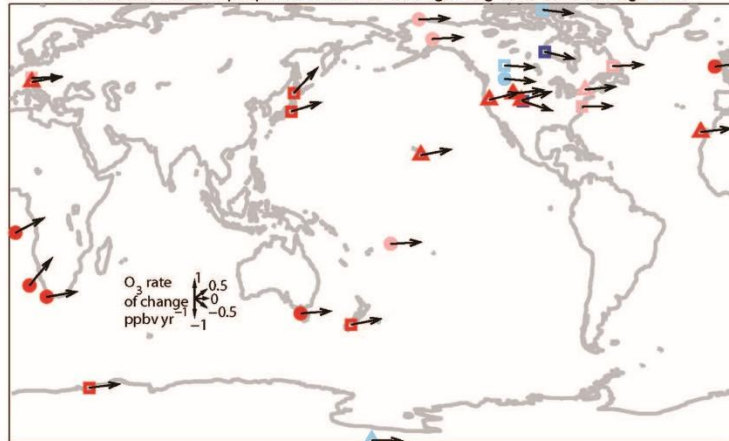
(courtesy of Barnes et al., 2011)

Tropospheric ozone trends

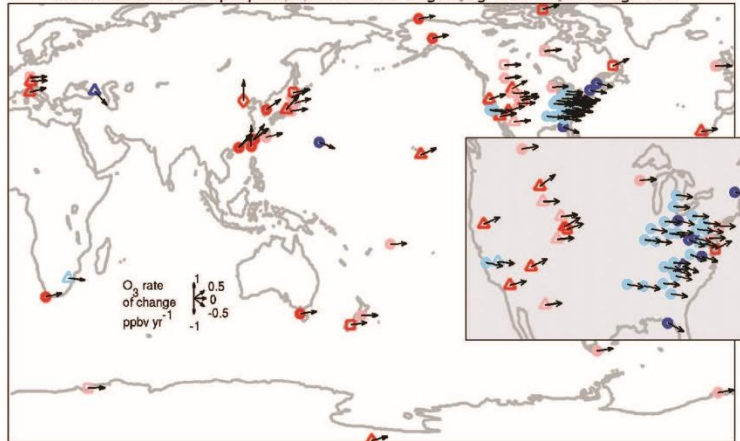
Surface and lower tropospheric ozone trends beginning 1950-1979 through 2010



Surface and lower tropospheric ozone trends beginning 1980-1989 through 2010



Surface and lower tropospheric ozone trends beginning 1990-1999 through 2010



(EDGARv4.1;
Cooper et al., 2016)

Ozone formation in CO oxidation

Ozone formation in the troposphere

(1) Why is CO not accumulating in urban air?

→ ,discovery' of the OH radical

CO volume mixing ratio in the lower troposphere: 100-200 ppbv



Chemical fate of OH globally: $\approx 2/3$ reacts with CO



$$k = 220 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$$



$$j \approx 5 \times 10^{-3}/\text{s}$$



$$k^{(1)} \approx 10^5/\text{s}$$



$$k^{(1)} \approx 10^{-2}/\text{s}$$



Ozone formation in the troposphere

Leighton relationship



$$dc_{\text{O}_3}/dt = 0 = k_5 c_{\text{O}} c_{\text{O}_2} c_{\text{M}} - k_6 c_{\text{NO}} c_{\text{O}_3}$$

$$\text{hence: } c_{\text{O}_3} = k_5 c_{\text{O}} c_{\text{O}_2} c_{\text{M}} / (k_6 c_{\text{NO}})$$

equilibrium within 2 min

quasi-constant ozone level ($f(j_{\text{NO}_2})$)

c_{O} available from:

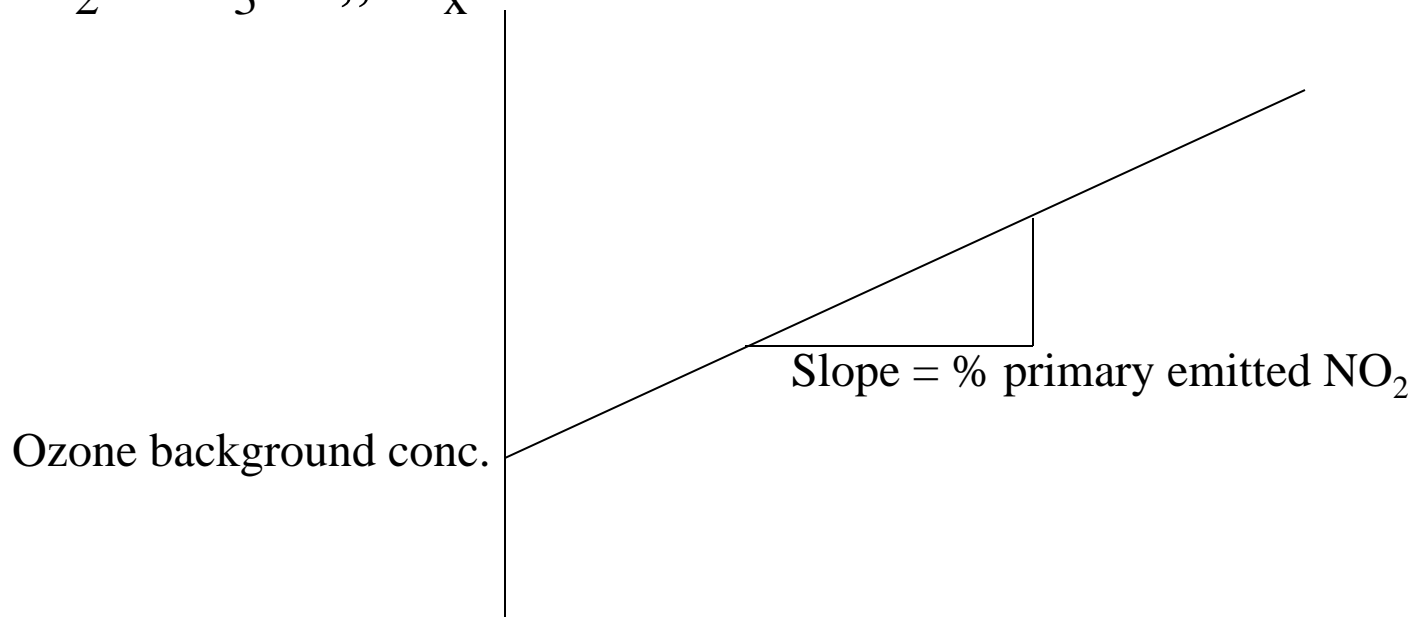
$$dc_{\text{O}}/dt = 0 = j_4 c_{\text{NO}_2} - k_5 c_{\text{O}} c_{\text{O}_2} c_{\text{M}} \quad (\text{hence: } c_{\text{O}} = j_4 c_{\text{NO}_2} / (k_5 c_{\text{O}_2} c_{\text{M}}))$$

$$\text{combined: } c_{\text{O}_3} = j_4 c_{\text{NO}_2} / (k_6 c_{\text{NO}}) \quad \text{or: } (c_{\text{O}_3} c_{\text{NO}}) / c_{\text{NO}_2} = \text{constant}$$

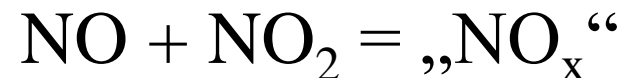
holds as long as there are no other O_3 loss reactions than (6)

Ozone formation in the troposphere

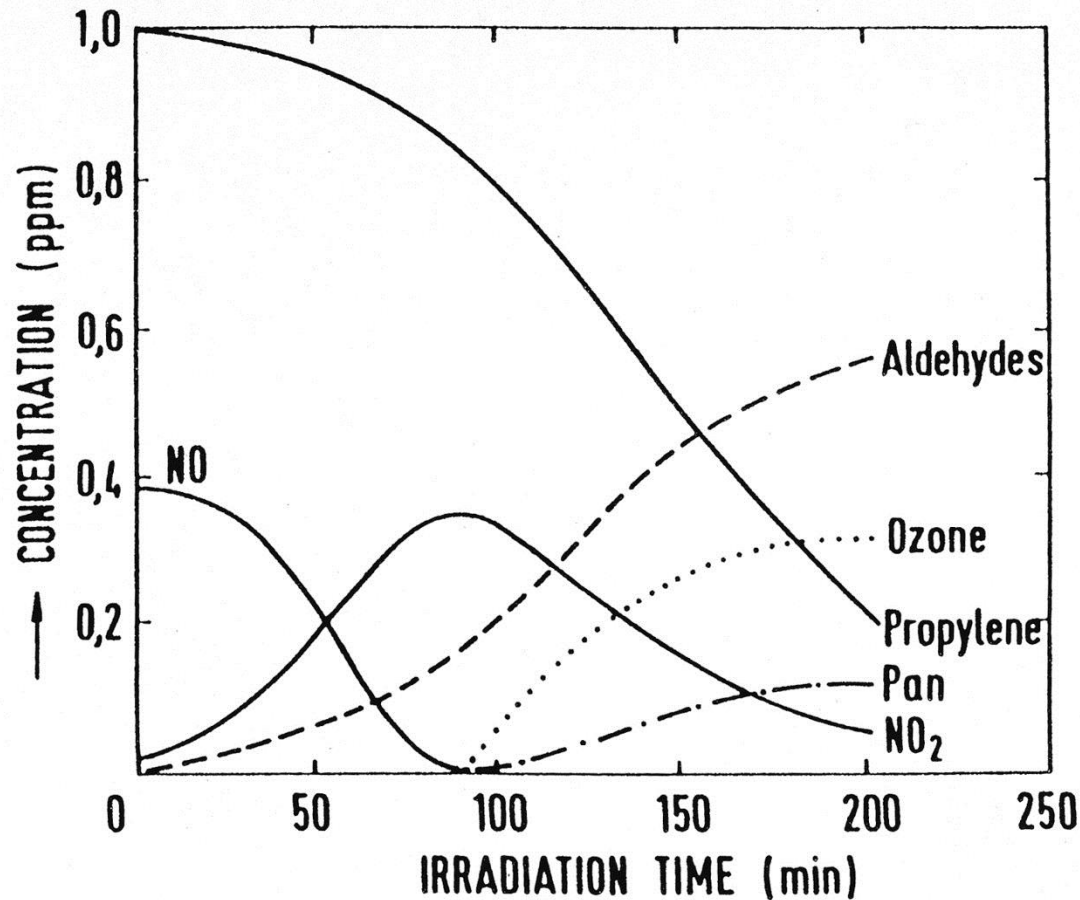
Ozone depends on the background level, on NO_x and on the ratio NO_2/NO upon emission:



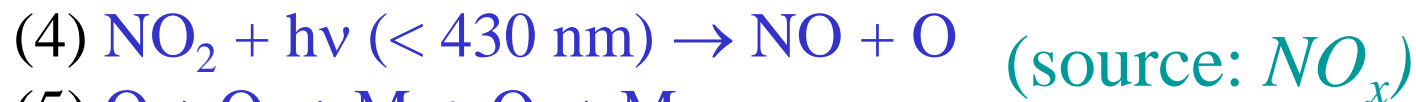
(Clapp & Jenkin, 2001)



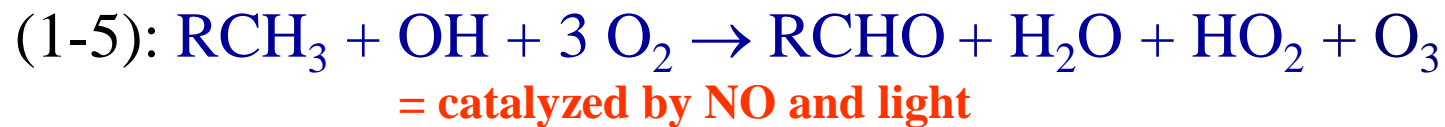
Ozone formation in synthetic atmosphere



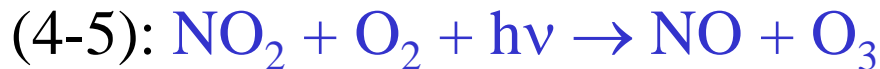
Ozone formation from *hydrocarbons*, HC_x , and NO_x



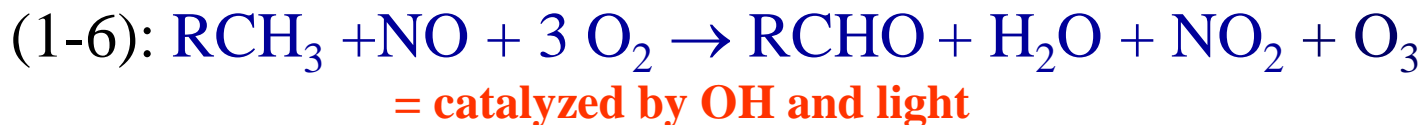
Sum



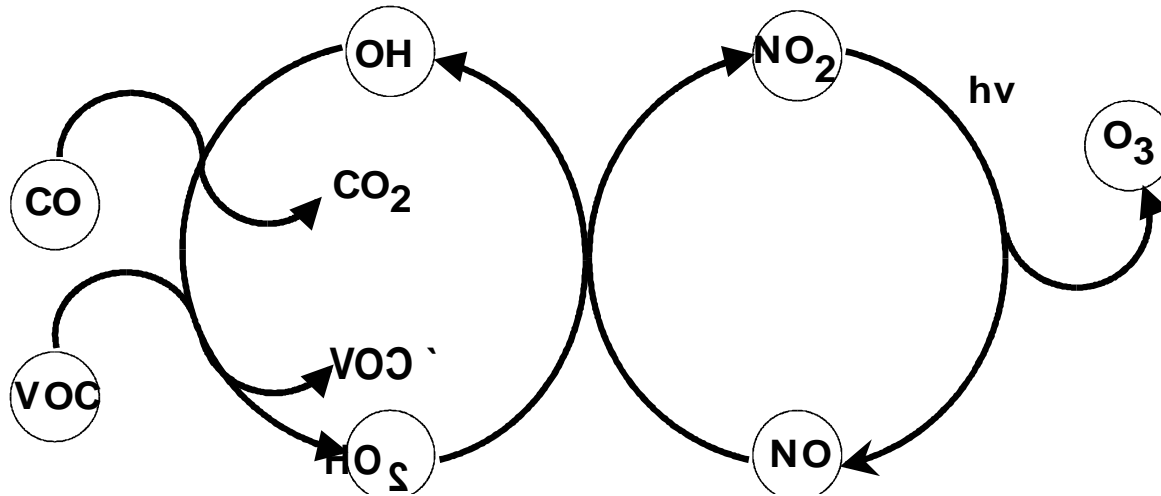
Sum



Sum



2 main pathways: CO or VOC oxidation



(courtesy: Möller, 2003)

HC_x: alkanes, example methane

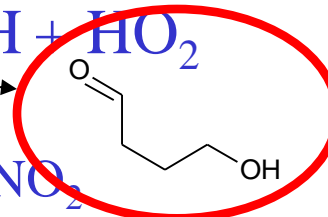
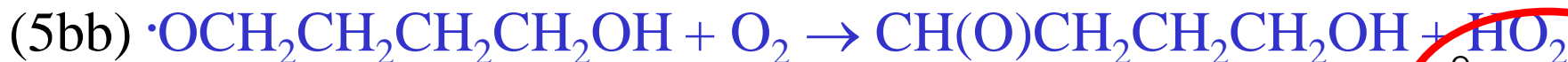
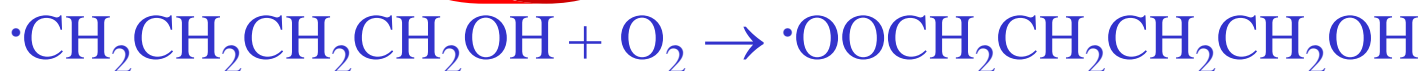
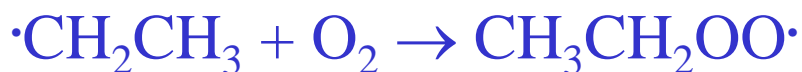
- Although slow, CH₄ is a major chemical sink for OH (globally ≈ 1/3 of OH reacts with CH₄).
- The so formed ozone is the major contribution to the background ozone.
- It increases with increasing methane emissions.



Sum:

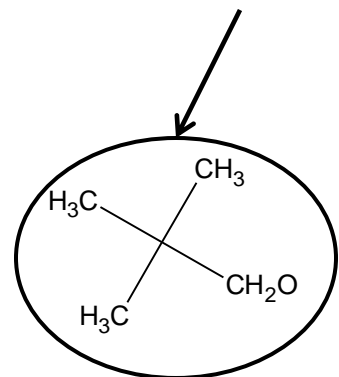


HC_x = alkanes: branching 1) C atom position attacked, 2) alkoxy radical



Alkoxy radicals: reactivity overview

RO [•]	k ⁽¹⁾ (10 ³ s ⁻¹)		
	decomposition	H-abstraction by O ₂	isomerization
CH ₃ CH ₂ CH ₂ CH ₂ O [•]	0.6	200	≈ 0
CH ₃ CH ₂ CH ₂ CHO [•] CH ₃	17	40	200
CH ₃ CH ₂ CHO [•] (CH ₂) ₂ CH ₃	34	40	200
CH ₃ CHO [•] (CH ₂) ₃ CH ₃	28	40	2000
CH ₃ C(CH ₃) ₂ CH ₂ O [•]	9.8	24	≈ 80



Nomenclature:

Saturated and unsaturated C chains: alkanes (*dt: Alkane*), alkenes and alkynes (*dt: Alkene, Alkine*)

Partly oxygenated hydrocarbons: ROH alcohols (*dt: Alkohole*), carbonyls: RCHO aldehydes (*dt: Aldehyde*) and R₂CO ketones (*dt: Ketone*), RCOOH and R(COOH)₂ mono- and dicarboxylic acids (*dt: Mono- und Dicarbonsäuren*)

Multifunctional partly oxygenated hydrocarbons:

RCHOHCHO α-hydroxyaldehydes, RCHOHCOOH α-hydroxyacids, ...

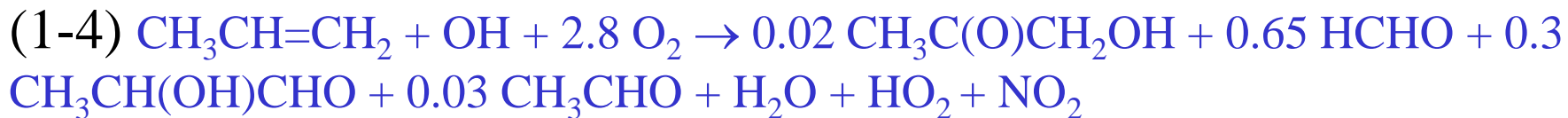
HC_x: alkene OH reaction, example C₃, i.e. propene

Alkenes are more reactive toward OH than alkanes: $k \leq 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

The higher substituted radical is more stable, hence, formed preferentially:



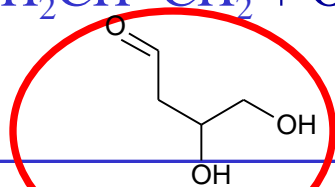
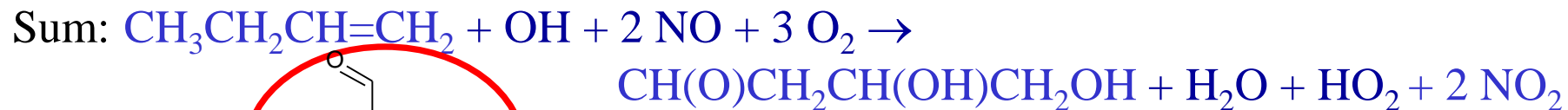
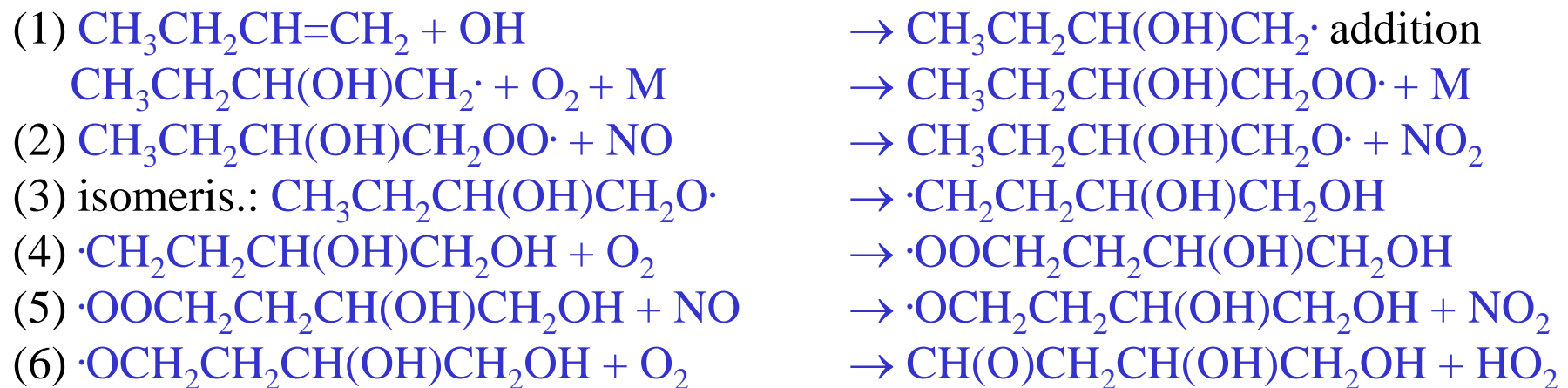
Sum



HC_x: alkene OH reaction

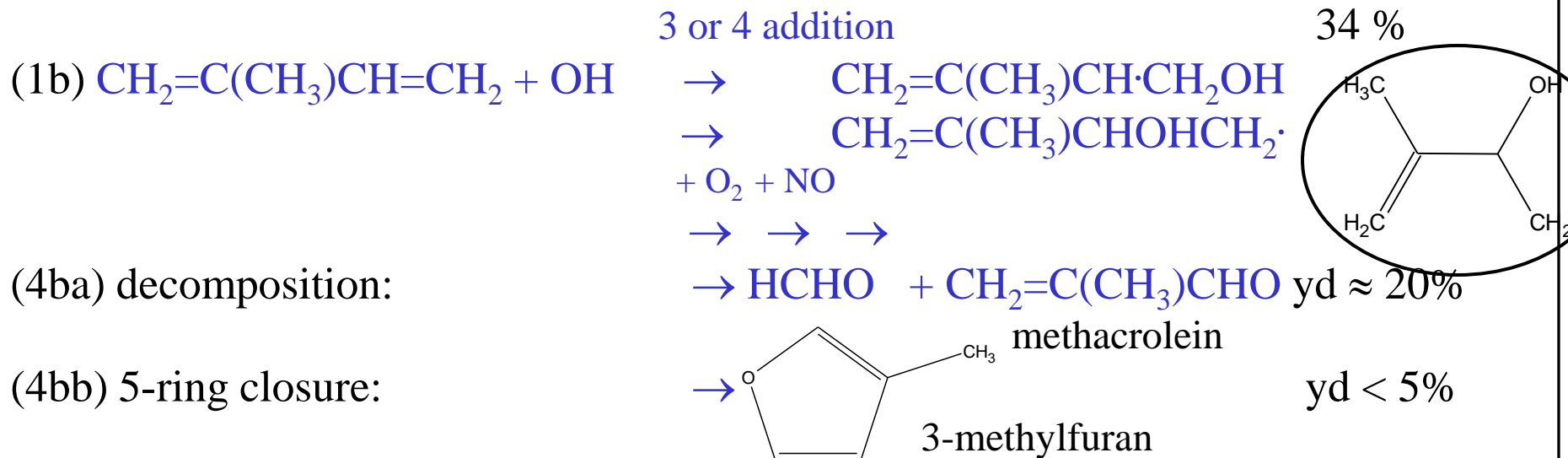
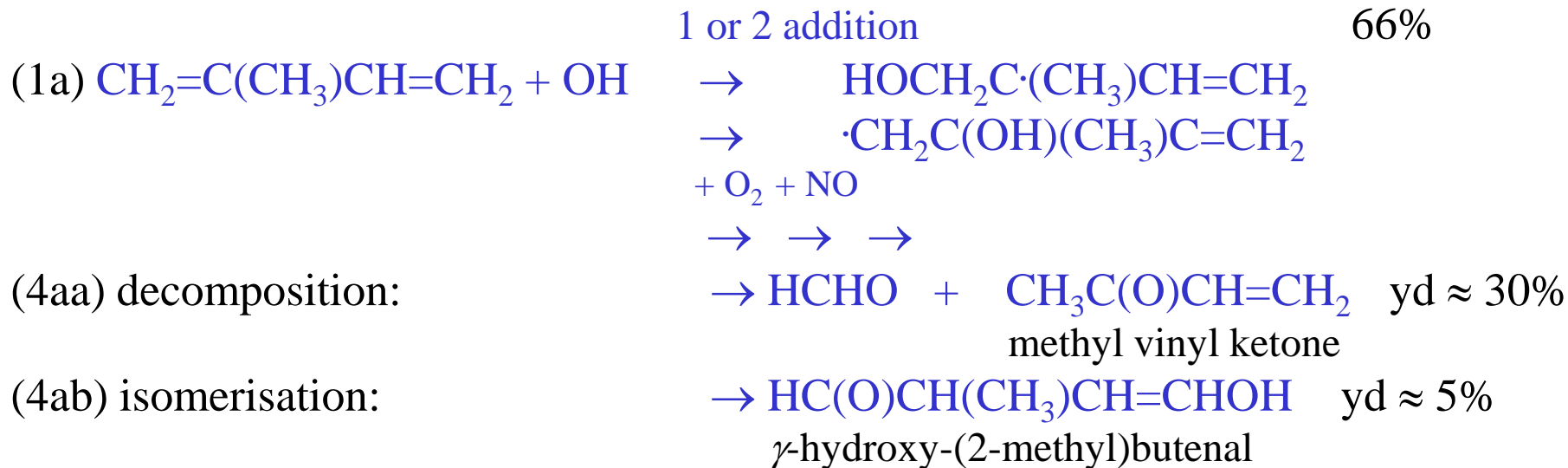
- Most alkenes react with OH addition to the double bond (positive p dependence of k_{OH}); only for the small alkenes the addition complex does not react further.
- H abstraction is more likely for large and branched alkenes.
- After the O₂ addition step ($\rightarrow ROO\cdot$), decomposition is the most probable path for $\leq C_4$ while isomerisation dominates for $> C_4$
(yields 0.04 for C₄ but 0.6 for C₈; Kwok et al., 1996)

Example n-butene:



← dihydroxycarbonyl

HC_x: alkene OH reaction: Example isoprene (= 2-methylbutadiene)



Ozone formation from *hydrocarbons*, HC_x , and NO_x



Sum (1-5):



= catalyzed by NO and light

Second option for NO:



= catalyst reacts with product

HC_x: OH reactivity, products overview

HC _x	k _{OH} 10 ⁻¹² cm ³ molec ⁻¹ s ⁻¹ (298 K)	oxygenated intermediates formed	No. of NO converted initial from total carbonyls (dep. neglected)		
Alkanes:					
CH ₄	0.006	HCHO	1	1	2
CH ₃ CH ₃	0.25	CH ₃ CHO	2	4	6
CH ₃ CH ₂ CH ₃	1.1	HCHO, CH ₃ CHO, CH ₃ COCH ₃	3	5	8
CH ₃ CH ₂ CH ₂ CH ₃	2.4				
CH ₃ CH(CH ₃)CH ₃	2.2				
CH ₃ (CH ₂) ₃ CH ₃	4.0				
<p>Lifetime with respect to OH reaction:</p> <p>k_{OH}⁽²⁾ = 0.01 × 10⁻¹² cm³ molec⁻¹ s⁻¹ ≈ k_{OH}⁽¹⁾ = 1 × 10⁻⁸ s⁻¹ → τ_{OH} = 4 months</p> <p>k_{OH}⁽²⁾ = 1 × 10⁻¹² cm³ molec⁻¹ s⁻¹ ≈ k_{OH}⁽¹⁾ = 1 × 10⁻⁶ s⁻¹ → τ_{OH} = 12 days</p> <p>k_{OH}⁽²⁾ = 50 × 10⁻¹² cm³ molec⁻¹ s⁻¹ ≈ k_{OH}⁽¹⁾ = 5 × 10⁻⁵ s⁻¹ → τ_{OH} = 6 hours</p>					
Alkenes:					
CH ₂ =CH ₂	8.5	2 HCHO	2	2	4
CH ₂ =CHCH ₃	26	HCHO, CH ₃ CHO	2	5	7
CH ₂ =CHCH ₂ CH ₃	31	HCHO, CH ₃ CH ₂ CHO	2	8	10
<i>cis</i> -CH ₃ CHCHCH ₃	56	2 CH ₃ CHO	2	8	10
<i>trans</i> -CH ₃ CHCHCH ₃	64	2 CH ₃ CHO	2	8	10
CH ₂ =C(CH ₃)CH ₃	51	HCHO, CH ₃ COCH ₃	2	5	7

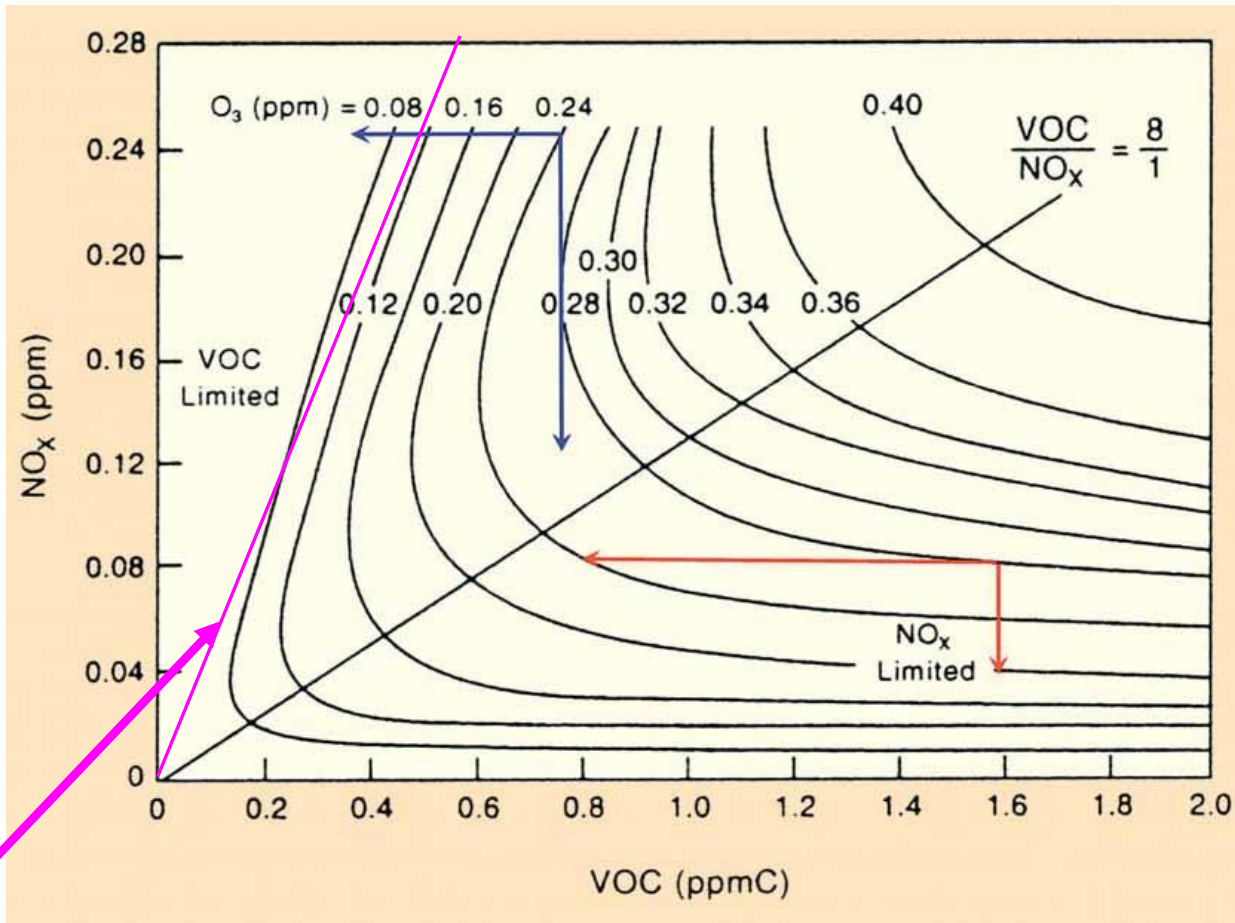
Ozone formation efficiency of various hydrocarbons

Characterisation of VOCs according to their *photochemical ozone creation potential*, POCP:

POCP : = $\Delta m_{O_3} / \Delta F_{VOC_i}$
under defined conditions (ozone formation during several days,
NO_x poor) (*Carter, 1994; EK, 1994*)

	POCP
C ₂ H ₄	100
CH ₄	0.7
C ₆ H ₆	18.9
CH ₃ OH	12.3
HCHO	42.1

Tropospheric ozone: Dependence on HC_x(VOC) and NO_x emission reductions perspectives



Emission ratio of road transport source

Example critical levels for natural and agroecosystems

Losses of harvested wheat > 5%, if accumulated dose exceeding 40 ppbv h;
 > 3000 ppbv h;
 similar: SOMO35 [ppbv d] – in 2000:

WHO air qual. Index SOMO35:= daily max of (8-h running average - 35ppbv ,bckgrd') added over 365 d

in 2030 under CLE
 (= current legislation)

in 2030 under MFR
 (= maximum feasible reduction)
 (Dentener et al., 2006)

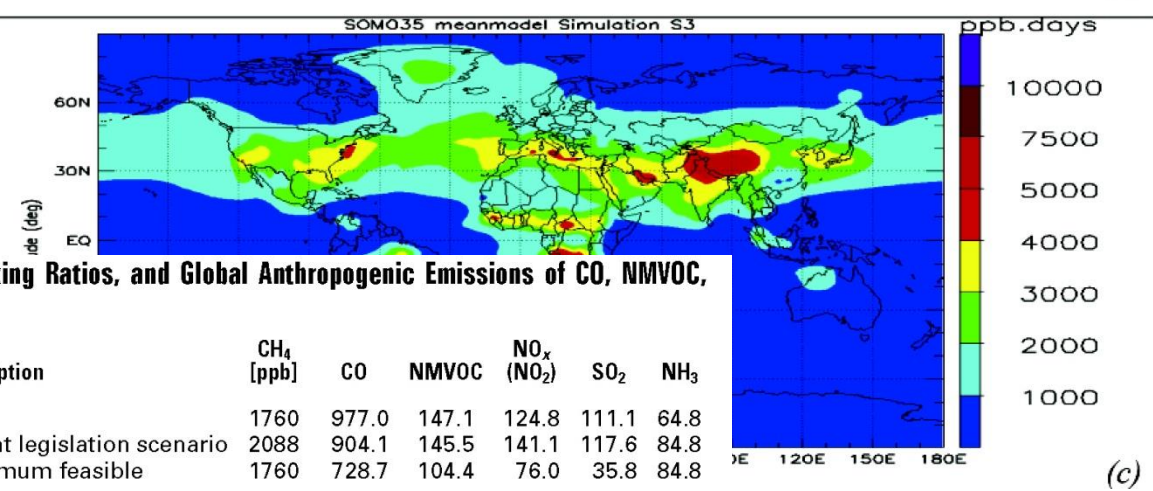
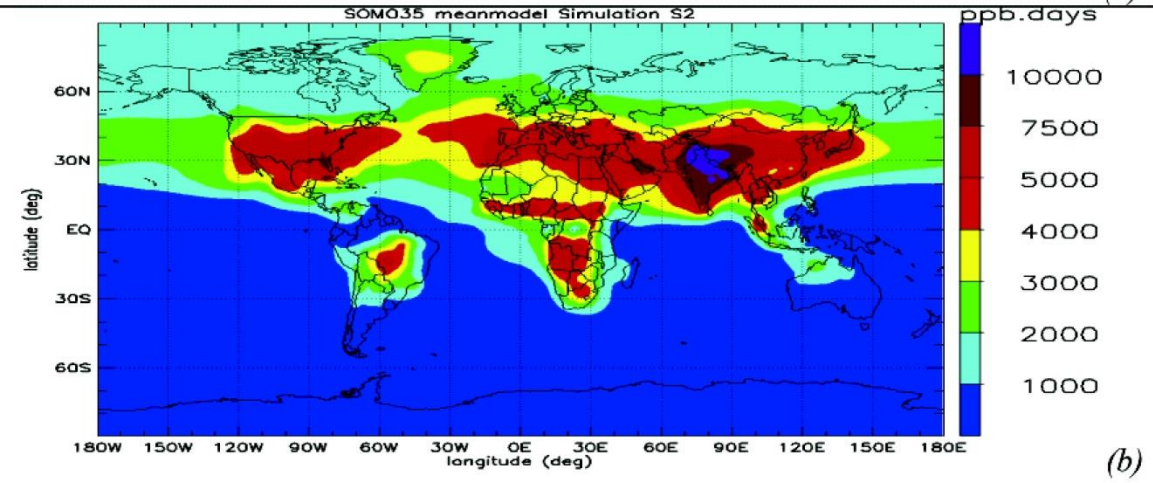
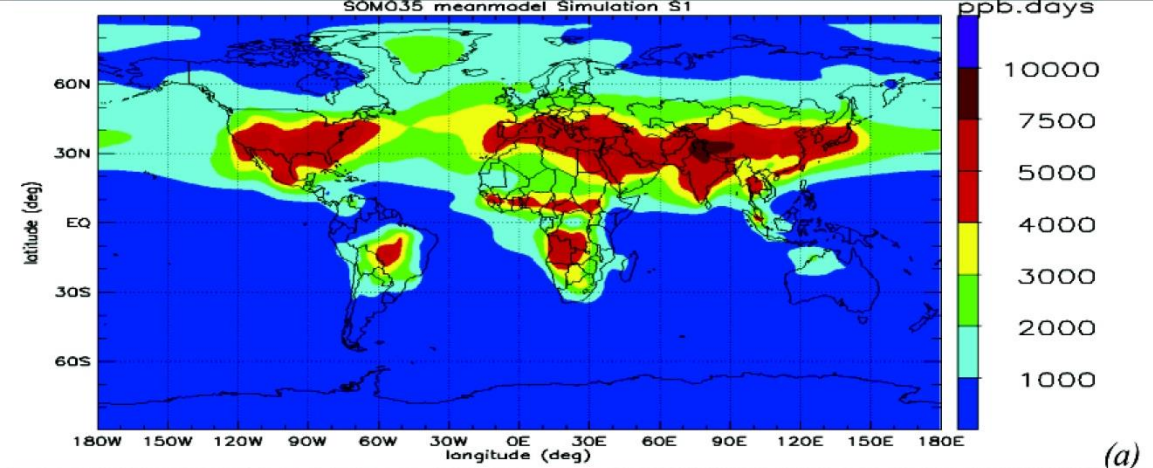


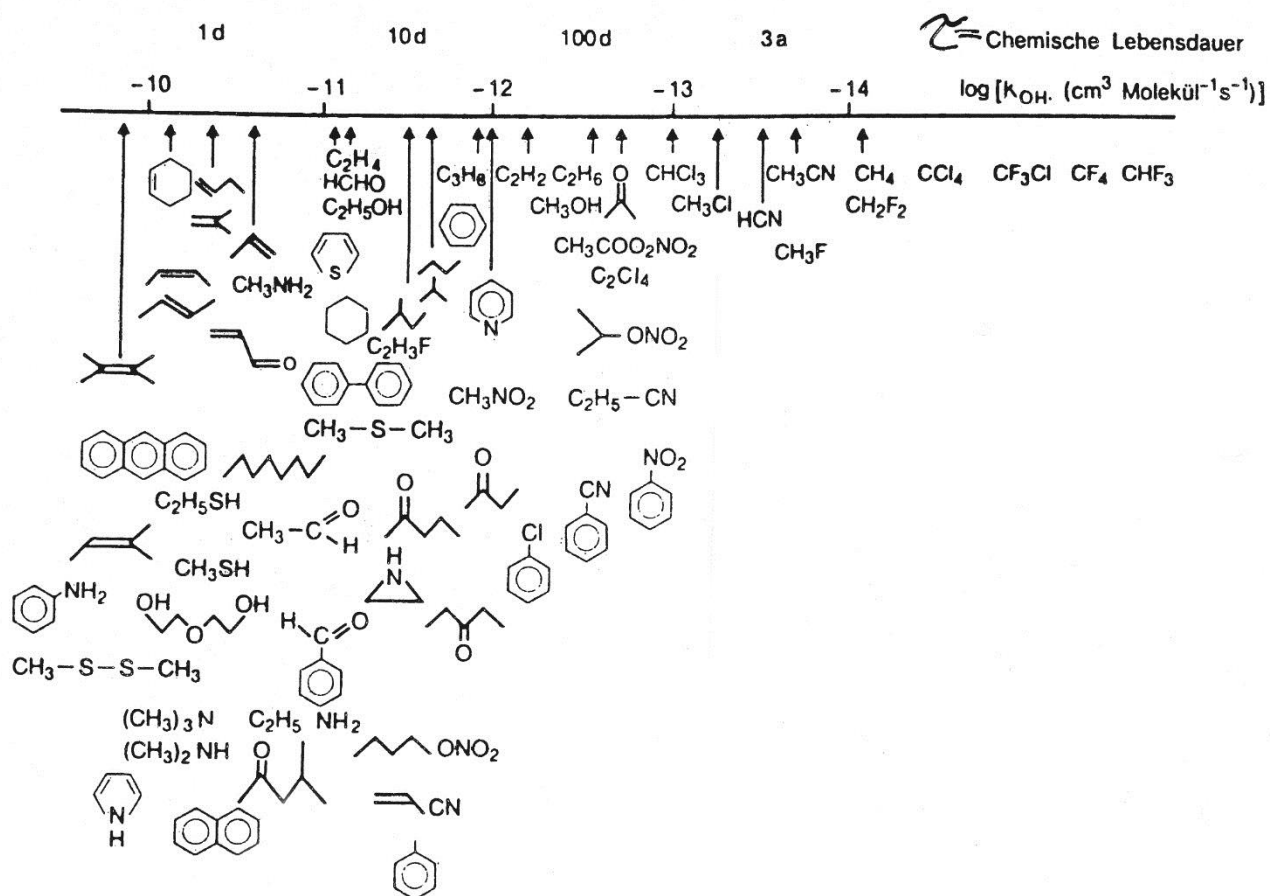
TABLE 1. Overview of Simulations, Prescribed Methane Volume Mixing Ratios, and Global Anthropogenic Emissions of CO, NMVOC, NO_x, SO₂, and NH₃^a

simulation	meteorology	description	CH ₄ [ppb]	CO	NMVOC	NO _x (NO ₂)	SO ₂	NH ₃
S1-B2000	CTM 2000 GCM SSTs 1990s	baseline	1760	977.0	147.1	124.8	111.1	64.8
S2-CLE/CLEc	CTM 2000 GCM SSTs 1990s	IIASA CLE 2030, current legislation scenario	2088	904.1	145.5	141.1	117.6	84.8
S3-MFR	CTM 2000 GCM SSTs 1990s	IIASA MFR 2030, maximum feasible	1760	728.7	104.4	76.0	35.8	84.8

HC_x, oxygenated, halogenated HC_x, and hetero atom organics OH reactivity overview

$$-\frac{dc_x}{dt} = k_{OH} c_{OH} c_x = \frac{c_x}{\tau}$$

Chemical residence time of organic substances in the atmosphere



Ozone formation in CO oxidation

Ozone formation in the troposphere

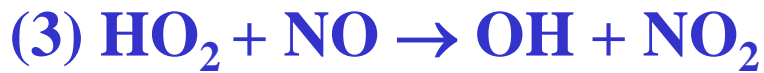
(1) Why is CO not accumulating in urban air?

→ ,discovery' of the OH radical

CO volume mixing ratio in the lower troposphere: 100-200 ppbv



Chemical fate of OH globally: $\approx 2/3$ reacts with CO



$k = 220 \times 10^{-12} \text{ cm}^3/\text{molec}/\text{s}$



$j \approx 5 \times 10^{-3}/\text{s}$



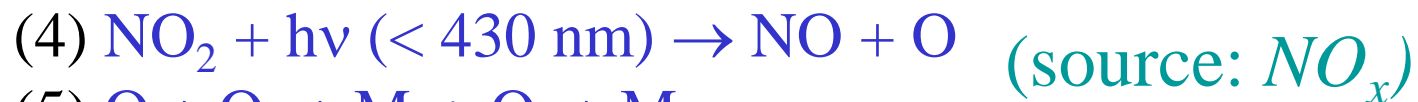
$k^{(1)} \approx 10^5/\text{s}$



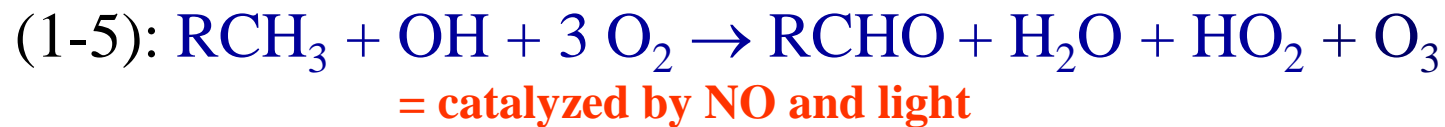
$k^{(1)} \approx 10^{-2}/\text{s}$



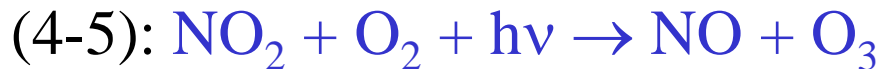
Ozone formation from *hydrocarbons*, HC_x , and NO_x



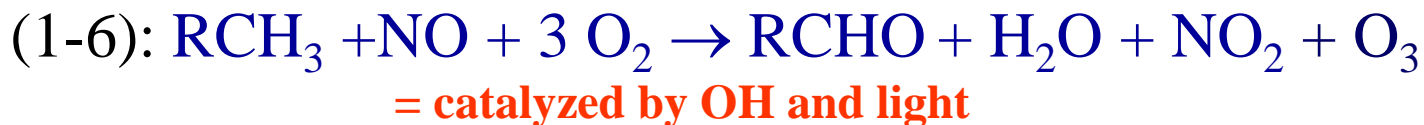
Sum



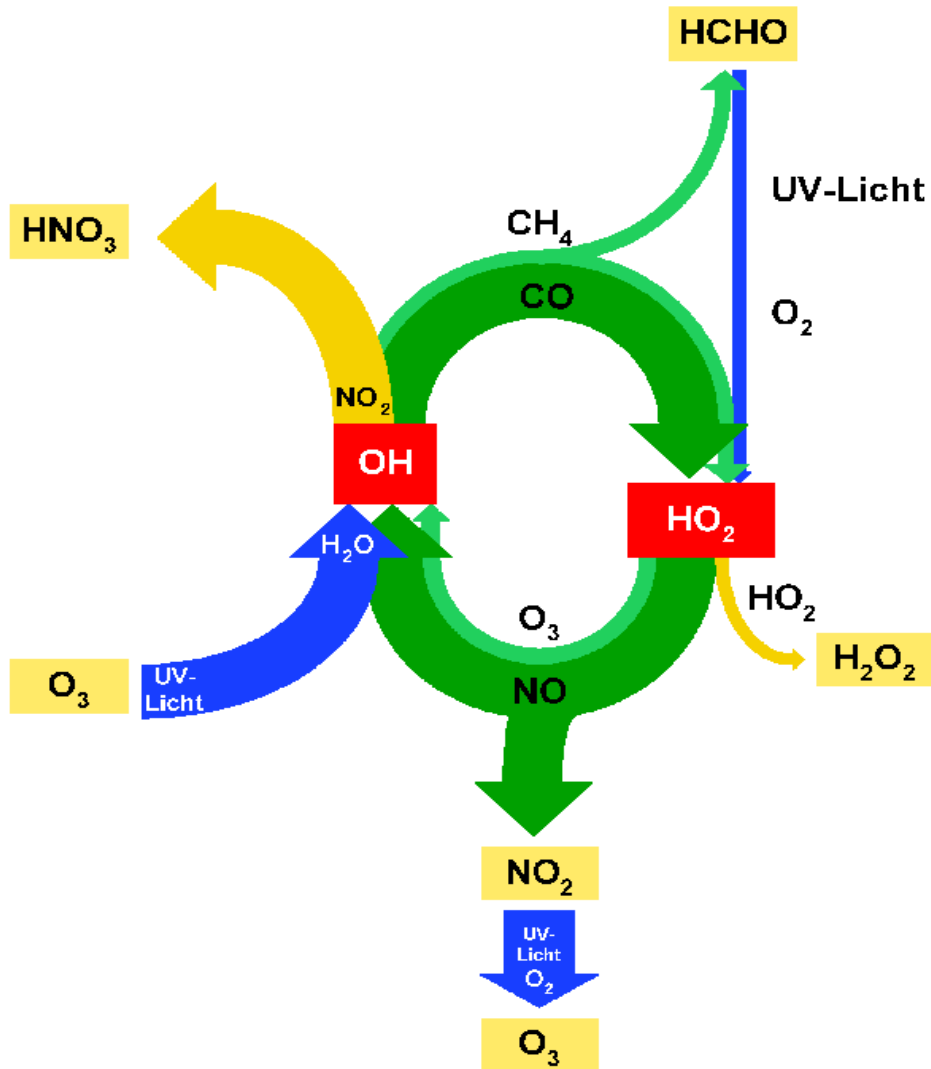
Sum



Sum



Tropospheric ozone formation from CO, CH₄: other products HCHO, H₂O₂, HNO₃ (radical sink reactions)

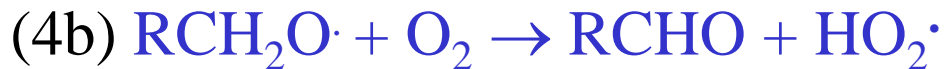


(courtesy: Ehhalt, 1999)

Sinks of tropospheric ozone

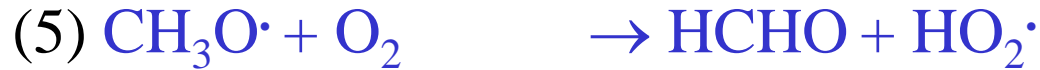
Hydrocarbon and CO chemistry in the absence of NO_x

Degradation of RH in NO-poor areas



→ Ozone loss. The threshold NO level for formation vs. loss is 5-10 pptv near the ground and ≈ 20 pptv near the tropopause

Degradation of methane in NO-poor areas



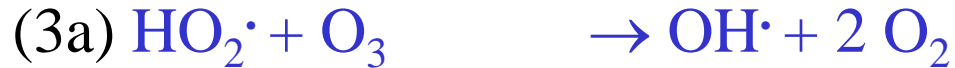
→ neutral with regard to ozone

Much of the CH₃OOH is washed out ($\tau \approx$ week)

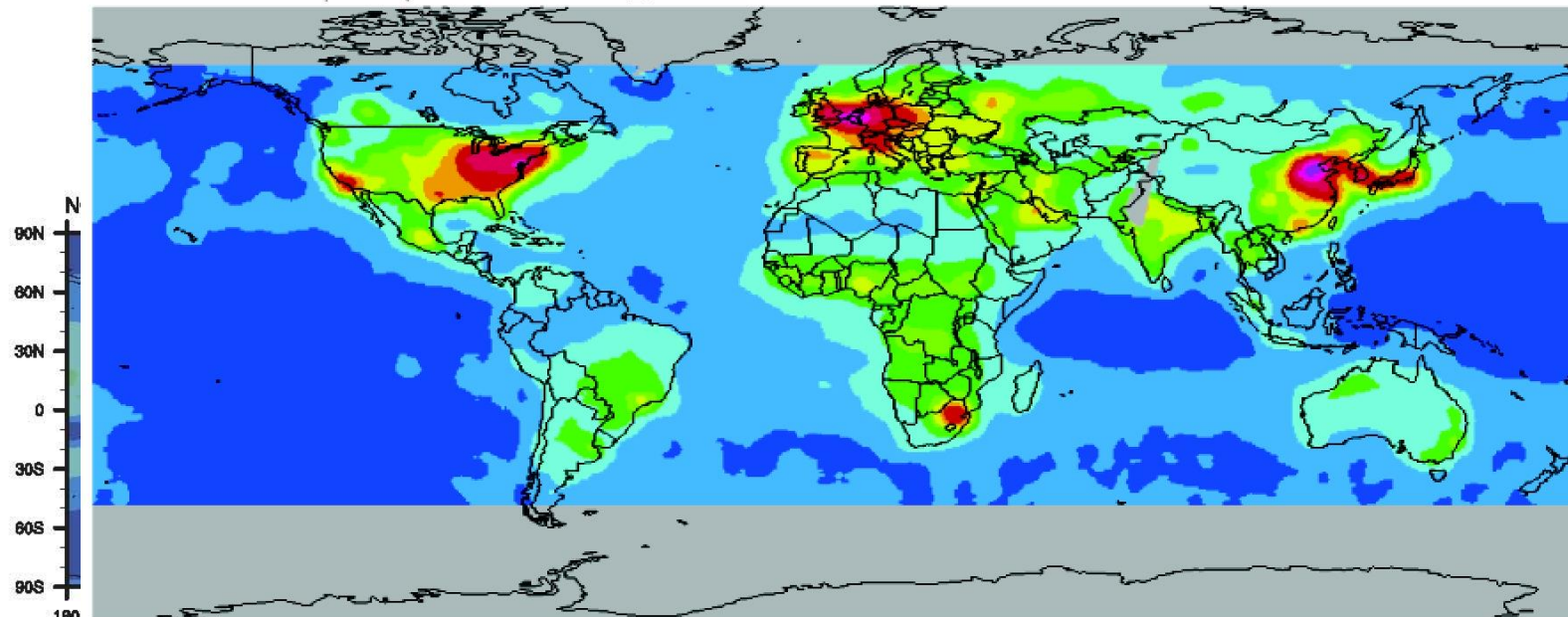
→ no oxidation to HCHO and CO, radical sink:



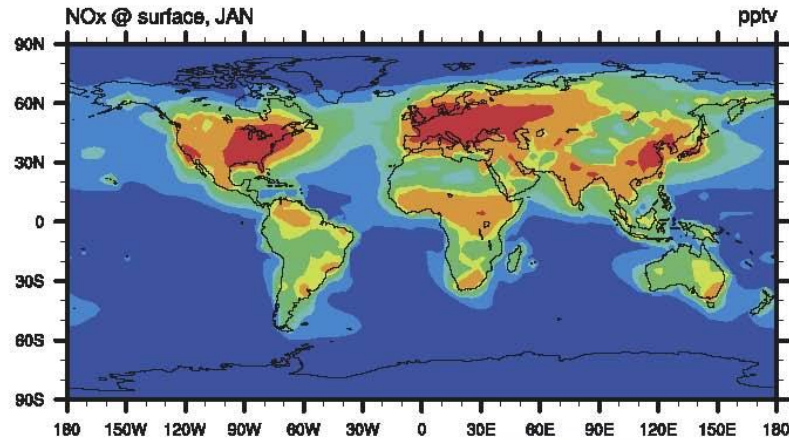
Degradation of CO in NO-poor areas



GOME tropospheric NO₂ – 2000 mean Retrieval mean

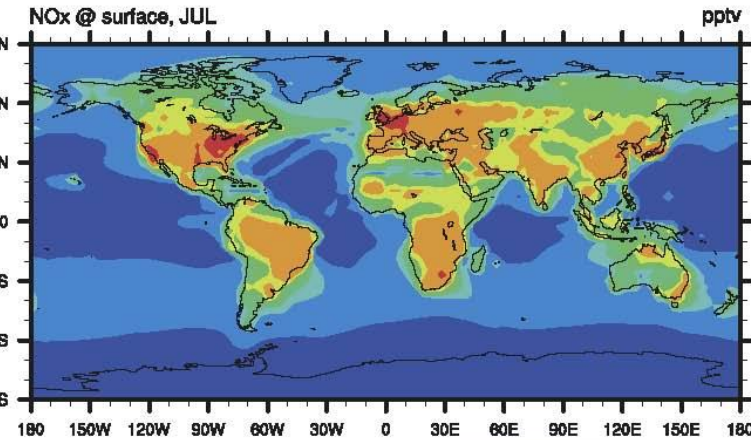


NO₂ column density [10^{15} molec/cm²]



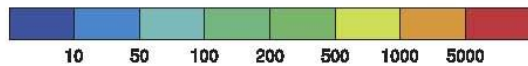
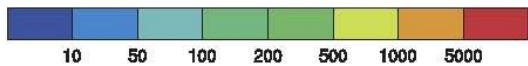
NO_x @ surface, JAN

pptv



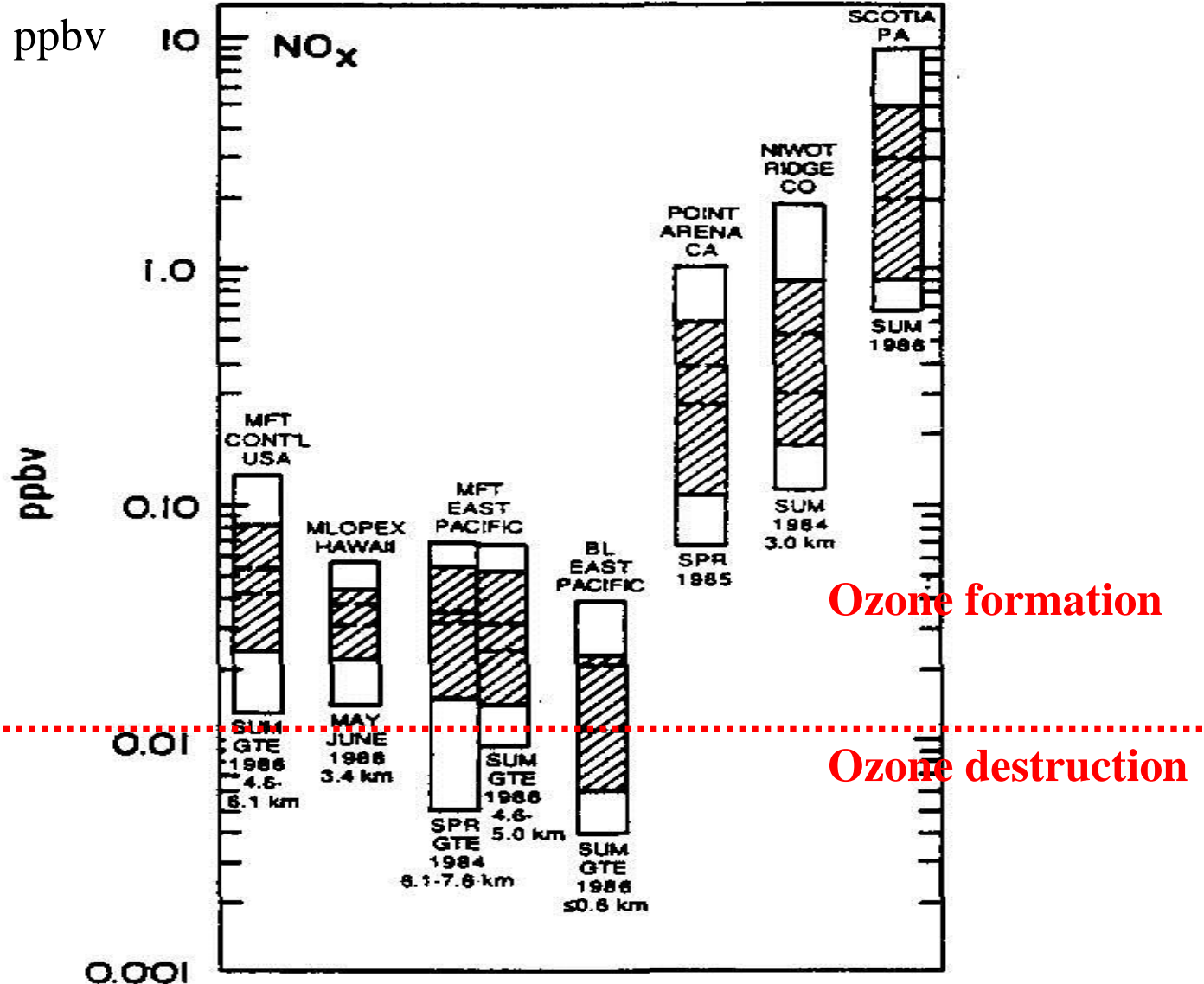
NO_x @ surface, JUL

pptv



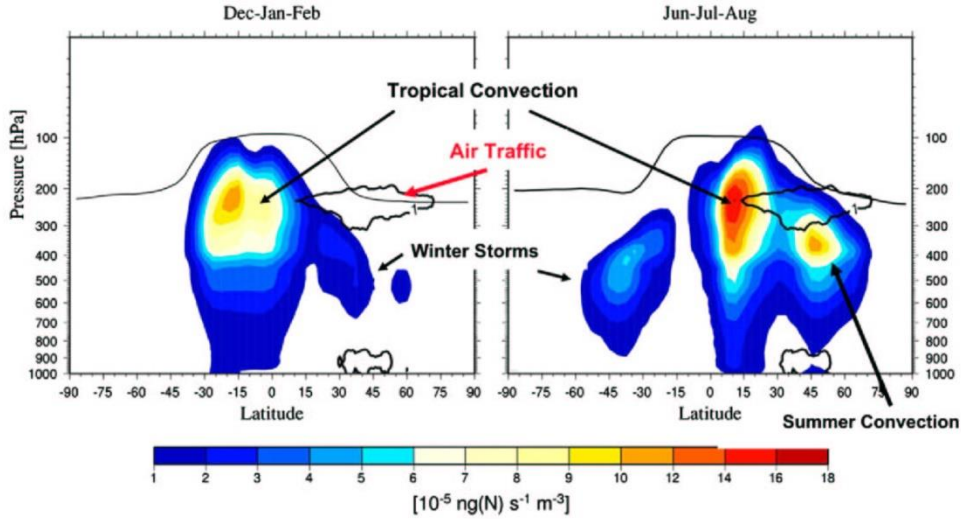
(Model results MOZART2; Horowitz et al., 2003)

NO_x distribution: NO_x-poor ?

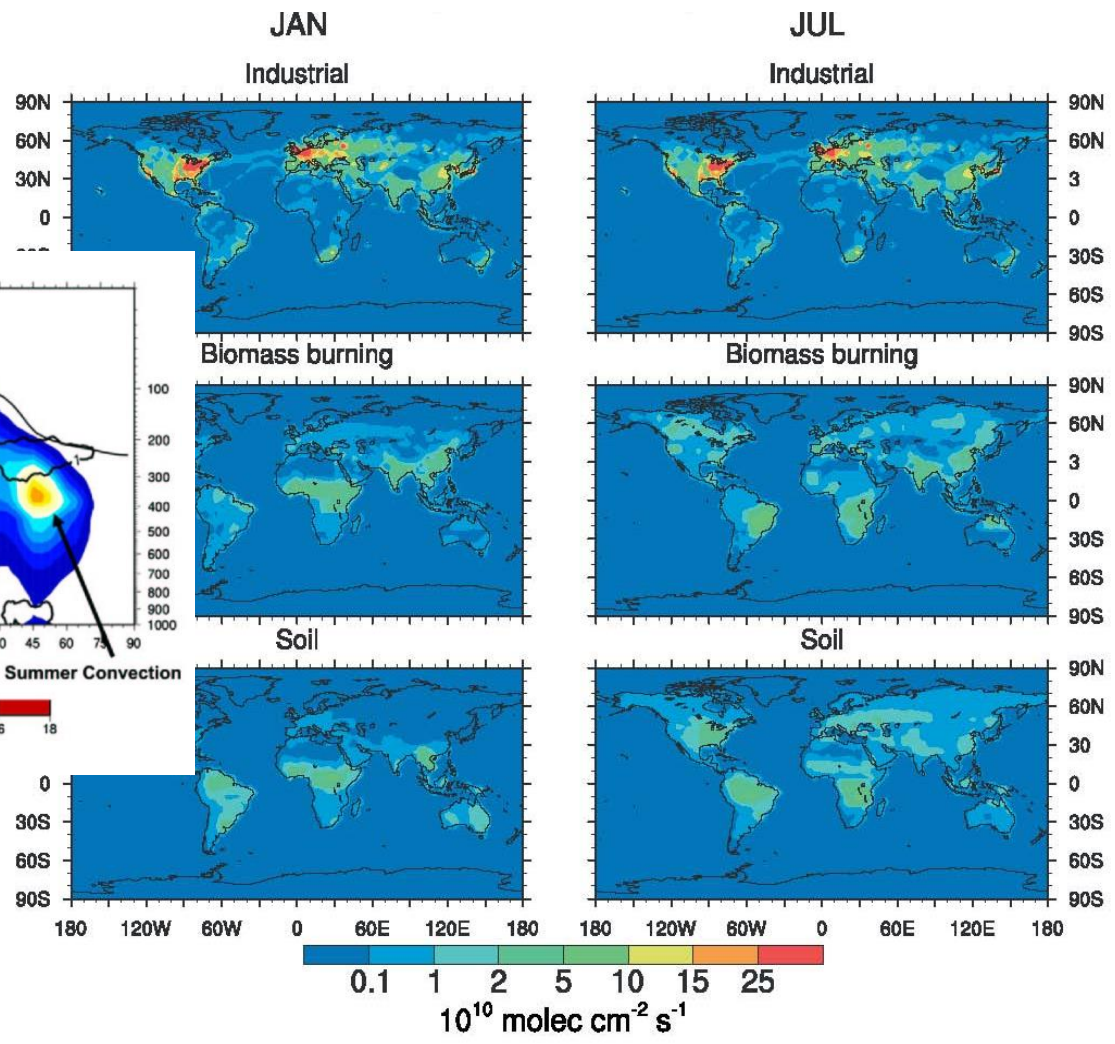


→ Most regions of the planetary boundary layer are above the NO_x threshold.

Global sources for N oxides, NO_x



simulation (Grewe, 2008)

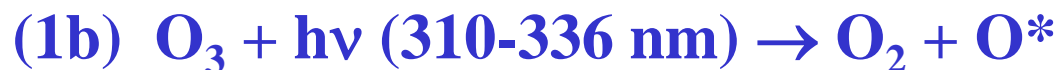


1990 (Tg N/a)	Natural	Anth
Lightning	3.0 (2-6)	
Soils and vegetation	3.2 (1.9-4.5)	
Agriculture (*)		2.3 (1.4-3.2)
Biomass burning	0.3	3.3 (2.1-5.5)
Fossil fuel burning		21 (20-23)
Sum	6.5 (4.2-11)	26.6 (23-32)

(*) Animal and plant production, without biomass burning

Radical sources

Radical source ozone



$E(mT)$

with element E , multiplicity $m = 2s + 1$ (singulett, dublett, triplett, ...), term symbol T (total orbital angular momentum number $L=0 \rightarrow S, L=1 \rightarrow P, L=2 \rightarrow D$)

s = spin angular momentum quantum number

Example $E = \text{O}$: Ground state O : $\text{O}(^3P)$

Excited state O^* : $\text{O}(^1D)$

(there is also another excited state O^* :

$\text{O}(^1S)$ formed from O_2 with $\lambda < 133 \text{ nm}$)



net effect: none



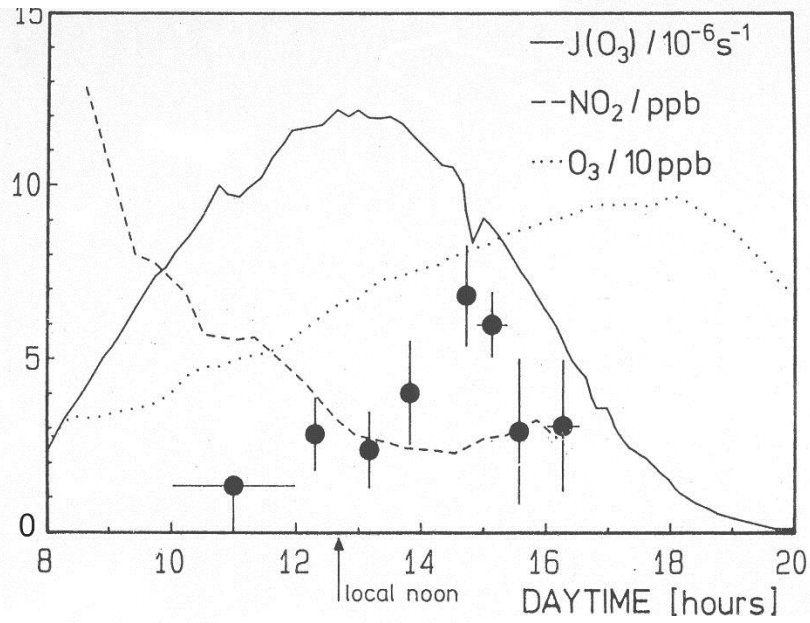
net effect: **radical formation**

Radical distributions - temporal

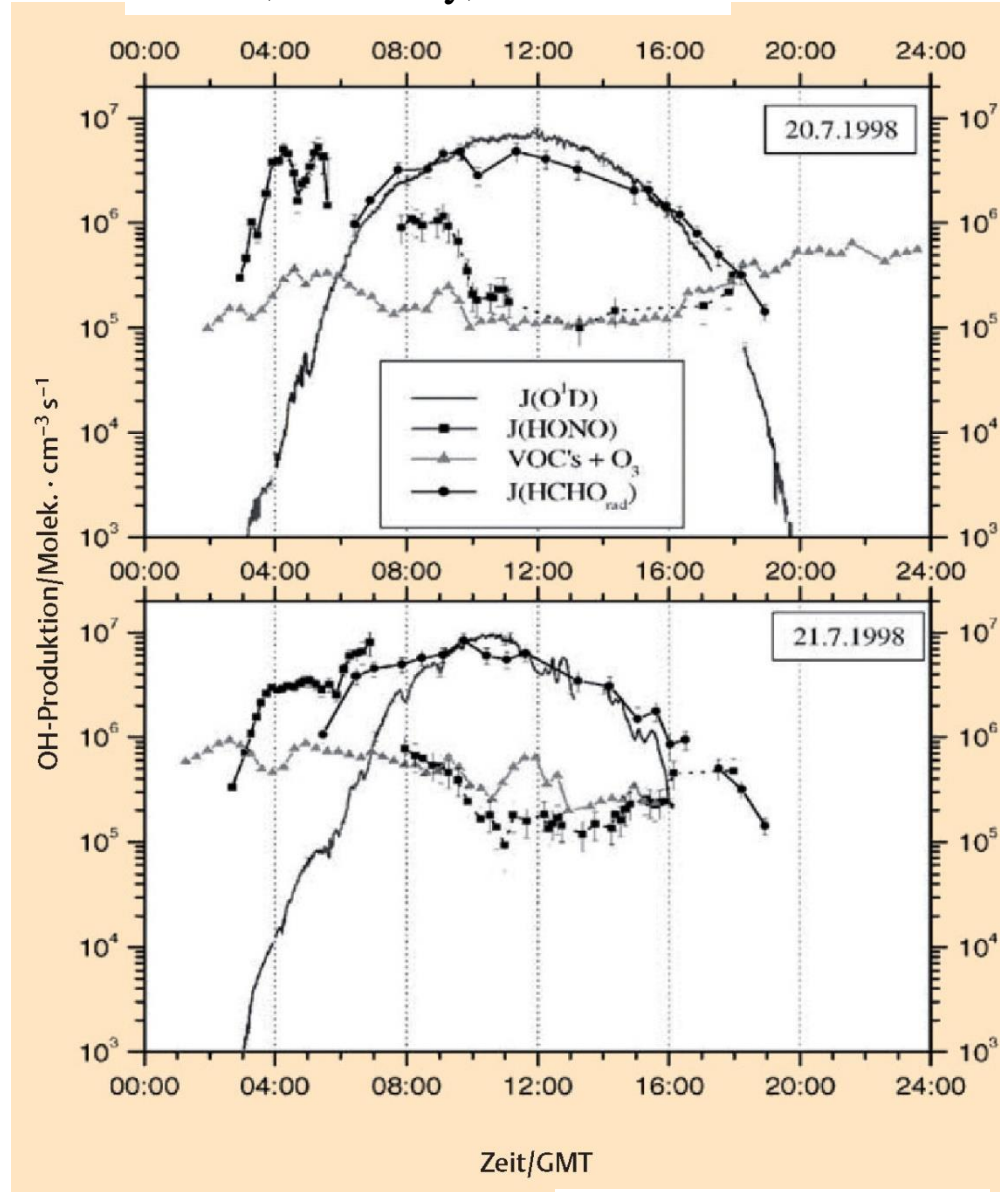
Berlin, Germany, 20.-21.7.98

Jülich, Germany, 14.7.1987

$$\text{OH} / 10^6 \frac{\text{molec}}{\text{cm}^3}$$

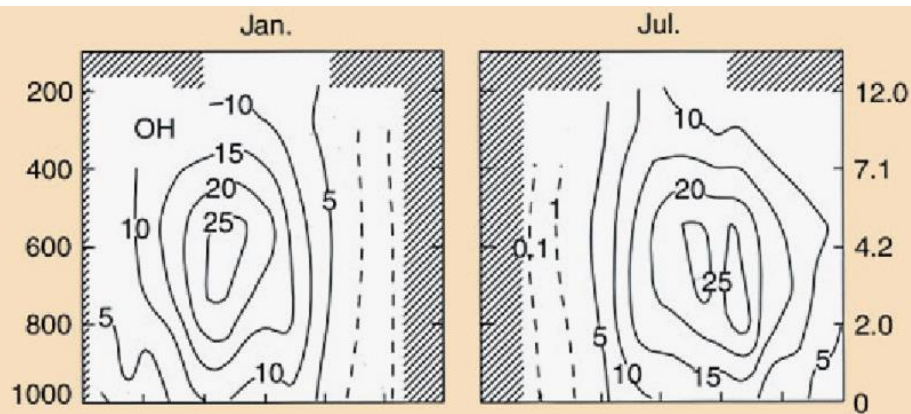


(Dorn et al., 1988)



(Barnes et al., 2007)

Radical distributions – spatial: OH



Zonally and monthly averaged data
(10^5 cm^{-3} ; *Spivakovsky et al., 2000*)

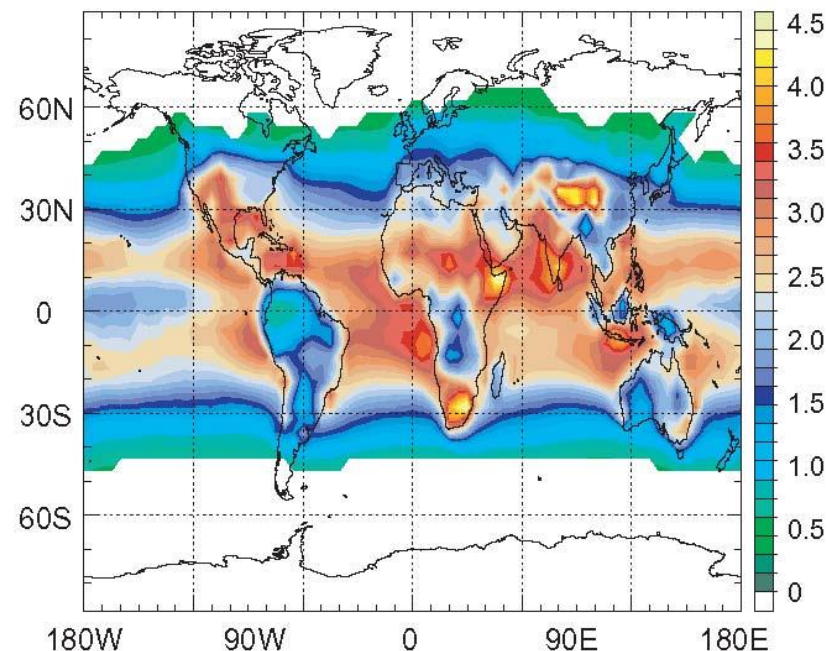


Fig. 1. Annual mean OH concentrations near the earth's surface, calculated with a chemistry-transport model (Lelieveld et al., 2002). The units are $10^6 \text{ radicals/cm}^3$. These results refer to OH in the boundary layer at low and middle latitudes where mean OH concentrations exceed $10^5 \text{ radicals/cm}^3$.

(*Lelieveld et al., 2002; Krol et al., 2003*)

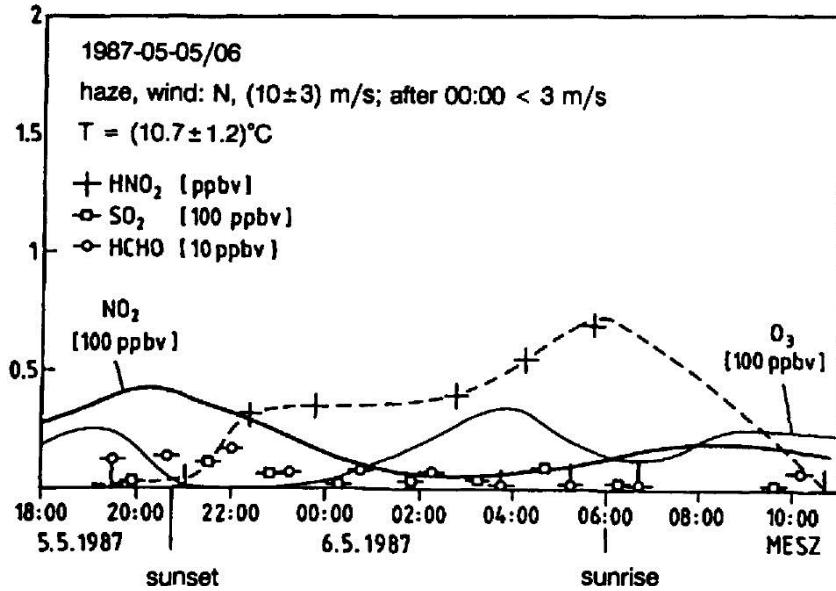
Common acronyms for hydrogen compounds:



another powerful OH source reaction: Photolysis of nitrous acid

Observations field: night-time accumulation

(Perner & Platt, 1979)



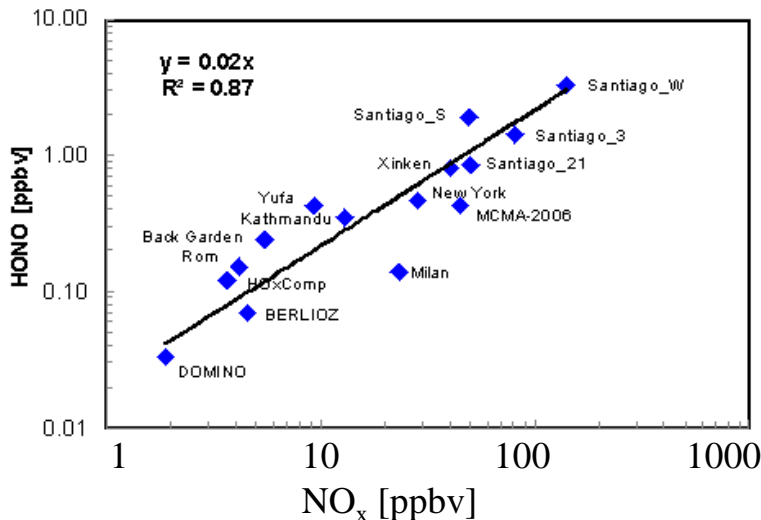
Correlated with NO₂

$c_{\text{HNO}_2 \text{ max}}$ ($\mu\text{g} / \text{m}^3$)	$c_{\text{HNO}_2 \text{ max}} / c_{\text{NO}_2}$ (% mol / mol)
5.2 (1.5 - 21)	4.34 (1.8 - 13)
1.7 (0.4 - 2.5)	3.26 (1.7 - 13)
0.092 (< 0.2 - 0.8)	> 20 (7)

(Lammel & Cape, 1996)

24 h mean

$c_{\text{HNO}_2} / c_{\text{NO}_2}$ (% mol / mol)
2.0 (1.0 - 5.0)



Urban areas
Rural areas
Remote

Urban and rural areas

(Elshorbany et al., 2012)

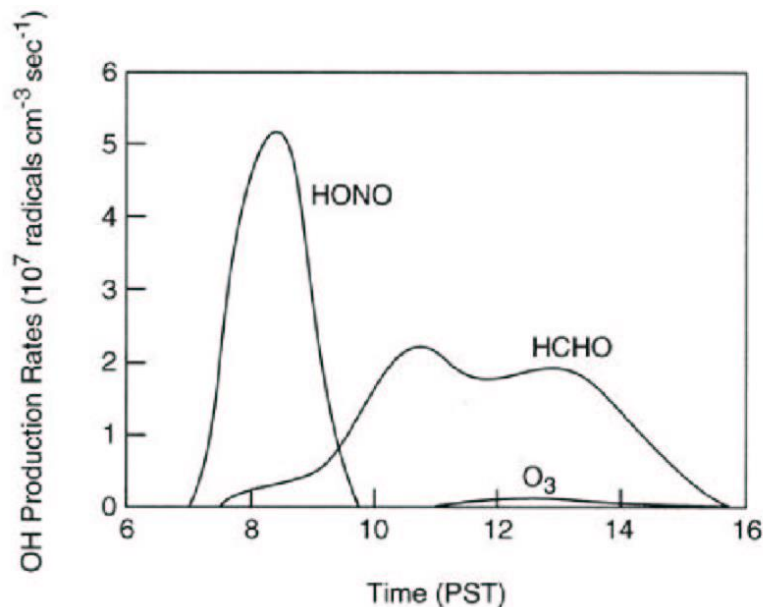
HNO₂: Significance

Efficient radical source, in particular in winter and in high latitudes (before visible sunrise in the UV)

dc_{OH}/dt [$\cdot 10^6/\text{cm}^3/\text{s}$] =

- from HNO₂ peak 34 ± 6 (09:00h)
from ozone 23 ± 4 (12:00h)
in urban California (Winer & Biermann, 1994)

- Integral (06:00-18:00 h) from HNO₂ 58 ± 9 ,
HCHO 33 ± 8 , O₃ 38 ± 6
in urban Italy (Acker et al., 2006)



Toxicology:

- Precursor of carcinogenic substances, i.e. nitrosamines, RNHNO

HO₂: Pernitric acid HOONO₂ – relevant in the upper troposphere



$$K_{10} = 1.8 \times 10^{-31} [\text{M}] (\text{T}/300)^{-3.2} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$K_{1\infty} = 4.7 \times 10^{-12} (\text{T}/300)^{-1.4} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} ; F_c = 0.6$$

$$K_{-10} = 4.1 \times 10^{-5} [\text{M}] e^{-10650/\text{T}} \text{ s}^{-1}$$

$$K_{-1\infty} = 4.8 \times 10^{15} [\text{M}] e^{-11170/\text{T}} \text{ s}^{-1} ; F_c = 0.6$$

(kinetic data taken from Atkinson et al., 2004)

Re-call: 1.3 Combinations of thermic reactions - Quasi steady state approximation

3. **between 2nd and 3rd order:** In the range of pressures and temperatures in the upper troposphere and stratosphere (c_M small) many reactions are in the region between 2nd and 3rd order reactions:

$$k = \frac{k_0 M}{1 + k_0 M / k_\infty} F_C^{(1 + \log(k_0 M / k_\infty))^2} \quad F_C \approx 0.6$$

$$k_0(T) = k_0^{300K} \left(\frac{T}{300K} \right)^{-n}, \quad k_\infty(T) = k_\infty^{300K} \left(\frac{T}{300K} \right)^{-m}$$

k_0, k_∞ = low, high pressure limiting rate constants
 F_C = broadening factor of falloff curve between atmospheric pressures

NO₂ + HO₂ + M → HO₂NO₂ + M
 $K_0 = k_0(T)c_M, n = -3.2$
 $K_\infty = k_\infty(T), m = -1.4 \rightarrow$
 $k_{288\text{ K}/1000\text{ hPa}} = 1.9 \times 10^{-12} \text{ cm}^3/\text{molec/s}$
 $k_{288\text{ K}/500\text{ hPa}} = 1.5 \times 10^{-12} \text{ cm}^3/\text{molec/s}$
 $k_{230\text{ K}/500\text{ hPa}} = 2.3 \times 10^{-12} \text{ cm}^3/\text{molec/s}$
 $k_{230\text{ K}/1000\text{ hPa}} = 3.0 \times 10^{-12} \text{ cm}^3/\text{molec/s}$

- NO + HO₂ → NO₂ + OH
- NO + CH₃O₂ → NO₂ + CH₃O
- NO + NO₃ → 2NO₂
- NO₂ + O(³P) → NO + O₂
- NO₂ + ClO → ClONO₂
- NO₂ + O₃ → NO₃ + O₂
- NO₂ + HO₂ → HO₂NO₂**
- NO₂ + OH → HNO₃
- NO₂ + NO₃ → N₂O₅
- HNO₃ + OH → H₂O + NO₂

- $R_{N10} = 3.7 \times 10^{-12} \exp(25/T)$
- $R_{N11} = 4.2 \times 10^{-12} \exp(18/T)$
- $R_{N12} = 1.5 \times 10^{-11} \exp(17/T)$
- $R_{N13} = 6.5 \times 10^{-12} \exp(12/T)$
- $R_{N14} = f(K_0, K_\infty), K_0 = 1.8 \times 10^{-31} [M] (300/T)^{3.2}, K_\infty = 4.7 \times 10^{-12} (300/T)^{1.4}$
- $R_{N15} = 1.2 \times 10^{-13} \exp(-2450/T)$
- $R_{N16} = f(K_0, K_\infty), K_0 = 2.6 \times 10^{-30} [M] (300/T)^{3.2}, K_\infty = 2.4 \times 10^{-11} (300/T)^{1.3}$
- $R_{N17} = f(K_0, K_\infty), K_0 = 2.2 \times 10^{-30} [M] (300/T)^{3.9}, K_\infty = 1.5 \times 10^{-12} (300/T)^{0.7}$
- $R_{N18} = f(K_0, K_\infty), K_0 = 2.2 \times 10^{-30} [M] (300/T)^{3.9}, K_\infty = 1.5 \times 10^{-12} (300/T)^{0.7}$
- $R_{N19} = K_1 + K_2 / (1 + K_2 / K_3), K_1 = 7.2 \times 10^{-15} \exp(785/T), K_2 = 1.9 \times 10^{-33} [M] \exp(725/T)$

HO₂: Pernitric acid HOONO₂ – relevant in the upper troposphere



$$k_{10} = 1.8 \times 10^{-31} [\text{M}] (\text{T}/300)^{-3.2} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$k_{1\infty} = 4.7 \times 10^{-12} (\text{T}/300)^{-1.4} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} ; F_c = 0.6$$

$$k_{-10} = 4.1 \times 10^{-5} [\text{M}] e^{-10650/\text{T}} \text{ s}^{-1}$$

$$k_{-1\infty} = 4.8 \times 10^{15} [\text{M}] e^{-11170/\text{T}} \text{ s}^{-1} ; F_c = 0.6$$

(kinetic data taken from Atkinson et al., 2004)

Examples	T (K)	p (hPa)	h (km)	τ (HNO ₄)	$\mu(\text{NO}_2)$ (nmol/mol)	$\mu(\text{HO}_2)$ (pmol/mol)	$\mu(\text{HNO}_4)$ (pmol/mol)
	230	300	9	6 d	0.01	1	54
					0.05	1	270
	270	700	3	9 min	0.02	0.4	0.08
					0.2	0.4	0.8
	273	1000	0	5 min	1	3	25
					30	3	750
	293	1000	0	25 s	1	3	1.7
					30	10	165

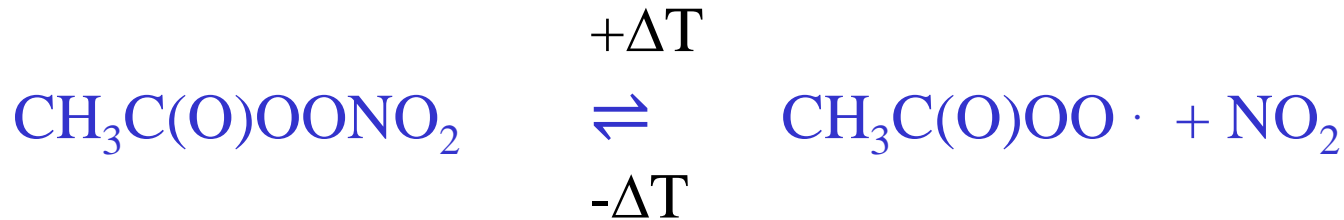
→ high solubility (acid): changes NO_x phase distribution and residence time

→ NO_x reservoir compound

Formation of peroxyacetyl nitrate



Peroxyacetyl nitrate (PAN): thermally labile



$$k = 1.95 \times 10^{16} e^{-13543/T} \text{ s}^{-1};$$

$$\tau = 2 \text{ years @ } 243\text{K}$$

$$\tau = 2 \text{ days @ } 273\text{K}$$

$$\tau = 45 \text{ min @ } 298 \text{ K}$$

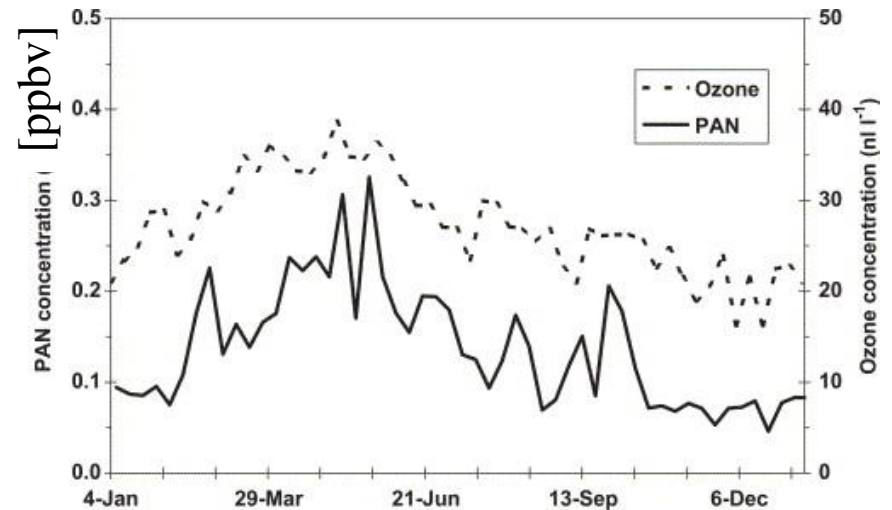
- **NO_x reservoir compound** ↔ **changes NO_x effective residence time**
- **delayed ozone formation**

PAN sink reactions:



Peroxyacetyl nitrate - occurrence

- 1) in the cold
- 2) in photochemical smog and in plumes of urban areas



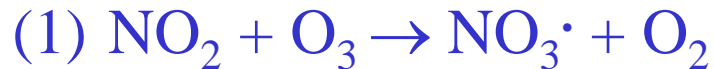
Rural Scotland (*McFadyen & Cape, 2005*)

- 3) ... even in plumes of whole regions:

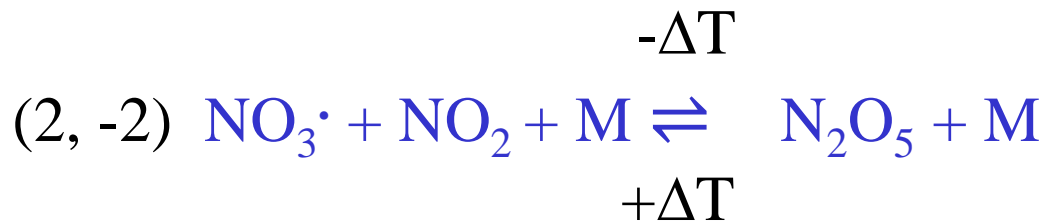
Nitrate radical

NO₂ oxidation by ozone: NO₃ formation
The adduct N₂O₅ – a thermally labile NO₃ reservoir

[pptv]



$$k_1 = 3.2 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$



[h]

$$k_{20} = 3.6 \times 10^{-30} [\text{M}] (\text{T}/300)^{-4.1} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

(Platt et al., 1980)

$$k_{2\infty} = 1.9 \times 10^{-12} (\text{T}/300)^{-0.2} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}; F_c = 0.35$$

$$k_{-20} = 1.3 \times 10^{-3} [\text{M}] (\text{T}/300)^{-3.5} e^{-11000/\text{T}} \text{ s}^{-1}$$

$$k_{-2\infty} = 6.2 \times 10^{14} (\text{T}/300)^{-0.2} e^{-11000/\text{T}} \text{ s}^{-1}; F_c = 0.35$$

(kinetic data taken from Atkinson et al., 2004)

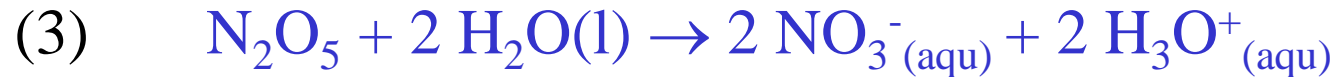
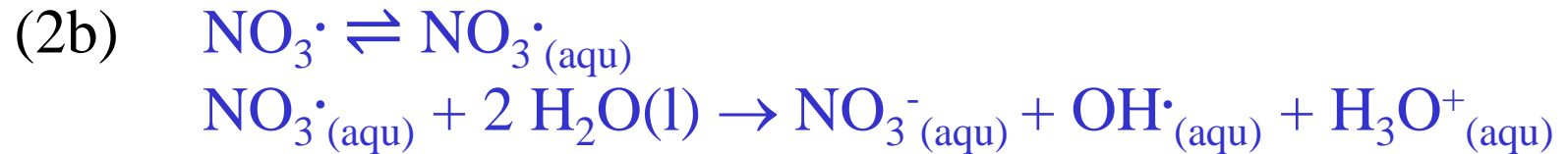
Equilibrium: $c_{\text{N}_2\text{O}_5} / (c_{\text{NO}_2} c_{\text{NO}_3}) = \mathbf{K} = k_2 / k_{-2}$

→ N₂O₅ not measurable, but can be inferred from c_{NO₂} and c_{NO₃}

Nitrate radical - sinks

Day-time: Rapid photolysis of NO_3

in clouds, on wet particles:



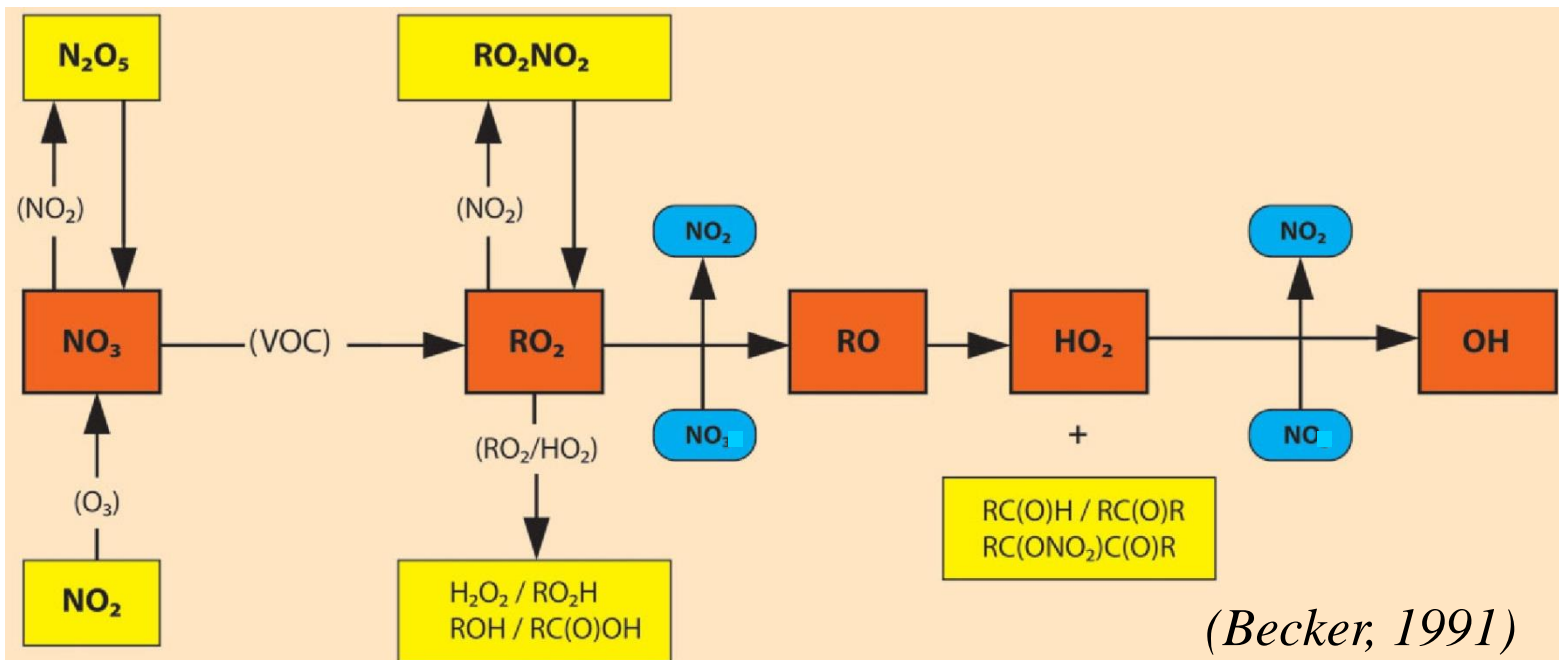
Examples	r.h. (%)	μ_{NO_2} (nmol/mol)	μ_{NO_3} (nmol/mol)	$\tau_{\text{NO}_3}^{\text{het}}$ (s)	$\tau_{\text{N}_2\text{O}_5}^{\text{het}}$ (s)	Yield OH (%)	Production $\text{dc}_{\text{OH}(\text{aqu})}/\text{dt}$ (molec cm ⁻³ s ⁻¹)
Marit. aerosol	60	1	0.042	1960	1890	8.0	9.1×10^4
	90	1	0.020	840	320	1.9	4.3×10^4
Continental aer.	60	10	0.90	5800	4200	3.3	32×10^4
	90	10	0.70	4500	3800	1.4	12×10^4
Coastal fog	> 96	1	1.8×10^{-5}	24	6.3	0.8	1.9×10^4
Radiation fog	> 96	10	1.1×10^{-5}	14	3.7	0.13	2.0×10^4

NO₃ chemistry: alkanes, example butane

Degradation of hydrocarbons during the night

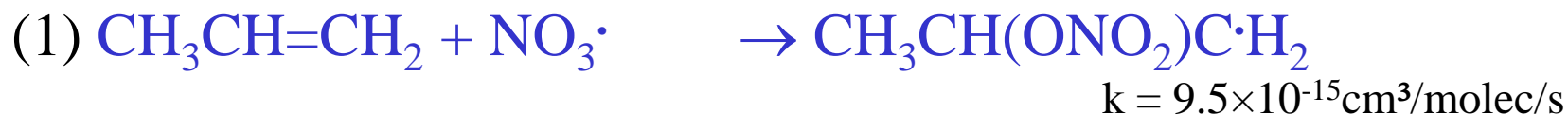


further similar to chemistry upon OH attack:

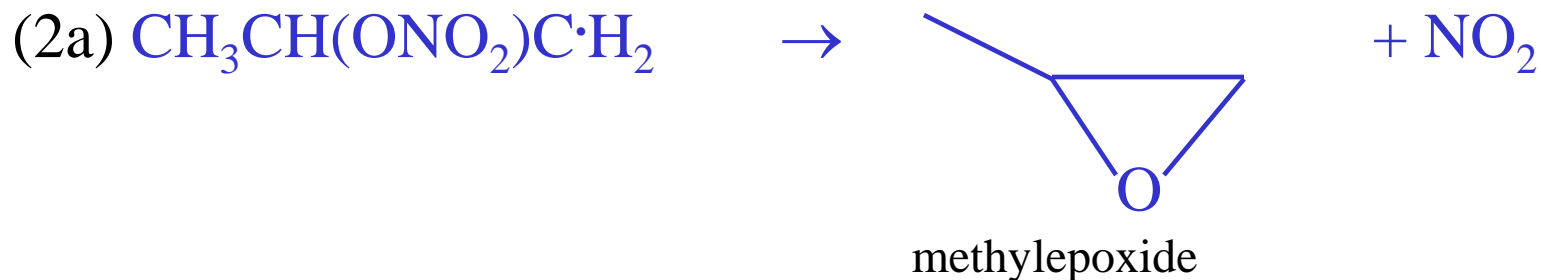


NO₃ chemistry: alkenes, example propene

Preferential is the addition to the higher substituted radical (like OH reaction):



diferent from chemistry upon OH attack, as adducts differ:



NO₃ reactivity towards hydrocarbons: overview

HC_x

k_{NO3}

10⁻¹⁵cm³ molec⁻¹s⁻¹

Alkanes:

CH ₄	< 0.001
CH ₃ CH ₃	0.0014
CH ₃ CH ₂ CH ₃	0.017
CH ₃ CH ₂ CH ₂ CH ₃	0.046
CH ₃ CH(CH ₃) ₂	0.11
CH ₃ (CH ₂) ₃ CH ₃	0.087

Alkenes:

CH ₂ =CH ₂	0.21
CH ₂ =CHCH ₃	9.5
CH ₂ =CHCH ₂ CH ₃	14
cis-CH ₃ CH=CHCH ₃	350
trans-CH ₃ CH=CHCH ₃	390
CH ₂ =C(CH ₃) ₂	330
α-pinene	590
β-pinene	210