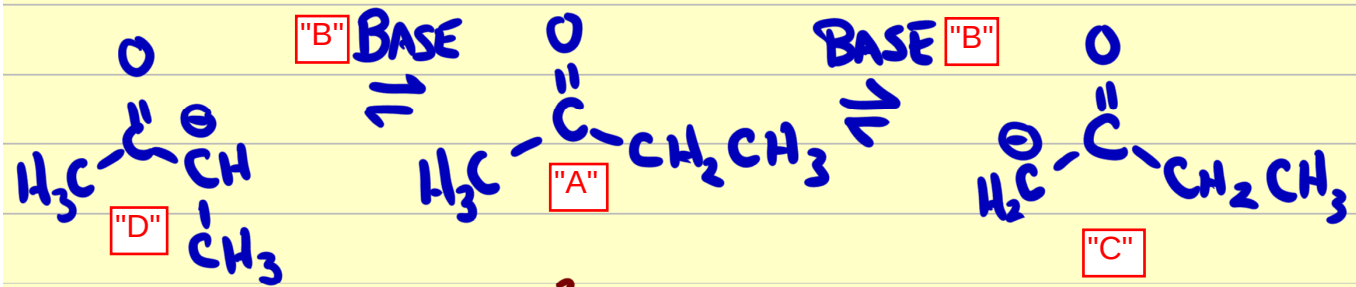
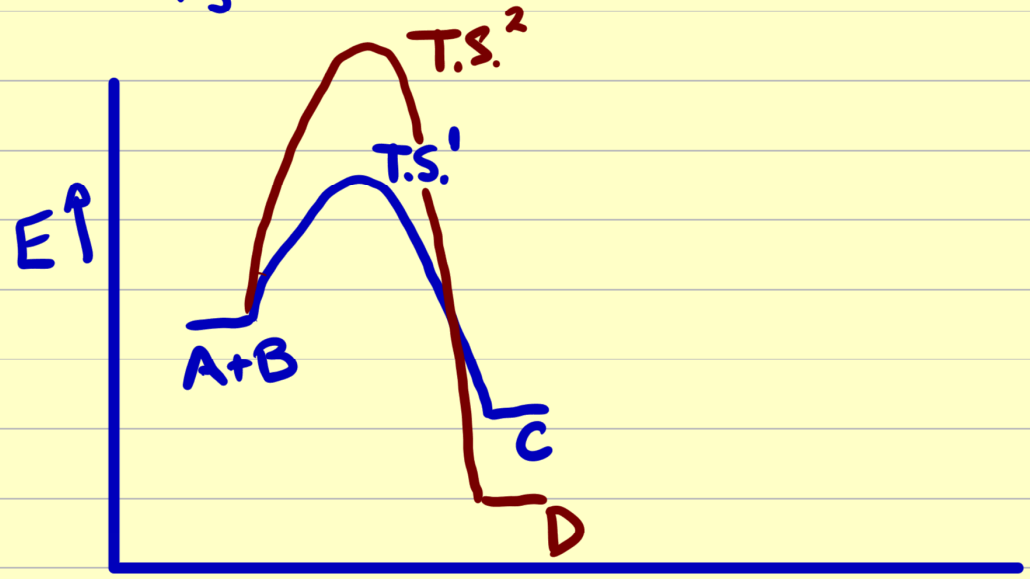
Kinetic Control vs. Thermodynamic Control.

Consider the following generic reaction

$$D \rightleftharpoons A + B \rightleftharpoons C$$

In fact, a real-world example is the alpha deprotonation of ketones, i.e.....





Two Situations.

1) If use Minimum Conditions to get Any Rxn To Go. - Rxn will be able get over TS' (Lowest Barrier) - You will

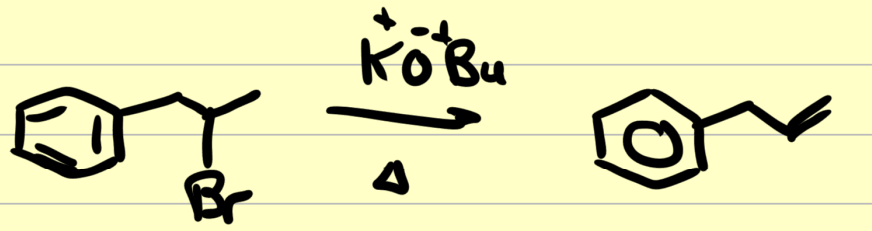
MAKE (MOSTLY) C. OPERATING UNDER

KINETIC CONTROL

ii) IF YOU USE HIGHER T, LONGER RXN TIME, YOU CAN GET BACK OVER T.S.$^{-1}$ TO A+B, AND OVER T.S.^{2}, TO GET D

∴ PRODUCTS WILL SIMPLY REFLECT ENERGIES OF MATERIALS - WILL GET D MOSTLY

THERMODYNAMIC CONTROL



OK, come to think of it, this pair isn't a perfect example

Rate Determining Step

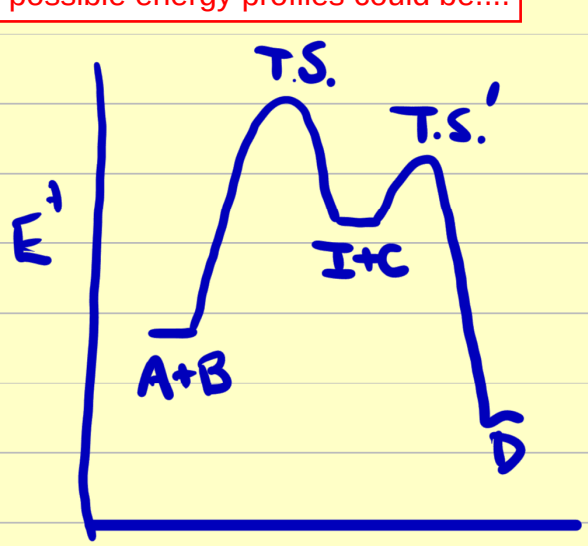
$A + B + C \longrightarrow D$.

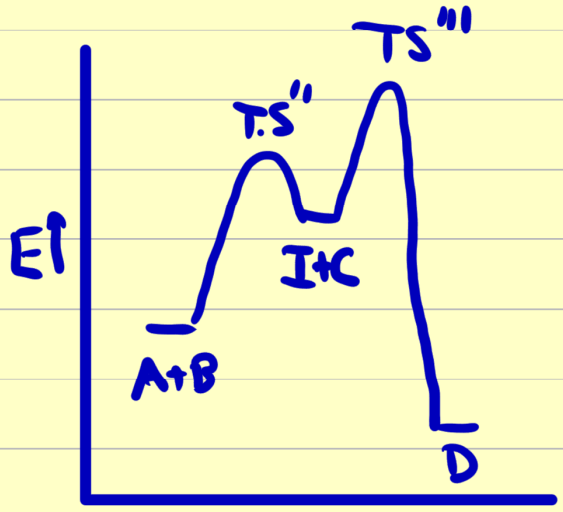
MECH There is >1 possible mechanism for this process, but a reasonable one would be.....

$A + B \rightleftharpoons I$ (Intermediate)

$I + C \rightleftharpoons D$.

-possible energy profiles could be....





rate = $k[A][B]$

2nd Order Overall

1st Step is Slow

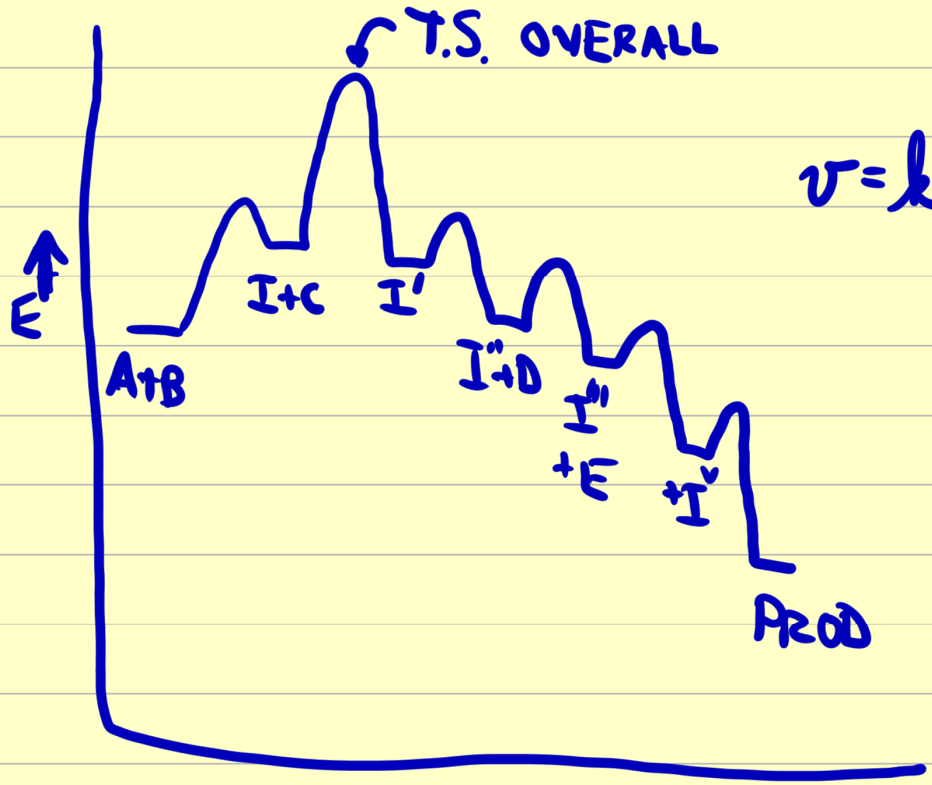
(Rate Determining)

rate = $k'[A][B][C]$

3rd Order Overall

2nd Step (r.d.s)

-situations can be far more complex, than above, i.e.,



$v = k[A][B][C]$

ONLY REAGENTS APPEARING BEFORE SLOWEST STEP APPEAR IN RATE EQN.

NUCLEOPHILES, ELECTROPHILES.

NUCLEOPHILE- ATOM OR GROUP OF ATOMS THAT BRING AN ELECTRON PAIR INTO A REACTION - EMPHASIS IS ON KINETICS

$Br^{\ominus}$, $I^{\ominus}$, , $Cl^{\ominus}$, $HO^{\ominus}$, $H_3N:$, 

- ALWAYS A POTENTIAL BASE, BUT NOT NECESSARILY A GOOD BASE

ELECTROPHILE - ATOM OR GROUP OF ATOMS THAT IS ATTACKED BY A NUCLEOPHILE

- e^- DEFICIENT IN SOME WAY.

Br^+, $^+CH_3$, CH_3-Cl,