Lecture 8

February 9, 2012

Chemistry of the Atmosphere

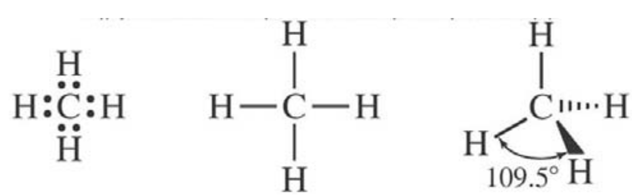
http://video.nytimes.com/video/2010/01/07/us/1247466441827/new-rules-proposed-for-smog-pollutants.html

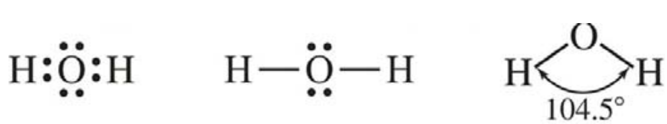
Air sampling reveals high emissions from gas field
Methane leaks during production may offset climate benefits of natural gas.

......the study estimates that natural-gas producers in an area known as the Denver-Julesburg Basin are losing about 4% of their gas to the atmosphere

Review: How to draw Lewis structures

1. Determine the sum of valence electrons
2. Use a pair of electrons to form a bond between each pair of bonded atoms
3. Arrange the remaining electrons to satisfy octet rule (duet rule for H)
4. Assign formal charges





but unlike methane, two electron pairs are bonding and two are non-bonding.

The non-bonding electron pairs take up more space than bonding pairs, so the H-to-O-to-H bond angle is compressed.

Valence Shell Electron Pair Repulsion Model allow us to predict the shape of other molecules.

Number of electron pairs around central atom	Shape of molecule	Bond angle
4 electron pairs, all bonding: CH_4, CF_4, CF_3Cl, CF_2Cl_2	tetrahedral	109.5^o
4 electron pairs, three bonding, one non-bonding: NH_3, PCl_3	Triangular pyramid	about 107^o
4 electron pairs, two bonding, two non-bonding: H_2O, H_2S	bent	about 105^o

Valence Shell Electron Pair Repulsion Theory assumes that the most stable molecular shape has the electron pairs surrounding a central atom as far away from one another as possible

Lewis Structures of Free Radicals

Free radicals possess an unpaired electron

The unpaired electron is not in actual use as a bonding electron

Carbon centered radical in which the carbon atom has one unpaired electron forms 3 bonds rather than four

H–Ċ–H
|
H

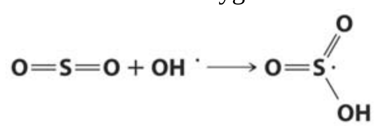
The procedure is more complicated in molecules that contain multiple bonds

For HOCO reasonable structure is

H–O–Ċ=O

Interactions with Hydroxyl Radical

- Hydroxyl radical is the prominent oxidizing species in the atmosphere
- Usually it reacts by adding itself to the molecule
- It can also abstract hydrogen atom to produce carbon centered radicals
- •OH addition does not occur to O-O bonds since the bonding that would result will be weak
- For example, in the case of SO_2, the OH radical adds to the sulfur atom forming a strong bond but not to an oxygen atom



- Hydroxyl radicals do not add to CO_2 (O=C=O) since C=O bonds are very strong
- However, it adds to CO since the addition favors conversion of triple bond to stable double bond

1. Hydrogen Abstraction Reactions

……Molecules with no multiple bonds but contain hydrogen

$$CH_4 + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_3 + H_2O$$

$$NH_3 + {}^{\bullet}OH \longrightarrow {}^{\bullet}NH_2 + H_2O$$

$$H_2S + {}^{\bullet}OH \longrightarrow {}^{\bullet}SH + H_2O$$

$$CH_3Cl + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_2Cl + H_2O$$

(CFCs such as CF_2Cl_2 are not readily oxidized by hydroxyl radicals)

•OH does not react with N_2, O_2 or fully oxidized species such as CO_2, SO_3 and N_2O_5 since these processes are highly endothermic

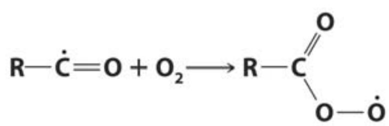
2. H atom abstraction by O_2 from nonperoxy radicals

$$CH_3O^\bullet + O_2 \longrightarrow H_2CO^\bullet + HOO^\bullet$$
$$HCO^\bullet + O_2 \longrightarrow CO + HOO^\bullet$$

Gases that undergo decomposition by absorbing UV-A or visible light can generate free radicals. For example,

$$H_2CO + \text{UV-A (338 nm)} \longrightarrow H^\bullet + HCO^\bullet$$

If there is no suitable hydrogen atom for O_2 to abstract then it adds.



3. Radicals Reaction with O_2 to produce peroxy and hydroperoxy radicals

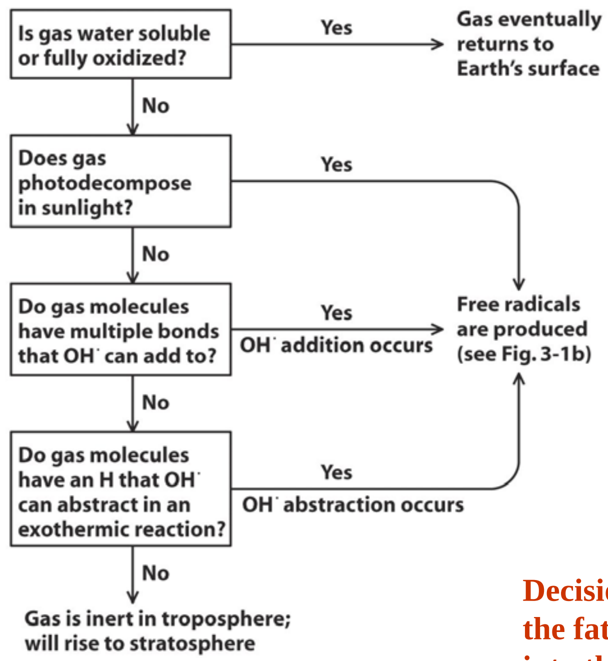
$$CH_4 + {}^\bullet OH \longrightarrow {}^\bullet CH_3 + H_2O$$

$${}^\bullet CH_3 + O_2 \longrightarrow CH_3OO^\bullet \qquad H^\bullet + O_2 \longrightarrow HOO^\bullet$$

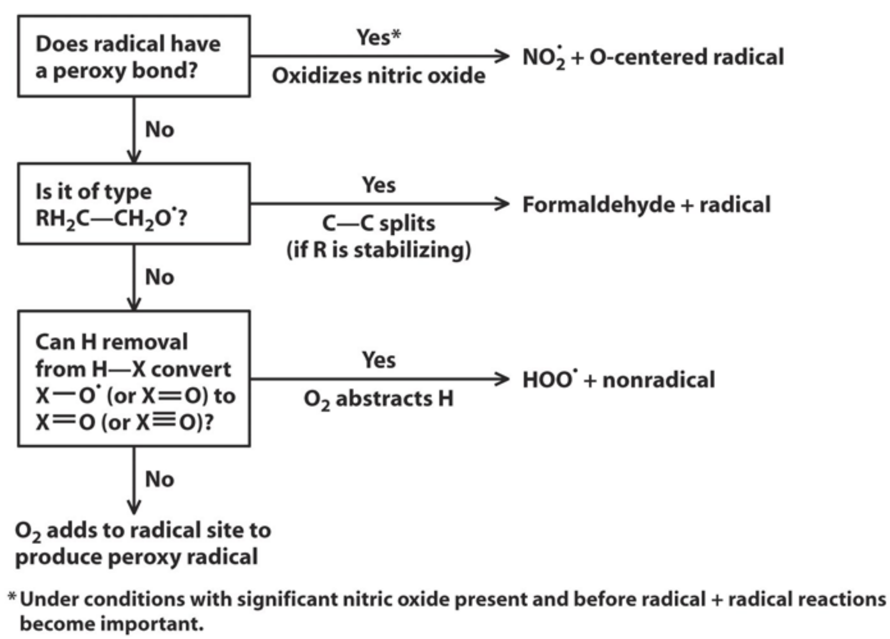
Peroxy radicals are less reactive and cannot abstract hydrogen like hydroxy radicals

The most common fate of peroxy radicals is its reaction with nitric oxide by the transfer of oxygen atom

$$HOO^\bullet + NO \longrightarrow HO^\bullet + NO_2$$
$$CH_3OO^\bullet + NO \longrightarrow CH_3O^\bullet + NO_2$$



Decision tree illustrating the fate of gases emitted into the air



Decision tree illustrating the fate of airborne free radicals

Troposphere oxidation of Methane

CH_4

Produced in inefficient (anaerobic) burning of fuels
No multiple bonds
Not soluble in water, do not absorb sunlight
Slow oxidation initiated by hydroxyl radical (hydrogen abstraction reaction)

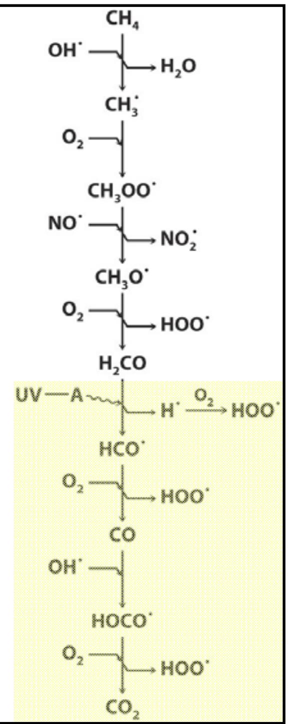
$$CH_4 + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_3 + H_2O$$

$${}^{\bullet}CH_3 + O_2 \longrightarrow CH_3OO^{\bullet}$$

$$CH_3OO^{\bullet} + NO \longrightarrow CH_3O^{\bullet} + NO_2$$

$$CH_3O^{\bullet} + O_2 \longrightarrow H_2CO + HOO^{\bullet}$$

…conversion of methane to formaldehyde



$$H_2CO + \text{UV-A (338 nm)} \longrightarrow H^{\bullet} + HCO^{\bullet}$$

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet}$$

$$HCO^{\bullet} + O_2 \longrightarrow CO + HOO^{\bullet}$$

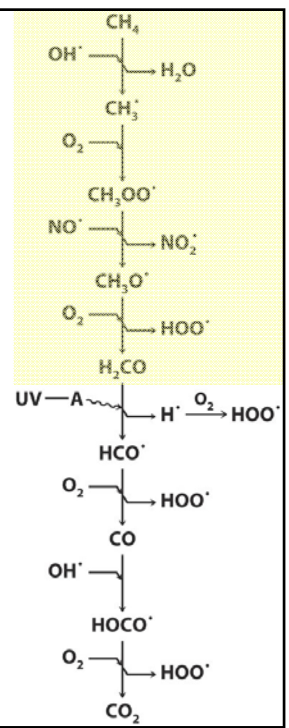
Note: CO is a stable intermediate and can further undergo transformations

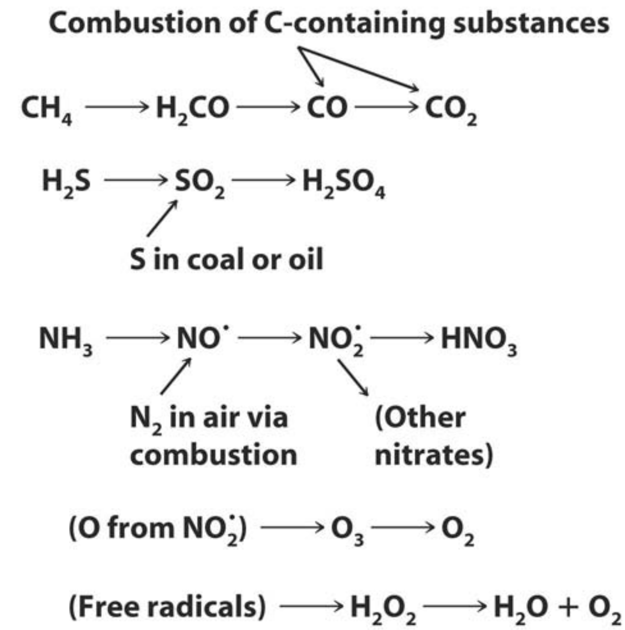
$$C \equiv O + OH^{\bullet} \longrightarrow HO\text{-}\dot{C}{=}O$$

$$H\text{–}O\text{–}\dot{C}{=}O + O_2 \longrightarrow O{=}C{=}O + HOO^{\bullet}$$

….. Production of CO_2 as the final product

$$CH_4 + 5O_2 + NO + 2OH^{\bullet} + UVA \longrightarrow CO_2 + H_2O + NO_2 + 4HOO^{\bullet}$$





Photochemical Smog

NO and unburnt hydrocarbons (VOC) are the primary reactants of photochemical smog formation

VOCs + NO + O_2 + sunlight ⟶ mixture of O_3, HNO_3, organics, free radicals

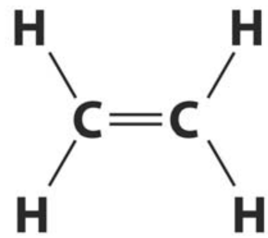
More free radicals are formed than consumed in smog because of the reaction of VOCs

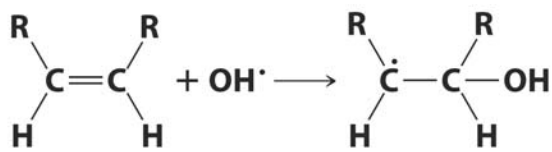
Reaction products such as aldehydes absorb UV-B and some UV-A to produce additional free radicals

Photochemical Smog : Oxidation of Reactive Hydrocarbons

Saturated hydrocarbons such as CH_4 react with hydroxyl radical by hydrogen abstraction

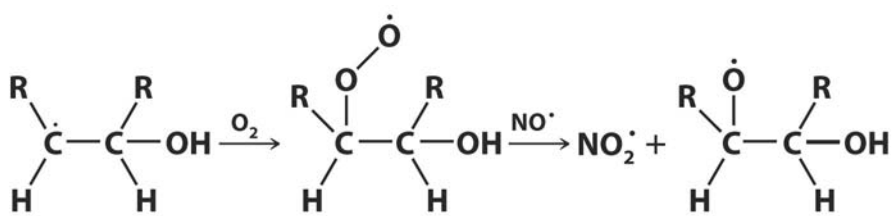
Hydrocarbons with double bond (e.g., ethylene) react with hydroxyl radical by addition because of lower activation energy





…formation of carbon centered radical

Carbon centered radical reacts with O_2 to produce a peroxy radical which in turn oxidizes NO to NO_2



Photochemical decomposition of NO_2 to NO and O and formation of ozone is responsible for photochemical smog

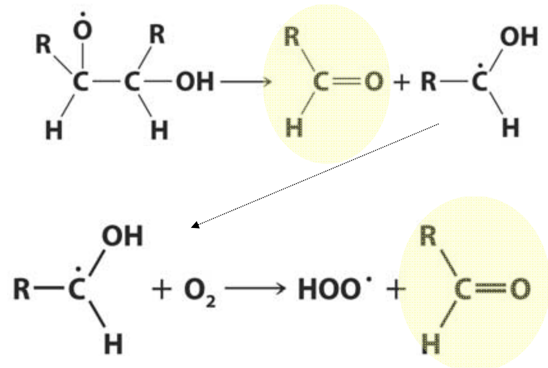
$NO_2 \longrightarrow NO + O$ (1)

$O + O_2 \longrightarrow O_3$ (2)

$NO + O_3 + \longrightarrow 2NO_2 + O_2$ (3)

Formation of Aldehyde

Decomposition of carbon centered radical

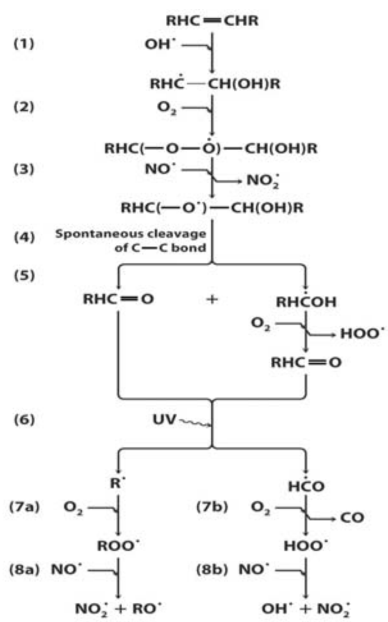


Aldehydes further decompose in sunlight

RHCO + sunlight ⟶ R• + HCO•

….further increase in the number of radicals

Mechanism of the RHC=CHR oxidation process in the smog



The Fate of Free Radicals

Rate of reaction between two radicals increases as the radical concentration increases

$$R^{\bullet} + R'^{\bullet} \longrightarrow \text{R-R}' \text{ stable molecule}$$

For example,

$$OH^{\bullet} + NO_2^{\bullet} \longrightarrow HNO_3$$

$$OH^{\bullet} + NO^{\bullet} \longrightarrow HNO_2 \xrightarrow{\text{sunlight}} OH^{\bullet} + NO^{\bullet}$$

(HONO accumulates only in the night)

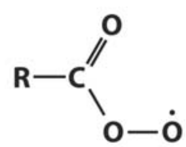
When the concentration of NOx is low,

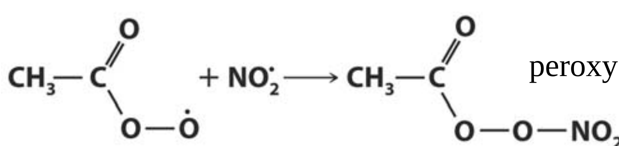
$$2OH^{\bullet} \longrightarrow H_2O_2$$

$$2HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

Fate of other radicals

O_2 + R–$\dot{C}$=O $\longrightarrow$





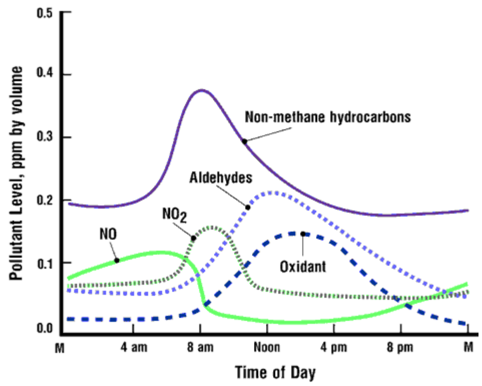
PAN

peroxyacetylnitrate

Peroxyacetylnitrate (PAN) is eye irritant and toxic to plants

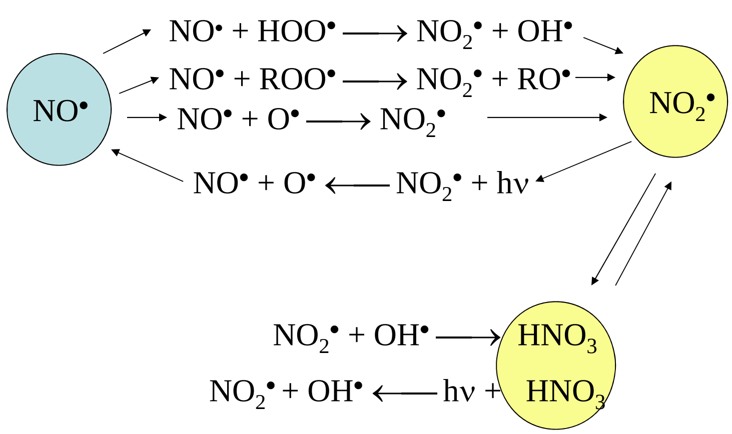
Thus in the afternoon hours a build up of oxidizing agents such as nitric acid, hydrogen peroxide and PAN is encountered

Variation of concentration of gases during the day



- Early morning traffic increases the emissions of both nitrogen oxides and VOCs as people drive to work.
- Later in the morning, traffic dies down and the nitrogen oxides and volatile organic compounds begin to react forming nitrogen dioxide, increasing its concentration.
- As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products form increasing concentrations of ozone.
- As the sun goes down, the production of ozone is halted. The ozone that remains in the atmosphere is then consumed by several different reactions.

http://jan.ucc.nau.edu/~doetqp-p/



Hydrogen abstraction reactions dominate chemistry in both stratosphere and troposphere

…….but the radicals that dictate the chemistry are different

Stratosphere: •OH, •O, •Cl, and •Br abstract H atom from stable molecule such as CH_4

Troposphere: hydroxyl and NOx radicals are the primary reactants

Processes involving loosely bound oxygen atoms

A Y-O structure from which O atom can be detached readily

TABLE 3-1 Molecules Containing Loose Oxygen Atoms

Molecule Y—O	Structure of Y—O	Y—O Bond Energy in kJ/mol	Comment
O_3	O_2—O	107	The most loose oxygen
$BrO^\bullet$	Br—O	235	
$HOO^\bullet$	HO—O	266	
$ClO^\bullet$	Cl—O	272	
$NO_2^\bullet$	ON—O	305	The least loose oxygen

Examples of “loose oxygen atom” reactions

Reaction with atomic oxygen

$$Y—O \rightarrow Y + O_2$$

Photochemical decomposition

$$Y—O + \text{sunlight} \rightarrow Y + O$$

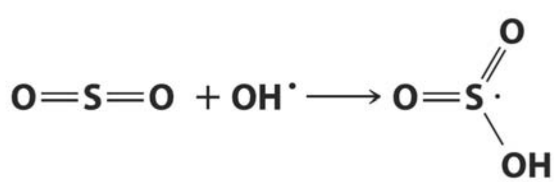
Reaction with NO

$$Y—O + NO \rightarrow Y + NO_2$$

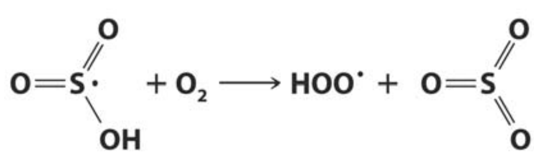
Abstraction of oxygen from Ozone

$$Y—O + X \rightarrow Y + XO$$
$$O_2—O + Cl \rightarrow O_2 + ClO$$

Oxidation of atmospheric SO_2 in gas phase



Addition of OH• followed by the formation of SO_3



$$SO_3 + H_2O(g) \longrightarrow H_2SO_4\ (g)$$
$$H_2SO_4(g) + nH_2O \longrightarrow H_2SO_4\ (aq)$$

Oxidation of atmospheric SO_2 in Aqueous Phase

Determination of total sulfur content and H^+ in water

SO_2 is soluble in water. It exists in the dissolved form if there is significant cloud or mist in the atmosphere. The oxidation to sulfuric acid occurs in the aqueous phase after rain drops accumulate on earth.

$$SO_2(g) + H_2O(aq) \rightleftharpoons H_2SO_3(aq)$$

Typical SO_2 conc. is 0.1 ppm or $(0.1/10^6) = 1\text{x}10^{-7}$ atm

From Henry's law, $K_H = [H_2SO_3]/P$ $\quad K_H = 1$ M atm^{-1}

$\therefore [H_2SO_3] = 1$ M atm$^{-1} \times 1\times10^{-7}$ atm $= 1\times10^{-7}$ M (or moles/L)

But H_2SO_3 dissociates readily with a dissociation constant of $K = 1.7\times10^{-2}$ M^{-1}

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3 \qquad K = 1.7\text{x}10^{-2}\ M^{-1}$$

As HSO_3 dissociates, more of SO_2 dissolves until it reaches an equilibrium with H^+ and HSO_3^-

$1.7\text{x}10^{-2}$ M^{-1} (or K) = $[H^+][HSO_3^-]/[H_2SO_3]$

$1.7\text{x}10^{-2}$ M^{-1} (or K) = $[H^+]^2/[H_2SO_3]$ = $[H^+]^2/1\text{x}10^{-7}$ M $\quad$ …$[H+]=[HSO_3^-]$

$[H^+]^2 = 1.7\text{x}10^{-9}$ M^2 $\quad$ or $[H+] \cong 4\text{x}10^{-5}$ M

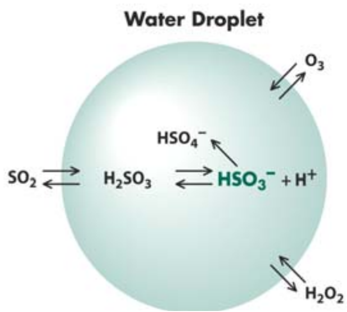
pH of rain water = $-\log [H^+] = 4.4$

Total $[H^+] = [HSO_3^-] = 4\text{x}10^{-5}$ M

$\therefore$ Total dissolved S is $4\text{x}10^{-5}$ M

The acidity of water is also affected by other pollutants.
What is the effect of excess H^+ on the HSO_3^- concentration?

Oxidation of atmospheric SO_2 in Aqueous Phase



- Dissolved SO_2 is oxidized by trace amounts of H_2O_2 and O_3
- Sunlight is a dominant factor in forming O_3 and H_2O_2
- If strong acids are present in the droplet they control the pH.
- Any freshly dissolved SO_2 has no effect

$$[HSO_3^-] = K \times [H_2SO_3]/[H^+]$$
$$= 1.7\times10^{-2} \times 10^{-7}/[H^+]$$
$$= 1.7\times10^{-9}/[H^+]$$

……inversely proportional to H^+

Since strong acids dissociate readily, $[H^+]$ concentration controls the overall concentration of HSO_3^-

- Acidity of the droplet has effect on the rate of SO_2 oxidation
- At pH below 5 H_2O_2 dominates oxidation and above pH 5 ozone or other catalytic reactions dominate the oxidation.