

6. Natural photochemical processes

6.1 Atmospheric photochemistry

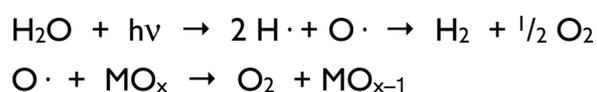
Origin of the current terrestrial atmosphere

Much geological evidence shows that Earth was without a primordial atmosphere. The primitive atmosphere resulted from the volcanic activity and from the bombardement of the Earth's surface by meteorites that caused the degasing of fused rocks. It must have contained mainly N₂, CO₂, and H₂O together with traces of reducing gases, such as H₂, CH₄, NH₃ and CO.

Despite the abundance of oxydes in the terrestrial crust, O₂ is not released by volcanic activity and no oxygen was originally present in the atmosphere. By comparison, the atmospheres of Mars and Venus contain less than 0.1 % O₂.

Gases	Volcanic effluents	Meteorites gases	Present atmosphere
H ₂ O	83 %	80 %	traces
CO ₂	12 %	15 %	0.03 %
N ₂	3 %	5 %	78.0 %
O ₂	0 %	0 %	20.9 %

In the absence of life, the main source of O₂ must have been photolysis of water by UV light ($\lambda < 195 \text{ nm}$):

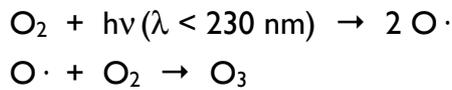


Origin of the current terrestrial atmosphere

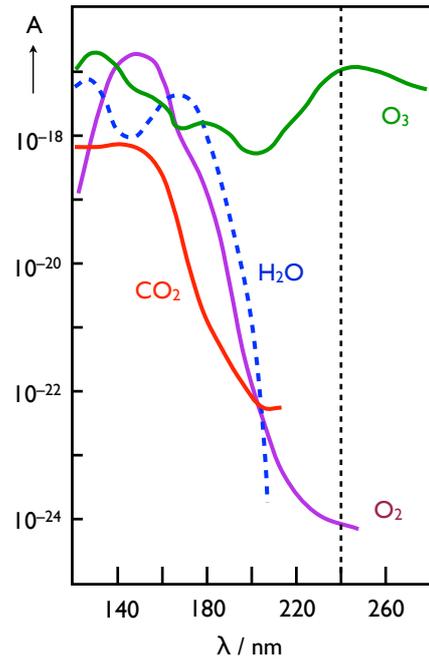
O₂ generated by water photolysis also absorbs UV ($\lambda < 230$ nm) causing a self-screening effect and limiting its concentration to $\sim 0.2\%$. 10^{-3} of the present atmosphere level (PAL) is consistent with geological evidence.

The rapid increase of O₂ concentration in the atmosphere was due to bacterial photosynthesis (cyanobacteria) and later by photosynthesis of blue-green algae during the precambrian era (-3.8 to -0.6 Gy).

Subsequent production of significant amounts of ozone through reactions:

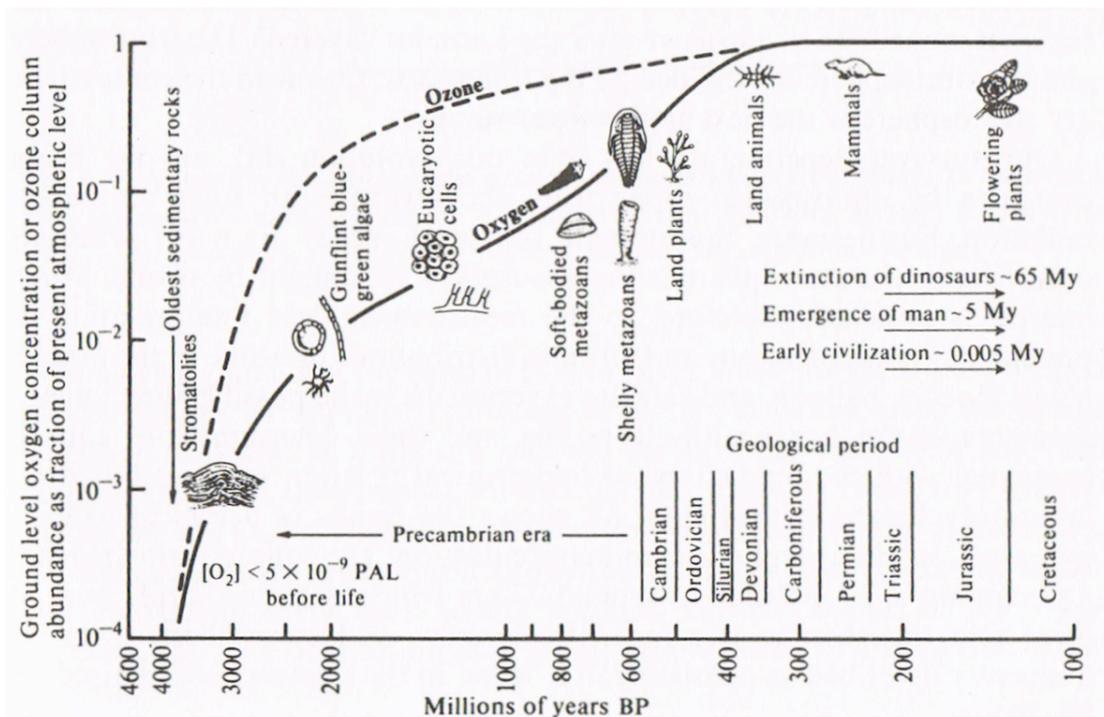


provided an efficient UV filter against nocive radiations ($\lambda < 290$ nm) and allowed for the development of life on dry land (ca. -570 My)



163

Origin of the current terrestrial atmosphere



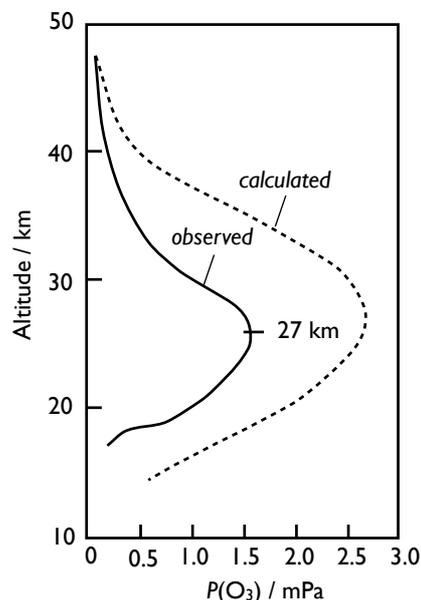
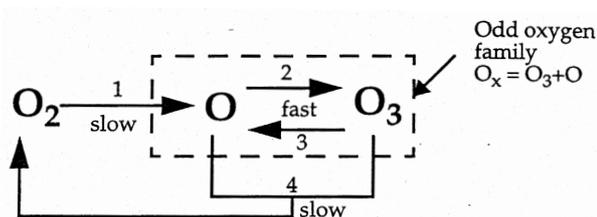
164

Stratospheric photochemistry (based on atomic oxygen)

Stratosphere is the second major layer of Earth's atmosphere, just above the troposphere. It is situated between about 10 km and 50 km altitude above the surface.

Chapman's mechanism for stratospheric ozone (1930)

- 1) $O_2 + h\nu \rightarrow 2 O\cdot \quad (\lambda < 240 \text{ nm})$
- 2) $O\cdot + O_2 \rightarrow O_3$
- 3) $O_3 + h\nu \rightarrow O_2 + O\cdot \quad (320 \text{ nm} > \lambda > 240 \text{ nm})$
- 4) $O\cdot + O_3 \rightarrow 2 O_2$



165

Stratospheric ozone sink

At high altitude, UV irradiation intensity is maximum, while O_2 concentration is low. The opposite is true at lower altitude. A peak of maximum O_3 concentration is thus observed at an altitude of 27 km.

The shape of the ozone partial pressure profile calculated from Chapman's kinetic model is verified experimentally. However, measured absolute concentrations are lower by a factor 2-3. This effect is due to the catalysis of reaction 4 by traces of various X species:

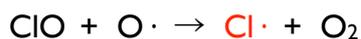
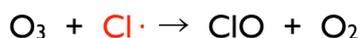
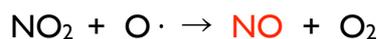
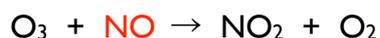
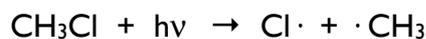
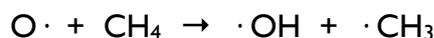
- 5) $X + O_3 \rightarrow XO + O_2$
- 6) $XO + O\cdot \rightarrow X + O_2$

At altitudes $h < 30 \text{ km}$, O_3 depletion is mainly due to $X = NO\cdot$ species. Above 30 km, the process is dominated by reaction with $\cdot OH$ radicals.

Precursors of these ozone-depleting substances (ODS) can be considered as being of natural origin. H_2O , CH_4 , N_2O and CH_3Cl may indeed be converted into catalytic X radicals within the stratosphere by reaction with $O\cdot$ atoms produced by the UV photolysis of ozone: $O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O\cdot(^1D)$.

166

Stratospheric ozone depletion



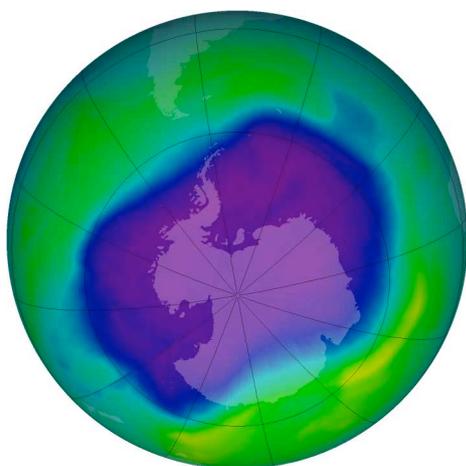
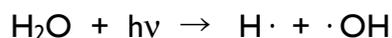
N_2O also stems from the use of fertilizers and must then be considered as being a pollutant of human origin.

Chlorine atoms $\text{Cl}\cdot$ are particularly efficient in catalyzing O_3 destruction. These atoms are essentially produced by the UV photolysis of chlorofluorocarbons (CFC, freons). Freon molecules, which were intensively used until they were banned by the Montréal protocol in 1987, slowly diffuse into the stratosphere, where they are photodissociated: $\text{CF}_2\text{Cl}_2 + h\nu \rightarrow \cdot\text{CF}_2\text{Cl} + \text{Cl}\cdot$

167

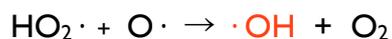
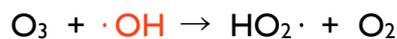
Ozone layer depletion

Over Antarctica, stratospheric clouds result from strong winds blowing around the continent during the austral winter forming a polar vortex. These clouds are constituted of ice micro-crystals. UV photolysis of H_2O produces $\cdot\text{OH}$ radicals and $\text{H}\cdot$ atoms at the surface of ice:



False color satellite picture of the antarctic ozone hole (NASA, Sept. 2006)

These two radical species present at the ice/air interface also act as catalysts of the decomposition of O_3 through homogeneous and heterogeneous mechanisms.



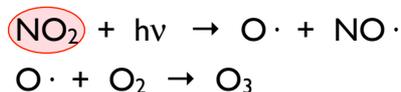
This natural photochemical process occurring over Antarctica is at the origin of the so-called winter ozone hole.

168

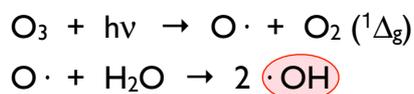
Tropospheric photochemistry (based on ·OH radicals)

About 90% of the total atmospheric mass resides in the troposphere. The Earth's surface acts as the main source of pollutant gases, although some NO_x and CO may be produced by thunderstorms. Hydroxyl radicals dominate the chemistry of the troposphere in the same way that oxygen atoms and ozone dominate stratospheric chemistry.

Stratospheric ozone layer filter limits the solar irradiation at the Earth's surface to wavelengths longer than 280 nm. At these wavelengths, the most photochemically active species are O₃, NO₂ and formaldehyde CH₂O. All three can yield ·OH or HO₂· indirectly. Ozone photolysis is, however a critical step. Some O₃ is transported from the stratosphere to the troposphere, but a mechanism also exist for generation of ozone in the troposphere itself.



NO· can be oxidized back to NO₂, as we shall see shortly. The formation of O₃, thus, is not stoichiometrically limited by the supply of NO₂.

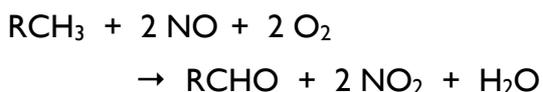
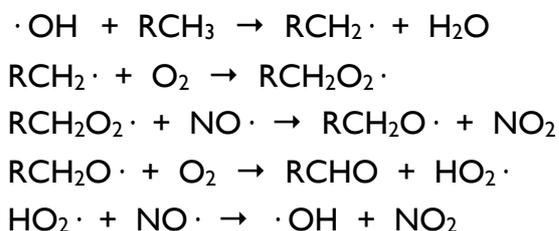


free radical chain initiator

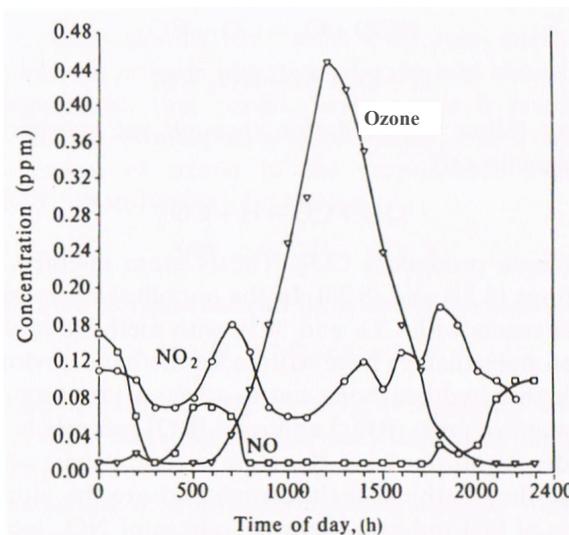
169

Tropospheric photochemistry

A first understanding of tropospheric photochemistry may be gained by considering RCH₃ as the only hydrocarbon pollutant. Attack of hydroxyl radicals on RCH₃ yields alkyl radicals and a sequence of oxidation steps yielding the aldehyde RCHO:



Hydroxyl radicals and NO₂ are regenerated within this cycle. Since NO₂ is the source of ozone photoproduction, the concentration of O₃ remains stationary.

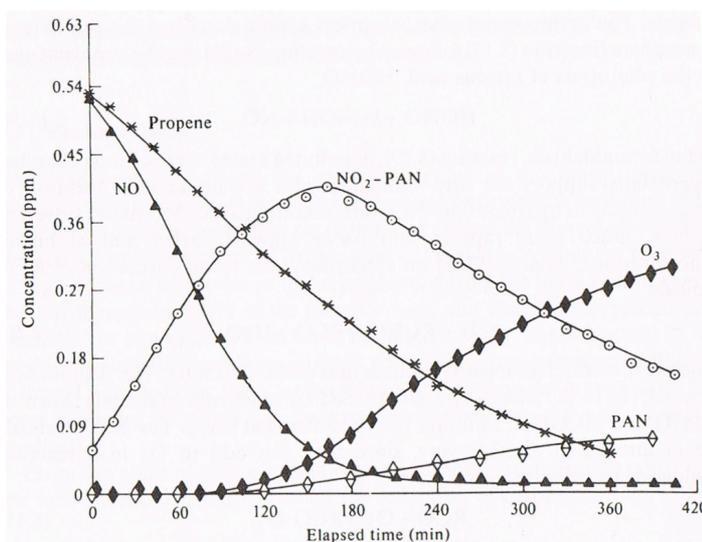
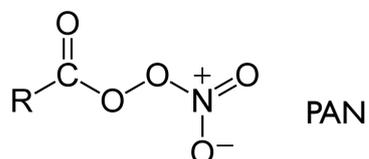
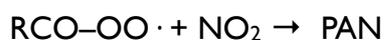
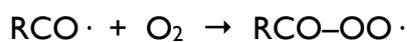
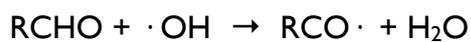


Variations in concentrations of O₃ and NO_x during the course of a smoggy day in Southern California

170

Tropospheric photochemistry

The aldehyde product can itself be photolyzed at $\lambda \leq 338$ nm. It can also react further with $\cdot\text{OH}$ radicals and NO_2 to yield peroxyacyl nitrate (PAN), which constitutes the irritating compound present in Summer smogs resulting from simultaneous air pollution and intense solar irradiation.



Concentration time-profiles of the major primary and secondary pollutants during irradiation of 0.53 ppm propene and 0.59 ppm NO_x in 1 atm of purified air in an evacuable smog chamber.