Atmospheric Chemistry
Oxidizing capacity of the troposphere

Pontus Roldin
Div. Nuclear Physics
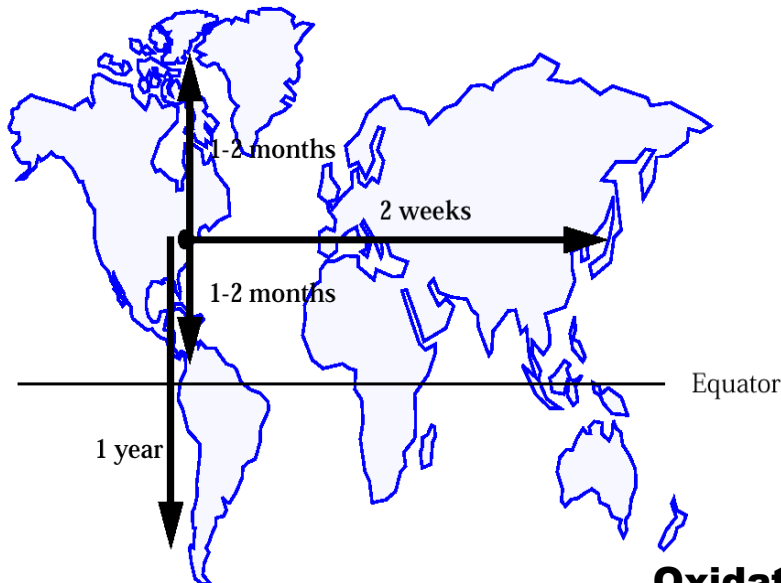## Dep. Physics
Lund University

Tropospheric chemistry Background

The troposphere is a chemical reservoir that is fairly well separated from the stratosphere.
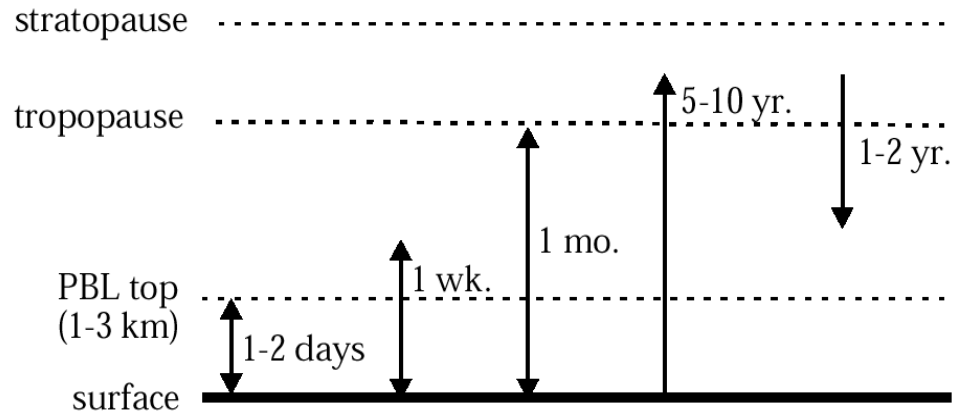
The mixing time in the troposphere is 1-2 months within each hemisphere.

Chemical substances with a lifetime shorter than ~1 year are transformed within the troposphere.

Horizontal mixing

Vertical mixing

1-2 months

2 weeks

1-2 months

Equator

1 year

stratopause

tropopause

5-10 yr.

1-2 yr.

1 mo.

PBL top
(1-3 km)

1 wk.

1-2 days

surface

Oxidation - troposphere

Tropospheric chemistry Background

The present day atmosphere is strongly affected by human activities.
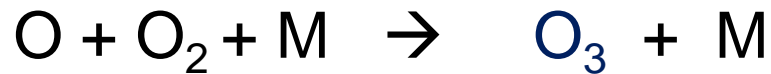
- Burning of fossil fuel and biomass emitts large amount of toxic carbon monoxide (CO) and hydrocarbons.

- Due to high temperatures in the combustion process, NO is also produced and emitted to the atmosphere:

$$O_2 \overset{\text{heat}}{\Longleftrightarrow} O + O$$

$$O + N_2 \Leftrightarrow NO + N$$

$$N + O_2 \Leftrightarrow NO + O$$
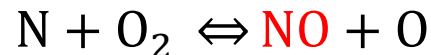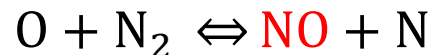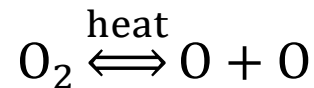
- Livestock, rice paddies and natural gas prod. emitt the GHG methane (CH_4).

- **What are the consequences of these emissions?**

Tropospheric chemistry

Scavenging of toxic CO by the detergent of the atmosphere, the hydroxyl radical OH.

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M \quad \text{(very fast)}$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

Oxidation - troposphere

Tropospheric chemistry

Scavenging of toxic CO by the detergent of the atmosphere, the hydroxyl radical OH.

$$CO + \cancel{OH} \rightarrow CO_2 + \cancel{H}$$

$$\cancel{H} + O_2 + \cancel{M} \rightarrow \cancel{HO_2} + \cancel{M} \qquad \text{(very fast)}$$

$$\cancel{HO_2} + \cancel{NO} \rightarrow \cancel{OH} + \cancel{NO_2}$$

$$\cancel{NO_2} + h\nu \rightarrow \cancel{NO} + \cancel{O}$$

$$\cancel{O} + O_2 + \cancel{M} \rightarrow O_3 + \cancel{M}$$

(Net): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$
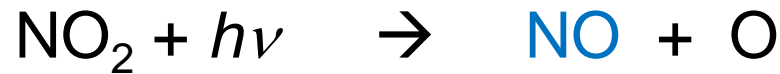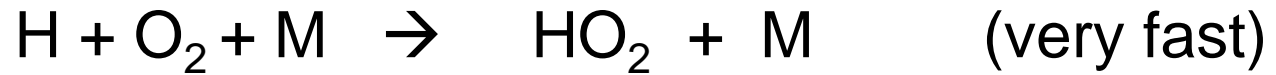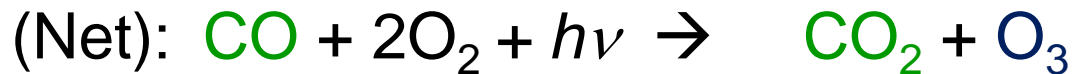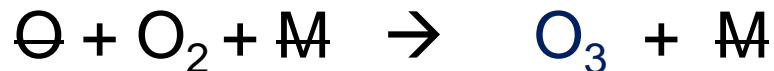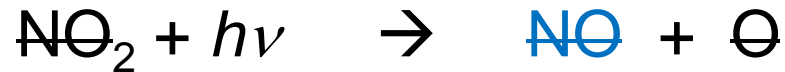
Tropospheric gas phase chemistry involves oxidation of CO and <u>organic hydrocarbons</u> ($C_xH_yO_z$) in the presence of <u>nitrogen oxides</u> ($NO_x \equiv NO + NO_2$) and <u>solar radiation ($h\nu$)</u>.

Oxidation - troposphere

Oxidants in the troposphere

The atmosphere is an **oxidizing** medium.

Examples   (oxidation numbers)

Hydrocarbons: $CH_4 \rightarrow CO_2$ i.e. $C(-IV) \rightarrow C(+IV)$

Sulphur species: $H_2S \rightarrow H_2SO_4$ i.e. $S(-II) \rightarrow S(+VI)$

Nitrogen species: $NO \rightarrow HNO_3$ i.e. $N(+II) \rightarrow N(+V)$

- The most abundant oxidants (O_2 and O_3) are relatively unreactive and therefore contribute very little to the oxidation of trace gases.
- Oxidation of non-radicals generally involves **radical** species, not O_2 and O_3.
- Exception: alkenes ($R\text{-}CH_2\text{=}CH_2\text{-}R$) can be oxidized by O_3 at carbon-carbon double bond

Oxidation - troposphere

Tropospheric chemistry

Tropospheric gas phase chemistry involves oxidation of organic compounds in the presence of nitrogen oxides and solar irradiation.

$h\nu$ ◄⋀⋀⋀
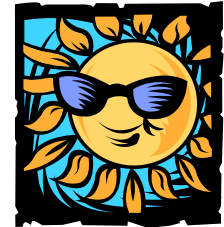
Similar to a hot flame, the oxidation proceeds with the aid of free radicals (radical concentrations in the troposphere are much lower than in the flame.)

Solar radiation is the external energy source driving the "combustion".

The organic compounds, for instance methane, is the "fuel".

Oxidation - troposphere

Tropospheric oxidation of trace gases

There must be strong sinks for nearly all gases emitted from Earth to the troposphere, since the concentrations of these gases do not increase in proportion to their source strengths.

Trace gases are oxidized, often in multiple steps.

Gases containing sulphur and nitrogen are oxidized to water-soluble compounds that are eventually wet deposited (acid rain).

Tropospheric oxidation is a vital sink for trace gases and greenhouse gases (e.g. CH_4 and CO that are both oxidized to CO_2).

Without the presence of strong oxidants in the troposphere the levels of a number of toxic trace gases would have risen to lethal concentrations (e.g. CO, SO_2).

Tropospheric ozone

Ozone is needed to initiate the radical production and thus also to maintain an oxidizing atmosphere.

Until the middle of the 1940-ies, it was believed that all tropospheric ozone originates from the stratosphere, where it was known to be produced via photolysis of O_2 ($\lambda < 240$ nm).

Since this UVc radiation is unable to penetrate down to Earth´s surface, it was thought that no ozone could be produced in the troposphere. Earth´s surface is an efficient ozone sink.

The Los Angeles smog made it apparent that there must be other strong sources of ozone also in the lower troposphere.

The Los Angeles Smog

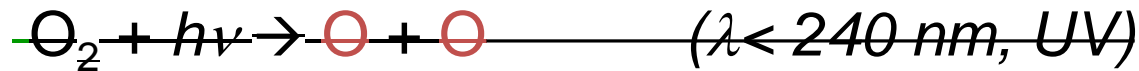Oxidation - troposphere

Ozone production in the troposphere

The only way to produce ozone is via

$$O + O_2 + M \rightarrow O_3 + M$$

with molecular oxygen O_2 and atomic oxygen O in its ground state $O(^3P)$,

This means that O has to be produced first.

Photolysis of O_2 does <u>not</u> occur in the troposphere (no UVc).

~~$O_2 + h\nu \rightarrow O + O$ ($\lambda < 240$ nm, UV)~~

There must be other sources of O in the troposphere.

Main source of O in the troposphere is via photolysis of NO_2

$$NO_2 + h\nu \rightarrow NO + O \quad (\lambda < 420 \text{ nm})$$

This reaction is very important for the tropopheric chemistry!

Oxidation - troposphere

Oxidants in the troposphere

NO_2 and solar radiation controls the production of O_3 , which in turn controls the production of HO_X radicals ≡ OH + HO_2 , which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.

NO_2 →$hν$→ O_3

$hν$

(There are also other ways of producing radicals in polluted air)

$hν$

HO_X radicals
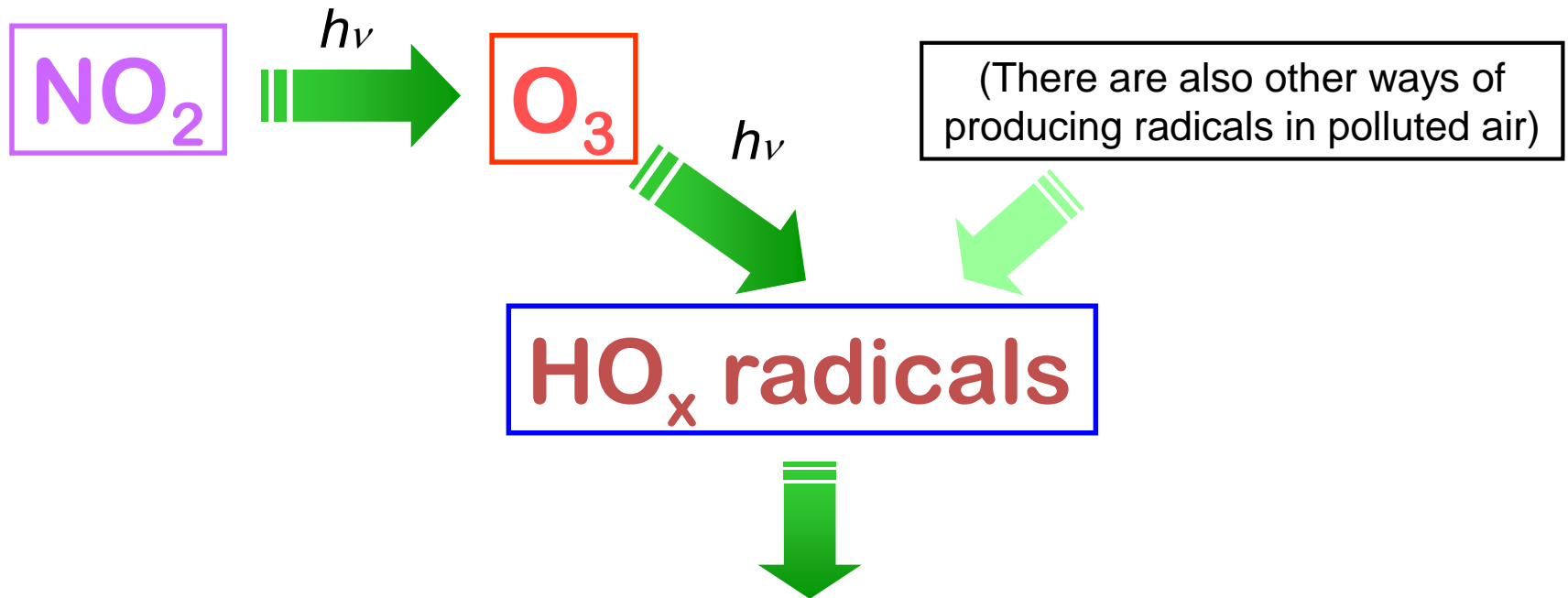
Oxidizing capacity of the troposphere

Oxidation - troposphere

Hydroxyl radical OH

- The hydroxyl radical is formed by photolysis of ozone and is the most important radical in the troposphere.

- It does not react with any of the major components of the atmosphere (N_2, O_2, CO_2, H_2O).

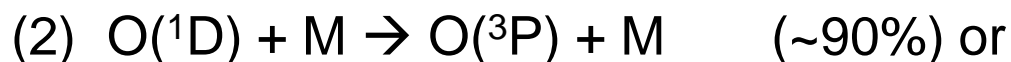- It reacts with most atmospheric trace gases. The "detergent" of the atmosphere.

Short lifetime (~1 s).

Exists in very low concentrations (10^5-10^7 molecules/cm^3).

Regenerated in catalytic cycles, since it would otherwise rapidly have been consumed.

Oxidation - troposphere
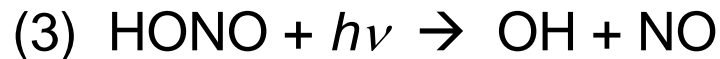
Hydroxyl radical OH

Production of hydroxyl radicals OH **via** O_3

(1) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

(2) $O(^1D) + M \rightarrow O(^3P) + M$ (~90%) or

(3) $O(^1D) + H_2O \rightarrow 2OH$ (~10%, one O_3 gives two OH)

Net 1 & 3: $O_3 + H_2O + h\nu \rightarrow 2OH + O_2$

Prerequisite: **Production of excited atomic oxygen** $O(^1D)$

Hydroxyl radical OH

Production of OH mainly proceeds via three reactions:

(1) $O_3 + H_2O + h\nu \rightarrow 2OH + O_2$

(2) $HO_2 + NO \rightarrow OH + NO_2$

(3) $HONO + h\nu \rightarrow OH + NO$
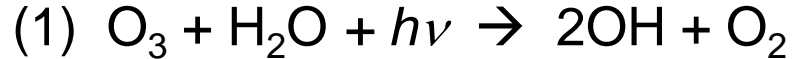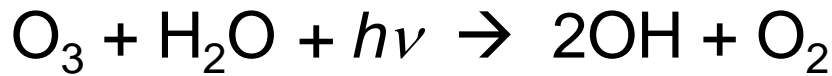
Reaction (1) dominates in clean background air ("low" NO_x, high RH).

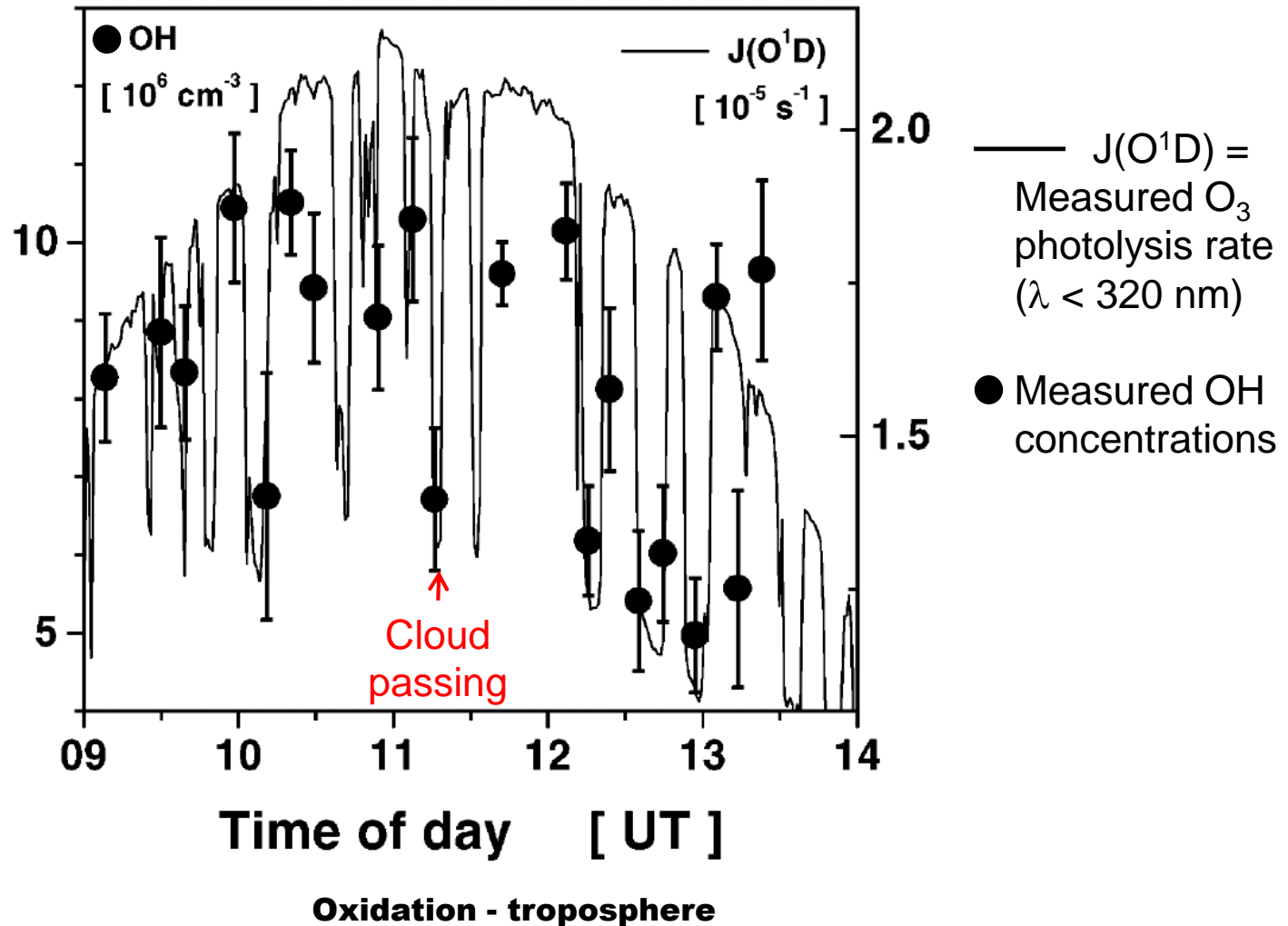Reaction (2) dominates in polluted air (high NO_x).

Reaction (3) from HONO only of importance at sunrise since HONO is rapidly photolyzed (within 10 min - 1 h).

Small amount of OH is also produced during the night when alkenes are oxidized by O_3

Oxidation - troposphere

Hydroxyl radical OH responds quickly to UV

$$O_3 + H_2O + h\nu \rightarrow 2OH + O_2$$

OH has short lifetime (~1 s).

— J(O¹D) = Measured O_3 photolysis rate (λ < 320 nm)

● Measured OH concentrations

Oxidation - troposphere

Production of the hydroxyl radical OH

Production of O(^{1}D) occurs in a narrow wavelength band between 300-320 nm.

Actinic flux (Ljusflöde) : I
Number of photons crossing the unit horizontal area per unit time (photons $\cdot$ m^{-2} $\cdot$ s^{-1})

Absorption cross-section : σ
"Target area" per molecule within which the photon is absorbed (m^2 $\cdot$ molecule $^{-1}$)

Quantum yield (Kvantutbyte) : q
Probability that absorption of a photon will cause photolysis (molecules $\cdot$ photon $^{-1}$)

Photolysis rate constant k :

$k = q \cdot \sigma \cdot I$ (s^{-1}, wavelength dependent)

Oxidation - troposphere

Ozone photolysis in the troposphere

Photolysis of O_3 in the troposphere

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

$k=q\sigma I$ where q, σ and I all vary with the wavelength of light.

<u>295 nm</u>: $q=0.95$, $\sigma=8\cdot10^{-19}$ $cm^2\cdot molecules^{-1}$, $I=1\cdot10^{10}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$

$k \approx 7.3\cdot10^{-9}$ $s^{-1}\cdot nm^{-1}$. Note that the unit is $s^{-1}\cdot nm^{-1}$ since this value only represents a small wavelength interval around 295 nm).

<u>305 nm</u>: $q=0.94$, $\sigma=2\cdot10^{-19}$ $cm^2\cdot molecules^{-1}$, $I=1.6\cdot10^{13}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$

$k \approx 2.9\cdot10^{-6}$ $s^{-1}\cdot nm^{-1}$.

<u>315 nm</u>: $q=0.25$, $\sigma=5\cdot10^{-20}$ $cm^2\cdot molecules^{-1}$, $I=6.9\cdot10^{13}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$

$k \approx 9.2\cdot10^{-7}$ $s^{-1}\cdot nm^{-1}$.

<u>325 nm</u>: $q=0$, $\sigma=1.6\cdot10^{-20}$ $cm^2\cdot molecules^{-1}$, $I= 1.2\cdot10^{14}$ $photons\cdot cm^{-2}\cdot s^{-1}\cdot nm^{-1}$

$k = 0$ $s^{-1}\cdot nm^{-1}$.

O3 Photolysis Rate Constant
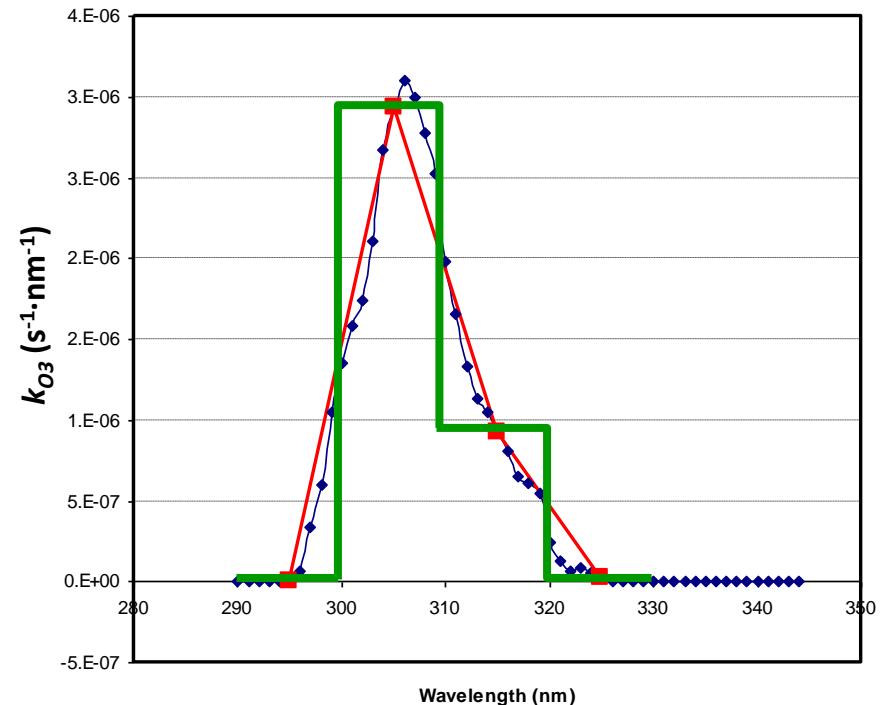
Integrate over all wavelenghts, that is $k=\int q(l)s(l)I(l)dl$. The unit is then s^{-1}. Multiply the values of the wavelength-dependent photolysis rate constants with the interval width (10 nm) and sum up. This **yields $k_{O3} = 3.9\cdot10^{-5}$ s^{-1}**. If one integrates (sums) only for 305 and 315 nm, you get almost the same result; $k_{O3} = 3.86\cdot10^{-5}$ s^{-1}.
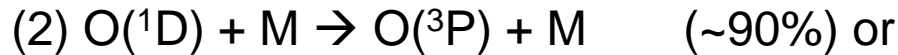
Oxidation - troposphere

Hydroxyl radical OH

Derive an expression for the Production of hydroxyl radicals OH via O_3 which should be a function of [M], [O_3] and [H_2O]

(1) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, λ < 320 nm)

(2) $O(^1D) + M \rightarrow O(^3P) + M$ (~90%) or

(3) $O(^1D) + H_2O \rightarrow 2OH$ (~10%, one O_3 gives two OH)

$O(^1D)$ short-lived, Hence you can assume "steady state" for $O(^1D)$

Oxidation - troposphere

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Prerequisite: Production of excited atomic oxygen
$O(^1D)$ short-lived $\rightarrow$ Assume "steady state" for $O(^1D)$

$$0 = \frac{d}{dt}\left[O(^1D)\right] = k_1[O_3] - k_2\left[O(^1D)\right][M] - k_3\left[O(^1D)\right][H_2O] \Rightarrow \left[O(^1D)\right] = \frac{k_1[O_3]}{k_2[M] + k_3[H_2O]} \quad \text{Eq. 1}$$

$$P_{OH} = \frac{d}{dt}[OH] = 2k_3\left[O(^1D)\right][H_2O] \quad \text{Eq. 2}$$

Insert Eq. 1 into Eq. 2 $\rightarrow$ $P_{OH} = \dfrac{2k_1 k_3 [O_3][H_2O]}{k_2[M] + k_3[H_2O]} \approx$

(2) Faster than (3), [M]>[H_2O] $\rightarrow$ $P_{OH} \approx \dfrac{2k_1 k_3}{k_2[M]}[O_3][H_2O] \quad \text{Eq. 3}$

Oxidation - troposphere

Hydroxyl radical OH

Production of the hydroxyl radical OH

$$P_{OH} \approx \frac{2k_1 k_3}{k_2 [M]} [O_3][H_2O] \quad \text{Eq. 3}$$

OH [10^5 molecules cm^{-3}]

Why is the [OH] highest in the tropics at 500 hPa?

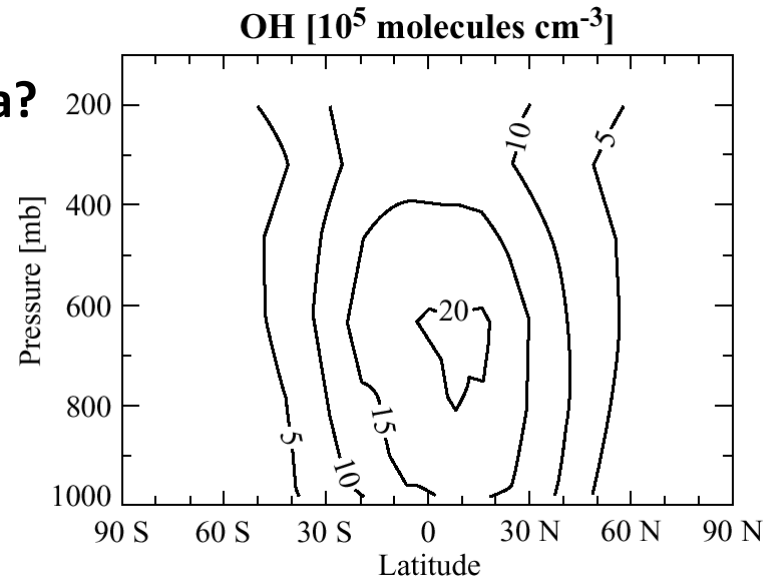Production of OH most efficient when
- plenty UVb radiation ($\lambda < 320$ nm, k_1)
- high ozone levels ([O_3])
- high humidity ([H_2O])
- low pressure ([M])

Production of OH largest in middle troposphere in the tropics.

It takes 1-2 months for an air mass at our latitudes to disperse to the tropics.

Large fractions of our air pollutants are processed in tropics.

Oxidation - troposphere

Hydroxyl radical OH – Modelling

The 3-dimensional global chemistry transport model GEOS-CHEM

GEOS3 OH for Jun 2002 Avg from L=1−30 (0.3−54.0 km)

molec / cm^{-3}
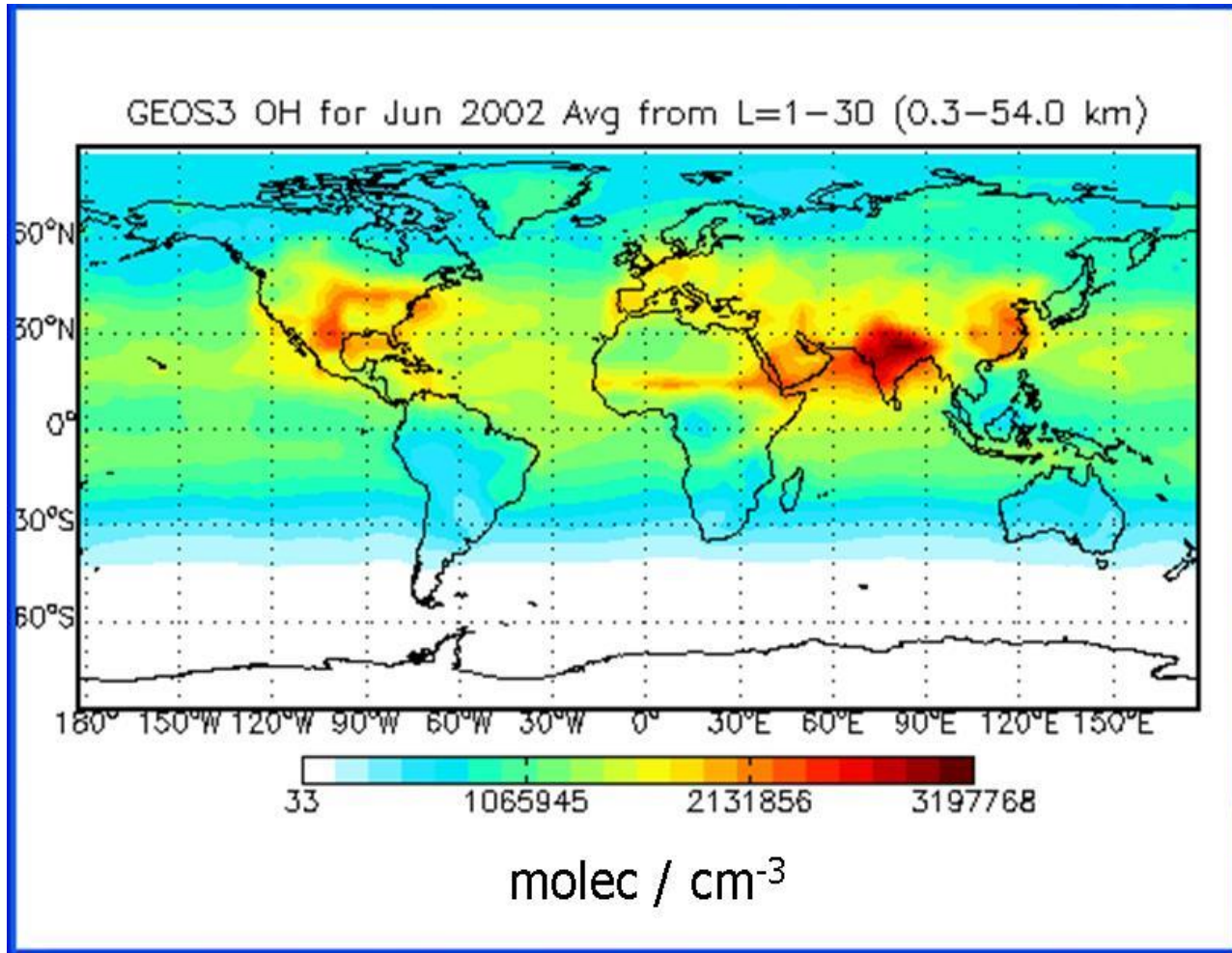
Lifetime for the hydroxyl radical OH

OH lifetime τ_{OH} can be estimated by knowing the most important sinks i

$$\tau_{OH} = \frac{1}{\sum\limits_i k_i n_i}$$

where n_i is the number concentration of molecule i and k_i is the corresponding rate constant.

The most important OH sinks (and for CO and CH_4) are

(4) $CO + OH \rightarrow CO_2 + H$
(5) $CH_4 + OH \rightarrow CH_3 + H_2O$

τ_{OH} = seconds   (τ_{CO} = 1-4 months, τ_{CH4} = ~10 years)

Titration of hydroxyl radical OH

The stratosphere is not a sufficient source of tropospheric ozone to account for the levels of OH in the troposphere.

The global sources of CO and CH_4 are strong enough to titrate out all tropospheric OH that originates from stratospheric ozone.

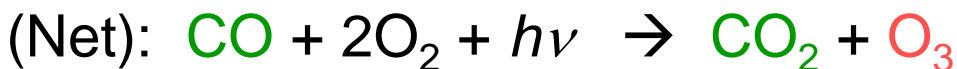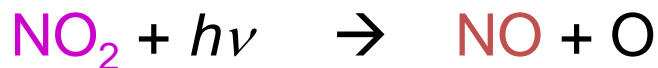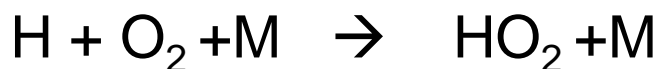Levels of CO and CH_4 should rise to catastrophic levels!

Presence of NO_X ($\equiv$ NO + NO_2) gives a catalytic regeneration of OH (and O_3) in the troposphere.

Presence of NO_X even at the low levels typically found in background air masses is very important for the oxidizing capacity of the troposphere and thereby life on Earth.
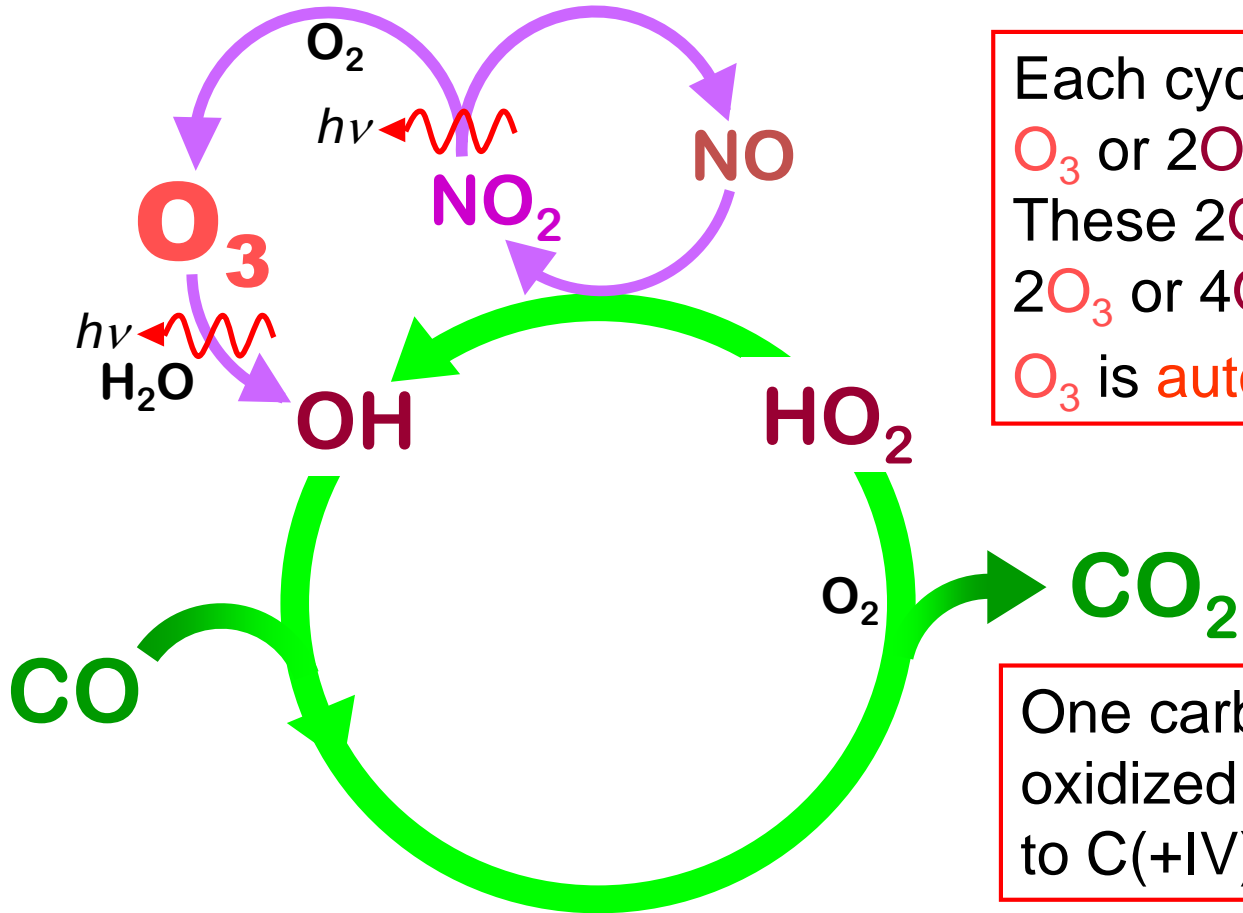
Oxidation - troposphere

Oxidation of carbon monoxide – high NO$_x$

Catalytic ozone production:

$CO + OH \rightarrow H + CO_2$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + NO \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

(Net): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ and $O(^1D) + H_2O \rightarrow 2OH$

Each cycle produces one net O$_3$ or 2OH.

Oxidation of carbon monoxide – high NO$_x$

O$_2$

$h\nu$

NO$_2$

NO

O$_3$

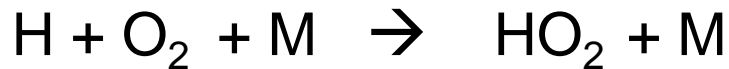$h\nu$

H$_2$O

OH

HO$_2$

CO

O$_2$

CO$_2$

Each cycle produces one O$_3$ or 2OH.
These 2OH can in turn give 2O$_3$ or 4OH and so on.

O$_3$ is autocatalytic.

One carbon atom is also oxidized from C(+II), CO, to C(+IV), CO$_2$.

(Net): $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$

Oxidation - troposphere
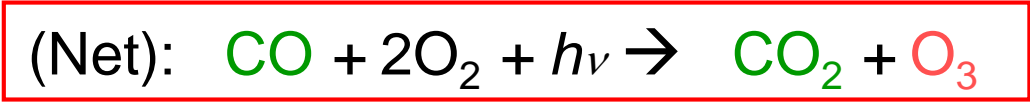
Oxidation of carbon monoxide – low NO$_x$

Catalytic ozone loss:

$$CO + OH \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

(Net): $CO + O_3 \rightarrow CO_2 + O_2$

Each cycle consumes one O_3.

Levels of NO are crucial to whether ozone is produced or consumed. Break-even lies at ~20 pptv NO (very low).

Ozone suffers a net loss only in very clean background air in the troposphere.

Such pristine air can still be found in large parts of the troposphere.

Oxidation - troposphere

Oxidation of carbon monoxide – low NO_x

O_3

HO_2

OH

CO

O_2

CO_2
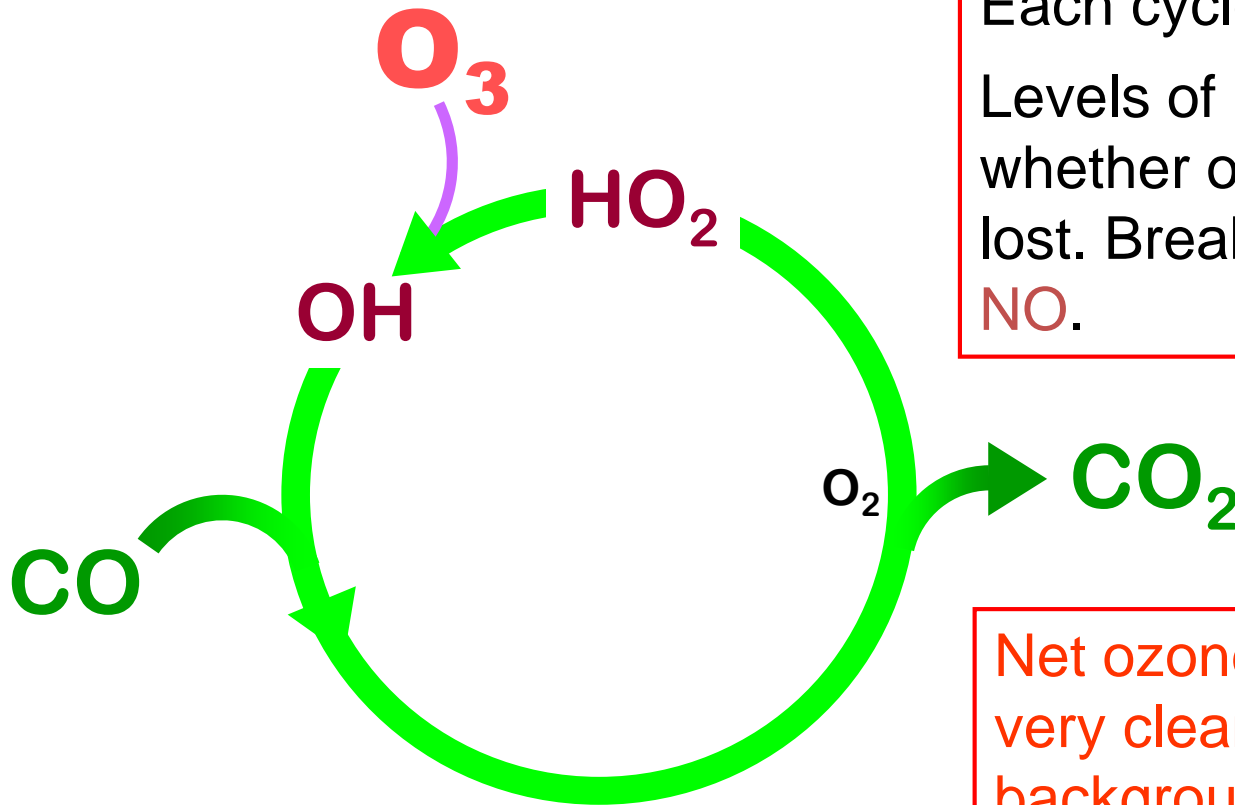
Each cycle consumes one O_3.

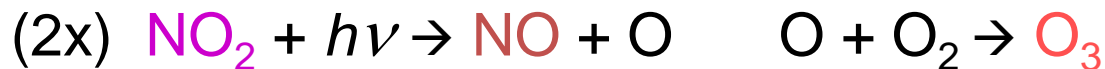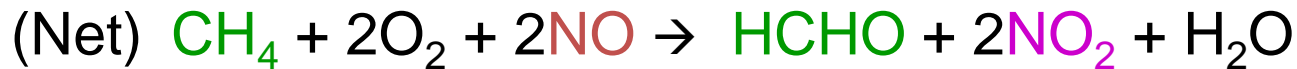Levels of NO determine whether ozone is produced or lost. Break-even lies ~20 pptv NO.

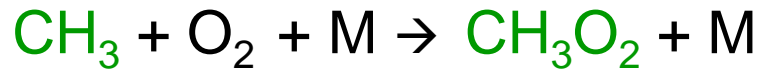Net ozone loss occurs only in very clean tropospheric background air.

(Net): $CO + O_3 \rightarrow CO_2 + O_2$

Oxidation - troposphere

Oxidation of methane

Catalytic ozone production:

$CH_4 + OH \rightarrow CH_3 + H_2O$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

(Net) $CH_4 + 2O_2 + 2NO \rightarrow HCHO + 2NO_2 + H_2O$

(2x) $NO_2 + h\nu \rightarrow NO + O$ $O + O_2 \rightarrow O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2OH$

Each cycle produces net $2O_3$ or $4OH$.

Oxidation of methane

(Net):
$CH_4 + 2O_2 + 2NO \rightarrow$
$HCHO + 2NO_2 + H_2O$

O_3

$h\nu$

NO_2

NO

$h\nu$

H_2O

OH

HO_2

CH_4
(methane)

O_2

O_2

HCHO
(formaldehyde)

CH_3O_2

CH_3O

Each cycle gives net
2 O_3 or 4 OH.

NO

NO_2

$h\nu$

O_2

O_3

Oxidation - troposphere

CH₄ → HCHO → CO → CO₂

$$CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2$$
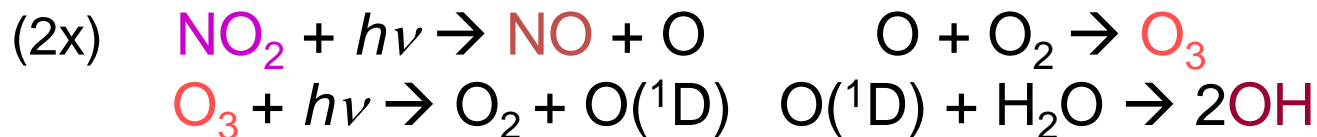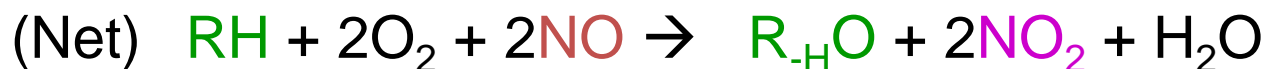
methane C(-IV) → formaldehyde C(0) → carbon monoxide C(II) → CO_2 C(IV)
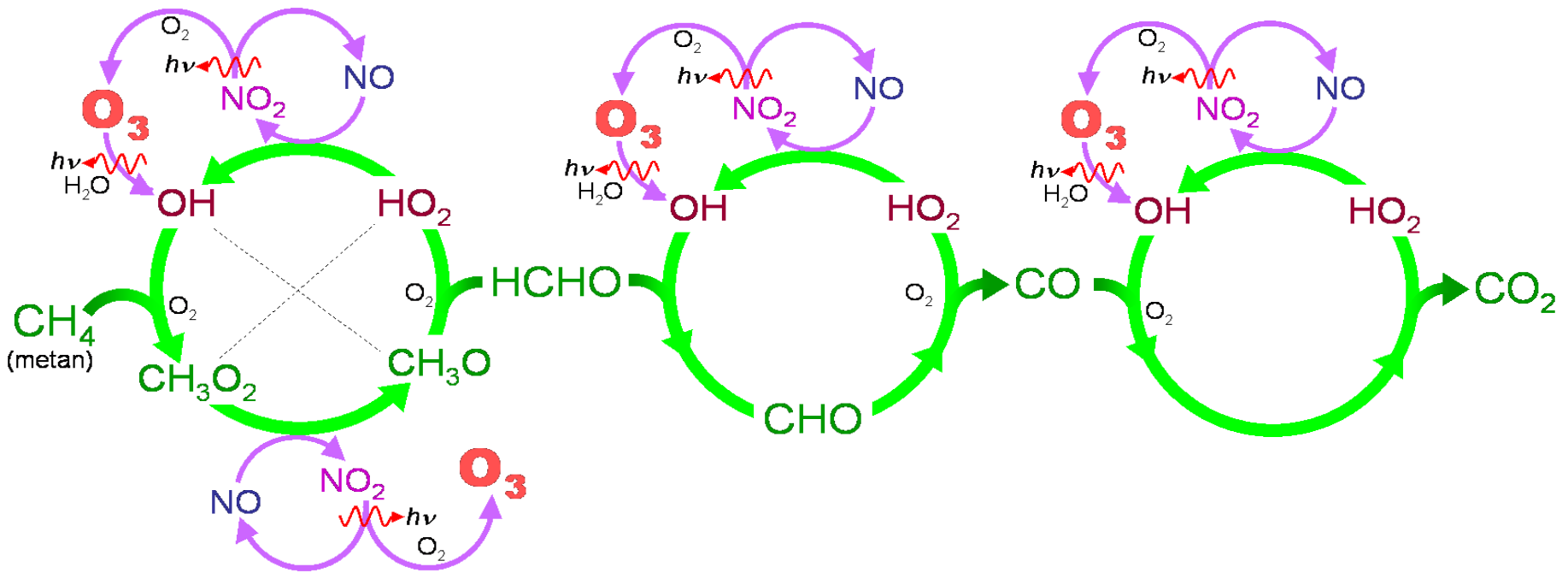
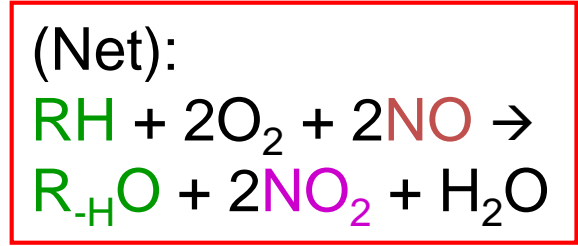**Oxidation - troposphere**

Oxidation of hydrocarbons RH

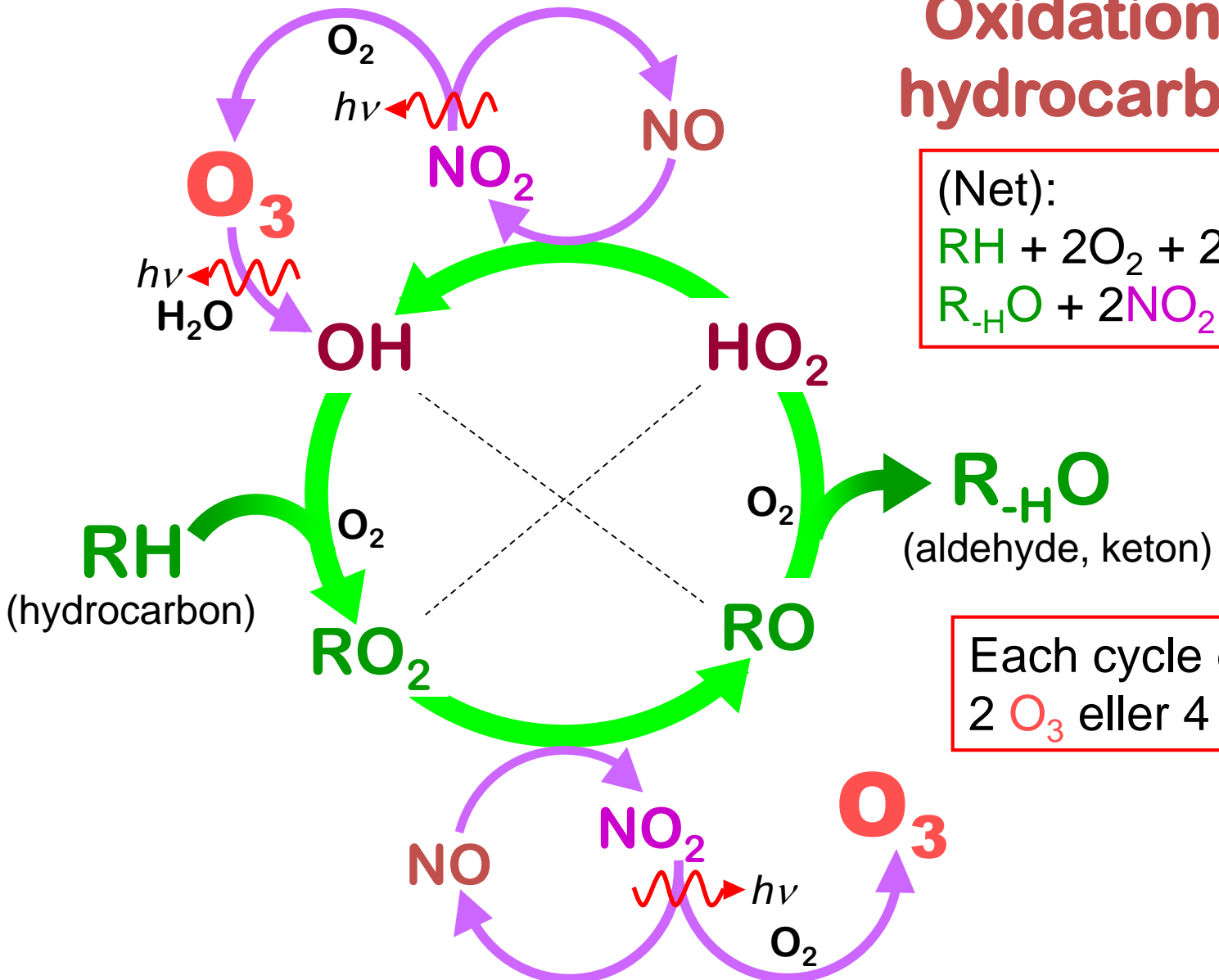**Examples: Alkanes RH**

$RH + OH \rightarrow R + H_2O$

$R + O_2 + M \rightarrow RO_2 + M$

$RO_2 + NO \rightarrow RO + NO_2$

$RO + O_2 \rightarrow R_{-H}O + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

(Net) $RH + 2O_2 + 2NO \rightarrow R_{-H}O + 2NO_2 + H_2O$

(2x) $NO_2 + h\nu \rightarrow NO + O$ $O + O_2 \rightarrow O_3$

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2OH$

Each cycle produces net $2O_3$ or $4OH$.

Oxidation - troposphere

Oxidation av hydrocarbons

(Net):
$RH + 2O_2 + 2NO \rightarrow$
$R_{-H}O + 2NO_2 + H_2O$

O_3

NO_2

NO

O_2

$h\nu$

$h\nu$

H_2O

OH

HO_2

O_2

O_2

$R_{-H}O$
(aldehyde, keton)

RH
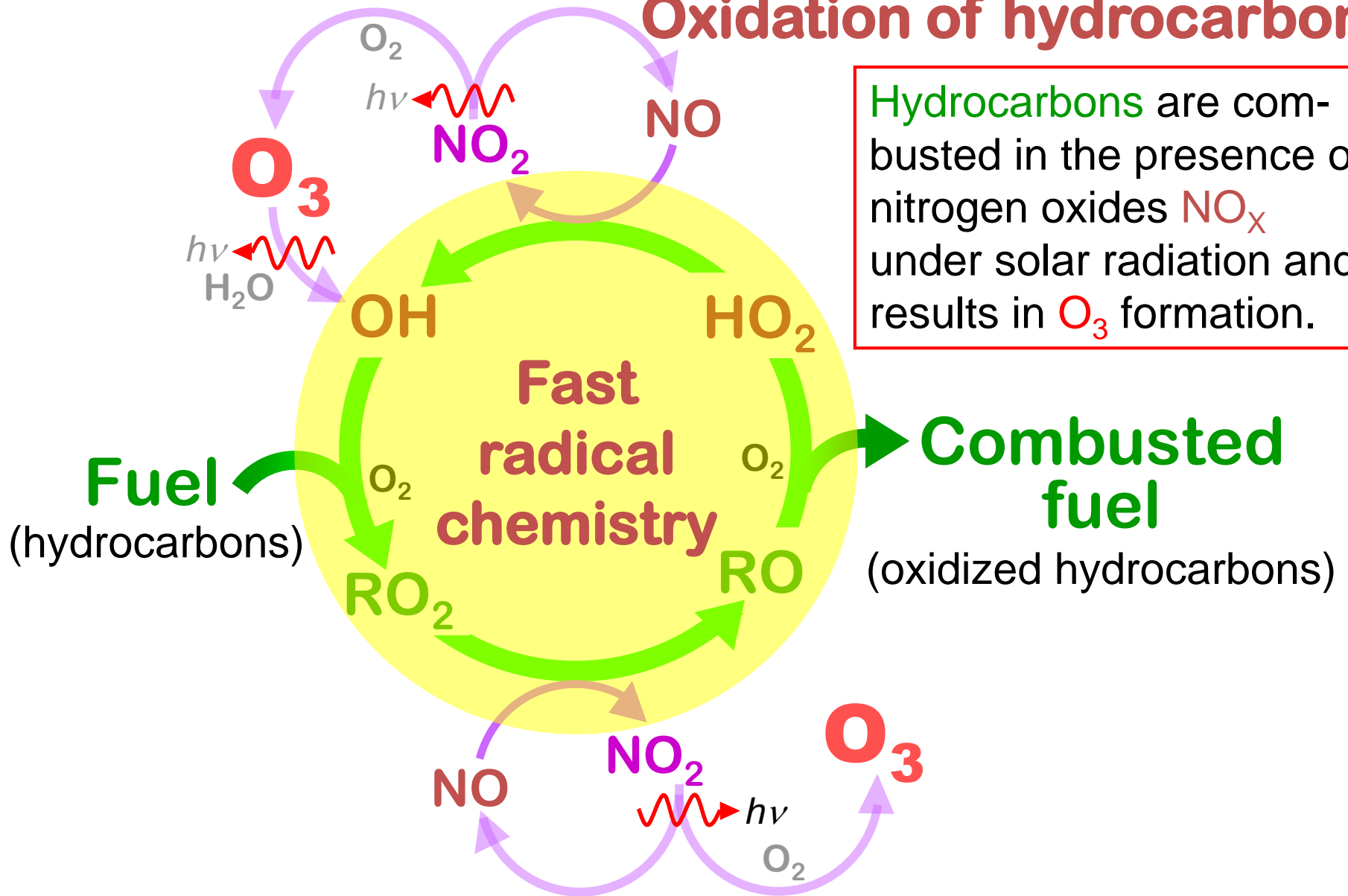(hydrocarbon)

RO_2

RO

NO

NO_2

O_3

$h\nu$

O_2

Each cycle gives net
2 O_3 eller 4 OH.

Oxidation - troposphere

Oxidation of hydrocarbons

Hydrocarbons are combusted in the presence of nitrogen oxides NO_X under solar radiation and results in O_3 formation.

Fast radical chemistry

Fuel (hydrocarbons)

Combusted fuel (oxidized hydrocarbons)

Oxidation - troposphere

Oxidation of hydrocarbons

Hydrocarbons (the fuel) are oxidized in the troposphere in multiple steps.

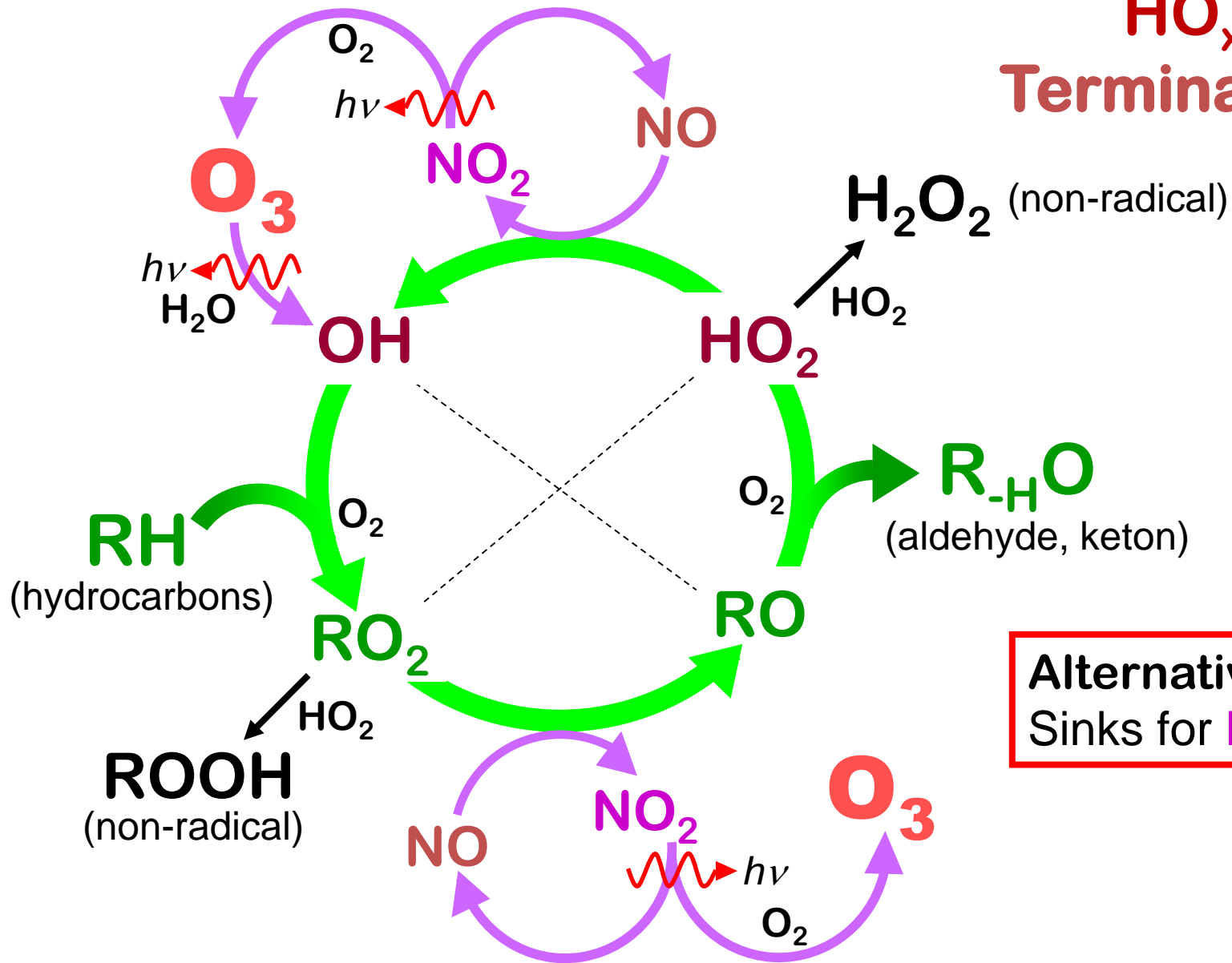Hydrocarbon → aldehyde → organic acid → carbon monoxide → CO_2

RH → $R_{-H}O$ → RCOOH → CO → CO_2

Oxidation number for carbon atom:
C(-IV) → C(0) → C(+II) → C(+II) → C(+IV)

Oxidation - troposphere

HO_x Termination

O_2

$h\nu$

NO_2

NO

H_2O_2 (non-radical)

HO_2

$h\nu$

O_3

H_2O

OH

HO_2

RH (hydrocarbons)

O_2

O_2

$R_{-H}O$ (aldehyde, keton)

RO_2

RO

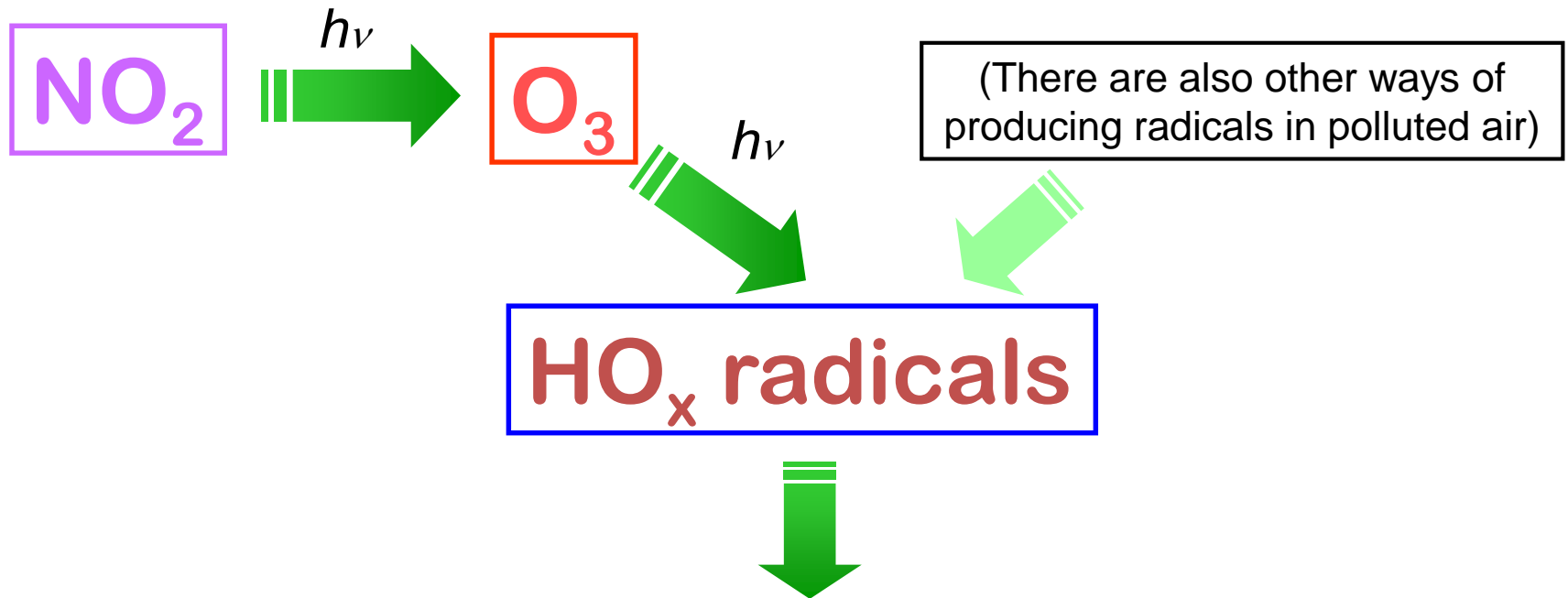ROOH (non-radical)

HO_2

NO

NO_2

$h\nu$

O_2

O_3

Alternative: Sinks for NO_X.

Oxidation - troposphere

Oxidants in the troposphere

NO_2 and solar radiation controls the production of O_3 , which in turn controls the production of HO_X radicals $\equiv OH + HO_2$, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.

$$\boxed{NO_2} \xrightarrow{h\nu} \boxed{O_3}$$

$h\nu$

(There are also other ways of producing radicals in polluted air)

$$\boxed{HO_X \text{ radicals}}$$

Oxidizing capacity of the troposphere

Oxidation - troposphere

Sources of NO$_x$

	Source (Tg N/yr)
Fossil fuel combustion	21 (45%)
Biomass combustion	12 (25%)
Soils	6 (13%)
Lightning	3 (7%)
Oxidation of NH_3	3 (7%)
Air traffic	0.5 (1%)
Transport from the stratosphere	0.1
Total	**~46**

Oxidation - troposphere

Sources of NO$_x$

Anthropogenic sources of NO$_x$ (caused by human activities) dominate compared to the natural sources.

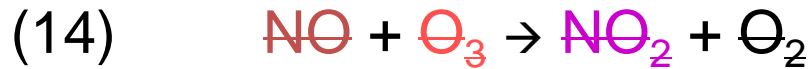Levels of NO$_2$ measured from a satellite.
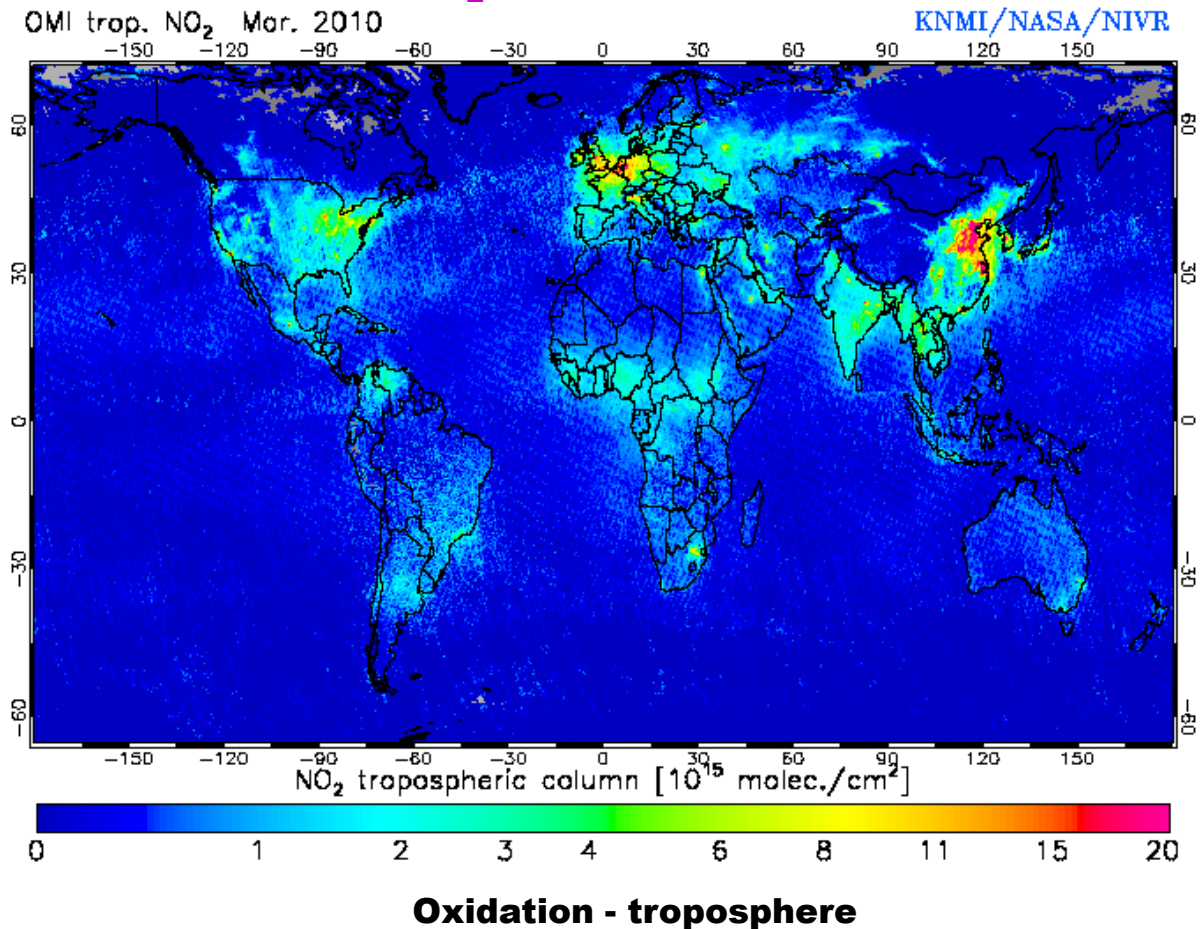
Oxidation - troposphere

Sinks for NO$_x$

NO$_X$ is mainly emitted as NO (at high temperatures).
NO$_X$ is cycled between NO and NO$_2$ (~1 minute).

(14)   NO + O$_3$ → NO$_2$ + O$_2$
(11)   NO$_2$ + $h\nu$ → NO + O   (λ < 420 nm)
(10.2)   O + O$_2$ + M → O$_3$ + M   (only way to produce O$_3$)

Oxidation - troposphere

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(10.2) ~~O~~ + ~~O$_2$~~ + ~~M~~ → ~~O$_3$~~ + ~~M~~   (only way to produce O$_3$)

(Net) No net formation or loss of either NO$_X$ or O$_3$

The above reactions represents a null-cycle for NO$_X$ and O$_3$

Sinks for NO$_x$

Apart from removal of HO$_X$ radicals, the catalytic ozone production cycle can also be broken by removing NO$_X$.

(30)   NO$_2$ + OH + M → HNO$_3$ + M (daytime)

Nigthtime:

(31)   NO$_2$ + O$_3$ → NO$_3$ + O$_2$ (NO$_3$ rapidly photolyzed)

(32)   NO$_3$ + NO$_2$ + M → N$_2$O$_5$ + M (N$_2$O$_5$ water-soluble)

(33)   N$_2$O$_5$ + H$_2$O → 2HNO$_3$ (on an aerosol particle)

τ_{NOx} = ~1 day

HNO$_3$ is very water-soluble and is washed out by precipitation (wet deposition).

HNO$_3$ is not a long-term reservoir for NO$_X$ (τ_{HNO3} = days).
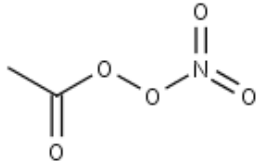
PAN - Reservoir for NO$_x$

Peroxyacetylnitrate (PAN) is an efficient reservoir for NO$_X$.

$$PAN = CH_3C(O)OONO_2$$

PAN enables NO$_X$ to be transported long distances and contribute to the levels of NO$_X$ in background air, which in turn adds to the oxidizing capacity in remote environments.

PAN is formed for instance when acetaldehyde reacts with OH radicals and then further with NO$_2$. Levels of PAN in polluted air can reach 1 ppb.
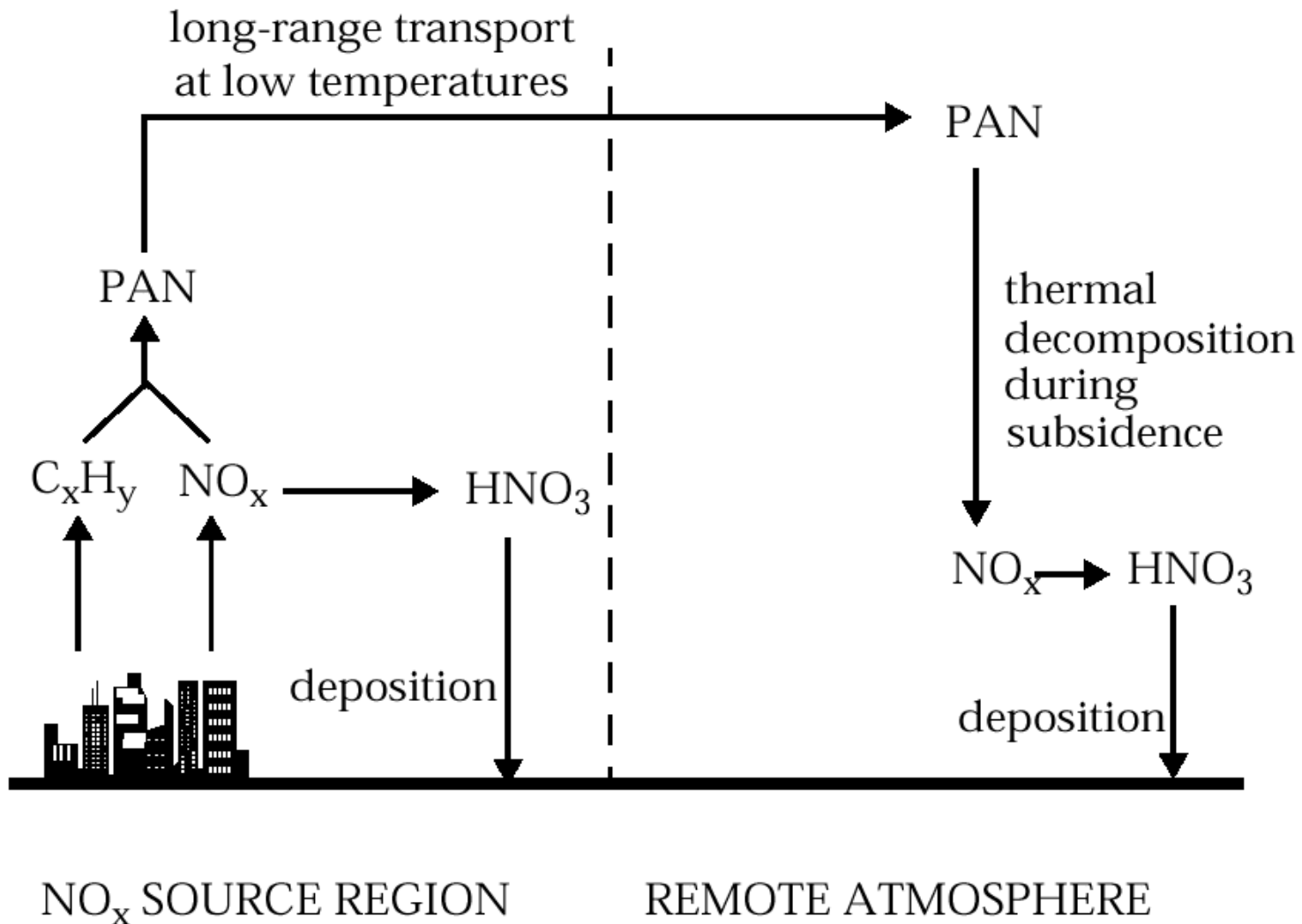
PAN is thermally unstable.

$$(37) \quad PAN \xrightarrow{\text{heat}} CH_3C(O)OO + NO_2$$
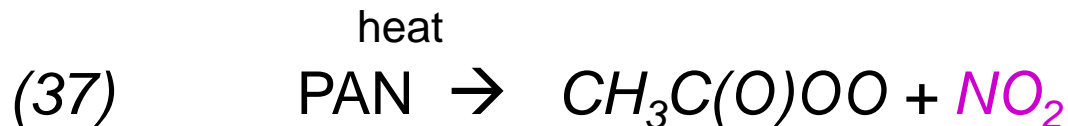
τ_{PAN} = ~1 hour at 295 K   (lower troposphere)
τ_{PAN} = months at 250 K   (upper troposphere)

Long-range transport of NO$_x$ via PAN

Global budget for tropospheric ozone

Ozone production in the troposphere is limited by the reactions

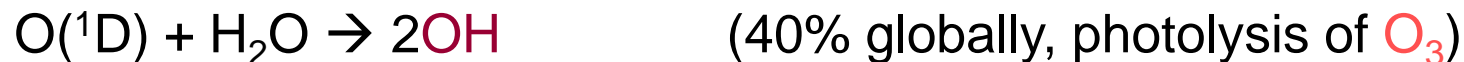HO_2 + NO   →   OH + NO_2 (70% globally)

CH_3O_2 + NO → CH_3O + NO_2 (20% globally)

RO_2 + NO → $R_{-H}O$ + NO_2 (10% globally)

followed by
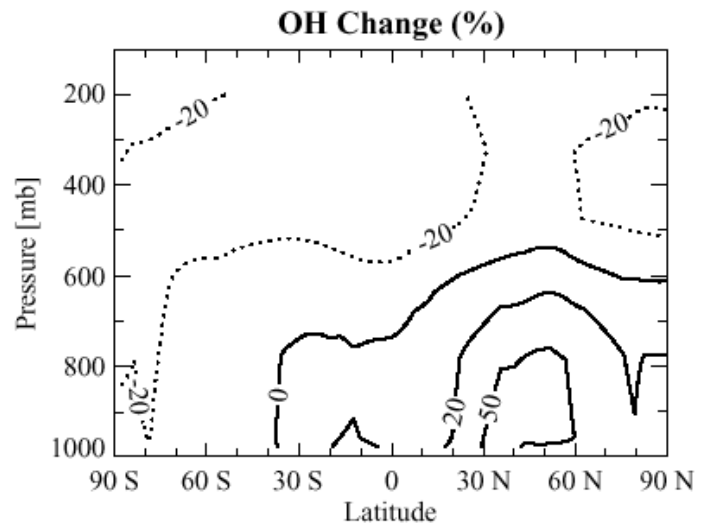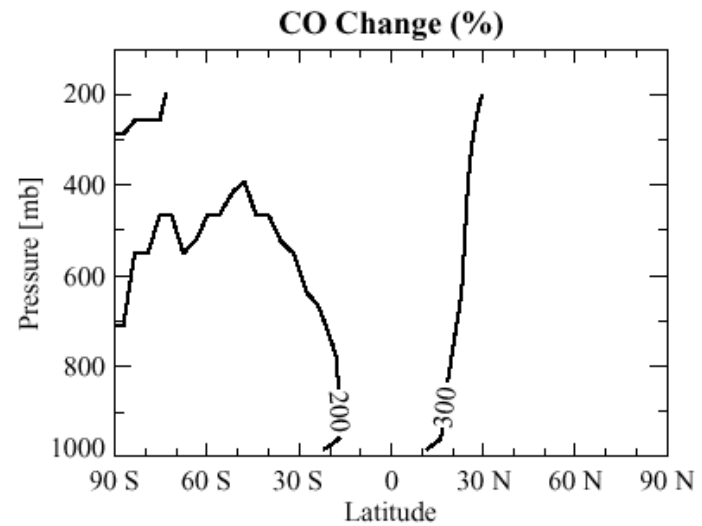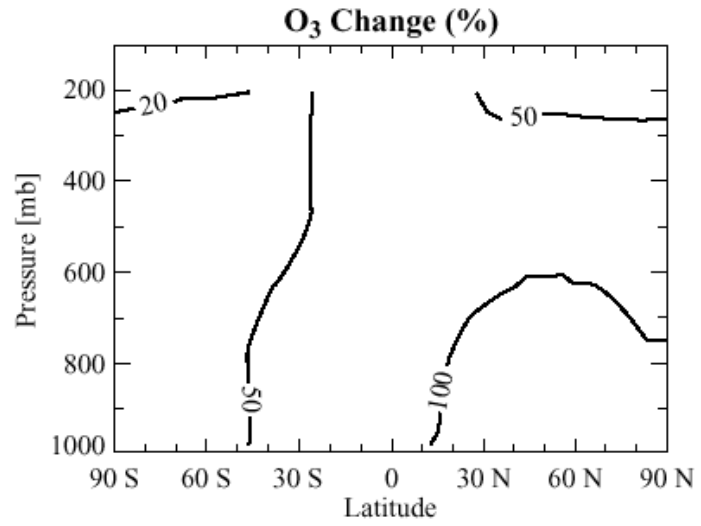
NO_2 + $h\nu$ → NO + O,   and O + O_2 → O_3

Down-mixing of stratospheric ozone is also a significant source.

Ozone loss in the troposphere is limited by the reactions

$O(^1D)$ + H_2O → 2OH   (40% globally, photolysis of O_3)

HO_2 + O_3 → OH + $2O_2$ (40% globally)
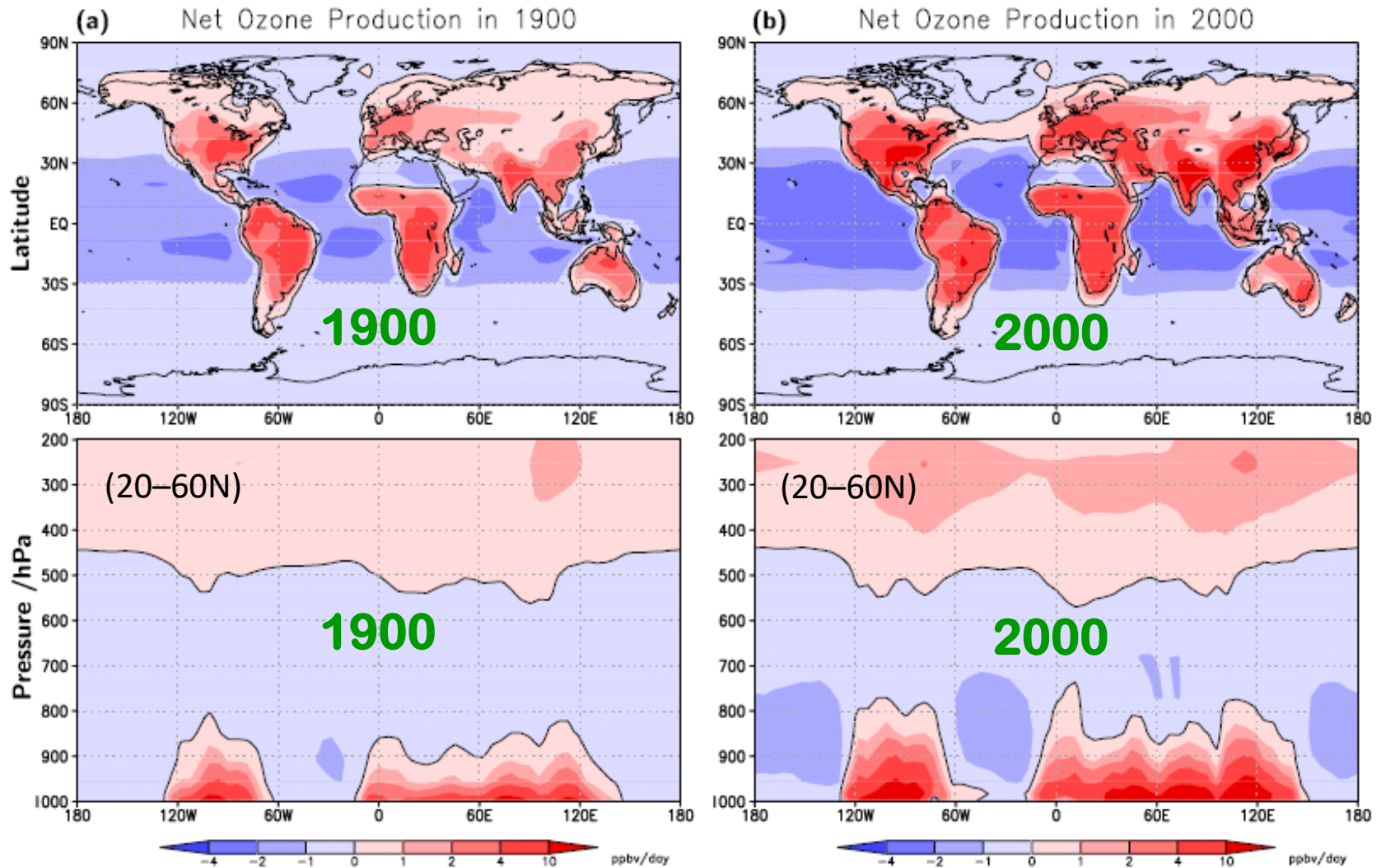
OH + O_3 → HO_2 + O_2 (10% globally)

Dry deposition of ozone is also a significant sink.

Anthropogenic modifications of the troposphere
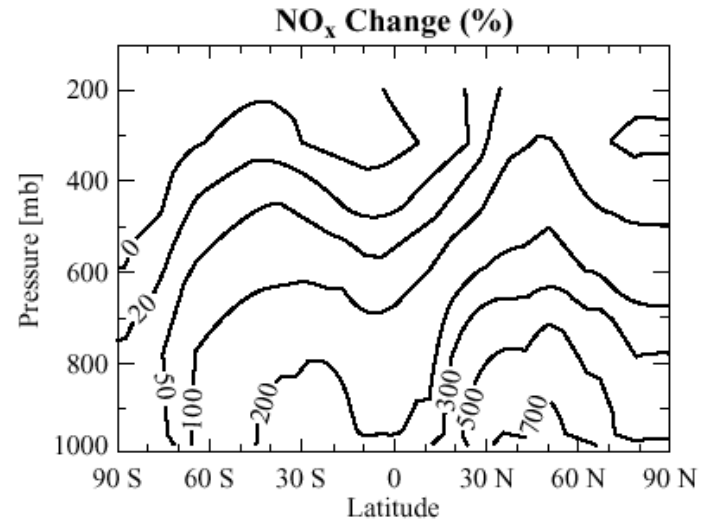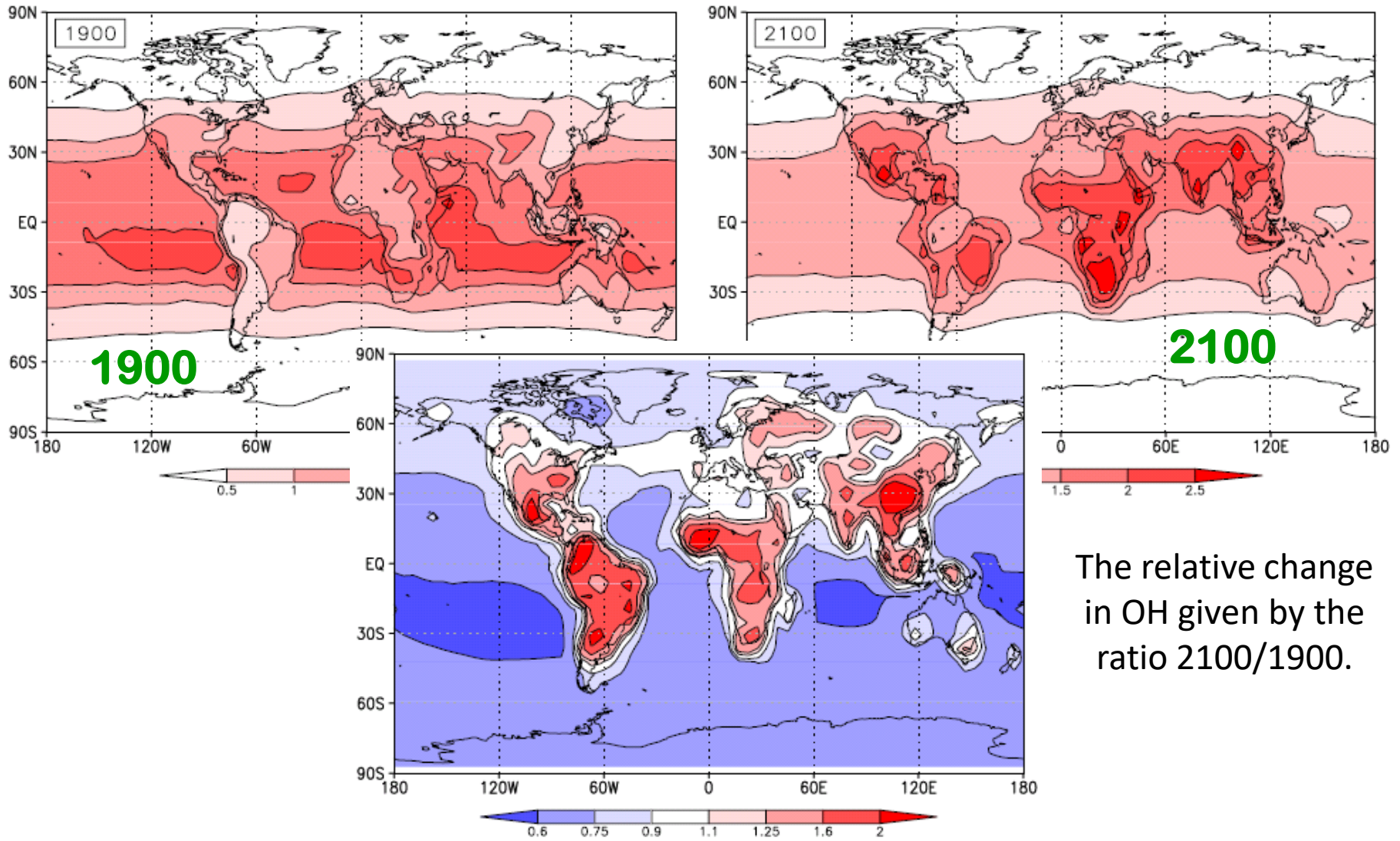
Modelled net O₃ production rates (ppbv/day)

Annual mean distribution of net O3 production in ppbv/day in (top) the boundary layer and (bottom) at northern mid-latitudes (20–60N) in (a) 1900, and (b) 2000. The contour line marks zero net production.
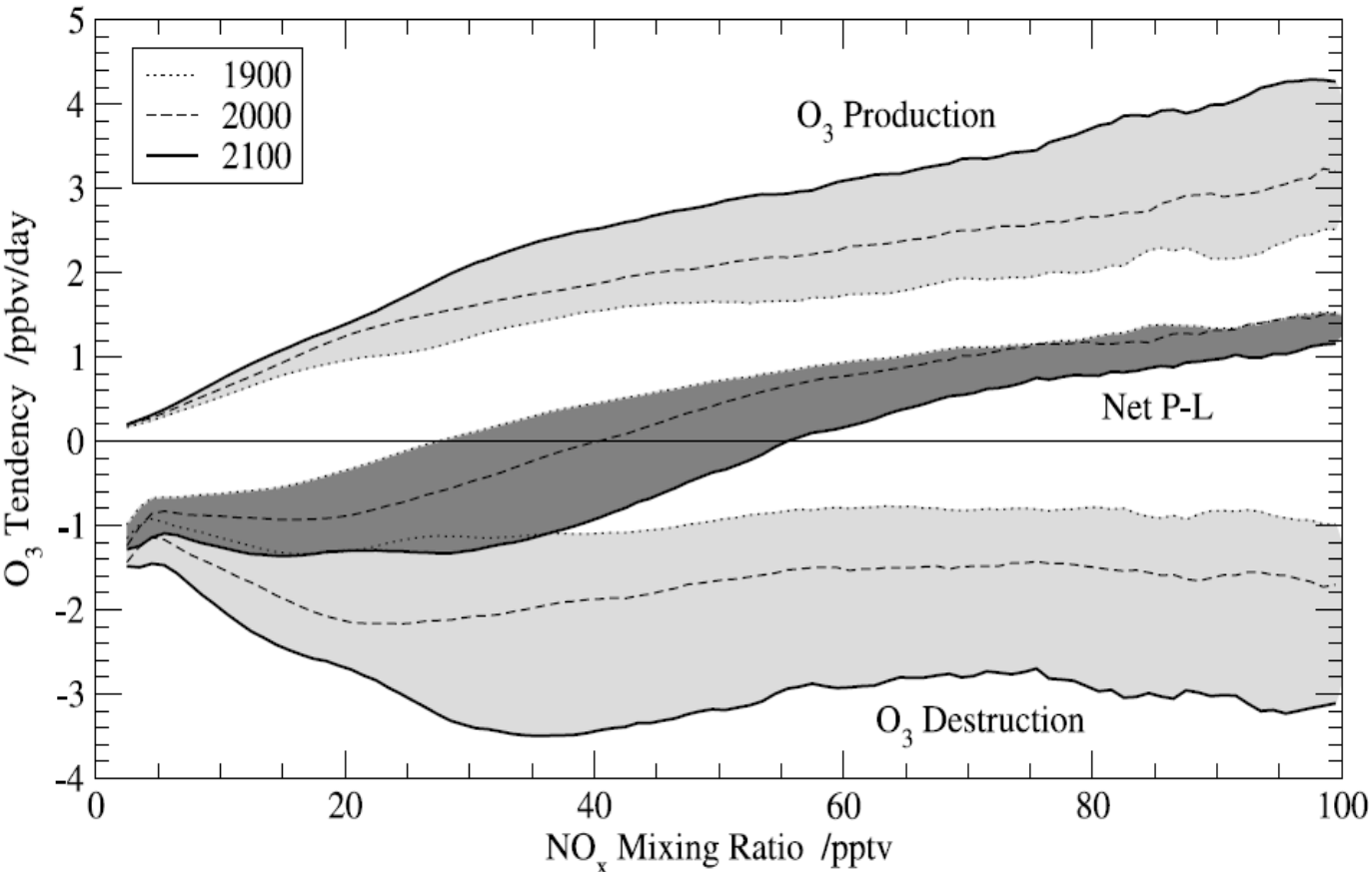
Modelled OH concentrations 1900 - 2100

The relative change in OH given by the ratio 2100/1900.

Annual mean distribution of OH (in units of 106 molecules cm−3**) in the boundary layer** in (left) 1900 and (right) 2100.
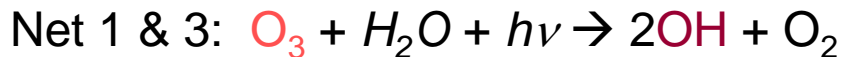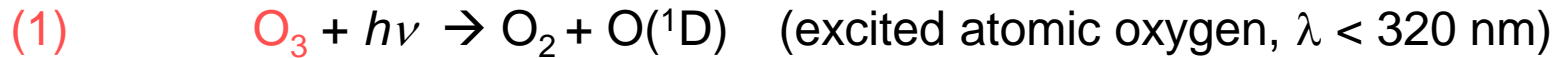
Modelled O$_3$ production and loss rates (ppbv/day)

Tropospheric O$_3$ production and loss rates (ppbv/day) below 250 hPa (10 km) as a function of NOx (pptv) for 1900, 2000, and 2100.

The critical NOx value for O$_3$ production occurs where net production (P-L) crosses zero, doubling between 1900 (28 pptv) and 2100 (55 pptv).

O. Wild, P.I. Palmer, How sensitive is tropospheric oxidation to anthropogenic emissions? GRL, VOL. 35, L22802, doi:10.1029/2008GL035718, 2008

How is the hydroxyl radical (OH) mainly produced in clean remote atmospheric regions?

(1) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ (excited atomic oxygen, $\lambda < 320$ nm)

(2) $O(^1D) + M \rightarrow O(^3P) + M$ (~90%) or

(3) $O(^1D) + H_2O \rightarrow 2OH$ (~10%, one O_3 gives two OH)

Net 1 & 3: $O_3 + H_2O + h\nu \rightarrow 2OH + O_2$

How is the hydroxyl radical (OH) mainly produced in polluted air?

$HO_2 + NO \rightarrow OH + NO_2$

Which are the two main sinks for hydroxyl radicals (OH) in the atmosphere?

(1) $CO + OH \rightarrow CO_2 + H$

(2) $CH_4 + OH \rightarrow CH_3 + H_2O$
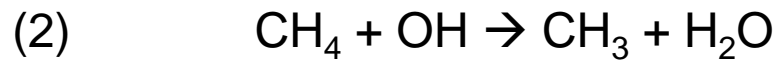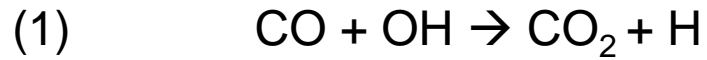
The Master Chemical Mechanism

mcm.leeds.ac.uk/MCM/

A searchable compilation of chemical reactions of atmospheric importance.

UNIVERSITY OF LEEDS

NASA JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

https://jpldataeval.jpl.nasa.gov/

A compilation of kinetic and photochemical data prepared by the NASA Panel for Data Evaluation.

Oxidation - troposphere