Atmospheric Chemistry

Lecture 17

Oxidizing Capacity of the Troposphere

- **Atmosphere is an oxidizing medium; trace gases are removed by being oxidized (e.g. CH_4, CO, HCFCs, etc.)**

- **Most abundant oxidants are O_2 and O_3; but have significant bond energies and are reactive only towards radicals**

- **Most important oxidizers are OH and H_2O_2 (hydrogen peroxide)**

- **We will begin by focusing on the hydroxyl radical, OH, which is particularly reactive to hydrogen-containing compounds through H-abstraction reactions to form water vapor**

Production of OH in the troposphere

$$h\nu + O_3 \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow OH + OH$$

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

$$P(OH) = 2\, k_{O1D,H2O}\, [O^1D]\, [H_2O]$$

$$= 2\, k_{O1D,H2O}\, [O^1D]/[O_3]\, [O_3]\, [H_2O]$$

$$= 2\, k_{O1D,H2O}\, J_{O3 \rightarrow O1D}/(k_{O1D,H2O}[H_2O]+k_{O1D,M}[M])\, [O_3]\, [H_2O]$$

$$\cong 2\, k_{O1D,H2O}\, J_{O3 \rightarrow O1D}/(k_{O1D,M}[M])\, [O_3]\, [H_2O]$$

How much $O(^1D)$ is there in the troposphere?

$P(O^1D) = J_{O3 \rightarrow O1D}\,[O_3]$

$L(O^1D) = k_{O1D,M}\,[O(^1D)]\,[M]$

$P=L \quad \rightarrow \quad [O(^1D)]/[O_3] = J_{O3 \rightarrow O1D}/(k_{O1D,M}[M])$

near surface: $[O(^1D)]/[O_3] = 10^{-4}/(3x10^{-11}\ 2.5x10^{19}) \approx 10^{-13}$

$[O_3] \approx 10^{12}$ cm^{-3} $\rightarrow$ $[O(^1D)] \approx 0.1$ cm^{-3}

Very small concentration of O^1D is key to initiating production of OH in the troposphere

The OH titration problem

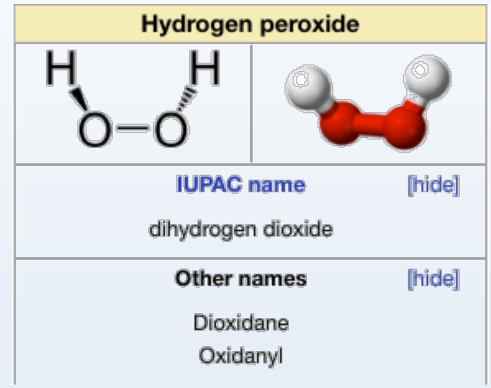
- OH is the key oxidant to start hydrocarbon oxidation
- Initial production of OH requires $O(^1D)$ that comes from O_3 photolysis
- What produces the O_3?
  - Transported from the stratosphere
  - Flux can be calculated to reasonable accuracy
  - Thus, an upper limit to the rate of formation of OH can be calculated
- OH is converted to HO_2 during oxidation of CO and CH_4
- Flux of CO from surface sources is greater than flux of O_3 from the stratosphere
- Thus, CO (and CH_4) could titrate the OH to HO_2 and reduce the loss of both CO and CH_4 such that they would build up large concentrations in the atmosphere

CO oxidation to CO_2

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$



Two paths for H_2O_2 loss

$H_2O_2 + hv \rightarrow 2OH$; regenerates OH

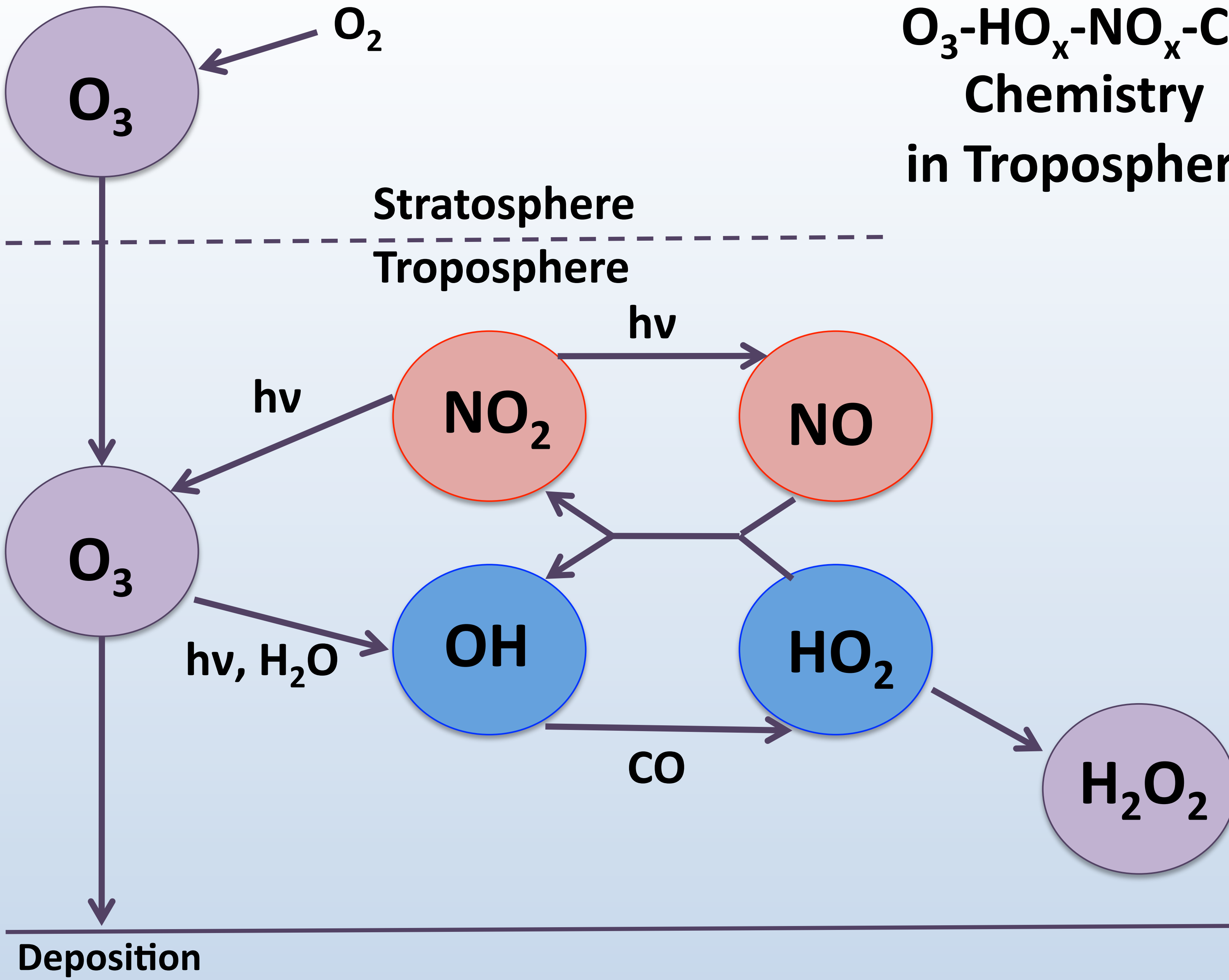
$H_2O_2 + OH \rightarrow HO_2 + H_2O$; consumes OH

But reaction of HO_2 with NO regenerates OH

$HO_2 + NO \rightarrow OH + NO_2$

Rescues us from the OH titration problem

Mechanism for O_3-HO_x-NO_x-CO Chemistry in Troposphere



Net result for CO oxidation

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

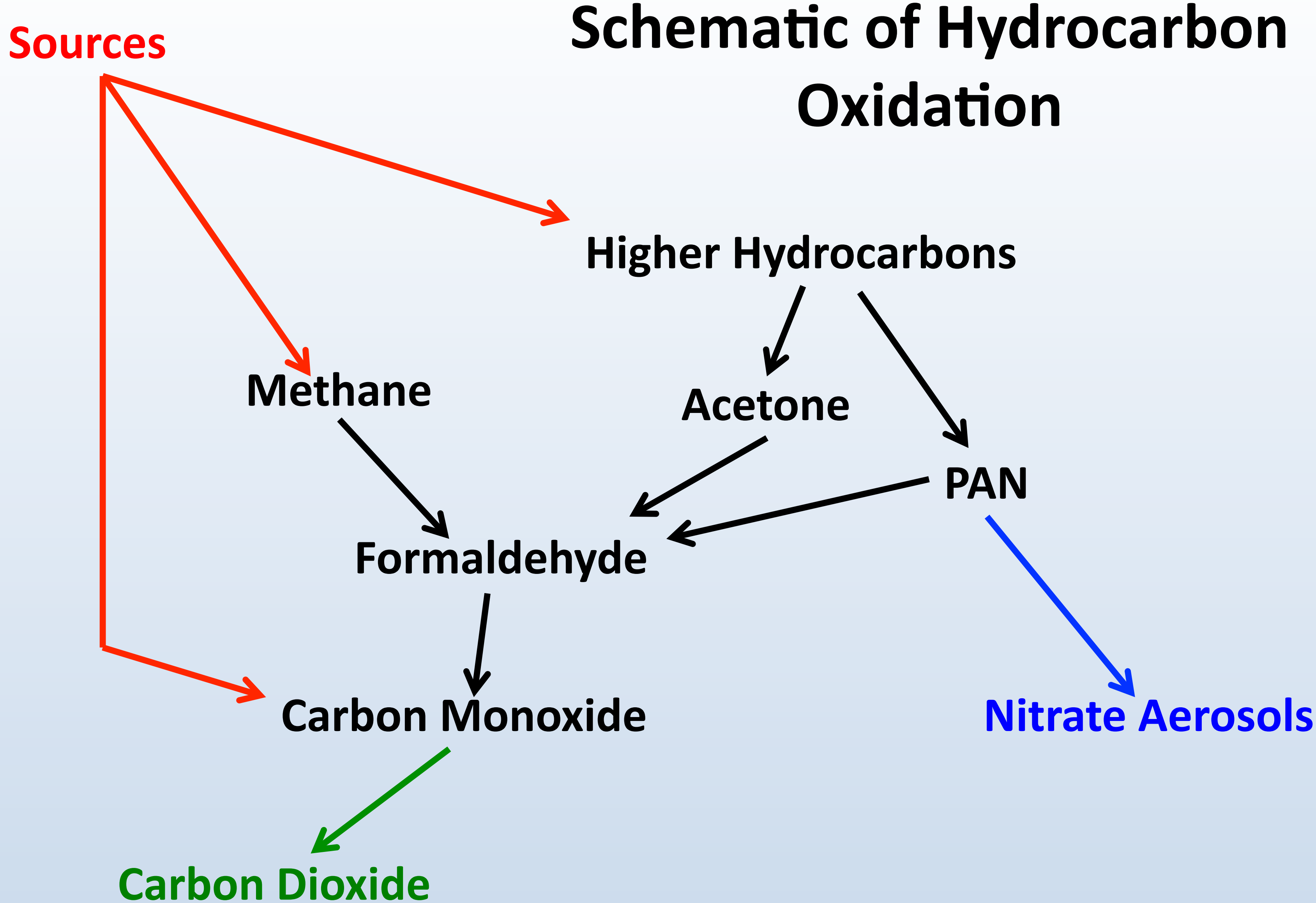
$HO_2 + NO \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

$CO + 2O_2 \rightarrow CO_2 + O_3$

Schematic of Hydrocarbon Oxidation



Summary points on atmospheric chemistry

- **We can make a large list of chemical reactions**
- **Which ones are important is dependent on conditions**
  - **Temperature**
  - **Pressure**
  - **Sources**
  - **Surfaces**
  - **Sunlight available**
  - **Mixing/transport**