Lindemann-Hinshelwood Mechanism

1 Multiple Reactions Mechanism

Normally we express the unimolecular reaction as:

$$A \xrightarrow{k_1} products \tag{1}$$

actually it is not due to single reaction, but multiple reaction mechanism. **Excitation:**

$$A + M \xrightarrow{\kappa_e} A^* + M \tag{2}$$

Here A^* is the activated complex. **De-Excitation:**

$$A^* + M \xrightarrow{k_{de}} A + M \tag{3}$$

Unimolecular Product Formation:

$$A^* \xrightarrow{k_{uni}} products$$
 (4)

Therefore, we can define:

$$\frac{d[prod]}{dt} = k_{uni}[A^*] \tag{5}$$

2 Steady State Assumption

To find the over production rate, we need to combine all steps to find $\frac{d[A^*]}{dt}$:

$$\frac{d[A^*]}{dt} = k_e[A][M] - k_{de}[A^*][M] - k_{uni}[A^*]$$
(6)

Now we introduce the **steady state assumption**. It refers to the assumption that the concentrations of some intermediates in the combustion reaction remain constant over time. This assumption often made for minor species to simplify kinetics problems.

Now we assume $[A^*]$ is in steady state, which means:

$$\frac{d[A^*]}{dt} = 0\tag{7}$$

Therefore:

$$[A^*] = \frac{k_e[A][M]}{k_{de}[M] + k_{uni}}$$
(8)

Then, combine with the product formation formula:

$$\frac{d[prod]}{dt} = k_{uni}[A^*] = k_{uni} \frac{k_e[A][M]}{k_{de}[M] + k_{uni}}$$
(9)

Recall the global reaction formula:

$$\frac{d[prod]}{dt} = k_1[A] \tag{10}$$

Finally we have:

$$k_1 = k_{uni} \frac{k_e[M]}{k_{de}[M] + k_{uni}} = \frac{k_e[M]}{1 + \frac{k_{de}[M]}{k_{uni}}}$$
(11)

Now we analyze the pressure dependence of k_1 . When the pressure is low, $[M] \approx 0$:

$$k_1 = \frac{k_e[M]}{1 + \frac{k_{de}[M]}{k_{uni}}} \approx \frac{k_e[M]}{1} = k_0$$
(12)

When the pressure is high:

$$k_{1} = \frac{k_{e}[M]}{1 + \frac{k_{de}[M]}{k_{uni}}} \approx \frac{k_{e}[M]}{\frac{k_{de}[M]}{k_{uni}}} = \frac{k_{e}k_{uni}}{k_{de}} = k_{\infty}$$
(13)