Atmospheric Chemistry
Oxidizing capacity of the troposphere

Erik Swietlicki
Avd. för Kärnfysik
Fysiska institutionen
Lunds universitet

Tropospheric chemistry

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.
Tropospheric chemistry

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

\[
CO + OH \rightarrow H + CO_2 \\
\ldots \ldots \rightarrow O_3
\]

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

Movie:
Example of how important oxidants are for life on Earth.
Concentrations of CO soon rise to toxic levels when left in the atmosphere.

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 involves radical species, not \( O_2 \) och \( O_3 \).
**Tropospheric chemistry**

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

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".

---

**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, $SO_2$).
Oxidants in the troposphere

The most important tropospheric oxidants are OH and other radicals in the HOx family (OH, HO2, RO, RO2).

OH: Hydroxyl radical, HO2: Hydroperoxyl radical
RO: Organic oxyl radical, RO2: Organic peroxyl radical

These radicals are formed in the troposphere in reactions that start with photolysis of ozone (radical initiation).

Initiation of the radical chain:
non-radical + hν → radical + radical’ (two unpaired electrons in total)

Propagation:
radical + non-radical → radical’ + non-radical’

Termination:
radical + radical’ → non-radical + non-radical’
radical + radical’ + M → non-radical + M

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 O2 (λ < 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.
Ozone production in the troposphere

**The only way to produce ozone is via**

\[ \text{O} + \text{O}_2 + M \rightarrow \text{O}_3 + M \]

with molecular oxygen \( \text{O}_2 \) and atomic oxygen \( \text{O} \) in its ground state \( \text{O}(^3P) \),

This means that \( \text{O} \) has to be produced first.

**Photolysis of \( \text{O}_2 \) does **not** occur in the troposphere** (no UVc).

\[ \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \quad (\lambda < 240 \text{ nm, UV}) \]

**There must therefore be other sources of \( \text{O} \) in the troposphere.**

Main source of \( \text{O} \) in the troposphere is via photolysis of \( \text{NO}_2 \)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad (\lambda < 420 \text{ nm}) \]

**This reaction is very important for the tropospheric chemistry!**
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, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.

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

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.
**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 $OH)$

Prerequisite: Production of excited atomic oxygen $O^{1D}$

---

**Hydroxyl radical OH**

Production of hydroxyl radicals $OH$ proceeds via three reactions:

(a) $O_3 + h\nu^{H_2O} \rightarrow 2OH + ...$
(b) $HO_2 + NO \rightarrow OH + ...$
(c) $HONO + h\nu \rightarrow OH + ...$

Reaction (a) dominates in background air ("low" $NO_x$, high RH).

Reaction (b) dominates in polluted air (high $NO_x$).

Reaction (c) from HONO only of importance at sunrise since HONO is rapidly photolyzed (within 10 min - 1 h).
Hydroxyl radical OH responds quickly to UV

\[ O_3 + h\nu \rightarrow H_2O + 2OH + \ldots \]

OH has short lifetime (~1 s).

Production of the hydroxyl radical OH

Production of \( O(^1D) \) 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\(^{-1} \))

- **Cross Section (Absorptionstvärsnitt) \( \sigma \)**
  "Target area" per molecule within which the photon is absorbed (m\(^2 \) \cdot molecule\(^{-1} \))

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

- **Photolysis rate constant \( k \)**:
  \[ k = q \sigma I \] (s\(^{-1} \), wavelength dependent)

\[ J(O^1D) = \text{Measured } O_3 \text{ photolysis rate (} \lambda < 320 \text{ nm)} \]

**Measured OH concentrations**

**Cloud passing**

Time of day [ UT ]

Oxidation - troposphere
**Ozone photolysis in the troposphere**

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \]  
(Excited atomic oxygen, \( \lambda < 320 \text{ nm} \))

**Exercise:**

Calculate the photolysis rate constant \( k \)

\[ k = q_x \cdot \sigma_x \cdot I \quad (\text{s}^{-1}, \text{wavelength dependent}) \]

Perform calculations in intervals centered around 295, 305, 315 and 325 nm.

---

**Photolysis**

Absorption cross section: \( \sigma_x \) (m²·molecule⁻¹)

Actinic Flux (Ljudsööde): \( I \)
Number of photons crossing the unit horizontal area per unit time (photons · m² · s⁻¹)

Quantum Yield (Kvantutbyte): \( q_x \)
Probability that absorption of a photon will cause photolysis of \( X \) (molecules · photon⁻¹)

Photolysis rate constant \( k \):

\[ k = q_x \cdot \sigma_x \cdot I \quad (\text{s}^{-1}, \text{wavelength dependent}) \]
Ozone photolysis in the troposphere

\[ O_3 + h\nu \rightarrow O_2 + O(1D) \quad \text{(excited atomic oxygen, } \lambda < 320 \text{ nm)} \]

Photolysis rate constant \( k \):

\[ k = q_x \cdot \sigma_x \cdot I \quad \text{(s}^{-1}, \text{wavelength dependent)} \]

- **Ozone Photolysis Quantum Yield**: Probability that absorption of a photon will cause photolysis.
- **O$_2$ UV Absorption Cross Sections**: "Target area" for the molecule within which the photon is absorbed.

Graphs showing actinic flux, photon flux, ozone photolysis quantum yield, and ozone UV absorption cross sections.
Oxidation - troposphere

### Ozone photolysis in the troposphere

**Photolysis of \( \text{O}_3 \) in the troposphere**

\[
\text{O}_3 + h \nu \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \quad \text{(excited atomic oxygen, } \lambda < 320 \text{ nm)}
\]

\( k = q \sigma l \) where \( q, \sigma \) and \( l \) all vary with the wavelength of light.

- **295 nm:** \( q = 0.95, \sigma = 8 \times 10^{-10} \text{ cm}^2 \text{ molecules}^{-1}, l = 1 \times 10^{10} \text{ photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1} \)
  \( k \approx 7.3 \times 10^{-5} \text{ s}^{-1} \text{ nm}^{-1} \). Note that the unit is s\(^{-1}\) nm\(^{-1}\) since this value only represents a small wavelength interval around 295 nm.

- **305 nm:** \( q = 0.94, \sigma = 2 \times 10^{-10} \text{ cm}^2 \text{ molecules}^{-1}, l = 1.6 \times 10^{10} \text{ photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1} \)
  \( k \approx 2.9 \times 10^{-4} \text{ s}^{-1} \text{ nm}^{-1} \).

- **315 nm:** \( q = 0.25, \sigma = 5 \times 10^{-20} \text{ cm}^2 \text{ molecules}^{-1}, l = 6.9 \times 10^{12} \text{ photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1} \)
  \( k \approx 9.2 \times 10^{-6} \text{ s}^{-1} \text{ nm}^{-1} \).

- **325 nm:** \( q = 0, \sigma = 1.6 \times 10^{-20} \text{ cm}^2 \text{ molecules}^{-1}, l = 1.2 \times 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1} \)
  \( k = 0 \text{ s}^{-1} \text{ nm}^{-1} \).

Integrate over all wavelengths, that is \( k = q \sigma I \) where \( q, \sigma \) and \( I \) all vary with the wavelength of light.

- **295 nm:** \( q = 0.95, \sigma = 8 \times 10^{-10} \text{ cm}^2 \text{ molecules}^{-1}, I = 1 \times 10^{10} \text{ photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1} \)
  \( k \approx 7.3 \times 10^{-5} \text{ s}^{-1} \text{ nm}^{-1} \). This yields \( k_{\text{O3}} = 3.9 \times 10^{-5} \text{ s}^{-1} \). If one integrates (sums) only for 305 and 315 nm, you get almost the same result; \( k_{\text{O3}} = 3.86 \times 10^{-5} \text{ s}^{-1} \).

Hydroxyl radical OH

**Production of hydroxyl radicals \( \text{OH} \) via \( \text{O}_3 \)**

1. \( \text{O}_3 + h \nu \rightarrow \text{O}_2 + \text{O}(^\text{1D}) \) \ (excited atomic oxygen, \( \lambda < 320 \) nm)
2. \( \text{O}(^\text{1D}) + \text{M} \rightarrow \text{O}(^\text{3P}) + \text{M} \) \ (90%) or
3. \( \text{O}(^\text{1D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \) \ (10%, one \( \text{O}_3 \) gives two \( \text{OH} \))

**Prerequisite:** Production of excited atomic oxygen \( \text{O}(^\text{1D}) \) short-lived \( \rightarrow \) Assume "steady state" for \( \text{O}(^\text{1D}) \) →

\[
0 = \frac{d}{dt} [\text{O}(^\text{1D})] = k_1 [\text{O}_3] - k_2 [\text{O}(^\text{1D})][\text{M}] - k_3 [\text{O}(^\text{1D})][\text{H}_2\text{O}] \\
[\text{O}(^\text{1D})] = \frac{k_1 [\text{O}_3]}{k_2 [\text{M}] + k_3 [\text{H}_2\text{O}]} 
\]
Hydroxyl radical OH

Production of the hydroxyl radical OH

\[
\frac{d}{dt}[OH] = 2k_2[O(D)]H_2O = \frac{2k_2k_3[M][H_2O]}{k_2[M] + k_3[H_2O]} \approx \frac{2k_2k_3}{k_2[M]}[O_3H_2O]
\]

(2) Faster than (3), \([M] > [H_2O]\)

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.

Hydroxyl radical OH – Modelling

The 3-dimensional global chemistry transport model GEOS-CHEM

http://www.chem.leeds.ac.uk/Atmospheric/Field/age/modelling.html
**Lifetime for the hydroxyl radical OH**

OH lifetime $\tau_{OH}$ in the troposphere can be estimated by knowing the most important sinks $i$

$$\tau_{OH} = \frac{1}{\sum_i k_i n_i}$$

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) $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + H$
(5) $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$

$\tau_{OH} =$ seconds ($\tau_{CO} =$ 1-4 months, $\tau_{CH_4} = \sim$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$_X$ (= 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 of carbon monoxide – high NOx

Catalytic ozone production:

\[ \text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2 \]
\[ \text{H} + \text{O}_2 (+M) \rightarrow \text{HO}_2 (+M) \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]
\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]
\[ \text{O} + \text{O}_2 (+M) \rightarrow \text{O}_3 (+M) \]

(Net): \[ \text{CO} + 2\text{O}_2 + h\nu \rightarrow \text{CO}_2 + \text{O}_3 \]

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(1D) \quad \text{oeh} \quad \text{O}(1D) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]

Each cycle produces one net \( \text{O}_3 \) or \( 2\text{OH} \).

Oxidation of carbon monoxide – high NOx

Each cycle produces one net \( \text{O}_3 \) or \( 2\text{OH} \). These \( 2\text{OH} \) can in turn give \( 2\text{O}_3 \) or \( 4\text{OH} \) and so on. \( \text{O}_3 \) is autocatalytic.

One carbon atom is also oxidized from C(+II), \( \text{CO} \), to C(+IV), \( \text{CO}_2 \).

(Net): \[ \text{CO} + 2\text{O}_2 + h\nu \rightarrow \text{CO}_2 + \text{O}_3 \]
Oxidation of carbon monoxide – low NO\textsubscript{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 net O\textsubscript{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 of methane

Catalytic ozone production:

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]
\[ \text{CH}_3 + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{O}_2 (+\text{M}) \]
\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]
\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]

(Net): \( \text{CH}_4 + 2\text{O}_2 + 2\text{NO} \rightarrow \text{HCHO} + 2\text{NO}_2 + \text{H}_2\text{O} \)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]
\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \quad \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]

Each cycle produces net 2\( \text{O}_3 \) or 4\( \text{OH} \).
CH₄ → HCHO → CO → CO₂

methane C(-IV) → formaldehyde C(0) → carbon monoxide C(II) → CO₂ C(IV)

Oxidation of hydrocarbons RH

Examples: Alkanes RH
RH + OH → R + H₂O
R + O₂ (+M) → RO₂ (+M)
RO₂ + NO → RO + NO₂
RO + O₂ → RXO₂ + HO₂
HO₂ + NO → OH + NO₂

(Net) RH + 2O₂ + 2NO → RHO₂ + 2NO₂ + H₂O

NO₂ + hν → NO + O O + O₂ → O₂
O₃ + hν → O₂ + O(¹D) O(¹D) + H₂O → 2OH

Each cycle produces net 2O₃ or 4OH.
Oxidation of hydrocarbons

(Net):
\[ RH + 2O_2 + 2NO \rightarrow R\cdot H_O + 2NO_2 + H_2O \]

Each cycle gives net 2 \( O_3 \) eller 4 \( OH \).

Fast radical chemistry

Hydrocarbons are combusted in the presence of nitrogen oxides \( NO_x \) under solar radiation and results in \( O_3 \) formation.
Oxidation of hydrocarbons

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

Hydrocarbon $\rightarrow$ aldehyde $\rightarrow$ organic acid $\rightarrow$ carbon monoxide $\rightarrow$ CO$_2$

$RH \rightarrow R_HO \rightarrow RCOOH \rightarrow CO \rightarrow CO_2$

Oxidation number for carbon atom:
C(-IV) $\rightarrow$ C(0) $\rightarrow$ C(+II) $\rightarrow$ C(+II) $\rightarrow$ C(+IV)

Termination

Termination (aldehyde, keton)
**Oxidants in the troposphere**

$\text{NO}_2$ and solar radiation controls the production of $\text{O}_3$, which in turn controls the production of $\text{HO}_x$ radicals, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.

![Diagram showing the process of oxidation in the troposphere](image)

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

**Oxidizing capacity of the troposphere**

---

**Sources of NO\textsubscript{x}**

<table>
<thead>
<tr>
<th>Source</th>
<th>Source (Tg N/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel combustion</td>
<td>21 (45%)</td>
</tr>
<tr>
<td>Biomass combustion</td>
<td>12 (25%)</td>
</tr>
<tr>
<td>Soils</td>
<td>6 (13%)</td>
</tr>
<tr>
<td>Lightning</td>
<td>3 (7%)</td>
</tr>
<tr>
<td>Oxidation of $\text{NH}_3$</td>
<td>3 (7%)</td>
</tr>
<tr>
<td>Air traffic</td>
<td>0.5 (1%)</td>
</tr>
<tr>
<td>Transport from the stratosphere</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>~46</td>
</tr>
</tbody>
</table>
**Sources of NO\textsubscript{x}**

Anthropogenic sources of NO\textsubscript{x} (caused by human activities) dominate compared to the natural sources.

Levels of NO\textsubscript{2} measured from a satellite.

**Sinks for NO\textsubscript{x}**

NO\textsubscript{x} is mainly emitted as NO (at high temperatures).

NO\textsubscript{x} is cycled between NO and NO\textsubscript{2} (~1 minute).

1. \(\text{NO}_2 + h\nu \rightarrow \text{NO} + O \) \((\lambda < 420 \text{ nm})\)
2. \(\text{O} + \text{O}_2 + M \rightarrow \text{O}_3 + M\) \((\text{only way to produce O}_3)\)
3. \(\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2\)

Net reaction:

\[\text{NO}_2 + \text{O}_2 \overset{h\nu}{\leftrightarrow} \text{NO} + \text{O}_3\]

This however is no sink for NO\textsubscript{x}.
Sinks for NOx

Apart from removal of HOX radicals, the catalytic ozone production cycle can also be broken by removing NOX.

\[(30) \quad \text{NO}_2 + OH + M \rightarrow \text{HNO}_3 + M \quad \text{(daytime)}\]

Nighttime:
\[(31) \quad \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(NO}_3 \text{ rapidly photolyzed)}\]
\[(32) \quad \text{NO}_3 + \text{NO}_2 + M \rightarrow \text{N}_2\text{O}_5 + M \quad \text{(N}_2\text{O}_5 \text{ water-soluble)}\]
\[(33) \quad \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad \text{(on an aerosol particle)}\]

\[\tau_{\text{NO}_x} = \sim1 \text{ day}\]

\text{HNO}_3 \text{ is very water-soluble and is washed out by precipitation (wet deposition).} \]
\text{HNO}_3 \text{ is not a long-term reservoir for NO}_x \quad (\tau_{\text{HNO}_3} = \text{days}).

PAN - Reservoir for NOx

Peroxyacetylinitrate (PAN) is an efficient reservoir for NOx.
\[\text{PAN} = \text{CH}_3\text{C(O)OO}_2\]

PAN enables NOx to be transported long distances and contribute to the levels of NOx 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 NO2. Levels of PAN in polluted air can reach 1 ppb.

PAN is thermally unstable.

\[(37) \quad \text{heat} \quad \text{PAN} \rightarrow \text{CH}_3\text{C(O)OO} + \text{NO}_2\]

\[\tau_{\text{PAN}} = \sim1 \text{ hour at } 295 \text{ K (lower troposphere)}\]
\[\tau_{\text{PAN}} = \text{months at } 250 \text{ K (upper troposphere)}\]
Oxidation - troposphere

Ozone production in the troposphere is limited by the reactions

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  
(70% globally)

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]  
(20% globally)

\[ \text{RO}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]  
(10% globally)

followed by

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \text{and} \quad \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]

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

Ozone loss in the troposphere is limited by the reactions

\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  
(40% globally, photolysis of \( \text{O}_3 \))

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]  
(40% globally)

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]  
(10% globally)

Dry deposition of ozone is also a significant sink.
Global models of tropospheric ozone

Anthropogenic modifications of the troposphere
Modelled net O$_3$ production rates (ppbv/day)

Annual mean distribution of net O$_3$ 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.
Tropospheric O$_3$ production and loss rates (ppbv/day) below 250 hPa (10 km) as a function of NO$_x$ (pptv) for 1900, 2000, and 2100.

The critical NO$_x$ value for O$_3$ production occurs where net production (P-L) crosses zero, doubling between 1900 (28 pptv) and 2100 (55 pptv).


**The Master Chemical Mechanism**

http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html

A searchable compilation of chemical reactions of atmospheric importance.

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

http://jpldataeval.jpl.nasa.gov/
http://jpldataeval.jpl.nasa.gov/download.html

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