Ozone
central to tropospheric chemistry

- Dominant producer of the ·OH radical through photolysis in the UV-B
  - source of atmospheric cleansing capacity
- Connected to NO$_x$ through the Null-Cycle
  - diurnal cycle
  - interdependence and titration
- Connected to HO$_x$ cycling
  - in-situ production AND loss from HO$_2$· reactions
- Connected to the direct removal of pollutants
  - ozonolysis
  - NO$_x$ oxidation
More reactions relevant for tropospheric ozone

• $HO_x$ sources …
  – Photolysis of ozone
  – Photolysis of formaldehyde and HONO
  – Ozonolysis of alkenes

• … and sinks (in order of importance)

\[
\begin{align*}
  NO_2 + \cdot OH (& M) & \rightarrow HNO_3 (& M) \\
  HO_2\cdot + HO_2\cdot (& M) & \rightarrow H_2O_2 + O_2 (& M) \\
  & \quad \rightarrow HO_2\cdot + ROO\cdot \rightarrow ROOH + O_2 \\
  HO_2\cdot + NO_2 (& M) & \rightarrow HO_2NO_2 (& M) \\
\end{align*}
\]

… and subsequent deposition of HNO$_3$, H$_2$O$_2$, and ROOH
HO\textsubscript{x} cycling in the troposphere (and stratosphere)

![Diagram of HO\textsubscript{x} cycling](image)

**Figure 6.2.** Schematic diagram of the important reactions involving hydrogen compounds in the troposphere and stratosphere. Interconversion of the reactive radicals results in the oxidation of reduced species of carbon, nitrogen, and sulfur. Loss of these reactive radicals occurs through physical and chemical removal of such species as HNO\textsubscript{3}, HO\textsubscript{2}NO\textsubscript{2}, and H\textsubscript{2}O\textsubscript{2} (not shown).

Brasseur, Orlando, Tyndall, 1999
The peroxy-radical loss reaction

\[(6.45)\] \[\text{CH}_3\text{O}_2^+ + \text{HO}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{O}_2 \]

stable peroxides, for example.

The reaction of \(\text{HO}_2\) with organic peroxy radicals also leads to the formation of

\[(6.46)\] \[\text{O}^6_2\text{H} + \text{O}^6_2\text{OH} \leftrightarrow \text{O}^6_2\text{H} + \text{O}^6_2\text{HO} + \text{O}^6_2\text{H} \]

\[(6.47)\] \[\text{O}^6_2\text{H} + \text{O}^6_2\text{OH} \leftrightarrow \text{O}^6_2\text{H} + \text{O}^6_2\text{HO} + \text{O}^6_2\text{H} \]

The peroxy-radical loss reaction
Ozone Deposition
(effective ozone loss)

FIGURE 5.10  Vertical profiles of ozone mixing ratio at a flatland station during the course of 1 day. Schematic representation of data obtained by Regener (1957).
Ozone budget in the troposphere

- transport from stratosphere
- *in-situ* production
- *in-situ* destruction
- deposition to the surface

<table>
<thead>
<tr>
<th>Sources</th>
<th>Present troposphere</th>
<th>Preindustrial troposphere</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>NH</td>
<td>SH</td>
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<tr>
<td>Stratosphere</td>
<td>335</td>
<td>145</td>
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<tr>
<td>HO$_2$ + NO</td>
<td>1970</td>
<td>1150</td>
</tr>
<tr>
<td>CH$_3$O$_2$ + NO</td>
<td>480</td>
<td>335</td>
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</table>

<table>
<thead>
<tr>
<th>Sinks</th>
<th>Present troposphere</th>
<th>Preindustrial troposphere</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH</td>
<td>SH</td>
</tr>
<tr>
<td>O($^1$D) + H$_2$O</td>
<td>1055</td>
<td>770</td>
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<td>HO$_2$/OH + O$_3$</td>
<td>865</td>
<td>480</td>
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<tr>
<td>Deposition</td>
<td>865</td>
<td>380</td>
</tr>
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</table>

Net chemical source: 530 235 765 55 95 150