EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

ATMOSPHERIC CHEMISTRY

Lecture No.: 11

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
  web: http://web.vscht.cz/~stafm/
  building A, Dept. 216, door No.162
  e-learning:
  https://e-learning.vscht.cz/course/view.php?id=106
- Scale of subject: winter semester
  14 lectures, 14 weeks, 2 hours/week
- Classification: Exam - written + oral form (depending on result of the test)

Scope of lecture 11

Reactions of ozone, chemistry of background troposphere, hydroxyl radical, hydroperoxyl radical

- Chemical and physical properties of ozone and its importance
- Mechanism of ozone decomposition, nitrogen cycle and chlorine cycle
- Consequences of damaging the ozonosphere for fauna, flora and human health
- Meaning of the terms „clean troposphere“ and „background troposphere“
- Reactions in background troposphere, hydroxyl radical and hydroperoxyl radical and cycles of their formation and extinction
- Characteristics of day and night phases of tropospheric reactions
- Natural sources of reactants for tropospheric reactions

Chemistry of ozone in atmosphere

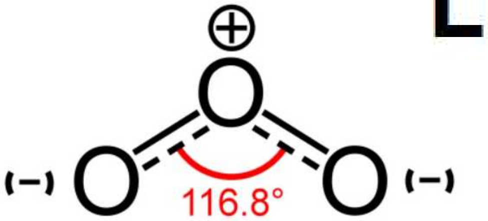
- **Ozone – trioxygen**
  - Compared to O_2 it has characteristic odour (ozein = to smell);
  - Detectable by the sense of smell from 0.01 ppm above;
  - Unlike O_2 gaseous ozone in thick layer has a blue colour.
  - Ozone is strongly oxidizing, reactive and at concentrations above 70 % vol. it is explosive.
  - O_3 is significantly more stable in acidic solutions than in alkali.
  - Compared to O_2 ozone is well soluble in water: at 20 °C 494 $cm^3.l^{-1}$;
  - O_3 is toxic ⇒ e.g. at workplaces in the Czech Rep. its permissible exposure limit (PEL) is 100 $\mu g.m^{-3}$ as an average value not to be exceeded within a shift, while Maximum permissible concentration (MPC) 200 $\mu g.m^{-3}$ must never be exceeded;
  - Ozone O_3 on Earth is always gaseous ⇒ melting point = -193 °C
    ⇒ boiling point = -112 °C

Chemistry of ozone in atmosphere

- **Ozone – trioxygen**
  - Unlike O_2 ozone is blue both in liquid and gaseous states.

Liquid O_3

Liquid O_2



Sourcec: http://sciencemadness.wikia.com, http://www.eielson.af.mil

Chemistry of ozone in atmosphere

- **Formation and extinction of ozone**
  - Ozone formation in stratosphere:

    Photolysis of molecular oxygen with subsequent termolecular synthesis – excessive energy is removed by a third particle (another molecule of O_2, N_2):

$$O_2 + h\nu \xrightarrow{\lambda<242,4\,nm} O + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

  - Extinction of ozone:

    Ozone is an unstable molecule – being exposed to radiation, it willingly decomposes: $2O_3 \rightarrow 3O_2$ or $O_3 + O \rightarrow O_2 + O_2$

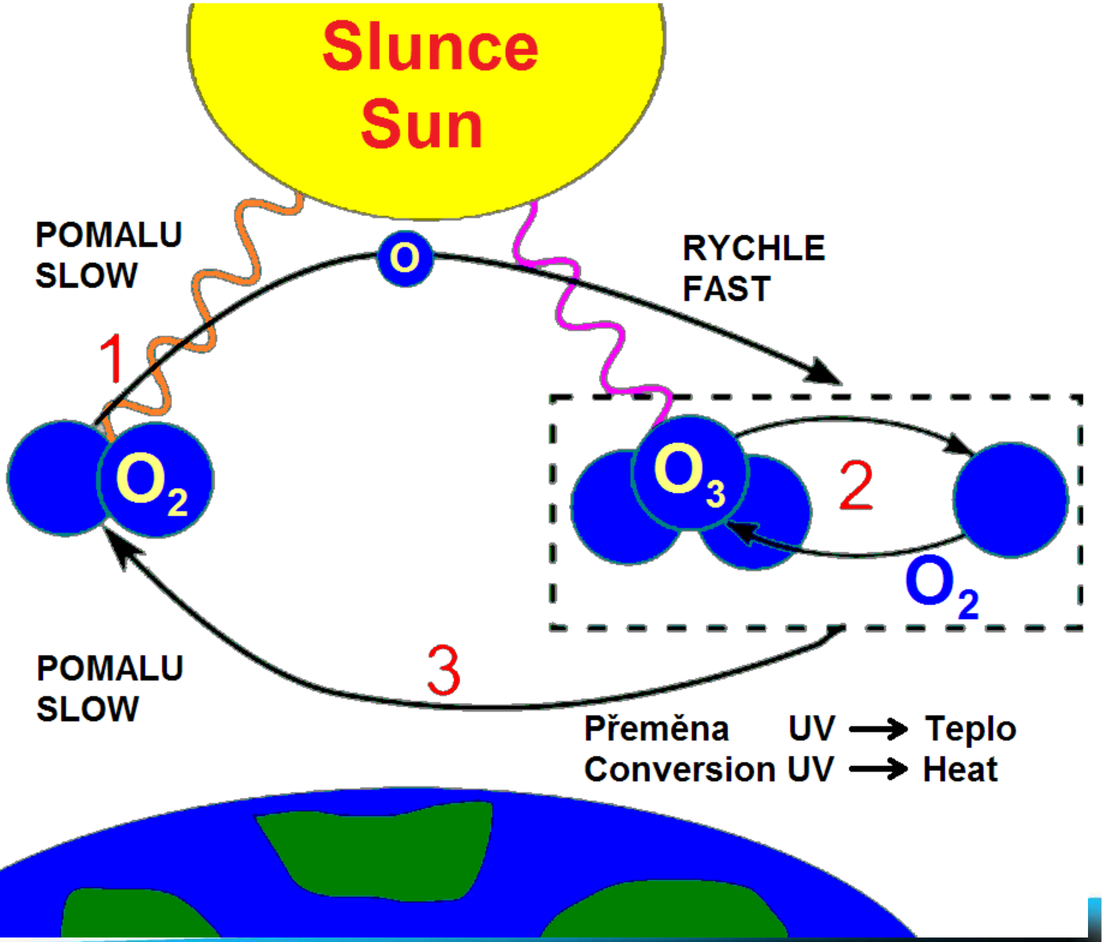
    Decomposition catalysed by biogenic or anthropogenic substances:

→ nitrogen oxides	NO, NO_2
→ hydrogen containing particles	$H^{\bullet}$, $HO^{\bullet}$, $HOO^{\bullet}$
→ halogen derivative residues	$ClO^{\bullet}$, Cl, Br, $BrO^{\bullet}$

Chemistry of ozone in atmosphere

- **Natural generation and decay of ozone**
  - Chapman cycle (majority of reactions run within Shumann-Runge interval λ = 175-200 nm and within the so called Hertzberg continuum up to 242.4 nm)

1. O_2 molecules undergo photolysis into 2 atoms of O
2. O_3 and O atoms convert cyclically (UV radiation splits O_3 and atoms of O react with another O_2 molecule
3. Ozone is decomposed by reaction with atom of O, with another O_3 molecule or with other gases (e.g. Cl, etc.)



Chemistry of ozone in atmosphere

- **Importance of ozone**
  - Importance of stratospheric ozone – absorption of UV radiation;
  - Ozonosphere (15 – 35 km); maximum concentration of O_3 between 25 – 30 km;
  - Ozone absorbs UV radiation with maximum 220 – 330 nm. During absorption UV radiation is transformed to heat.
  - Temperature maximum, caused by UV absorption by O_3 molecules, has been measured at the altitude of 50 km – ozone is able to absorb effectively even at its low concentrations.
  - The ozonosphere itself remains cold, but essential for terrestrial life.
  - At altitudes below **30 km** gradual decrease of O_3 concentration because:

    photodissociation of O_2 essential for O_3 synthesis runs up to 242.4 nm, while O_3 decomposition continues up to 1,200 nm

    $\Rightarrow$ decomposition of O_3 dominates

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere**
  - The lowest O_3 concentrations are measured in Antarctica;
  - According to the Montreal Protocol (from 1987), the majority of chlorofluorinated hydrocarbons are banned;
  - Due to their long lasting persistence, high CFC concentrations are still present in the atmosphere;
  - Diameter of the „ozone hole“ depends on weather:

    During the winter on the southern hemisphere (summer on the north), the atmosphere upon Antarctica is isolated due to the polar atmospheric vortex and mass exchange is therefore limited;

    Formation of stratospheric clouds with very low temperature;

    In the polar stratospheric clouds (PSC), the maximum O_3 decomposition occurs;

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere – note:**

During September + October (spring in Antarctica)

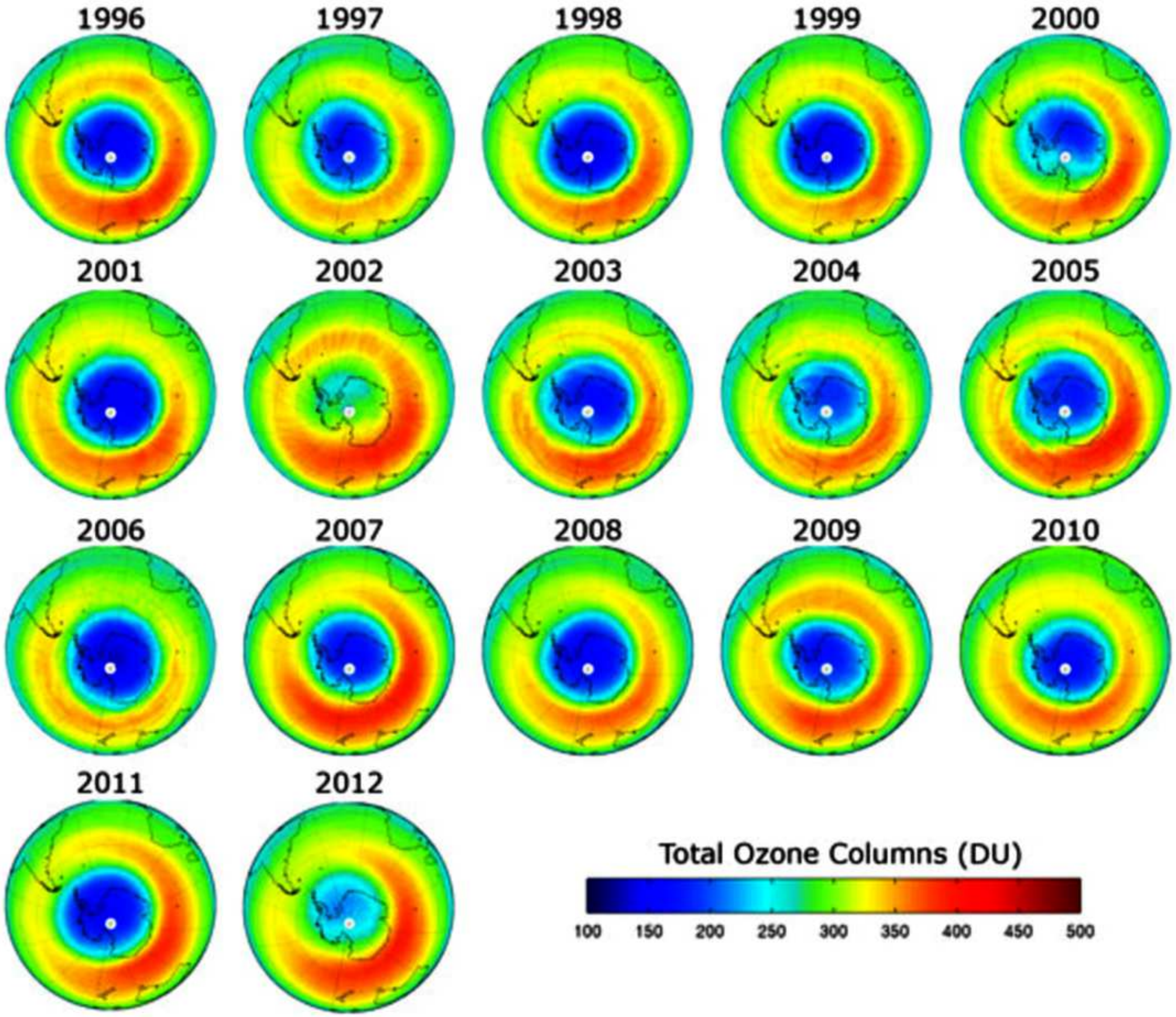
⇒ more intensive sunshine + presence of PSC

⇒ activation of $Cl^{\bullet}$ radicals

⇒ intensive decay of O_3.

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere** (Source: Deutsches Zentrum für Luft- und Raumfahrt e.V.)
  - Proven CFCs decrease in atmosphere – better for O_3 restoration:



DU = Dobson Unit = 2.69×10^{20} molecules O_3 per m^2

1 DU = layer of pure O_3 having the height of 10 µm

(at normal conditions).

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere**
  - General mechanism:

$$O_3 + X \longrightarrow O_2 + OX$$
$$OX + O \longrightarrow X + O_2$$

  - X is in fact a catalyst;
  - 3 main cycles of O_3 decomposition:
    - HO_x cycle
    - Nitrogen cycle
    - Chlorine cycle
  - HO_x cycle:

Radicals $H^\bullet$, $HO^\bullet$,$HOO^\bullet$ are generated naturally from water vapour, methane and molecular hydrogen;

Radical $HO^\bullet$ contributes to the O_3 decomposition in the lower stratosphere (16 – 20 km) by up to 50 %, but it is predominating at the altitudes above 40 km.

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Nitrogen cycle (discovered in 1970):

    Catalysts X can be NO or NO_2, generated in the stratosphere due to oxidation of N_2O (unlike the troposphere – see the lecture about acidic gases) or they are generated by photodissociation of N_2 and subsequent oxidation:

$$\text{above 30 km: } N_2O + h\nu \xrightarrow{UV} N_2 + O^*$$

$$O^* + N_2O \longrightarrow NO + NO$$

$$\text{above 80 km: } N_2 + h\nu \xrightarrow{UV} N + N$$

$$N + O_2 \longrightarrow NO + O$$

NO$_x$ react with radicals $HO^\bullet$ and $ClO^\bullet$ ⇒ creating collectors of ozone destructive agents having the form of $ClNO_3$ and HNO_3:

$$ClO^\bullet + NO_2 \longrightarrow ClONO_2$$

$$ClONO_2 + h\nu \xrightarrow{UV} ClO^\bullet + NO_2$$

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Chlorine cycle (predicted in 1974, confirmed later):

    Catalysts X are: $ClO^{\bullet}$, Cl

    Sources of Cl can be alternatively chlorinated or chlorofluorinated hydrocarbons (CFC). The mechanism is following:

    Reservoir compounds are accumulated in the stratosphere (HCl, $ClONO_2$)

    On the active surface of an aerosol (see PSC clouds) crystals of $H_2O + HNO_3.3H_2O$ are formed with H_2SO_4 on the top together with a thin layer of a water condensate, where reactions take place

$$ClONO_2\,(g) + H_2O\,(l) \longrightarrow HClO\,(l) + HNO_3\,(l)$$

$$HCl\,(g) \xrightarrow{dissociation\ in\ H_2O\,(l)} H^+ + Cl^-$$

$$Cl^- + HClO\,(l) \longrightarrow Cl_2\,(g) + OH^-$$

$$OH^- + H^+ \longrightarrow H_2O$$

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Chlorine cycle – next step:

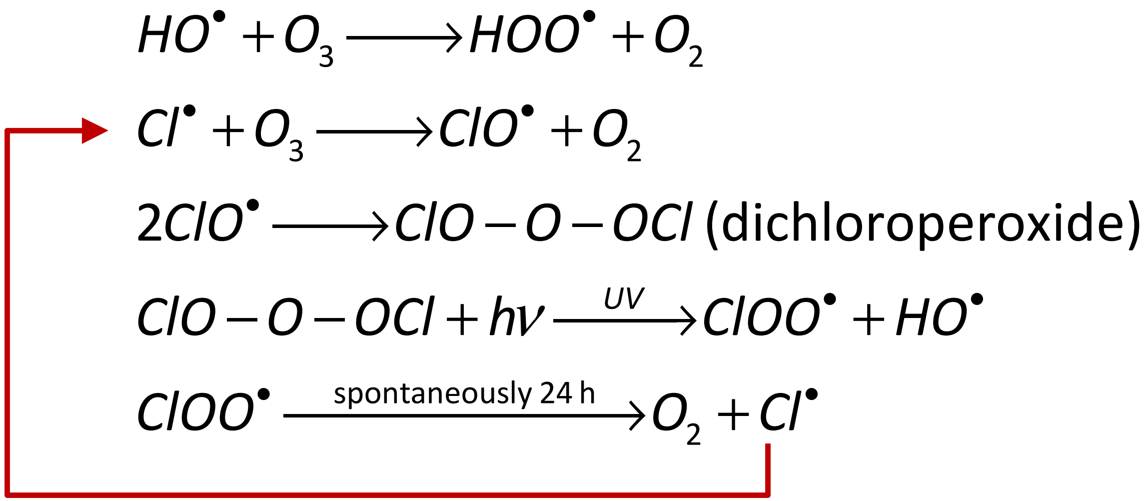
During the polar night accumulation of HClO and Cl_2 occurs;

When the sunrise begins, the photolysis starts:

$$Cl_2\,(g) + h\nu \longrightarrow 2Cl^\bullet$$

$$HClO\,(g) + h\nu \longrightarrow Cl^\bullet + HO^\bullet$$

Initiation of ozone destruction follows:



$$HO^\bullet + O_3 \longrightarrow HOO^\bullet + O_2$$

$$Cl^\bullet + O_3 \longrightarrow ClO^\bullet + O_2$$

$$2ClO^\bullet \longrightarrow ClO-O-OCl \text{ (dichloroperoxide)}$$

$$ClO-O-OCl + h\nu \xrightarrow{UV} ClOO^\bullet + HO^\bullet$$

$$ClOO^\bullet \xrightarrow{\text{spontaneously 24 h}} O_2 + Cl^\bullet$$

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Chlorine cycle – temporary deactivation:

The main process of Cl radicals deactivation is the reaction with NO_2;

Until PSC is present deactivation does not occur – NO_2 is bonded in the PCS crystals as HNO_3;

When PSC disappears, the deactivation starts:

$$HNO_3 + h\nu \longrightarrow NO_2 + HO^\bullet$$

$$ClO^\bullet + NO_2 \longrightarrow ClONO_2$$

At the moment when PSC is formed again, the process of $ClNO_3$ cleavage starts again: $ClONO_2 \rightarrow HClO \rightarrow Cl_2 \rightarrow Cl^\bullet$ and so on!

Warning! Persistence of chlorine reservoirs is roughly 100 years!

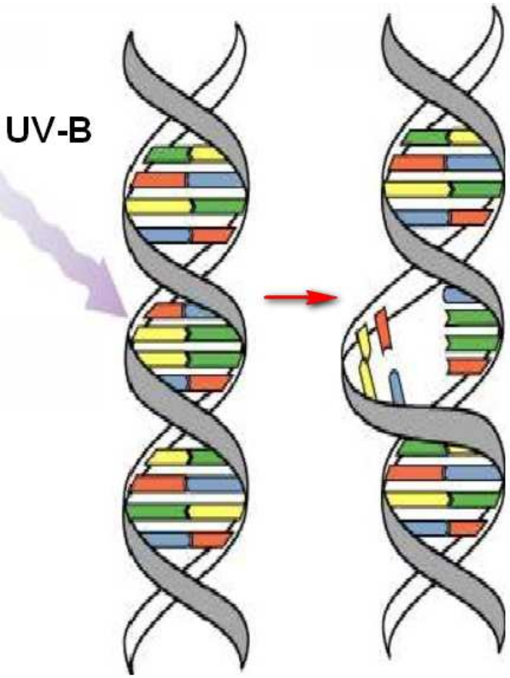
Chemistry of ozone in atmosphere

- **Consequences of ozone layer damaging**
  - Penetration of UV-B radiation on the Earth‘s surface has negative impacts on animals and plants.
  - Impact to skin ⇒ tumours (e.g. melanoma);
  - Impact to eye cornea ⇒ eye tumours + cataract;
  - Impact to plants ⇒ inhibition of photosynthesis
  - Impact to immunity ⇒ decrease of resistance against infections;
  - Influencing aquatic organisms ⇒ extinction of small species living in surface layers = damaging trophic chains.
  - Damaging material property ⇒ accelerated degradation of lacquers, varnishes, plastics and wood.
  - Influencing climate ⇒ changes in structures of temperature distribution in atmosphere and changes in circulation flows.

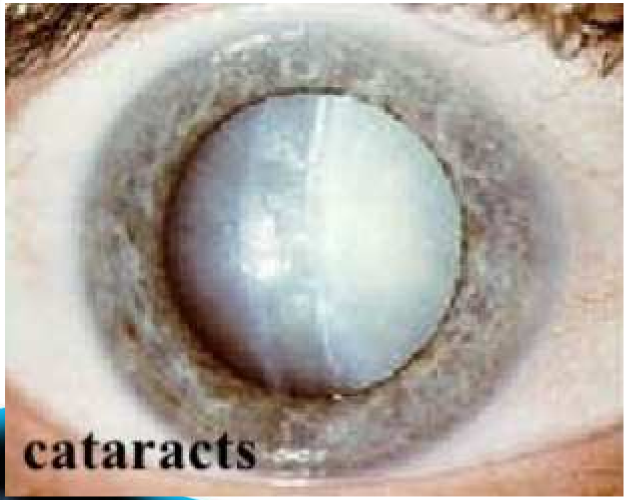
Chemistry of ozone in atmosphere

- **Consequences of ozone layer damaging – exposition to UV-B light**

Extinction of krill



Damaging DNA



Damaging eyes

Background troposphere

- **General rules**
  - Background troposphere = clean troposphere
  - 2 possible meanings of the term „clean troposphere“
  - Mechanistic definition:

    Clean troposphere = part of the troposphere, where the concentration of non-methane hydrocarbons is so low that it does not influence the formation and decay of HO• radical

    HO• radical is then created only by the reaction of excited singlet ^{1D}O with water vapour and is decomposed by the reaction with CH_4 and CO.
  - Environmental definition:
    Clean troposphere = troposphere without anthropogenic pollutants.
  - Different reactions run at day time (photochemical) and at night:

Background troposphere (HO•)

- **Synthesis of hydroxyl radical (lifetime ca. 1 second)**
  - Photolysis of ozone (UV radiation 290 – 360 nm)

    Main mechanism of its formation

    $$O_3 + h\nu \xrightarrow{\lambda\ 290-360\ nm} {}^{3P}O + O_2$$

    $$O_3 + h\nu \xrightarrow{\lambda\ 319\ nm} {}^{1D}O + O_2$$

    $${}^{1D}O + H_2O \longrightarrow 2HO^\bullet$$

    ^{1D}O very unstable ⇒ at relative air humidity 50 % only 4.5 % atoms of ^{1D}O are converted to HO$^\bullet$

  - Photolysis of nitrous acid (UV radiation < 400 nm)

    Minority mechanism

    $$HNO_2 + h\nu \xrightarrow{\lambda < 400\ nm} HO^\bullet + NO$$

  - Photolysis of hydrogen peroxide (UV radiation < 370 nm)

    Minority mechanism

    $$H_2O_2 + h\nu \xrightarrow{\lambda < 370\ nm} 2HO^\bullet$$

Background troposphere (HO•)

- **Decomposition of hydroxyl radical (lifetime ca. 1 second)**
  - Reaction with methane or CO

    Dominating mechanism of decomposition

$$HO^{\bullet} + CH_4 \longrightarrow H_3C^{\bullet} + H_2O$$

$$HO^{\bullet} + CO \longrightarrow CO_2 + H^{\bullet}$$

Due to anthropogenic emissions of CO and hydrocarbons ⇒ on the northern hemisphere, the concentration of HO• radicals is by 20 % lower;

- **Regeneration of hydroxyl radical**
  - Reaction of hydroperoxyl radical with nitrogen monoxide

    Dominating mechanism

$$HOO^{\bullet} + NO \longrightarrow NO_2 + HO^{\bullet}$$

Background troposphere (HOO•)

- **Synthesis of hydroperoxyl radical**
  - Reaction of hydrogen radical with oxygen

    (second phase of HO• decomposition)

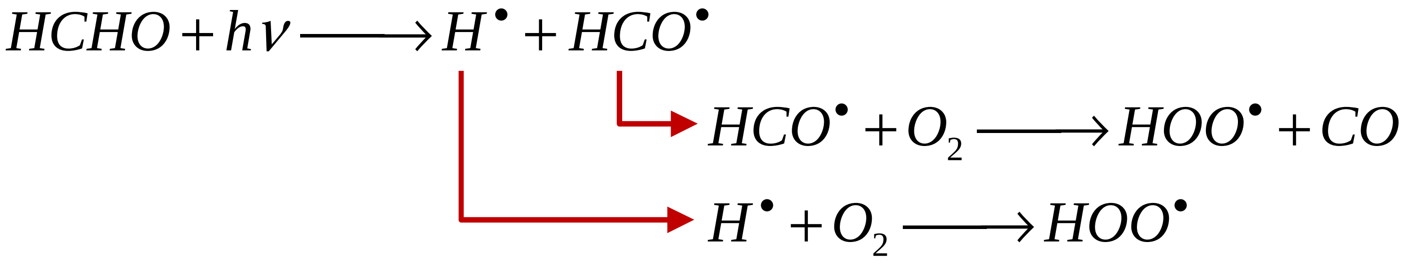
    Main mechanism

$$HO^{\bullet} + CO \longrightarrow CO_2 + H^{\bullet}$$

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet}$$

  - Photolysis of aldehydes (as intermediates of hydrocarbon oxidation)

    Main mechanism



$$HCHO + h\nu \longrightarrow H^{\bullet} + HCO^{\bullet}$$

$$HCO^{\bullet} + O_2 \longrightarrow HOO^{\bullet} + CO$$

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet}$$

Background troposphere (HOO•)

- **Decomposition of hydroperoxyl radical**
  - Reaction with hydroxyl radical

$$HOO^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$$

  - Reaction with another hydroperoxyl radical

$$HOO^{\bullet} + HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

  - Reaction with nitrogen monoxide (see regeneration of hydroxyl radical)

$$HOO^{\bullet} + NO \longrightarrow NO_2 + HO^{\bullet}$$

  - Reaction with ozone (also regeneration of hydroxyl radical)

$$HOO^{\bullet} + O_3 \longrightarrow 2O_2 + HO^{\bullet}$$

Background troposphere

- **Characteristics of day phase of tropospheric reactions**

  - In the clean troposphere low temperature, multiphase oxidation of admixtures, released due to natural processes from the Earth surface in their reduced form.
  - Ozone represents the initial oxidation agent, secondary it is a hydroxyl radical.
  - Following compounds undergo the oxidation:

Methane	CH_4
Carbon monoxide	CO
Formaldehyde	$HCHO$
Nitrogen monoxide and dioxide	NO and NO_2

Background troposphere

- **Natural sources of reactants for tropospheric reactions**
  - Sources of methane

    Biogenic sources
    (anaerobic fermentation)

    Leakages from lithosphere
  - Sources of carbon monoxide

    Oxidation of methane by HO•
    (50 % of the overall CO concentration is generated this way)

    Oxidation of natural terpenes

    Incineration processes

Big emissions of methane – wetlands in Siberia

Coniferous forests – source of natural terpenes

Background troposphere

- **Natural sources of reactants for tropospheric reactions**
  - Sources of nitrogen oxides

    Soil and oceanic processes

    Combustion processes

    Electric discharges

  - Sources of ozone (tropospheric)

    Photochemical reactions

    Transfer from stratosphere

    (only ca. ¼ of the total conc.)

Flash – source of NO_x (and minority of O_3)

Forest fires – source of NO_x

Background troposphere

- **Daytime tropospheric reactions**
  - Reaction of hydroxyl radical with methane

$$CH_4 + HO^\bullet \longrightarrow H_3C^\bullet + H_2O$$

$$H_3C^\bullet + O_2 + M \longrightarrow CH_3OO^\bullet + M$$

subsequent reaction of methylperoxyl radical with nitrogen monoxide

$$CH_3OO^\bullet + NO \longrightarrow NO_2 + CH_3O^\bullet$$

$$CH_3O^\bullet + O_2 \longrightarrow HCHO + HOO^\bullet$$

  - Reaction of hydroxyl radical with carbon monoxide

$$HO^\bullet + CO \longrightarrow CO_2 + H^\bullet$$

$$H^\bullet + O_2 + M \longrightarrow HOO^\bullet + M$$

subsequent reaction of hydroperoxyl radical with nitrogen monoxide

$$HOO^\bullet + NO \longrightarrow NO_2 + HO^\bullet$$

Background troposphere

- **Daytime tropospheric reactions**
  - Reaction of hydroxyl radical with formaldehyde

$$HCHO + HO^{\bullet} \longrightarrow CHO^{\bullet} + H_2O$$

$$CHO^{\bullet} + O_2 \longrightarrow CO + HOO^{\bullet}$$

- **Termination reactions of hydroxyl and hydroperoxyl radical**
  - Reaction of hydroxyl radical with nitrogen dioxide

$$HO^{\bullet} + NO_2 \longrightarrow HNO_3$$

  - Reaction of hydroperoxyl radical with another hydroperoxyl

$$HOO^{\bullet} + HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \longrightarrow 2HO^{\bullet} \quad \text{(only small part)}$$

Hydrogen peroxide represents a temporary collector (reservoir) of hydroxyl radicals.

Background troposphere

- **Night tropospheric reactions**
  - All nitrogen oxides are converted to NO_2, which reacts with ozone.
    Nitrate radical reacts with another nitrogen dioxide.
    Subsequently, dinitrogen pentoxide is formed and converted to the acid:

$$NO_2 + O_3 \longrightarrow NO_3^\bullet + O_2$$

$$NO_3^\bullet + NO_2 + M \longrightarrow N_2O_5 + M$$

$$N_2O_5\ (g) + H_2O\ (l) \longrightarrow 2HNO_3\ (l)$$

  - Nitrate radical is unstable during the day (photolysis to NO or NO_2 depends on λ).
  - During the night, $NO_3^\bullet$ stable $\Rightarrow$ reaction with hydrocarbons (mostly alkenes) and forming alky peroxynitrates.

    Alkyl peroxynitrates react with oxygen to alkylperoxy radicals or they stay unchanged till morning when their photolysis occurs.