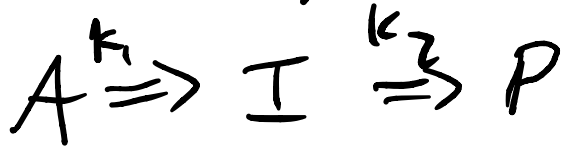


How can we distinguish multistep from single step?

good example comes from



Real example $OClO \rightleftharpoons Cl + O_2$

actually $OClO \rightleftharpoons ClOO$



with $v_f^1 \gg v_b^1$ and $v_f^2 \gg v_b^2$

so $OClO \Rightarrow ClOO \Rightarrow Cl + O_2$

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dI}{dt} = k_1 A - k_2 I$$

$$\frac{dP}{dt} = k_2 I$$

Solve for $A = A_0$

$$A(t) = A_0 e^{-k_1 t}$$

$$I(t) = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$P = A_0 - I - A$$

$$= A_0 \left(1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right)$$

prob 29-5
not doing

For a single step reaction

$$P = A_0 (1 - e^{-k_1 t})$$

So when can these be distinguished?

if $k_2 \gg k_1$

$$P = [A]_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]$$

$\uparrow \quad \uparrow$
 $\approx -k_c$ decays fast

$$\approx [A]_0 (1 - e^{-k_1 t}), \text{ can't distinguish}$$

if $k_1 \gg k_2$

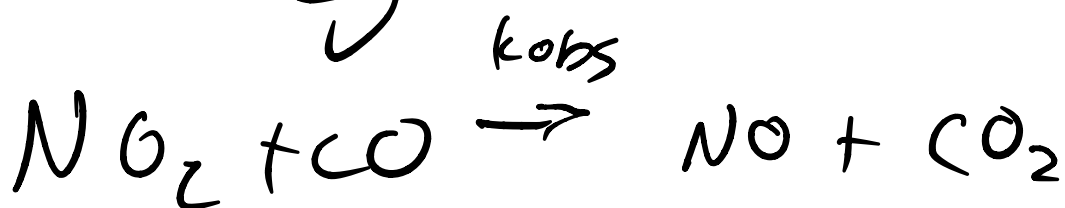
$$P \approx [A]_0 (1 - e^{-k_2 t})$$

Measure $-\frac{dA}{dt}$ & $\frac{dP}{dt}$, distinguishable!

Rate determining step

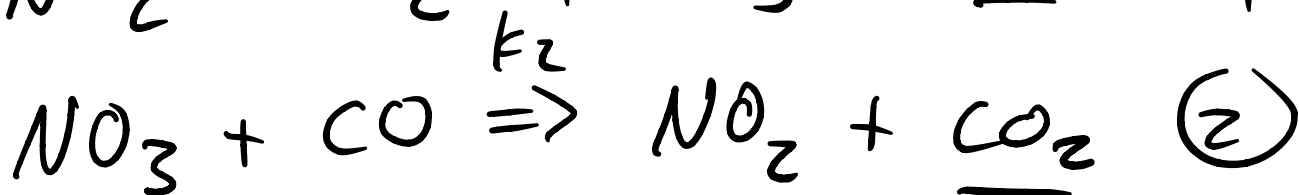
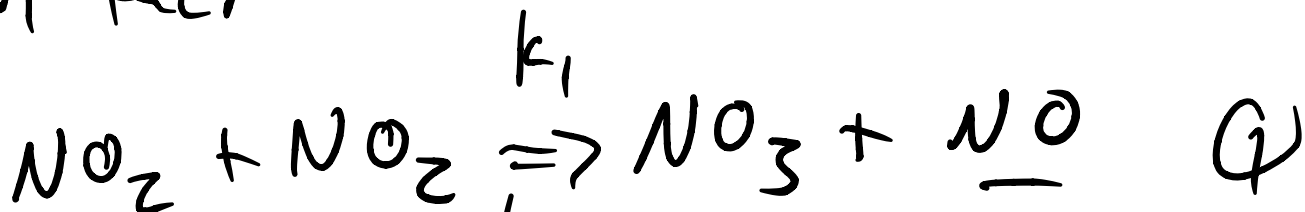
If one step is very slow,
sets apparent reaction mechanism

eg



★ not $v = k [\text{NO}_2] [\text{CO}]$

in fact

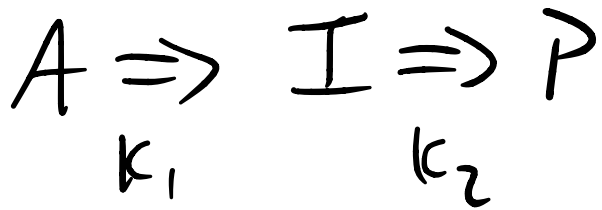


$$v_1 \ll v_2$$

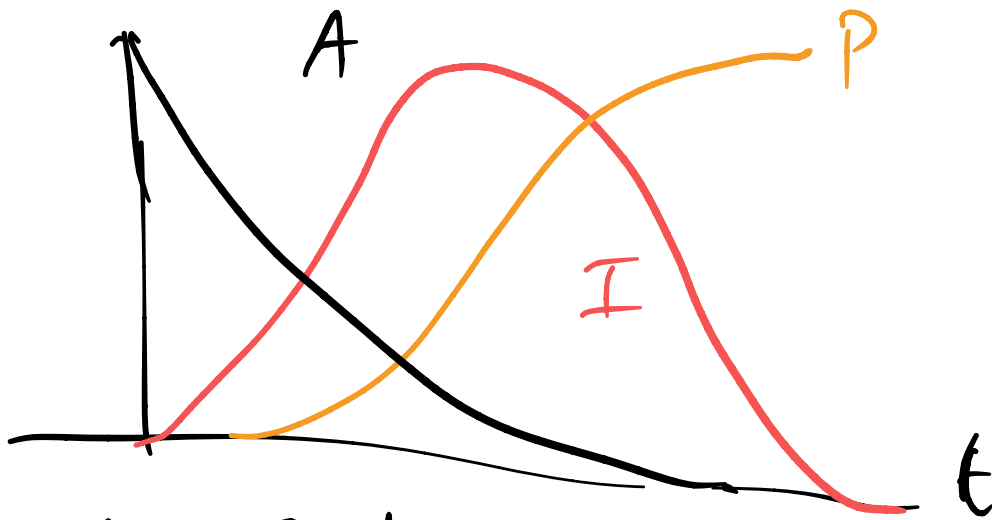
$$\text{so } v = k_1 [\text{NO}_2]^2$$

as long as sufficient CO
waiting around

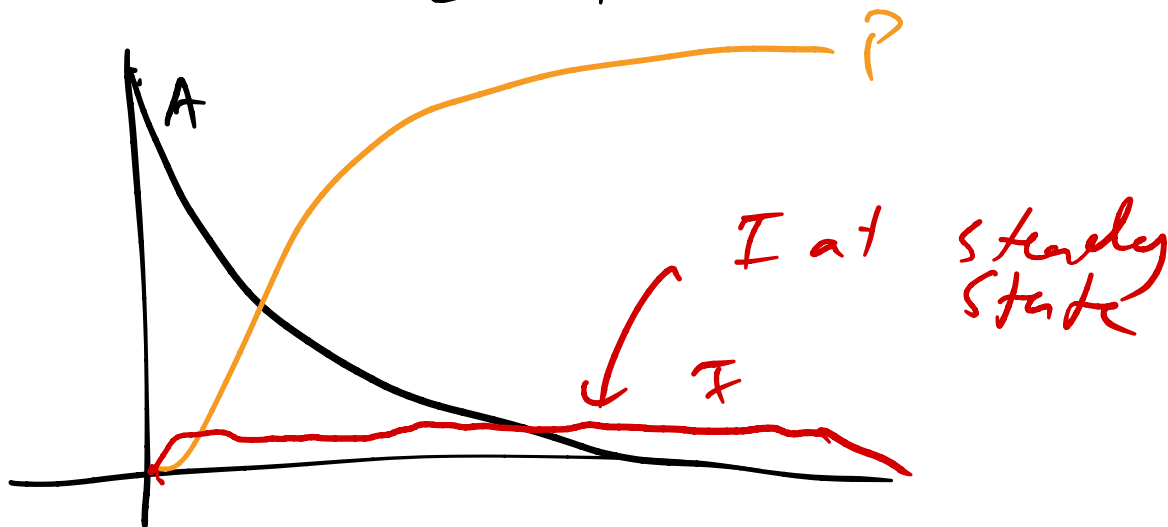
Steady state Approx helps solve
many rate problems



if $k_1 \gg k_2$, get a lot of I ,
which slowly reacts



but if $k_2 \gg k_1$



Also true for a set of
reversible reactions at eq.
Before had!

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dI}{dt} = k_1 A - k_2 I = 0 \quad \leftarrow \text{if steady state}$$

$$\frac{dP}{dt} = k_2 I \quad \leftarrow I = \frac{k_1 A}{k_2}$$

$$\Rightarrow A = A_0 e^{-k_1 t}$$

$$I_{ss} = \frac{k_1}{k_2} A_0 e^{-k_1 t}$$

$$\rightarrow P = A_0 (1 - e^{-k_1 t})$$

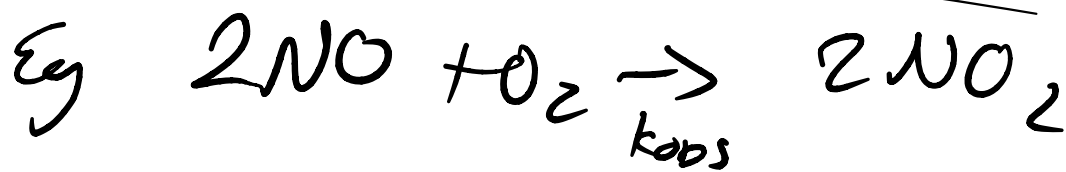
appears
single step

$$\frac{dI_{ss}}{dt} = -\frac{k_1^2 A_0}{k_2} e^{-k_1 t}$$

so $\frac{k_1^2}{k_2} A_0$ must
be small!

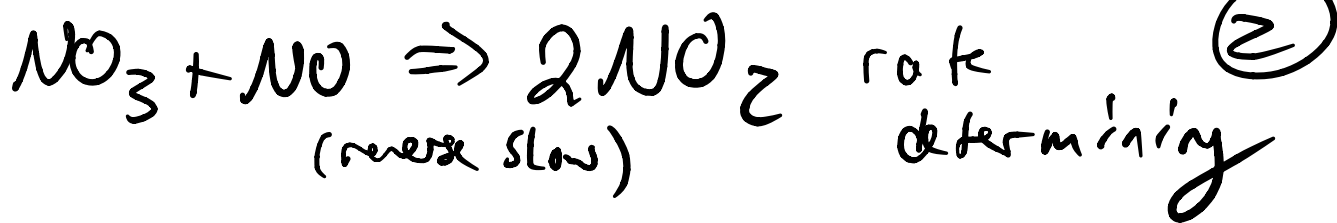
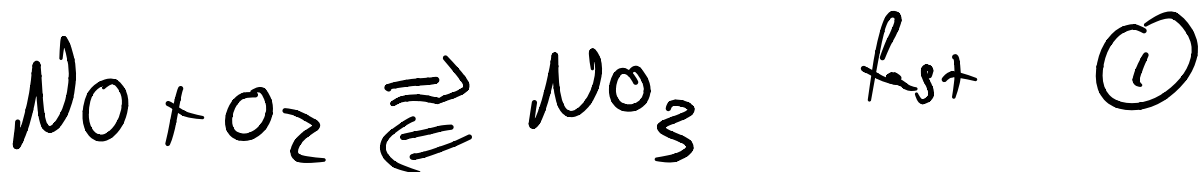
Otherwise not ≈ 0

Rate law \rightarrow mechanism



$$v(t) = k_{\text{obs}} [\text{NO}]^2 [\text{O}_2] \quad !?$$

What about mechanism:



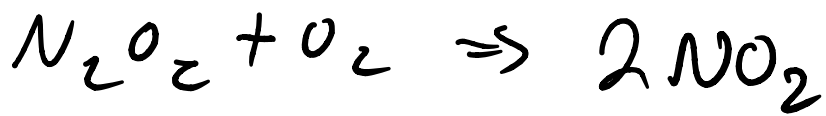
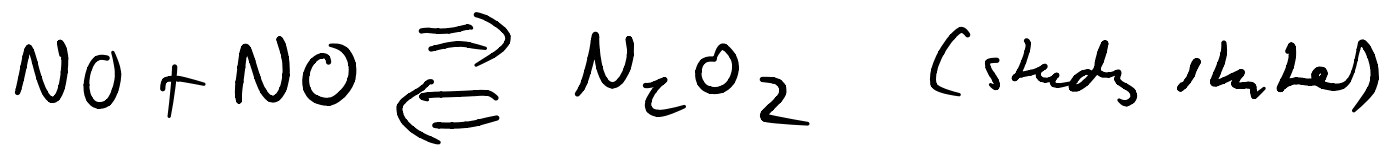
(1) @ Eq

$$\text{so} \quad \frac{k_f'}{k_b'} = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}$$

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \text{rate} = k_2 [\text{NO}_3][\text{NO}]$$

$$= \frac{k_2 k_f'}{k_b'} [\text{NO}]^2 [\text{O}_2]$$

Alternative, Mech 2



$$\text{rate} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2 [\text{N}_2\text{O}_2] [\text{O}_2]$$

can solve for

$$[\text{N}_2\text{O}_2]_{ss} = \frac{k_f' [\text{NO}]^2}{k_b' + k_2 [\text{O}_2]}$$

$$\approx \frac{k_f'}{k_b'} [\text{NO}]^2 \quad \text{if } k_2 [\text{O}_2] \text{ small}$$

$$\text{rate} = k_2 \frac{k_f'}{k_b'} [\text{NO}]^2 [\text{O}_2]$$

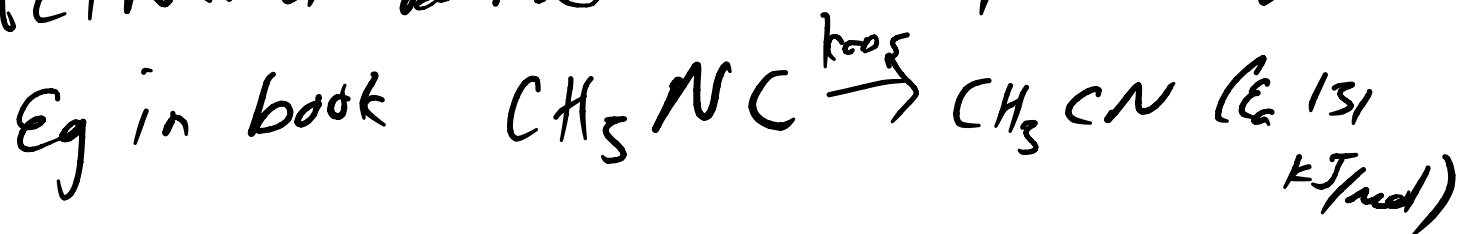
same as mech 1!

other expts favor mech 2

Lindemann Mechanism

Mentioned previously that must have enough energy to overcome activation barrier
— in gases, comes from direct collision

Activation barrier can be quite high



At high conc:

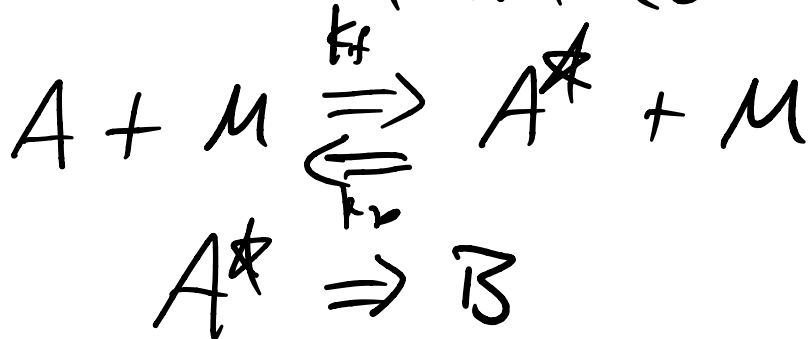
$$v = k [\text{CH}_3\text{NC}]$$

low conc

$$v = k [\text{CH}_3\text{NC}]^2$$

Need a collision to get enough energy to react

Lindemann proposed a transition state
from collision w/ molecule M



$[A^*]$ is small so $\frac{d[A^*]}{dt} \approx 0$

$$\frac{d[B]}{dt} = k_f' [A^*] \quad *$$

$$0 = \frac{d[A^*]}{dt} = k_f [A][M] - k_f' [A^*] - k_b [A^*]$$

$$[A^*] = \frac{k_f' [A][M]}{(k_f' + k_b [M])}$$

$$\frac{d[B]}{dt} = \frac{k_f' k_f}{(k_f' + k_b [M])} [A][M] = k_{obs} [A]$$

$$k_{obs} = \frac{k_f' k_f}{(k_f' + k_b [M])} [M]$$

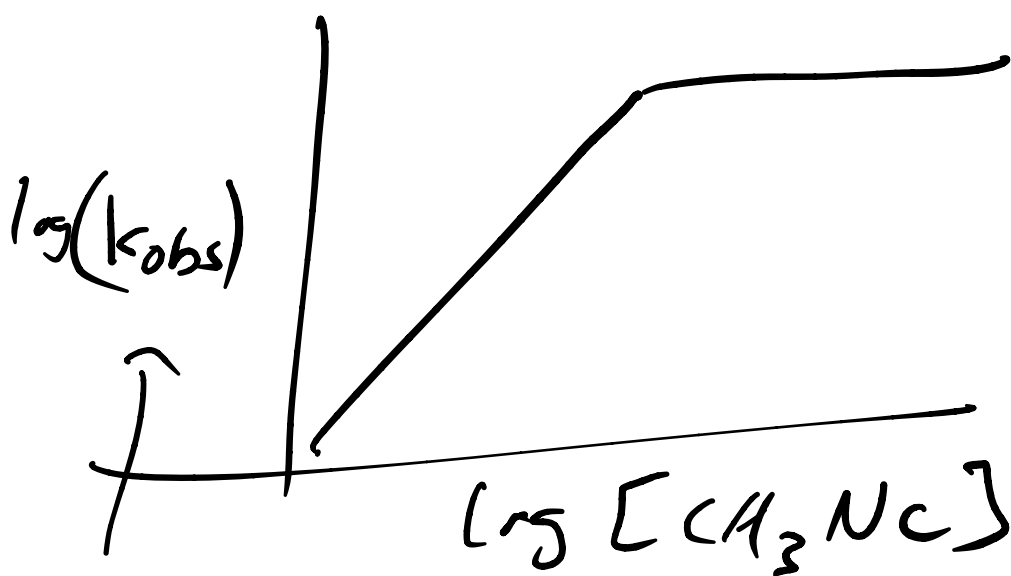
At high concentration M ,
other deactivated &

$$K_{obs} = \frac{k_f^1 k_f^2}{k_b^1}$$

at low conc, $k_{obs} = k_f^1 [M]$

so, second order at low conc

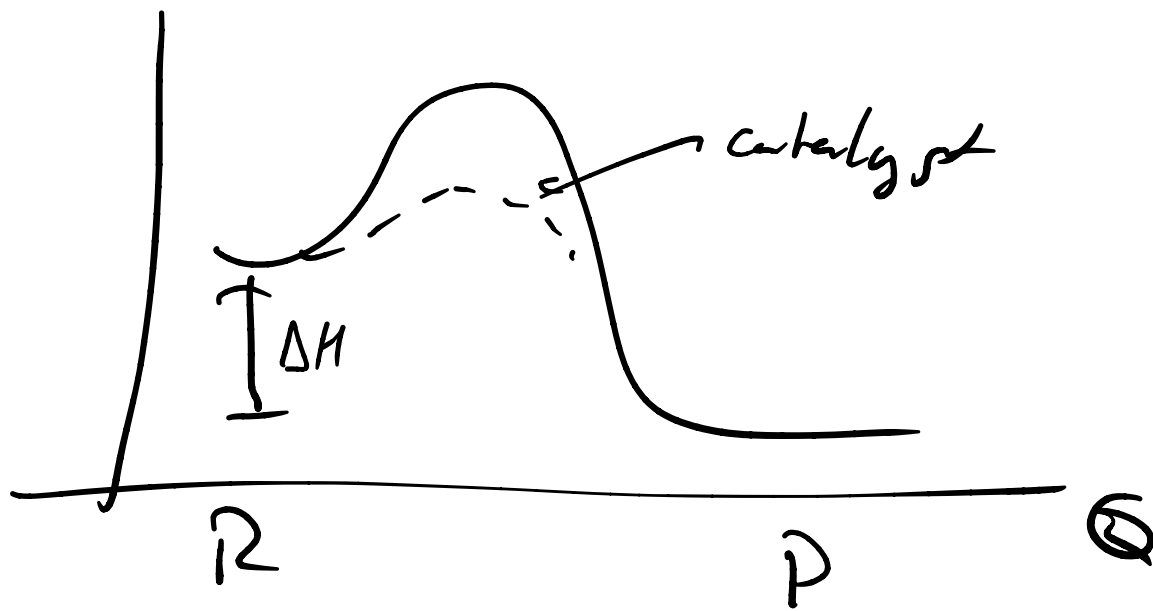
Explicit data for CH_3NC isomerization



linear observed rate constant

(skipping chair reactions, 29-7)

Catalysts



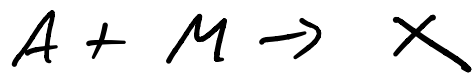
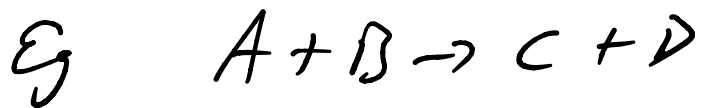
Important - different reaction paths!

Homogeneous catalysis -
in solution mixed in

Heterogeneous catalysis (different phase)

Eg metal surface

Catalyst takes place in reaction
but is not used up



Enzymes are biological catalysts

Greatly accelerate reactions

and can be very specific & stereoselective