Gaseous Pollutants

- General considerations on gaseous air pollutants
- Oxidizing power of the atmosphere and chemical reactivity
- Gas-phase chemistry of photochemical air pollution
- Emission control strategies
- Chemical kinetic mechanisms for air pollution modeling
Different Phases in the Atmosphere

• Gases
  – Main gases (N₂, O₂)
  – Trace gases (pollutants)
• Liquid water
  – Cloud and fog droplets
  – Rain drops
• Solid water
  – Ice
  – Snow
• Particles
  – Solid
  – Liquid
Molecules: for example, NO, NO$_2$, O$_3$, etc.; chemically stable species
Radicals: for example, OH, HO$_2$, NO$_3$, etc.; very reactive species, very low concentrations
Atoms: for example, O$^{3P}$, Hg$^0$; reactive or stable species, depending on their electronic state
Excited species: for example, O$^{1D}$; highly reactive species, very low concentrations

\[
\text{NO} + \text{HO}_2 \Rightarrow \text{NO}_2 + \text{OH}
\]

molecule \hspace{1cm} radical \hspace{1cm} molecule \hspace{1cm} radical
Types of Chemical Species

- Pollutants: adverse health and environmental effects
- Precursors: chemical species that produce a pollutant via a chemical reaction
- Oxidants: chemical species that oxidize other species

\[ \text{NO} + \text{HO}_2 \Rightarrow \text{NO}_2 + \text{OH} \]

preursor oxidant pollutant
Ideal Gas Law

Ideal gas law:

\[ P \ V = n \ R \ T \]

\( P \) (atm): Atmospheric pressure
\( V \) (m\(^3\)): Volume of air
\( T \) (K): Temperature
\( R = 8.31 \) J K\(^{-1}\) mole\(^{-1}\) = 8.2 x 10\(^{-5}\) atm m\(^3\) K\(^{-1}\) mole\(^{-1}\): Ideal gas law constant
\( n \) (moles): number of moles

At \( P = 1 \) atm and \( T = 298 \) K (25 ° C): \( n / V = 40.9 \) moles / m\(^3\)

\( N = 6.02 \times 10^{23} \) molecules per mole ; 1 atm = 2.46 x 10\(^{25}\) molec m\(^{-3}\)
Unit Conversions

1 atm = 2.46 x 10^{25} \text{ molecules m}^{-3} = 40.9 \text{ moles / m}^{3}

At $P = 1$ atm:
1 ppb = $10^{-9}$ atm = $2.46 \times 10^{10}$ molecules cm$^{-3}$ \hspace{1cm} (ppb: parts per billion)

Conversion of $\mu$g/m$^3$ to ppb
(MW is the molar weight of the chemical species in g/mole):

1 $\mu$g/m$^3$ = $10^{-6}$ / MW mole/m$^3$ = $10^{-6}$/ (40.9 MW) atm = $10^3$ / (40.9 MW) ppb

1 ppb = (40.9 MW) / $10^3$ $\mu$g/m$^3$

For example, for ozone (MW = 48 g/mole): 1 ppb = 2 $\mu$g/m$^3$
Pollutant Categories

- $\text{NO}_x$: NO and NO$_2$
- $\text{NO}_y$: all nitrogen oxides (except N$_2$O), i.e., NO, NO$_2$, NO$_3$, HNO$_3$, HNO$_2$, N$_2$O$_5$, organic nitrates
- $\text{NO}_z$: $\text{NO}_y$ - $\text{NO}_x$
- $\text{SO}_x$: SO$_2$, SO$_3$, and H$_2$SO$_4$
- $\text{VOC}$: volatile organic compounds, i.e., alkanes, alkenes, aldehydes, alcohols, aromatic compounds, etc.
- $\text{HC}$: hydrocarbons (organic compounds with C and H)
- $\text{NMHC}$: non-methane hydrocarbons
Primary and Secondary Pollutants

- Primary pollutants: they are emitted directly into the atmosphere
  - NO and NO\textsubscript{2} (NO\textsubscript{x}), SO\textsubscript{2}, VOC (for example, HCHO, C\textsubscript{6}H\textsubscript{6}), etc.

- Secondary pollutants: they are formed in the atmosphere via chemical reactions
  - O\textsubscript{3} (formed from NO\textsubscript{x} and VOC), NO\textsubscript{2}, HCHO, H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3}, etc.
Main Gaseous Pollutants

- **Sulfur dioxide (SO\textsubscript{2}):** Regulated air pollutant (respiratory health effects) and precursor of secondary particulate matter (PM) and sulfuric acid (contributor to acid rain)
- **Carbon monoxide (CO):** Regulated air pollutant (anoxia) and precursor of ozone
- **Ozone (O\textsubscript{3}):** Regulated secondary pollutant (respiratory health effects)
- **Nitrogen oxides (NO and NO\textsubscript{2}):** Precursors of secondary PM, ozone, and nitric acid (contributor to acid rain), precursor of nitrogenous species contributing to eutrophication, NO\textsubscript{2} is a regulated air pollutant (respiratory health effects)
- **Volatile organic compounds (VOC):** Precursors of secondary PM and ozone, some VOC are carcinogenic
- **Semi-volatile organic compounds (SVOC):** Precursors of secondary PM
- **Ammonia (NH\textsubscript{3}):** Precursor of secondary PM
Urban Air Pollution

Urban air pollution is due to gaseous and particulate (aerosols) air pollutants.

Air pollution has adverse effects on health, atmospheric visibility, vegetation, and materials.

Currently, emissions of $\text{SO}_2$ and CO from vehicles and industries are regulated in North America and Europe and the corresponding ambient concentrations have decreased considerably over the past decades.

Today, the focus of urban air quality policies for gaseous air pollutants concerns mostly ozone ($\text{O}_3$) and nitrogen dioxide ($\text{NO}_2$).
Photochemical “Smog”

“Smog”: Smoke + fog

Pollutants + solar radiation => photochemical pollution

Photochemical smog:
- Gaseous pollutants (ozone, nitrogen dioxide, formaldehyde, acroleine …)
- Particles
Some pollutants have a lifetime of several days and can, therefore, be transported over long distances by the wind and thereby contribute to continental and regional background pollution.

Urban pollution results not only from pollutant emissions from local sources but also from the long-range transport of pollutants from distant sources.
Importance of Atmospheric Ozone

- Radiative properties in the stratosphere: Problem of the destruction of the stratospheric ozone layer

- Air pollutant in the lower atmosphere (troposphere): adverse health effects (pulmonary irritant) and damage to vegetation

- Greenhouse gas

- Precursor of the hydroxyl radical, OH, which is the main oxidant in the atmosphere
Daytime Chemistry and Nighttime Chemistry

• Daytime chemistry:
  – Photolysis => atoms and radicals => high reactivity of the atmosphere

• Nighttime chemistry
  – No photolysis => few radicals => low reactivity of the atmosphere
Stratosphere and Troposphere

- **Stratosphere**:
  - $O_2$ and $O_3$ absorb ultraviolet solar radiation ($\lambda < 290$ nm)
  - Source of atomic oxygen to form $O_3$:
    $$O_2 + h\nu \Rightarrow O + O \quad \lambda < 242 \text{ nm}$$

- **Troposphere**
  - Solar radiation, which is effective for photolysis, is in the range:
    $$290 \text{ nm} < \lambda < 730 \text{ nm}; \text{i.e., there is no } O_2 \text{ photolysis.}$$
  - Source of atomic oxygen to form $O_3$:
    $$NO_2 + h\nu \Rightarrow NO + O \quad 300 < \lambda < 420 \text{ nm}$$
Stratosphere and Troposphere

Actinic flux as a function of wavelength at different altitudes in the atmosphere

Source: DeMore et al., 1997, Publication 97-4, Jet Propulsion Laboratory, Pasadena, California.
Oxidizing Power of the Atmosphere

- Production of OH
  - Ozone photolysis leads to OH production:

\[
O_3 + hv (\lambda < 310 \text{ nm}) \rightarrow O_2 + O(^1D)
\]

The excited oxygen atom becomes stable by reaction with a molecule:

\[
O(^1D) + M \rightarrow O(^3P) + M
\]

\[
O(^1D) + H_2O \rightarrow 2 \text{ OH}
\]
Oxidizing Power of the Atmosphere

• The cleansing of the atmosphere occurs mostly via the oxidation of organic and inorganic chemical species
  – Organic species => CO₂ and H₂O
  – Inorganic species => acids, nitrates, sulfates…

• The three main oxidants are: OH, O₃, and NO₃
  – OH: mostly during daytime (product of photolysis)
  – O₃: both during daytime and nighttime
  – NO₃: mostly at night (photolyzed during the day)
Chemical Lifetime of a Chemical Species

- The lifetime indicates the chemical stability of the chemical species
- For example, oxidation reaction of chemical species $X_i$ by OH:
  $$X_i + OH \rightarrow \ldots,$$
  with $k_{OH}(T)$ as the kinetic constant

Destruction term: $-k_{OH} [OH] [X_i]$, which leads to a characteristic time:

$$t_{l,i} = 1 / (k_{OH} [OH])$$

$t_{l,i}$ is also called the chemical lifetime or residence time.

It should not be confused with the half-life, which corresponds to the time at which half of the reactant, $X_i$, has been consumed:

$$t_{1/2} = \ln(2) / (k_{OH} [OH]) = 0.7 \ t_{l,i}$$
**Lifetimes of some VOC in the Lower Troposphere**

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Photolysis(^a)</th>
<th>OH</th>
<th>NO(_3)</th>
<th>O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_2)</td>
<td>-</td>
<td>30 h</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>-</td>
<td>12 d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>48 d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methane</td>
<td>-</td>
<td>5 a</td>
<td>&gt; 300 a</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>-</td>
<td>11 d</td>
<td>&gt; 4 a</td>
<td>-</td>
</tr>
<tr>
<td>n-Butane</td>
<td>-</td>
<td>5 d</td>
<td>7 a</td>
<td>-</td>
</tr>
<tr>
<td>Hexane</td>
<td>-</td>
<td>2 d</td>
<td>3 a</td>
<td>-</td>
</tr>
<tr>
<td>Octane</td>
<td>-</td>
<td>36 h</td>
<td>20 mo</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene</td>
<td>-</td>
<td>33 h</td>
<td>19 mo</td>
<td>7 d</td>
</tr>
<tr>
<td>Propylene</td>
<td>-</td>
<td>11 h</td>
<td>12 d</td>
<td>28 h</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>-</td>
<td>4 h</td>
<td>7 h</td>
<td>90 min</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>-</td>
<td>4 h</td>
<td>28 h</td>
<td>44 h</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>-</td>
<td>8 h</td>
<td>-</td>
<td>25 h</td>
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<tr>
<td>trans-3-Hexene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100 min</td>
</tr>
<tr>
<td>trans-4-Octene</td>
<td>-</td>
<td>4 h</td>
<td>-</td>
<td>2 h</td>
</tr>
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</tr>
<tr>
<td>o-Xylene</td>
<td>-</td>
<td>20 h</td>
<td>9 mo</td>
<td>-</td>
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<tr>
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<td>18 h</td>
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<tr>
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<td>18 h</td>
<td>45 d</td>
<td>-</td>
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<td>Isoprene</td>
<td>-</td>
<td>3 h</td>
<td>4 h</td>
<td>22 h</td>
</tr>
<tr>
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<td>5 min</td>
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Discovery of “Photochemical Smog”

- Arie Haagen-Smit, a professor of biochemistry at the California Institute of Technology (Caltech), proposed and demonstrated in 1952 that air pollution in Los Angeles was due to reactions among nitrogen oxides (NO$_x$) and volatile organic compounds (VOC) in the presence of solar radiation.

Photochemical Smog: Ozone Formation

\[ \text{O}_3 \]

Ozone is formed from nitrogen oxides and volatile organic compounds reacting in the presence of sunlight: It is a non-linear system.

\[ \text{NO}_x \]
Nitrogen oxides: NO and NO\(_2\)

\[ \text{VOC} \]
Volatile organic compounds: alkanes, alkenes, aromatics, aldehydes, alcohols…
Oxidants of Photochemical Smog

- **Hydroxyl radical: OH**
  
  \[
  \text{O}_3 + h\nu \rightarrow O^{(1)D} + \text{O}_2 \\
  O^{(1)D} + \text{H}_2\text{O} \rightarrow 2 \text{OH} \\
  \text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{OH} \\
  \text{HNO}_2 + h\nu \rightarrow \text{NO} + \text{OH}
  \]

- **Ozone: \(\text{O}_3\)**
  
  \[
  \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \\
  \text{O} + \text{O}_2 \rightarrow \text{O}_3
  \]

- **Nitrate radical: \(\text{NO}_3\)**
  
  \[
  \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2
  \]
The Photostationary State

Ozone formation:
\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]
\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]

Ozone destruction:
\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

The net chemical budget is zero

This is also known as the Leighton cycle.
The Photostationary State

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad k_1$$

$$\text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad k_2$$

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad k_3$$

Philip A. Leighton, Professor of chemistry at Stanford University, introduced the concept of a photostationary state among these three reactions: at equilibrium, all reaction rates are equal. This is the photostationary state of Leighton

$$k_1 \ [\text{NO}_2] = k_2 [\text{O}] \ [\text{O}_2] = k_3 [\text{NO}] \ [\text{O}_3]$$
The Photostationary State of Leightonon

\[ \begin{align*}
    &\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad k_1 \\
    &\text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad k_2 \\
    &\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad k_3
\end{align*} \]

At equilibrium (photostationary state), all reaction rates are equal:

\[ k_1 [\text{NO}_2] = k_2[\text{O}][\text{O}_2] = k_3 [\text{NO}][\text{O}_3] \]

thus:

\[ [\text{O}_3] = \frac{(k_1 [\text{NO}_2])}{(k_3 [\text{NO}])} \]

The ozone concentration produced by this reaction cycle is low.
Chain of Oxidation of Carbon Monoxide

CO

Propagation reactions

\[
\begin{align*}
\text{CO} + \text{OH} & \Rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \Rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{NO} & \Rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]

\[
\text{CO} + \text{NO} + \text{O}_2 \Rightarrow \text{CO}_2 + \text{NO}_2
\]

Ozone formation

\[
\begin{align*}
\text{NO}_2 + h\nu & \Rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \Rightarrow \text{O}_3
\end{align*}
\]

\[
\text{NO}_2 + \text{O}_2 \Rightarrow \text{NO} + \text{O}_3
\]

Net budget

\[
\text{CO} + 2 \text{O}_2 \overset{\text{NO}_x}{\Rightarrow} \text{CO}_2 + \text{O}_3
\]

Thus, the oxidation of one molecule of carbon monoxide leads to one additional ozone molecule.
Chain of Oxidation of Carbon Monoxide (CO)

Propagation reactions

\[
\begin{align*}
CO + OH &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
\hline
CO + NO + O_2 &\rightarrow CO_2 + NO_2
\end{align*}
\]

Ozone formation

\[
\begin{align*}
NO_2 + hv &\rightarrow NO + O \\
O + O_2 &\rightarrow O_3 \\
\hline
NO_2 + O_2 &\rightarrow NO + O_3
\end{align*}
\]

Net budget

\[
CO + 2 O_2 \stackrel{NO_x}{\rightarrow} CO_2 + O_3
\]

Thus, the oxidation of one molecule of carbon monoxide leads to one additional ozone molecule.
Ozone Formation
Perturbation of the Photostationary Cycle

Ozone formation

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

Oxidation of NO to NO$_2$ with destruction of O$_3$

\[ \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2 \quad (3) \]

Oxidation of NO to NO$_2$ without destruction of O$_3$

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (4) \]

Budget of reactions (1), (2) and (4):

\[ \text{HO}_2 + \text{O}_2 \rightarrow \text{OH} + \text{O}_3 \]
Photochemical Smog

The oxidation of CO perturbs the photostationary cycle by converting NO to NO₂ without O₃ destruction and leads to ozone formation.

\[ \text{O}_3 \quad \text{NO} \rightarrow \text{NO}_2 \rightarrow \text{HO}_2 \rightarrow \text{OH} \rightarrow \text{CO}_2 \rightarrow \text{CO} \]

The oxidation of volatile organic compounds (VOC) leads to ozone formation in the same manner.
The main categories of VOC are the following:

- **Alkanes**: hydrocarbons (C and H) with single C-C bonds
- **Alkenes**: hydrocarbons (C and H) with one or more double C=C bonds
- **Aromatic compounds**: a phenyl ring
- **Aldehydes**: a carbonyl group (-HC=O)
- **Ketones**: An oxo group (C=O)
- **Alcohols**: C-OH
- **Ethers**: C-O-C
The oxidation pathways for VOC are the following:

- Photolysis (mostly for aldehydes)
- Reaction with OH
- Reaction with NO₃
- Reaction with O₃ (for alkenes only)
- Reaction with O(^3P) (negligible)
Oxidation of Formaldehyde (HCHO)

\[
\begin{align*}
\text{HCHO} + h\nu & \Rightarrow \text{H} + \text{HCO} \\
\text{H} + \text{O}_2 & \Rightarrow \text{HO}_2 \\
\text{HCO} + \text{O}_2 & \Rightarrow \text{HO}_2 + \text{CO}
\end{align*}
\]

\[
\begin{align*}
\text{HCHO} + h\nu + 2\text{O}_2 & \Rightarrow 2\text{HO}_2 + \text{CO}
\end{align*}
\]

\[
\begin{align*}
\text{HCHO} + h\nu & \Rightarrow \text{H}_2 + \text{CO}
\end{align*}
\]

\[
\begin{align*}
\text{HCHO} + \text{OH} & \Rightarrow \text{HCO} + \text{H}_2\text{O} \\
\text{HCO} + \text{O}_2 & \Rightarrow \text{HO}_2 + \text{CO}
\end{align*}
\]

\[
\begin{align*}
\text{HCHO} + \text{OH} + \text{O}_2 & \Rightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O}
\end{align*}
\]
Oxidation of Formaldehyde (HCHO)

HCHO + hv => H + HCO
H + O₂ => HO₂
HCO + O₂ => HO₂ + CO

HCHO + hv + 2 O₂ => 2 HO₂ + CO

HCHO + hv => H₂ + CO

HCHO + OH => HCO + H₂O
HCO + O₂ => HO₂ + CO

HCHO + OH + O₂ => HO₂ + CO + H₂O

Hydroperoxyl radical
Oxidation of Formaldehyde (HCHO)

On average:

\[
\begin{align*}
\text{HCHO } + (hv, \text{OH}) + \text{O}_2 & \Rightarrow \text{HO}_2 + \text{CO} + (1/2 \text{H}_2, \text{H}_2\text{O}) \\
\text{NO} + \text{HO}_2 & \Rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + hv & \Rightarrow \text{NO} + \text{O}_3
\end{align*}
\]

\[
\text{HCHO } + (hv, \text{OH}) + 2 \text{O}_2 \Rightarrow \text{O}_3 + \text{CO} + (1/2 \text{H}_2, \text{H}_2\text{O}) + \text{OH}
\]

Therefore, the oxidation of one molecule of formaldehyde leads to \textit{two} additional molecules of ozone.
**Oxidation of Acetaldehyde (CH$_3$CHO)**

\[
\begin{align*}
\text{CH}_3\text{CHO} + hv & \rightarrow \text{CH}_3 + \text{HCO} \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 \\
\text{HCO} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CO} \\
\hline
\text{CH}_3\text{CHO} + hv & \rightarrow \text{CH}_3\text{O}_2 + \text{HO}_2 + \text{CO} \\
\text{CH}_3\text{CHO} + hv & \rightarrow \text{CH}_4 + \text{CO} \\
\text{CH}_3\text{CHO} + \text{OH} & \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O} \\
\text{CH}_3\text{CO} + \text{O}_2 & \rightarrow \text{CH}_3\text{C(O)O}_2 \\
\text{CH}_3\text{C(O)O}_2 + \text{NO}_2 & \leftarrow \rightarrow \text{CH}_3\text{C(O)O}_2\text{NO}_2 \quad \text{[peroxyacetyl nitrate or PAN]} \\
\text{CH}_3\text{C(O)O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{C(O)O} + \text{NO}_2 \\
\text{CH}_3\text{C(O)O} + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 + \text{CO}_2
\end{align*}
\]
Oxidation of Methane (CH$_4$)

\[
\begin{align*}
\text{CH}_4 + \text{OH} & \rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \\
\text{CH}_3\text{O}_2 + \text{NO}_2 & \Leftrightarrow \text{CH}_3\text{ONO}_3 \\
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \\
2 \text{NO}_2 + \text{hv} & \rightarrow 2 \text{NO} + 2 \text{O}_3 \\
\text{CH}_4 + 4 \text{O}_2 & \rightarrow 2 \text{O}_3 + \text{HCHO} + \text{H}_2\text{O}
\end{align*}
\]

Therefore, the oxidation of one molecule of methane leads to four additional molecules of ozone; however, it is slow.
Oxidation of Alkanes by OH

\[
\begin{align*}
\text{RH} + \text{OH} & \quad \Rightarrow \quad \text{R} + \text{H}_2\text{O} \quad \text{(for CH}_4, \text{ R} = \text{CH}_3) \\
\text{R} + \text{O}_2 & \quad \Rightarrow \quad \text{RO}_2 \\
\text{RO}_2 + \text{NO} & \quad \Rightarrow \quad \text{RO} + \text{NO}_2 \\
\text{RO} + \text{O}_2 & \quad \Rightarrow \quad \text{R’CHO} + \text{HO}_2 \quad \text{(R’ = R – 1 CH}_2) \\
\text{NO} + \text{HO}_2 & \quad \Rightarrow \quad \text{NO}_2 + \text{OH} \\
2 \text{NO}_2 + hv & \quad \Rightarrow \quad 2 \text{NO} + 2 \text{O}_3 \\
\hline
\text{RH} + 4 \text{O}_2 & \quad \Rightarrow \quad 2 \text{O}_3 + \text{R’CHO} + \text{H}_2\text{O}
\end{align*}
\]

Therefore, the oxidation of one alkane molecule leads to two ozone molecules and one aldehyde, which will lead to at least two ozone molecules.
Oxidation of Alkanes by OH

\[
\begin{align*}
\text{RH} + \text{OH} & \rightarrow \text{R} + \text{H}_2\text{O} \\
\text{R} + \text{O}_2 & \rightarrow \text{RO}_2 \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \\
\text{RO} + \text{O}_2 & \rightarrow \text{R'}\text{CHO} + \text{HO}_2 \quad (\text{R'} = \text{R} - \text{1 CH}_2) \\
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \\
2 \text{NO}_2 + \text{hv} & \rightarrow 2 \text{NO} + 2 \text{O}_3 \\
\text{RH} + 4 \text{O}_2 & \rightarrow 2 \text{O}_3 + \text{R'}\text{CHO} + \text{H}_2\text{O}
\end{align*}
\]

Therefore, the oxidation of one alkane molecule leads to two ozone molecules and one aldehyde, which will lead to at least two ozone molecules.
The reaction rate increases with the number of carbon atoms of the alkane molecule.
Alkane Oxidation by NO$_3$

The first step differs from that of oxidation by OH:

$$RH + OH \rightarrow R + H_2O$$

$$RH + NO_3 \rightarrow R + HNO_3$$

The oxidation of alkanes by NO$_3$ is very slow (i.e., negligible).
Alkene Oxidation by OH

The oxidation path differs from that of alkanes because, instead of the abstraction of a hydrogen atom, the OH radical is added to the double bond.

Example of ethylene (ethene):

\[
\begin{align*}
H_2C=CH_2 + OH & \rightarrow HOCH_2CH_2 \\
HOCH_2CH_2 + O_2 & \rightarrow HOCH_2CH_2O_2 \\
HOCH_2CH_2O_2 + NO & \rightarrow HOCH_2CH_2O + NO_2 \\
& \quad \text{(72 %)} \\
HOCH_2CH_2O & \rightarrow 2 \text{ HCHO} + \text{ HO}_2 \\
& \quad \text{(28 %)} \\
HOCH_2CH_2O & \rightarrow HOCH_2CHO + \text{ HO}_2 \\
\end{align*}
\]

\[C_2H_4 + OH + 2 \text{ NO} \rightarrow 1.4 \text{ HCHO} + 0.3 \text{ HOCH}_2\text{CHO} + \text{ OH} + 2 \text{ NO}_2\]
A terminal alkene has the double-bond at the end of the molecule.
Kinetics of Terminal and Internal Alkene Oxidation by OH

Oxidation is faster if the double-bond is not at the end of the molecule (internal).
The oxidation path differs from that of alkanes because, instead of the abstraction of a hydrogen atom, the NO$_3$ radical is added to the double bond.

$$R_1R_2C=CR_3R_4 + NO_3 \Rightarrow R_1R_2C(NO_2)-CR_3R_4$$

$$R_1R_2C(NO_2)-CR_3R_4 + O_2 \Rightarrow R_1R_2C(NO_2)-C(O_2)R_3R_4$$

$$R_1R_2C(NO_2)-C(O_2)R_3R_4 + HO_2 \Rightarrow \text{organic nitrate, ketones}$$

$$R_1R_2C(NO_2)-C(O_2)R_3R_4 + CH_3O_2 \Rightarrow \text{organic nitrate, ketones}$$

Note that the organic peroxyl radical does not react with NO to form NO$_2$, because NO concentrations are negligible when NO$_3$ is present (O$_3$ reacts much faster with NO than with NO$_2$); therefore, oxidation by NO$_3$ does not lead to O$_3$ formation.
Alkene Oxidation by $O_3$

Oxidation by $O_3$ is specific to alkenes:

$$R_1R_2C=C+R_3R_4C\rightarrow O_3 \rightarrow \text{Ozonide}$$

$$\text{Ozonide} \rightarrow \text{Carbonyl compounds} + \text{Criegee biradicals}$$

$$R_1R_2\text{COO} \rightarrow \text{stable products} + \text{radicals} \Rightarrow \text{formation of } O_3$$
The oxidation of aromatic compounds differs from that of alkanes because the abstraction of a hydrogen atom by OH (to form H$_2$O) is a minor oxidation path (< 10 %; formation of benzaldehyde in the case of toluene).

The main oxidation path is the addition of OH to the aromatic ring to form an aromatic radical. The products may (1) maintain the aromatic ring or (2) result from a break-up of the ring. Example of toluene:

(1) Toluene + OH $\rightarrow$ cresol  
   (about 18 %)

(2) Toluene + OH $\rightarrow$ aldehydes (glyoxal, methylglyoxal, methyl butene dial, 1,4-butenedial)  
   (> 70 %)
Some VOC are more reactive than others and one can define VOC reactivity scales.

Comparison of reactivity scales for VOC based on (1) “Maximum incremental reactivity” (MIR; black bars, left side scale) and (2) OH kinetics (grey bars, right side scale). The MIR can be measured in the laboratory (smog chamber experiment) or calculated with a chemical kinetic mechanisms (here, simulation with SAPRC-07, WPL Carter, Univ. of California at Riverside).
VOC Reactivity

Some VOC are more reactive than others and one can define VOC reactivity scales.

VOC reactivity is a combination of kinetics (how fast is the VOC oxidized) and mechanism (how many O₃ molecules are formed per VOC molecule oxidized).
Termination of the VOC Oxidation Cycles

The cycle is mostly catalyzed by the oxidation of NO into NO$_2$ and the photolysis of NO$_2$. Therefore, the reaction of NO$_2$ with a radical (OH or an organic radical) can terminate an oxidation cycle

Formation of a sink species:
NO$_2$ + OH $\Rightarrow$ HNO$_3$

Formation of a reservoir species:
NO$_2$ + CH$_3$C(O)O$_2$ $\Leftrightarrow$ CH$_3$C(O)O$_2$NO$_2$ (PAN)
Termination of the VOC Oxidation Cycles

The cycle can also be terminated by reactions between peroxyl radicals

For example:

\[
\begin{align*}
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 \text{ (Hydrogen peroxide)} \\
\text{HO}_2 + \text{RO}_2 & \rightarrow \text{ROOH} \text{ (Organic peroxide)}
\end{align*}
\]
Nitrogen Oxides in the Atmosphere

PAN

Nitrogen Oxides in the Atmosphere

**Decomposition**

**Dry deposition**

**Organic radicals**

**OH, O₃**

**Wet and dry deposition**

**very slow**

**fast**

**Emissions**

**Dry deposition**

**HNO₃**

**Dry deposition**
Chemical Regimes
NO$_x$-limited vs VOC-limited

• High-NO$_x$ regime (VOC-limited): Termination occurs mostly via nitric acid (HNO$_3$) formation.
  \[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]

• Low-NO$_x$ regime (NO$_x$-limited): The governing termination reaction is between peroxyl radicals.
  \[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]
  which leads to hydrogen peroxide (H$_2$O$_2$) formation

• The relative importance of the two reaction pathways depends on the [VOC]/[NO$_x$] ratio.
Schematic Representation of O$_3$ Formation

O$_3$: Oxidized VOC
Schematic Representation of O$_3$ Formation Precursors: VOC and NO$_x$
Schematic Representation of O$_3$ Formation
Pollutants: O$_3$ and NO$_2$
Schematic Representation of O₃ Formation
Oxidants: OH, HO₂, and RO₂
Temporal Variation of O$_3$ and NO$_2$

The O$_3$ maximum occurs in midday when solar radiation is the most important, thereby leading to radical formation (OH) and VOC oxidation.

The NO$_2$ maximum occurs in the morning during rush-hour traffic, because (1) emissions are maximum at that time and (2) during midday photolysis decreases NO$_2$ concentrations.
In a “low-NO_x“ regime, the [VOC]/[NO_x] ratio is high and the production of peroxyl radicals RO_2 is high; therefore, NO reacts preferentially with RO_2 or HO_2 rather than with O_3 and leads to O_3 formation.
High-NO$_x$ Regime

In a “high-NO$_x$” regime, the [VOC]/[NO$_x$] ratio is low and the production of peroxyl radicals (RO$_2$) is low; therefore, NO may react preferentially with O$_3$ rather than with RO$_2$ or HO$_2$ and leads to O$_3$ destruction.
Example of “Indicators”
Sensitivity of O$_3$ to VOC and NO$_x$

- $H_2O_2$ / (HNO$_3$ + particulate nitrate) as an indicator

High values:
Sensitive to NO$_x$

Low values:
Sensitive to VOC
Two chemical regimes:

- "Low-NO\textsubscript{x}\" regime when NO\textsubscript{x} concentrations are low compared to VOC concentrations (for example, remote areas): ozone formation is limited by NO\textsubscript{x}, therefore, a reduction in NO\textsubscript{x} leads to a reduction in ozone.

- "High-NO\textsubscript{x}\" regime when NO\textsubscript{x} concentrations are high compared to VOC concentrations (for example, urban areas): ozone formation is limited by VOC, therefore, a reduction in VOC leads to a reduction in ozone and a reduction in NO\textsubscript{x} may lead to an increase in ozone.
Isopleths of ozone (lines of constant ozone concentration, typically for the maximum daily regulatory value, i.e., 8-hour average maximum) as a function of the emissions (or early-morning concentrations) of NO\textsubscript{x} and VOC.
The Weekend Effect

- The change in the $[\text{VOC}]/[\text{NO}_x]$ ratio between week days and weekends affects ozone formation (fewer diesel trucks on weekends in the U.S.)

- The lower $\text{NO}_x$ emissions on weekends lead to more ozone formation in a high-$\text{NO}_x$ regime: this has been observed for example in Los Angeles and Chicago

- Air quality model simulations reproduce this weekend effect (e.g., in the Los Angeles basin)
Strategy for Reducing Ozone Precursors

• Developing an effective emission control strategy is complex because the chemical regime for ozone formation varies in space and time.

• Typically (but not always)
  – Ozone formation is VOC-limited in urban areas
  – Ozone formation is NO$_x$-limited in rural areas
Strategy for Reducing Ozone Precursors

VOC / NO\textsubscript{x} ratio calculated with a model simulation (Polyphemus model of Cerea).

The dotted line corresponds to [VOC]/[NO\textsubscript{x}] = 8 and depicts the approximate boundary between the NO\textsubscript{x} and VOC-limited regimes; VOC limited in blue/green and NO\textsubscript{x} limited in red/yellow. Source: Cerea
Strategy for Reducing Ozone Precursors

Model simulation results (Polyphemus model of Cerea):
Effect of 15 % reductions in NO$_x$ or VOC emissions over the Paris region on maximum 8-hour average O$_3$ concentrations ($\mu$g/m$^3$)

Source: Cerea
Importance of Long-Range Atmospheric Transport for the Paris Region

Model simulation results (Polyphemus model of Cerea):
Relative decrease (%) of VOC concentrations due to a 15 % decrease of VOC emissions in the Paris region

Source: Cerea
The Role of Long-Range Transport on Ozone Concentrations

- Lifetime of ozone: one to two weeks $\Rightarrow$ trans-Pacific Ocean and trans-Atlantic Ocean transport

- Some studies estimate that
  - 5 to 10 ppb of ozone concentrations in California are due to Asian emissions (mostly in April and May)
  - 3 to 5 ppb of ozone concentrations in western Europe are due to North American emissions

- Challenge: local emissions must decrease sufficiently to account for the potential increase of the global ozone background concentrations.
Evolution of Ozone Concentrations in Los Angeles, California

Significant decrease of ozone concentrations in Los Angeles (with inter-annual variability)

![Graph showing the evolution of ozone concentrations from 1980 to 2015.](Source: SCAQMD, http://www.aqmd.gov)
Evolution of Ozone Concentrations in Paris

Little decrease of ozone concentrations in Paris (with inter-annual variability)

Heat wave of 2003

Maximum 8-hour average concentrations
(Regulatory value: 120 µg/m³ averaged over 8 hours, to be exceeded 25 times)

Evolution of Ozone Concentrations in Paris

Possible explanations

- **Chemistry**: Joint reductions in NO\textsubscript{x} and VOC emissions led to little change in the VOC/NO\textsubscript{x} ratio and, therefore, little change in ozone concentrations.

- **Physics (Long-range transport)**: The limited decrease in ozone concentrations overall in Europe leads to a nearly constant ozone background, which contributes significantly to ozone concentrations in the Paris region.
Primary and Secondary NO$_2$
Evolution of NO$_2$ Concentrations in Paris

Two hypotheses:

- **Secondary NO$_2$:** NO$_2$ is formed by reaction of NO with O$_3$; as O$_3$ decreases little, NO$_2$ decreases little (there is more NO than O$_3$, therefore, O$_3$ is the limiting species for NO$_2$ formation).

- **Primary NO$_2$:** The NO$_2$ fraction in NO$_x$ emissions increased because of the effect of some particle diesel filters on NO oxidation to NO$_2$. 
Evolution of NO$_2$ Concentrations in Paris

Simulations conducted at Cerea suggest that the first hypothesis (greater NO$_2$ fraction in NO$_x$ emissions) is the most likely (Roustan et al., *Atmos. Environ.*, 2011)

The use of diesel particle filters in some diesel vehicles has led to an increase of the NO$_2$ fraction in NO$_x$ emissions; as a result, NO$_2$ concentrations in the Paris region remained nearly constant for several years. Nevertheless, they have started to decrease.

Annual concentrations of NO$_2$ (µg/m$^3$) at a near-road monitoring station in the Paris region

Source of data: Airparif
Evolution of NO$_2$ Concentrations in Los Angeles, California

Significant decrease (3 % per year) of NO$_2$ hourly concentrations in Los Angeles (with inter-annual variability)

Maximum 1-hour average concentrations
(Regulatory value: 100 ppb averaged over 1 hour, to be exceeded 7 times)

Evolution of NO$_2$ Concentrations in Paris

Significant decrease (3 % per year) of NO$_2$ annual concentrations in Paris over the long term (with inter-annual variability)

Maximum annual average background concentrations (Regulatory value: 40 µg/m$^3$)

Chemical Mechanisms of Photochemical Air Pollution

A chemical kinetic mechanism must represent the reactions that take place among the different chemical species and correctly simulate the evolution of the concentrations of the main air pollutants.

The chemical kinetic mechanism must be incorporated into an air quality model that simulates also the atmospheric transport processes (chemical-transport model or CTM); therefore, it is necessary to have an efficient numerical scheme for the chemical kinetic equations.
Chemical Mechanisms of Photochemical Air Pollution

• Mechanism for inorganic chemistry (NO$_x$, SO$_2$, CO, O$_3$, etc.)
  – About 20 species and 50 reactions

• Detailed mechanisms for organic chemistry (VOC)
  – Several hundreds of species and several thousands of reactions

• Reduced mechanisms for organic chemistry
  – 30 to 100 species and about one to three hundred reactions
Two main categories of mechanisms for VOC

1. Mechanisms with surrogate molecular species: SAPRC99, RACM, RACM2, MELCHIOR, CACM...

2. Mechanisms based on the decomposition of organic chemical species into functional groups ("carbon-bond" mechanisms): CBIV, CB05…
Mechanisms with Surrogate Species

Example of RACM2:

- n-butane : HC3 (alkanes, alcohols, esters, and alkynes with a rate constant for reaction with OH < $3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$)

- 1-hexene : OLT (terminal alkenes)

- propionaldehyde : ALD (aldehydes with 3 carbons or more)
Carbon-Bond Mechanisms

Example of CB05:

- n-butane: 4 PAR (carbon atoms with single bonds)

- 1-hexene: 1 OLE (2 carbon atoms with a double bond) + 4 PAR

- propionaldehyde: 1 PAR + 1 ALDX (acetaldehyde)
## Kinetics of Oxidation of Alkanes by OH

<table>
<thead>
<tr>
<th>Number of carbon atoms</th>
<th>Rate constant (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>CB05 : $k($# C$)$</th>
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</tbody>
</table>
Kinetics of Oxidation of Alkanes by OH

Number of carbon atoms

Rate constant (cm$^3$ molecule$^{-1}$ s$^{-1}$) x 10$^{-12}$

CB05 : $k(#\text{C})$

RACM2 : $k(#\text{C})$
Kinetics of Terminal and Internal Alkene Oxidation by OH

Number of carbon atoms

Rate constant (cm$^3$ molecule$^{-1}$ s$^{-1}$)
Chemical Mechanisms of Photochemical Air Pollution

Chemical kinetic mechanisms are evaluated against experimental data obtained in smog chambers.

Those smog chambers may be indoor or outdoor, small or large, in Teflon or stainless steel…

If needed, the chemical kinetic mechanism is improved to obtain better agreement with the experimental data.