

EWCE 105

ENVIRONMENTAL CHEMISTRY

Lecture – 9

Lecture Outlines

- Photochemical Reactions in the Atmosphere

Atmospheric Chemistry and Photochemical Reactions



- **Atmospheric chemistry** refers to **chemical processes** that occur **in the atmosphere.**
- **Atmospheric chemistry occurs** in the **gas phase** where **molecules are** relatively **far apart.**
- A **second major aspect** of **atmospheric chemistry** is the **occurrence of photochemical reactions.**

Steps followed in Photochemical Reactions

- Initiated when **a photon of ultraviolet radiation** is **absorbed by a molecule**.
- The energy of a photon, E, is given by E = hv, where h is Planck's constant and v is the frequency of the radiation.
- **Electromagnetic radiation** of a sufficiently **short wavelength can cause chemical bonds to break** in molecules.
- This can **lead to the formation of reactive species** that **can participate in reaction sequences** called chain reactions.

Atmospheric Chemical Processes

Two constituents of utmost importance in atmospheric chemistry are:

- Radiant energy from the sun - Photons put high energy into individual molecules.
- The hydroxyl radical, $HO^{\bullet}$ - Most important highly reactive intermediates.

Atmospheric Chemical Processes Important Terms / Facts

- **Photo-dissociation, photolysis, or photodecomposition** is a **chemical reaction** in which **a chemical compound** is **broken down by photons**. It is defined as the interaction of one or more photons with one target molecule.
- **UV radiation has a higher frequency than visible light** and **more energetic** and more likely **to break chemical bonds** in molecules that absorbs it.
- **Excited State***: Product of photochemical reaction may be electronically energized in an excited state and may make the excited species chemically more reactive.

$$NO_2 + h\nu \rightarrow NO_2^*$$

Atmospheric Chemical Processes Important Terms / Facts

- **Free Radicals**: Contain an unpaired electron (·), because of strong pairing tendency of electron, free radicals are normally highly reactive and cause most of the important chemical processes in atmosphere. Free radicals with unpaired electrons: $H_3C^{\bullet}$, $HO^{\bullet}$.

Representation of Major Atmospheric Chemical Processes

- Third Body, M: An important reaction in the stratosphere is that between an oxygen atom and an O_2 molecule to produce stratospheric ozone. In the reaction below, M is a third body, almost always a molecule of O_2 or N_2 ,that absorbs the energy released in the reaction, which otherwise would cause the product molecule to fall apart.

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

Important Gaseous Atmospheric Chemical Species

- Chemical species fall into following arbitrary and overlapping classifications:

1. Inorganic oxides (CO, CO_2, NO_2, SO_2),
2. Oxidants (O_3, H_2O_2, HO^o radical, $HO_2{}^o$ radical)
3. Reductants (CO, SO_2, H_2S),
4. Organics (also reductants; in the unpolluted atmosphere, CH_4 is the predominant organic species),
5. Oxidized organic species (carbonyls, organic nitrates),
6. Photo chemically active species (NO_2, formaldehyde),
7. Acids (H_2SO_4),
8. Bases (NH_3),
9. Salts (NH_4HSO_4,),
10. Unstable reactive species (electronically excited NO_2, $HO^{\bullet}$ radical).

Chemical and Photochemical Reactions in the Atmosphere

1. Emission of a photon (light):

$$NO_2^* \rightarrow NO_2 + h\nu$$

2. Direct reaction of an excited species:

$$O_2^* + O_3 \rightarrow 2O_2 + O$$

3. Dissociation:

$NO_2^* \rightarrow NO + O$ (tropospheric reaction)

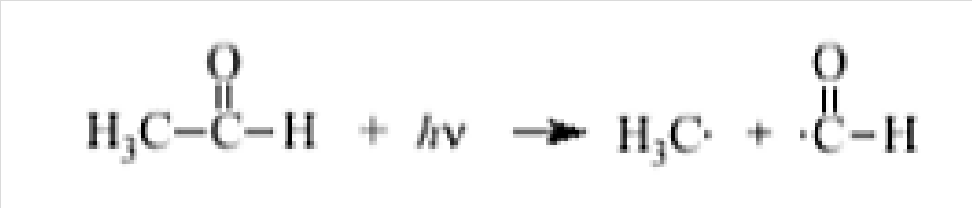
$O_2^* \rightarrow O + O$ (stratosphere leading to O_3)

4. Photoionization (formation of ions in the ionosphere)

$$N_2^* \rightarrow N_2^+ + e^-$$

Free Radicals

- **Free radicals** are atoms, molecules, or molecular fragments with **unpaired electrons**.



- Free radicals are **highly chemically reactive** because of the strong pairing tendency of their unpaired electrons.
    - Undergo series of **chain reactions** generating more free radicals.
    - Chain termination such as , $H_3C\bullet + H_3C\bullet \rightarrow C_2H_6$
- Although highly chemically reactive, **free radicals can be quite stable** in **the upper atmosphere** where there are **few other species with which they can react**.

Free Radicals: Hydroxyl ($HO^{\bullet}$) Radical

- How Hydroxyl (HO•) is formed?

  $HO^{\bullet}$ formed by photolysis of water at higher altitudes :

$$H_2O + h\nu \rightarrow HO\bullet + H\bullet$$

  As the result of ozone photolysis in lower atmosphere :

$$O_3 + h\nu(\lambda < 315\ nm) \rightarrow O^* + O_2$$

$$O^* + H_2O \rightarrow 2HO\bullet$$

- Other the sources of Hydroxyl (HO•) in the atmosphere?

$HONO + h\nu\ (\lambda < 400\ nm) \rightarrow OH + NO$

Nitrous acid vapour (Photolysis)

$H_2O_2 + h\nu\ (\lambda < 370\ nm) \rightarrow 2OH$

Hydrogen peroxide(Photodissociation)

Free Radicals: Hydroxyl ($HO^{\bullet}$) Radical

- $HO^{\bullet}$ is the single most important intermediate species in atmospheric chemical processes.
- Hydroxyl ($HO^{\bullet}$) radical drives the daytime chemistry of both polluted and clean atmosphere and acts as an atmospheric detergent.

Hydroxyl Radical: The Atmosphere's Detergent

The major route for the reformation of the hydroxyl radical in the troposphere is :

$$NO_2 + h\nu \rightarrow NO_2^*$$

$$NO_2\bullet + h\nu\ (\lambda < 400\ nm) \rightarrow NO\bullet + O\bullet$$

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

$$O_3 + h\nu\ (\lambda < 315\ nm) \rightarrow O_2 + O^*$$

$$O^* + H_2O \rightarrow 2\ \bullet OH$$

$$NO_2\bullet + H_2O \rightarrow NO\bullet + 2\ \bullet OH$$

Free Radicals: Hydroxyl ($HO^{\bullet}$) Radical

- How Hydroxyl ($HO^{\bullet}$) Radicals React with different species in the atmosphere?

- HO• reacts with many electron rich (multiple bonded) species in the atmosphere
  - CO, SO_2, H_2S, CH_4, NO
- HO• can also react by abstraction of hydrogen, e.g.

$$CH_4 + \bullet OH \rightarrow \bullet CH_3 + H_2O$$

$$NH_3 + \bullet OH \rightarrow \bullet NH_2 + H_2O$$

$$H_2S + \bullet OH \rightarrow \bullet SH + H_2O$$

$$CH_3Cl + \bullet OH \rightarrow \bullet CH_2Cl + H_2O$$

- HO• commonly removed by reaction with CO or CH_4

$$HO\bullet + CO \rightarrow CO_2 + H\bullet$$

$$HO\bullet + CH_4 \rightarrow H_3C\bullet + H_2O$$

Methyl Radical

Lecture Summary

- Photochemical Reactions in the Atmosphere

The End