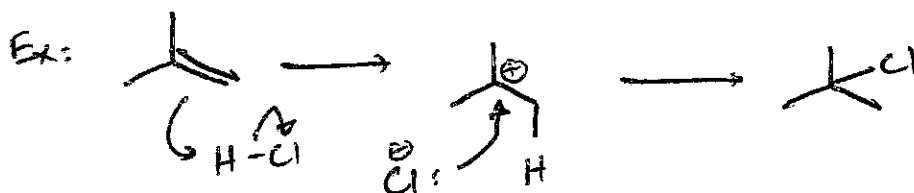


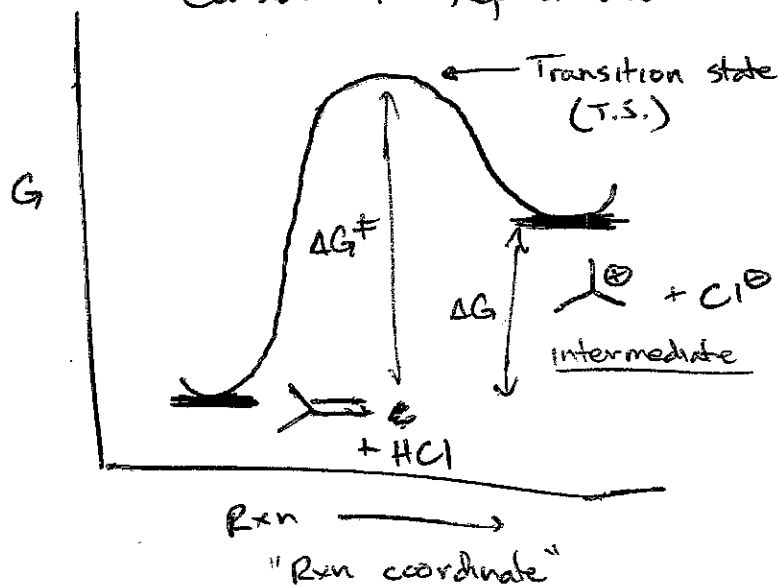
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Recall: Arrow formation for rxn mechanism (hypotheses)



- Complementary graphical formalism for rxn mechanisms - reaction energy diagram (focus on relative energies of S.M., intermediates, products, transition states)

Consider 1st step of above rxn



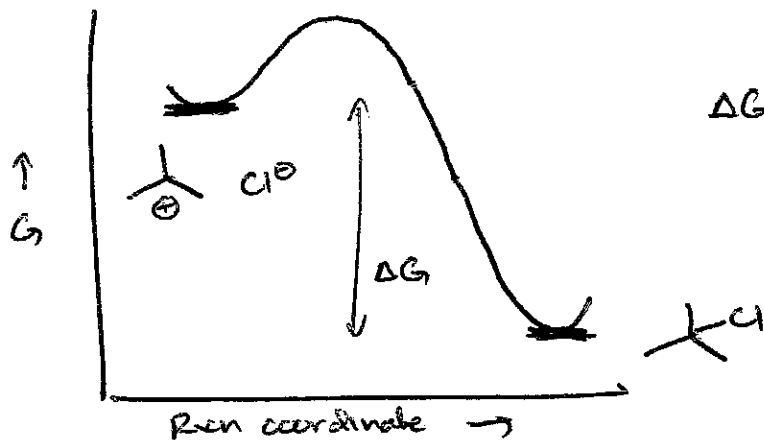
Note:

- 1) $\Delta G > 0$, rxn is thermodynamically unfavorable. (Carbocations are unstable)
- 2) ΔG^\ddagger - related to rxn rate (i.e., to the "reactivity" of S.M.)

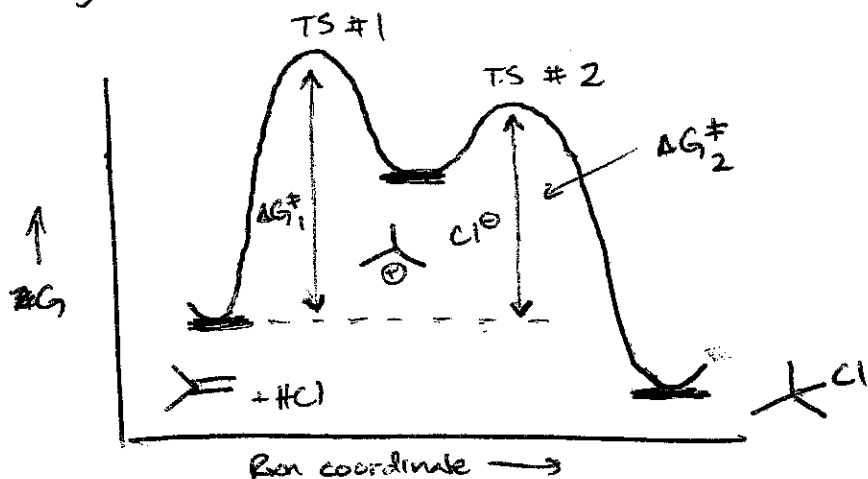
3) "Rxn coordinate" - X axis of graph - a measure of reaction progress. E.g., inverse of H...C distance (H from HCl)

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• For 2nd step of reaction:



• Diagram for entire mechanism:



New insight

$$\Delta G_1^\ddagger > \Delta G_2^\ddagger$$

∴ First step (C⁺ formation) is the rate-determining step (RDS) for the rxn.

• Correlation between "curved arrows" and "energy diagram" - SM, intermediates, products are always energy minima

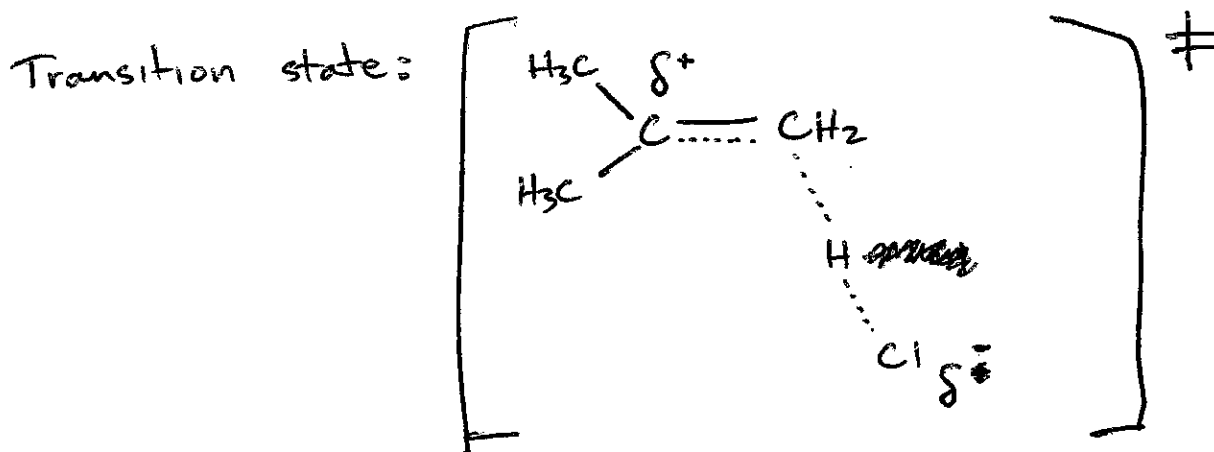
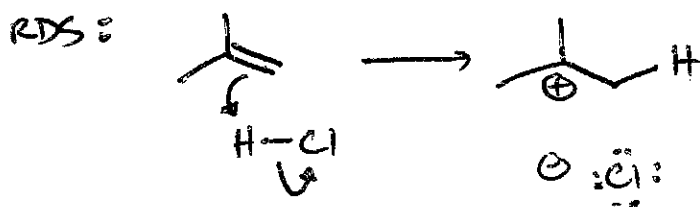
• Between every pair of minima, there is a maximum - this corresponds to the Transition State

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• How do we come to understand factors that influence T.S. (transition state) energy?

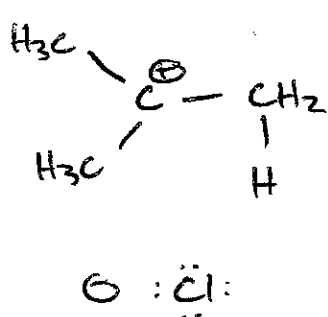
Hammond Postulate: T.S. that is adjacent to a high-energy intermediate will be similar in structure to ~~the~~ that ~~the~~ intermediate

• Apply Hammond Postulate to HCl addition:



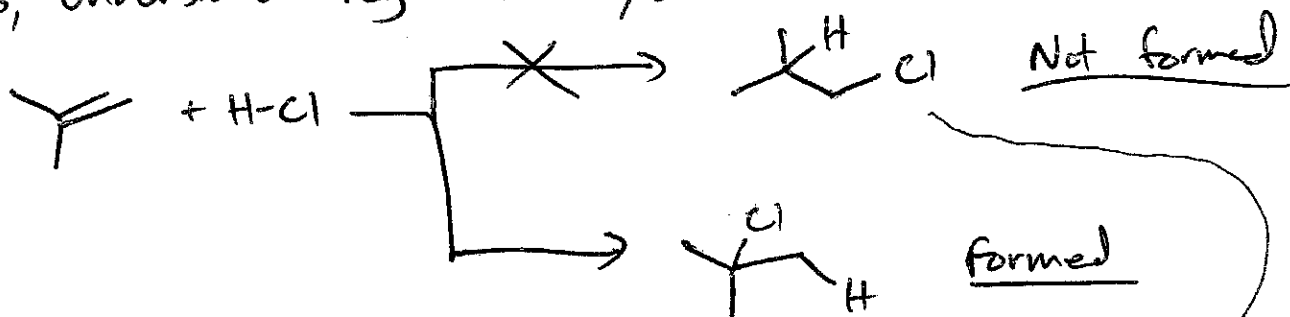
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• Hammond ~~post~~ postulates:

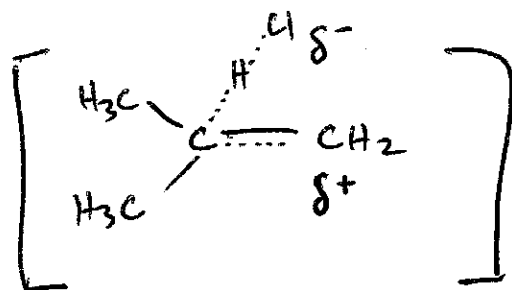


Factors that would stabilize this C^{\oplus} would also stabilize the rate-determining T.S., and vice versa.

• Thus, understand regioselectivity:



- Rationalize: T.S. that would have required:



This T.S. is highly unstable because you are beginning to form a 1° carbocation. (BAD)

⇒ High-energy T.S. ⇒ this product not favored

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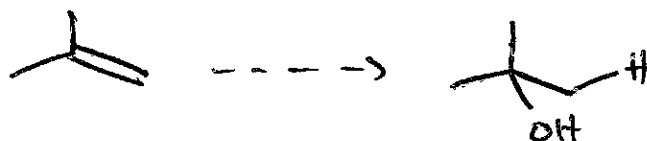
• Catalysis: catalyst is a species that lowers ΔG^\ddagger

(i.e., makes vertical ~~diff~~ distance between SM + TS smaller on energy diagram)

... but is not consumed in the reaction.

Ex: Acid-catalyzed hydration of alkenes (add H_2O across $C=C$)

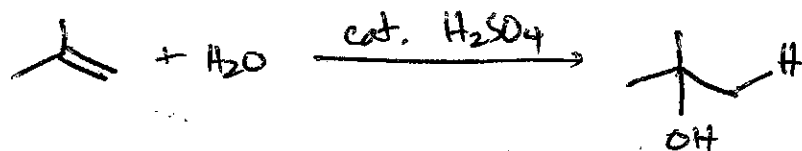
Overall process:



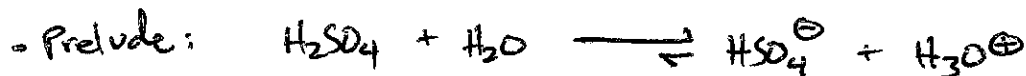
(variation on HX addition)

BUT - no reaction under pH-neutral conditions. An acid catalyst is required

• Thus:

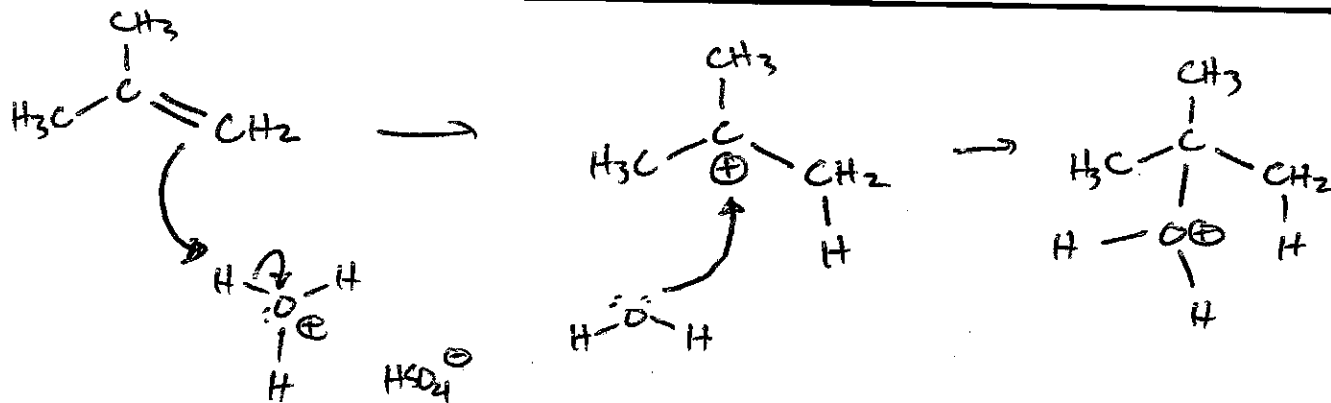


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Continued on Wed.