29.6: The Lindemann Mechanism

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. Frederick Lindemann discovered the concept in 1921 and Cyril Hinshelwood developed it. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step. The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

General Mechanism

The schematic reaction $A + M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A + M \rightleftharpoons A^* + M \tag{29.6.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^* \overset{k_2}{\rightarrow} P \tag{29.6.2}$$

with

- forward reaction rate: k_2

Assuming that the concentration of intermediate A^* is held constant according to the quasi steady-state approximation, what is the rate of formation of product P?

Solution

First, find the rates of production and consumption of intermediate A^*. The rate of production of A^* in the first elementary step (Equation 29.6.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^*]}{dt} = \underset{\text{(forward first step)}}{k_1[A][M]} - \underset{\text{(reverse first step)}}{k_{-1}[A^*][M]} - \underset{\text{(forward second step)}}{k_2[A^*]} \tag{29.6.3}$$

According to the steady-state approximation,

$$\frac{d[A^*]}{dt} \approx 0 \tag{29.6.4}$$

Therefore the rate of production of A^* (first term in Equation 29.6.3) equals the rate of consumption (second and third terms in Equation 29.6.3):

$$k_1[A][M] = k_{-1}[A^*][M] + k_2[A^*] \tag{29.6.5}$$

Solving for $[A^*]$, it is found that

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \tag{29.6.6}$$

The overall reaction rate is (Equation 29.6.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{29.6.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 29.6.6 into Equation 29.6.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} \tag{29.6.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 29.6.8 can be simplified.

📌 Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 29.6.1)
2. There is a time delay Δt between collision and reaction (Equation 29.6.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 29.6.1)

✔ Example 29.6.1 : Dissociation of

The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide

$$N_2O_5 \rightarrow NO_2 + NO_3$$

is postulated to take place via two elementary steps, which are similar in form to the schematic example given above:

1. $N_2O_5 + N_2O_5 \rightleftharpoons N_2O_5^* + N_2O_5$
2. $N_2O_5^* \rightarrow NO_2 + NO_3$

Using the quasi steady-state approximation soluioten (Equation 9) with $[M] = [N_2O_5]$, then rate equation is:

$$\text{Rate} = k_2[N_2O_5]^* = \frac{k_1 k_2 [N_2O_5]^2}{k_{-1}[N_2O_5] + k_2}$$

Experiment has shown that the rate is observed as first-order in the original concentration of N_2O_5 sometimes, and second order at other times.

- If $k_2 >> k_{-1}$, then the rate equation may be simplified by assuming that $k_{-1} \approx 0$. Then the rate equation is

$$\text{Rate} = k_1[N_2O_5]^2$$

which is *second order*.
- If $k_2 << k_{-1}$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is

$$\text{Rate} = \frac{k_1 k_2 [N_2O_5]}{k_{-1}} = k_{obs}[N_2O_5]$$

which is *first order* with

$$k_{obs} = \frac{k_2 k_2}{k_{-1}}.$$
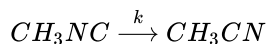

❓ Exercise 29.6.1

The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

$k_{obs}(s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5](mol/m^{-3})$	10	25	50

> Confirm that these data are consistent with the Lindemann mechanism and derive a rate constant and a ratio of two rate constants for elementary reactions in the mechanism. What are the units of the two quantities.

Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1st order rate kinetics. Experimentally, however, 1st order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2nd order rate law:

$$\frac{d[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{29.6.9}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\text{A} + \text{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{A}^* + \text{M} \tag{29.6.10}$$

$$\text{A}^* \xrightarrow{k_2} \text{B} \tag{29.6.11}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of A^* is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species B with time:

$$\frac{d[\text{A}^*]}{dt} = k_1[\text{A}][\text{M}] - k_{-1}[\text{A}^*]_{ss}[\text{M}] - k_2[\text{A}^*]_{ss} \approx 0 \tag{29.6.12}$$

Solving for $[\text{A}^*]$,

$$[\text{A}^*] = \frac{k_1[\text{M}][\text{A}]}{k_2 + k_{-1}[\text{M}]} \tag{29.6.13}$$

The reaction rates of species A and B can be written as

$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} = k_2[\text{A}^*] = \frac{k_1 k_2[\text{M}][\text{A}]}{k_2 + k_{-1}[\text{M}]} = k_{\text{obs}}[\text{A}] \tag{29.6.14}$$

where

$$k_{\text{obs}} = \frac{k_1 k_2[\text{M}]}{k_2 + k_{-1}[\text{M}]} \tag{29.6.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}[\text{M}] \gg k_2$. Equation 29.6.14 then becomes

$$-\frac{d[\text{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\text{A}] \tag{29.6.16}$$

which follows 1st order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}[\text{M}] \ll k_2$. In this scenario, Equation 29.6.14 becomes

$$-\frac{d[\text{A}]}{dt} = k_1[\text{A}][\text{M}] \tag{29.6.17}$$

which follows second order rate kinetics, consistent with experimental observations.

References

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