CK-23

Chapter 29: Reaction Mechanisms

Always remember….

- One can <u>never prove</u> a reaction mechanism, although evidence may disprove a mechanism.

- Verifying proposed mechanisms requires extensive experimental verification of each proposed step!

Let's examine a reaction …

$$A \xrightarrow{k_{obs}} P$$

Reaction could progress in multiple ways… How can we distinguish?

Case 1: One elementary step

$$A \xrightarrow{k_1} P$$

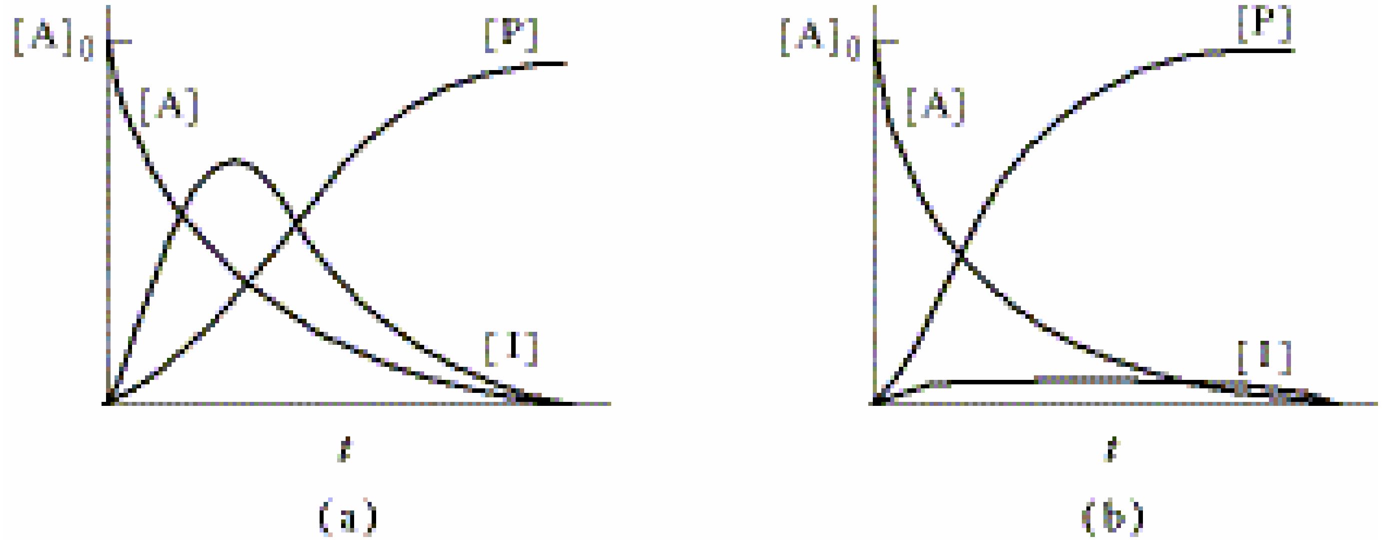
Case 2: Two step reaction

$$A \xrightarrow{k_1} I$$

$$I \xrightarrow{k_2} P$$

Now let's focus on the intermediate… CK-26

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



How do k_1 and k_2 relate in case a? in case b?

(a) I forms quickly but decays slowly…

(b) I builds up to a constant, nearly negligible, concentration until near end of reaction. …

EX-CK5

Rate Laws do not yield unique mechanisms

An empirically determined rate law does not imply a unique reaction mechanism!

Consider reaction: $2\mathrm{NO}(g) + \mathrm{O}_2(g) \xrightarrow{k_{obs}} 2\mathrm{NO}_2(g)$

Experimentally, it was determined that the rate is given by:

$$v(t) = k_{obs}[\mathrm{NO}]^2[\mathrm{O}_2]$$

Researchers proposed two possible mechanisms. They need to determine if one of them is correct.

So how would researchers distinguish between the mechanisms?

Remember the Chain Rxn from CK-6? CK-28

$H_2(g) + Br_2\ (g) \rightarrow 2HBr\ (g)$

$$v(t) = \frac{2k'[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k''[\mathrm{HBr}][\mathrm{Br_2}]^{-1}}$$

Proposed Mechanism

Initiation: $Br_2(g) + M(g) \xrightarrow{k_1} 2Br^{\cdot}(g) + M(g)$

Propagation:

$$\left.\begin{aligned} Br^{\cdot}(g) + H_2(g) &\xrightarrow{k_2} HBr(g) + H^{\cdot}(g) \\ H^{\cdot}(g) + Br_2(g) &\xrightarrow{k_3} HBr(g) + Br^{\cdot}(g) \end{aligned}\right.$$

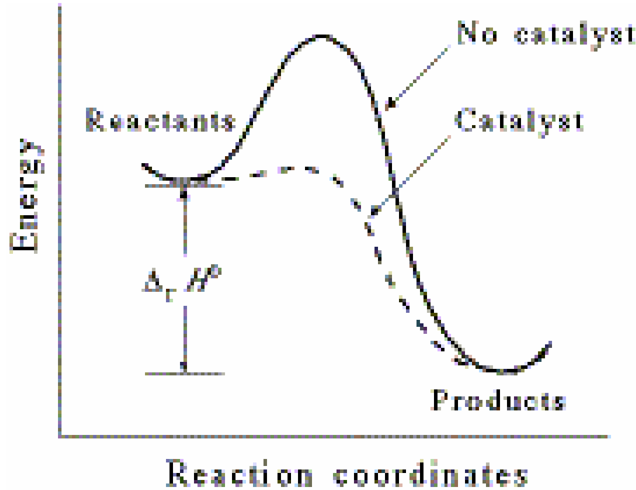
Inhibition: $HBr(g) + H^{\cdot}(g) \xrightarrow{k_{-2}} Br^{\cdot}(g) + H_2(g)$

Termination: $2Br^{\cdot}(g) + M(g) \xrightarrow{k_{-1}} Br_2(g) + M(g)$

What about the solution kinetics lab?!

- Now that we’ve explored reaction mechanisms and rate laws, let’s try to derive the rate laws from the solution kinetics lab…

Catalyst: A substance that participates in the chemical reaction but is not consumed. Provides a new mechanism for reaction and can cause reaction to occur faster.



In an experiment involving a catalyst, there are two competing reactions:

$$A \rightarrow \text{products} \qquad\qquad A + \text{catalyst} \rightarrow \text{products} + \text{catalyst}$$

If both reactions are elementary, overall rate is given by:

$$-\frac{d[A]}{dt} = k[A] + k_{cat}[A][catalyst]$$