February 2009

Addendum to Chapter 5

For the spontaneous decomposition of ozone triggered by activation caused by UV radiation, we have seen that the following mechanism is in agreement with the observed rate form.

$$O_3 \underset{k_2}{\overset{k_1}{\rightleftarrows}} O + O_2 \qquad (1)$$

$$O + O_3 \xrightarrow{k_3} 2O_2 \qquad (2)$$

The overall stoichiometry is

$$2O_3 = 3O_2 \qquad (3)$$

The first step, shown is reversible, is essentially the UV triggered initiation step, from left to right, and extinction (termination) step for the free radical, from right to left.

We have seen that application of PSSA to the above mechanism leads to the following rate form:

$$-R_{O_3} = \frac{2k_1k_3C_{O3}^{\,2}}{k_2C_{O_2} + k_2C_{O_3}} \qquad (4)$$

Since the first term in the denominator dominates at most conditions, the rate can be represented as

$$-R_{O_3} = 2k_3K_1\frac{C_{O3}^{\,2}}{C_{O_2}} \qquad (5)$$

where $K_1 = k_1/k_2$ is the equilibrium constant for the first step.

Observing our previous result for the concentration of the active intermediate, C_O, we note that

$$C_O = K_1\frac{C_{O3}}{C_{O2}} \qquad (6)$$

so that the rate can be represented by

$$-R_{O_3} = 2k_3(C_O)(C_{O3}) \qquad (7)$$

which is the rate for step 2, which is the rate-limiting step (RLS).

The value of the rate constant is reported as:

$$k_3 = 1.9x10^{-11} e^{-2300/T} (cm^3 / molecule\ s) \qquad (8)$$

[Convert this to usual molar units such as (cm^3/mol s) or (L/mol s)]

We are interested in estimating by how much can this rate be accelerated in the presence of the catalyst such as chlorine atoms or radicals that occur in the stratosphere due to the presence of fluorochlorocarbons like freons.

This catalyzed decomposition of ozone can be represented by a simplified Rowland-Robinson mechanism

$$CF_2C\ell_2 \xrightarrow[<220_{nm}]{h\upsilon} C\ell + CF_2C\ell \qquad (9)$$

The above is the initiation step that gives rise to the following catalytic sequence (cycle)

$$C\ell + O_3 \xrightarrow{k_{c_1}} O_2 + C\ell O \qquad (10)$$

$$C\ell O + O \xrightarrow{k_{c_2}} C\ell + O_2 \qquad (11)$$

The sum of (10) and (11) leads to

$$O + O_3 \xrightarrow{C\ell} 2O_2 \qquad (12)$$

and we want to compare the rate of the catalyzed ozone decomposition (reactions (10) and (11)) to step (2) of the uncatalyzed mechanism. It is known that

$$k_{c1} = 5x10^{-11} e^{-140/T} (cm^3 / molecule\ s) \qquad (13)$$

$$k_{c2} = 1.1x10^{-10} e^{-2.20/T} (cm^3 / molecule\ s) \qquad (14)$$

Notice the much lower activation energy for the rate constants of the catalyzed steps.

Using PSSA we set the net rate of formation of $C\ell O$ to zero.

$$R_{C\ell O} = k_{c1} C_{C\ell} C_{O3} - k_{c2} C_{C\ell O} C_O = 0 \qquad (15)$$

Since the sequence is catalytic we recognize that the total concentration of Chlorine atoms available $(C\ell \text{ and } C\ell O)$ is constant

$$C_{C\ell} + C_{C\ell O} = C_{C\ell}^o \qquad (16)$$

Since from eq (15) it follows that

$$C_{C\ell} = \frac{k_{c2}C_O}{k_{c1}C_{O3}} C_{C\ell O} \qquad (17)$$

Upon substitution for $C_{C\ell O}$ *from eq*(16) into eq (17) we get

$$C_{C\ell} = \frac{k_{C2}C_O C_{C\ell}^o}{k_{c1}C_{O3} + k_{c2}C_O} \qquad (17a)$$

and

$$C_{C\ell O} = \frac{k_{C1}C_{03}C_{C\ell}^O}{k_{c1}C_{O3} + k_{c2}C_O} \qquad (17b)$$

The catalyzed rate of ozone decomposition becomes

$$-R_{O_{3C}} = k_{c1}C_{C\ell}C_{O3} = \frac{k_1 k_{c2} C_{C\ell}^o C_O C_{O3}}{k_{c1}C_{O3} + k_{c2}C_O} \qquad (18)$$

Typically, $k_{c2}C_O << k_{c1}C_{O3}$ so that the rate can be represented by

$$-R_{O3} = k_{c2}C_{C\ell}^O C_O \qquad (19)$$

Now let us compare the above catalytic rate of ozone decomposition and the spontaneous rate of eq (2).

$$\frac{-R_{O3_C}}{-R_{O3}} = \frac{k_{c2}C_{C\ell}^O C_O}{k_3 C_O C_{O2}} = \frac{k_{C2}C_{C\ell}^O}{k_3 C_{O3}} \qquad (20)$$

In the freons contaminated stratosphere

$$\frac{C_{C\ell}^O}{C_{O3}} = \frac{C_{C\ell} + C_{C\ell O}}{C_{O3}} \approx 10^{-3} \qquad (21)$$

Using he reported rate constants we get

$$\frac{-R_{O_{3C}}}{-R_{O3}} = \frac{1.1x10^{-10}e^{-220/T}}{1.9x10^{-11}e^{-2300/T}} x10^{-3} = 5.79x10^{-3}e^{2080/T} \qquad (22)$$

At T=200K (-73˚C) this become

$$\frac{-R_{O3C}}{-R_O} = 190 \qquad 23)$$

Thus the presence of CFCs accelerates ozone decomposition almost 200 times! For full explanation of the dynamics of the ozone hole above Antarctica read the Rowland and Molina’s paper,. Now you have the tools to understand it.

Remember that other components such as oxides of nitrogen contribute significantly to ozone dynamics.