Introduction to Photochemistry

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Outline

- Layers of the atmosphere
- Photochemistry – definitions
- Energy for photochemistry
- Consequences of photochemistry in stratosphere (ozone depletion)
- Consequences of photochemistry in troposphere (smog, haze, and acid rain)
Layers of the atmosphere
- Troposphere
- Stratosphere

Ozone depletion

Haze, smog, global warming

Troposphere (90%)

Mesosphere (0.5%)

Stratosphere (9.5%)

Ozone maximum

Tropopause

Stratopause

Mesopause

Altitude (kilometers)

Temperature (°C)
Photochemistry

- **Photochemistry** – Chemistry of the atmosphere driven by sunlight
- **Photodissociation** – Cleavage of a molecule into two or more (smaller) molecules (or atoms) by absorption of light
Photolysis Processes

\[
XY + hv \rightarrow XY^* 
\]
When \( XY^* \) is unstable, it may decompose into its constituent atoms

\[
XY^* \rightarrow X + Y \ (\text{ground state}) \\
XY^* \rightarrow X^* + Y \ (\text{excited state})
\]
Photodissociation Rate

\[ R_1 = J_1 n_1 \]

- \( J_1 \) = wavelength dependent coefficient that depends on absorption properties of molecule (s\(^{-1}\))
- \( n_1 \) = number density (molecules/cm\(^3\))
Photodissociation

- $J_1$ is large ($> 10^{-6}$/s), molecule unstable
  - Atmospheric lifetime: sec to days (example: O$_3$ and NO$_2$)
- $J_1$ is small ($< 10^{-7}$/sec), molecule stable
  - Long lifetimes (~yrs)
  - Most atmospheric gases (N$_2$, O$_2$, CH$_4$)
  - Other loss mechanisms important (chemical reaction, physical removal)
Solar Energy Needed for Photochemistry

- Stratosphere: high energy UV
- Troposphere: low energy UV and VIS
- Also IR in troposphere, but not strong enough to break bonds (excites vibrations and rotations, but not dissociation)
Earth’s Energy Balance

Solar in $\rightarrow$ Infrared out

UV-VIS-IR $\rightarrow$ IR
Solar In – IR Out
Energy In (from Sun)

![Energy In (from Sun) diagram](image)
How much UV-VIS energy makes it to troposphere?

- VIS - all
- UV-A: 320-380 nm (tanning salons) – all
- UV-B: 290-320 nm (sunburn) - most absorbed by O₃ layer
- UV-C: 250-290 nm (biocidal) – completely absorbed by O₂ and O₃ in stratosphere
UV (strat); UV-VIS (trop)
Photochemistry in Stratosphere (High-Energy UV)

- Natural formation of ozone
  - \( \text{O}_2 + \text{hv} \rightarrow \text{O} + \text{O} \)
  - \( \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 \)
- Natural destruction of ozone
  - \( \text{O}_3 + \text{hv} \rightarrow \text{O} + \text{O}_2 \)
  - \( \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \)
Photochemistry in Stratosphere (High energy UV) [cont.]

- Destruction of ozone (human-caused)
  - $\text{CF}_2\text{Cl}_2 + \text{light} \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$
  - $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
  - $\text{ClO} + \text{O}_3 \rightarrow \text{Cl} + \text{O}_2 + \text{O}_2$
Photochemistry in Troposphere (UV-VIS)

- UV-B and UV-A (and some VIS)
  - $\text{N}_2 + \text{light (trop)} \rightarrow \text{no reaction}$
  - $\text{O}_2 + \text{light (trop)} \rightarrow \text{no reaction}$
  - $\text{CO}_2 + \text{light (trop)} \rightarrow \text{no reaction}$
  - $\text{H}_2\text{O} + \text{light (trop)} \rightarrow \text{no reaction}$
  - CFCs + light (trop) $\rightarrow$ no reaction
- “Stable” molecules, bonds too strong
So is there PC in the trop?

- Yes – the two most important reactions
  - $O_3 + h\nu \rightarrow O_2 + O^*$
  - $NO_2 + h\nu \rightarrow NO + O^*$

- Both provide source of O atom (free radical, highly reactive) – this in turn, drives much of troposphere chemistry
Free Radicals

- Atoms or molecules with unpaired electron in outer shell (neutral)
- Two important free radicals in troposphere
  - O (from photodissociation of O\(_3\) & NO\(_2\))
  - OH (hydroxyl radical, made from O)

\[
O + H_2O \rightarrow OH + OH
\]
The Hydroxyl Radical OH

- Minor (trace) constituent, but very important! \([\text{OH}] \sim 1 \text{ ppm}\)
- “Ajax” of atmosphere – OH reacts with almost everything with H
  - \(\text{CH}_4 \text{ (methane)} + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}\)
  - \(\text{H}_2\text{S} + \text{OH} \rightarrow \text{HS} + \text{H}_2\text{O}\)
  - \(\text{CF}_2\text{ClH (H-CFC)} + \text{OH} \rightarrow \text{CF}_2\text{Cl} + \text{H}_2\text{O}\)
Atmospheric Lifetimes

- “Short” lifetimes (< 10 yr)
  - Photochemically unstable (NO₂ and O₃)
  - React with OH (CH₄, reactive hydrocarbons, H-CFCs, SO₂)
  - Wash out (soluble in water)

- “Long” lifetimes (10-200 yr)
  - CO₂ (greenhouse gas)
  - N₂, O₂ (major gases in atmosphere)
Consequences of Tropospheric Photochemistry

- Direct photochemistry (reactions with hv)
  - Photolysis of NO$_2$
  - Photolysis of O$_3$

- Indirect photochemistry (rxns with OH)
  - HCFCs (as shown before)
  - Photochemical SMOG
  - Haze/acid rain (sulfate and nitrate aerosols)
Photochemical (LA) Smog

- London smog (1952) – 4000 deaths
  - Coal (sulfur) + heat $\rightarrow$ H₂SO₄
  - Smoke (coal) + fog = smog
- Los Angeles smog is different
  - Primary pollutants (from cars) [e.g. NO, CO]
  - Light (sun) and warmth (above 15 °C)
  - Topography (inversion)
EPA Criterion Pollutants: Smog

- CO  carbon monoxide ($1^\circ$)
- $\text{NO}_x$  NO + NO$_2$  ($1^\circ$ and $2^\circ$)
- O$_3$  ozone ($2^\circ$)
- RH (VOC)  reactive hydrocarbons or volatile organic carbon ($1^\circ$)
Chemistry of Smog

$$\text{RH} + \text{OH} + \text{NO} \rightarrow \text{O}_3 + \text{NO}_2 + \text{HC}$$

O$_2$, light

RH (VOC) = reactive hydrocarbon or volatile organic carbon (e.g. CH$_4$, octane, terpenes)
HC = unreactive hydrocarbon (CO$_2$)
OH = hydroxyl radical (requires light)
NO(NO$_2$) = nitrogen oxide (nitrogen dioxide)
O$_3$ = ozone
The Chemical Reactions
(simplified)

Early Morning (sun and cars)

\[ \text{CO(cars)} + \text{OH} \rightarrow \text{H} + \text{CO}_2 \]

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 \]

Late Morning (interconversion of NO\textsubscript{x})

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

\[ \text{NO}_2 + \text{light} \rightarrow \text{NO} + \text{O} \]
The Chemical Reactions

Early afternoon (formation of ozone)

\[ O + O_2 + M \rightarrow O_3 \]

Same as formation of stratospheric \( O_3 \), but source of \( O \) atom is \( NO_2 \), not \( O_2 \)

Stratosphere: \( O_2 + \text{UV light} \rightarrow 2O \)

Troposphere: \( NO_2 + \text{UV light} \rightarrow NO + O \)
Photochemical Smog

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{H} + \text{CO}_2 \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + \text{light} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

Net: \( \text{CO} + 2\text{O}_2 + \text{light} \rightarrow \text{CO}_2 + \text{O}_3 \)
Smog Scenario

- Early AM rush hour
  - Temperature inversion
  - NO, CO, RH (from cars)
- Mid-morning (photochemistry, sun)
  - NO$_2$, CO$_2$, HC
- Mid-afternoon (~3-5 PM)
  - O$_3$ peaks
  - Land warms, sea breeze pushes smog to mountains
Smog Scenario (cont.)

- **Evening**
  - Rush hour traffic (more RH, CO, NO)
  - No sunlight, little O$_3$ formation
  - Sea breeze pushes O$_3$ inland

- **Late evening**
  - Land cools, sea breeze dies down
  - Temperature inversion
Evolution of Smog over Time

6-9 AM

10 AM

3-5 PM

9 PM

NO, CO, RH

NO, CO₂, HC

NO₂, CO₂, HC, aerosols

O₃, GC
Haze and Acid Rain

- Conversion of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$
- Conversion of NO to $\text{HNO}_3$
Formation of $\text{H}_2\text{SO}_4$

$\text{SO}_2 \rightarrow \rightarrow \text{H}_2\text{SO}_4$

1. Gas-phase (homogeneous) (SLOWER)

$\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3$

$\text{HSO}_3 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$

$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$
Formation of $\text{H}_2\text{SO}_4$ (cont.)

$$\text{SO}_2 \rightarrow \rightarrow \text{H}_2\text{SO}_4$$

2. In water (heterogeneous) FASTER

$$\text{SO}_2 + \text{H}_2\text{O} \text{ (l)} \rightarrow \text{H}_2\text{O SO}_2(\text{l})$$

$$\text{H}_2\text{O SO}_2(\text{l}) + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$$
Formation of $\text{HNO}_3$

$\text{NO} \rightarrow \rightarrow \text{HNO}_3$

1. Gas-phase (homogeneous) (FAST)

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

$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$
Fate of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$

- Gases ($\text{H}_2\text{SO}_4$ and $\text{HNO}_3$) dissolve in water to form acid rain
- Gases ($\text{H}_2\text{SO}_4$ and $\text{HNO}_3$) nucleate to form particles
- Particles ($\sim 0.1 \, \mu\text{m}$) scatter light and cause haze
A Clear Day (Raleigh Day)
(just molecular scattering)
Aerosol Scattering (Backward)
Aerosol Scattering (Forward)