12.10: Catalysis

There are many examples of reactions that involve catalysis. One that is of current importance to the chemistry of the environment is the catalytic decomposition of ozone (Fahey, 2006). The overall reaction

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

can be catalyze by atomic chlorine by the following mechanism.

$$O_3 + Cl \xrightarrow{k_1} ClO + O_2$$

$$ClO + O \xrightarrow{k_1} Cl + O_2$$

The rate of change of the intermediate (ClO) concentration is given by

$$\frac{[ClO]}{dt} = k_1[O_3][Cl] - k_2[ClO][O]$$

Applying the steady state approximation to this relationship and solving for $[ClO]$ produces

$$ClO] = \frac{[O_3][Cl]}{k_2[O]} \tag{12.10.1}$$

The rate of production of O_2 (which is two times the rate of the reaction) is given by

$$\frac{d[O_2]}{dt} = k_2[O_3][Cl] + k_2[ClO][O]$$

Substituting the expression for $[ClO]$ (Equation 12.10.1) into the above expression yields

$$\begin{aligned}\frac{d[O_2]}{dt} &= k_2[O_3][Cl] + k_2\left(\frac{[O_3][Cl]}{k_2[O]}\right)[O] \\ &= k_1[O_3[Cl] + k_1[O_3][Cl] \\ &= 2k_1[O_3][Cl]\end{aligned}$$

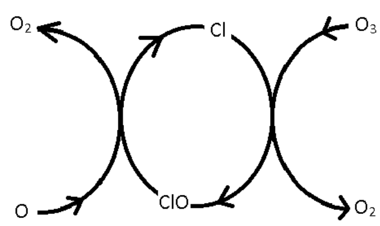
And so the rate of the reaction is predicted to be first order in $[O_3]$, first order in the catalyst $[Cl]$, and second order overall.

$$\text{rate} = k[O_3][Cl]$$

If the concentration of the catalyst is constant, the reaction kinetics will reduce to first order.

$$\text{rate} = k[O_3]$$

This catalytic cycle can be represented in the following diagram:



On the left, atomic oxygen picks up an oxygen atom from ClO to form O_2 and generate a Cl atom, which can then react with O_3 to form ClO and an O_2 molecule. The closed loop in the middle is characteristic of the catalytic cycle involving Cl and ClO. Further, since Cl acts as a catalyst, it can decompose many O_3 molecules without being degraded through side reactions.

The introduction of chlorine atoms into the upper atmosphere is a major environmental problem, leading to the annual thinning and eventual opening of the ozone layer over Antarctica. The source of chlorine is from the decomposition of chlorofluorocarbons which are sued as refrigerants and propellants due to their incredible stability near the Earth's surface. However, in the upper atmosphere, these compounds are subjected to ultraviolet radiation emitted by the sun and decompose to form the radicals responsible for the catalytic decomposition of ozone. The world community addressed this issue by drafting the **Montreal Protocol (Secretariat, 2015)**, which focused on the emission of ozone-destroying compounds. The result of this action has brought about evidence of the Antarctic ozone hole healing (K, 2015). This is one very good example science-guided political, industrial, and economic policies leading to positive changes for our environment.