ATMOSPHERIC CHEMISTRY

A) What is global warming all about?

CO_2
CH_4
N_2O

B) First a review

Low pH of rain

1) Carbonic acid production due to atmospheric CO_2.

2) Further lowered by SO_2…

3) …and NO_2.

C) Chemical reactions in the atmosphere

The most important reactive intermediate species in atmospheric chemical processes is the hydroxyl radical ($OH^{\bullet}$) formed by:

1) photochemical decomposition of ozone …

$O_3 + h\nu \rightarrow$

*** indicates an excited molecule (temporarily reactive)**

… which reacts with water

$O^{*} + H_2O \rightarrow$

$^{\bullet}$ indicates a free radical (unpaired e-)

2) direct hydrolysis of water

$H_2O + h\nu \rightarrow$

The concentration of $OH^{\bullet}$ in the atmosphere is very small, how can it be so important?

$CH_4 + OH^{\bullet} \rightarrow$

$NH_3 + OH^{\bullet} \rightarrow$

$H_2S + OH^{\bullet} \rightarrow$

$CH_3Cl + OH^{\bullet} \rightarrow$

These reactions are all _____ and occur very rapidly.

The resultant radicals can then interact with other radicals, sometimes forming more $OH^{\bullet}$ and generating other radicals

Examples:

$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow$

$CH_3^{\bullet} + O_2 \rightarrow$

Other important radicals

Methylperoxyl radical

Hydroperoxyl radical

D) Atmospheric oxidation of methane to CO_2

Initiated by the rxn:

$CH_4 + OH^{\bullet} \rightarrow$

Overall rxn:

$CH_4 + 5O_2 + 5NO^{\bullet} + UV\text{-}C \rightarrow$

The result is an overall increase in radicals that can interact with other atmospheric gases.

E) Ozone

I Creation of ozone (Fig. 1-5)

Layers in atmosphere:

Troposphere -

Stratosphere –

Formation of O <u>above</u> the stratosphere

O_2 + UV-C →

Ozone formation occurs in the stratosphere. Why?

O + O_2 →

The ozone layer exists between 15 - 35 km above ground.

II Noncatalytic destruction of ozone (Chapman cycle Fig. 1-12)

O_3 + UV →

O + O_3 →

III Catalytic destruction of ozone

Naturally occurring nitrous oxide

$N_2O + O^* \rightarrow 2NO^\bullet$

Overall rxn?

So how does increasing N_2O concentrations influence ozone?

IV Chlorine as a catalyst

Where does $Cl^{\bullet}$ come from?

Initial sources: methyl chloride; production of chlorinated gases (such as CFCs)

$HCl + OH^{\bullet} \rightarrow$

CH_3Cl + UV-C $\rightarrow$

$ClONO_2 \rightarrow$

What is the overall rxn for the destruction of ozone by $Cl^{\bullet}$?

Note that $Cl^{\bullet}$ is regenerated.

The avg $Cl^{\bullet}$ destroys 10,000 ozone molecules.