12.7: The Lindemann Mechanism

The **Lindemann mechanism** (Lindemann, Arrhenius, Langmuir, Dhar, Perrin, & Lewis, 1922) is a useful one to demonstrate some of the techniques we use for relating chemical mechanisms to rate laws. In this mechanism, a reactant is collisionally activated to a highly energetic form that can then go on to react to form products.

$$A + A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A^*$$

$$A^* \xrightarrow{k_2} P$$

If the steady state approximation is applied to the intermediate A^*

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] \approx 0$$

an expression can be derived for $[A^*]$.

$$A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

Substituting this into an expression for the rate of the production of the product P

$$\frac{d[P]}{dt} = k_2[A^*]$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$$

In the limit that $k_{-1}[A] \ll k_2$, the rate law becomes first order in $[A]$ since $k_{-1}[A] + k_2 \approx k_{-1}[A]$.

$$\frac{d[P]}{dt} = \frac{k_2 k_1}{k_{-1}}[A]$$

This will happen if the second step is very slow (and is the rate determining step), such that the reverse of the first step "wins" in the competition for [A*]. However, in the other limit, that $k_2 \gg k_{-1}[A]$, the reaction becomes second order in $[A]$ since $k_{-1}[A] + k_2 \approx k_2$.

$$\frac{d[P]}{dt} = k_1[A]^2$$

which is consistent with the forward reaction of the first step being the rate determining step, since A^* is removed from the reaction (through the formation of products) very quickly as soon as it is formed.

Third-body Collisions

Sometimes, the **third-body collision** is provided by an inert species M, perhaps by filling the reaction chamber with a heavy non-reactive species, such as Ar. In this case, the mechanism becomes

$$A + M \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

And in the limit that $[A^*]$ can be treated using the steady state approximation, the rate of production of the product becomes

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

And if the concentration of the third body collider is constant, it is convenient to define an **effective rate constant**, k_{uni} .

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

The utility is that important information about the individual step rate constants can be extracted by plotting $1/k_{uni}$ as a function of $1/[M]$.

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_2 k_1} + k_2 \left(\frac{1}{[M]} \right)$$

The plot should yield a straight line, the slope of which gives the value of k_2, and the intercept gives $(k_{-1}/k_2 k_1)$.
