

## Tropospheric Chemistry – Radical Reactions

### Topics covered in today's class.

We will discuss how radicals react in the stratosphere

- Interactions with hydroxyl radical
- Tropospheric oxidation of methane
- Processes leading to photochemical smog formation
- Oxidation of atmospheric SO<sub>2</sub>

### Note:

- The class website is <http://www.nd.edu/~pkamat/chem20204.html> (Presentation List, Lecture Notes and Assignments are posted)
- If you have any questions or need help, please get in touch with me.

### Keypoints :

#### Hydroxyl Radical Reactions

- Hydroxyl radical is the prominent oxidizing species in the atmosphere
- Usually it reacts by adding itself to the molecule if it has multiple bonds
- It abstract hydrogen atom from molecules that do not have multiple bonds to produce carbon centered radicals
- •OH addition does not occur to O-O bonds since the bonding that would result will be weak

#### Peroxy radical reactions

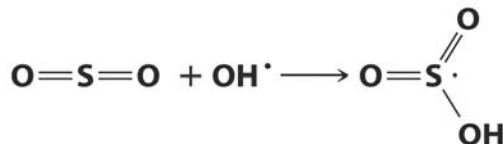
- Formed by reaction of carbon centered radicals with oxygen
- Peroxy radicals are less reactive and do not abstract hydrogen.
- Most common reaction of peroxy radical is with NO to produce NO<sub>2</sub>

#### Free radical reactions with nonperoxy radicals

- Creates additional bonds and usually generates HOO•.
- In the absence of H abstraction it can also add

#### Photolysis of NO<sub>2</sub>, HNO<sub>3</sub> and formaldehyde produce reactive radicals

Radical reactions play an important role in the oxidation of CH<sub>4</sub>, VOCs and atmospheric SO<sub>2</sub>.



#### Solve:

SO<sub>2</sub> dissolves in water (Henry's constant  $K_H = 1 \text{ M atm}^{-1}$ ) to form H<sub>2</sub>SO<sub>3</sub>.

Determine the pH of the rain water in equilibrium with SO<sub>2</sub> of 0.1 ppm

{Note: H<sub>2</sub>SO<sub>3</sub> dissociates and it is in equilibrium with H<sup>+</sup> and HSO<sub>3</sub><sup>-</sup> ( $K = 1.7 \times 10^{-2} \text{ M}^{-1}$ ) }

