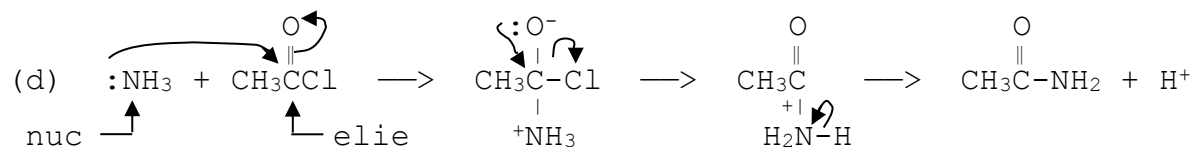
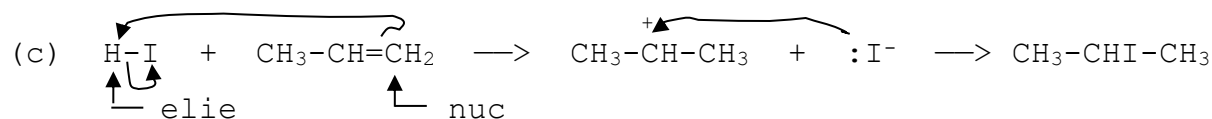
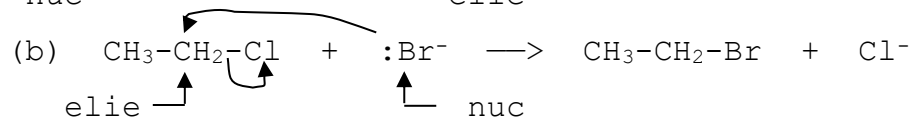
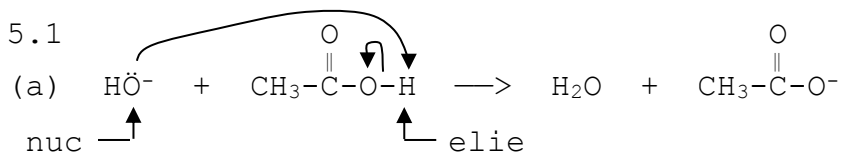
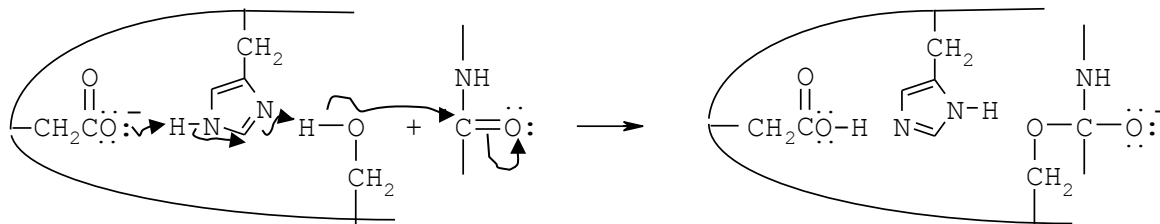


Answers to Puzzles of Chapter 5
The Mechanics of Reactions

5.1



5.2



5.3 (a) $\Delta G^\circ = -RT \ln K = -(8.31 \text{ J/K}\cdot\text{mol})(298 \text{ K})(\ln 10) = -5690 \text{ J/mol} = -5.69 \text{ kJ/mol}$

(b) $\Delta G^\circ = -8.31(298)\ln 100 = -11.4 \text{ kJ/mol}$

(c) $\Delta G^\circ = -8.31(298)\ln 0.10 = +5.69 \text{ kJ/mol}$

5.4 (a) same ΔH° (b) same ΔS° (c) same ΔG° (d) same K

5.5 (a) $\text{rate} = k[\text{CH}_3\text{Cl}][\text{HO}^-]$

Because all reactants are included in the rate law, the mechanism may or may not be one-step.

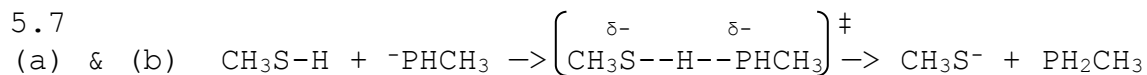
(b) $\text{rate} = k[\text{Me}_3\text{CCl}]$

If the mechanism were one-step, the rate would be directly proportional to **all** reactants.

Therefore, the mechanism must be multistep, not one-step.

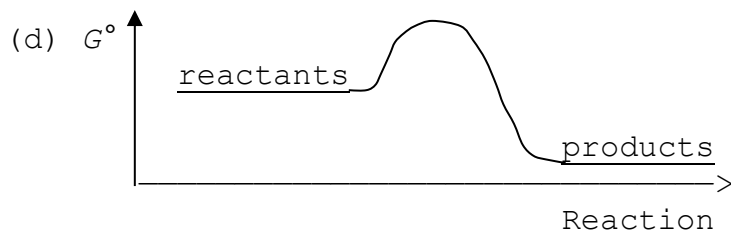
5.6 By binding reactants in a correct orientation, the enzyme helps reactants collide properly.

5.7

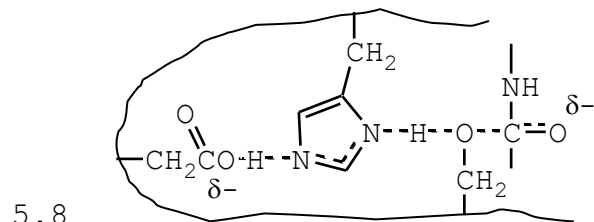


(c) compare bases: in basicity: $\text{:PHCH}_3 > \text{CH}_3\text{S}^-$

The base atoms P & S are in 1 row, so EN is the decisive factor. The base e's are stabler on the more EN S. So the reactant base and acid are stronger.



(d) yes, positive for both



5.9 (a) As $T \downarrow$, $k \downarrow$ and rate \downarrow (b) As [reactant] \downarrow , k is constant and rate \downarrow
 (c) As catalyst \uparrow , $k \uparrow$ and rate \uparrow (d) As steric hindrance \uparrow , $k \downarrow$ and rate \downarrow

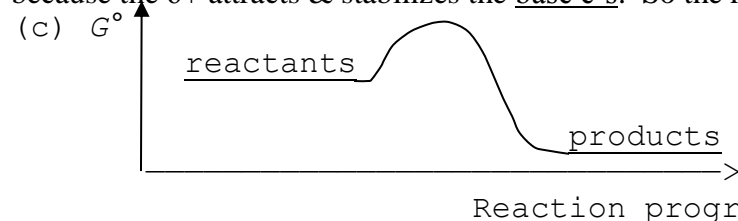
5.10 By deforming and inactivating the enzyme, raising the temperature might slow the reaction.

5.11 In the first reaction the base can remove 1 of 6 equivalent Hs to reach products, whereas the base in the second reaction can remove 1 of only 3 Hs. So, the first reaction has more lenient orientation needs, a larger S_{TS} , a larger ΔS^\ddagger , and a smaller ΔG^\ddagger .

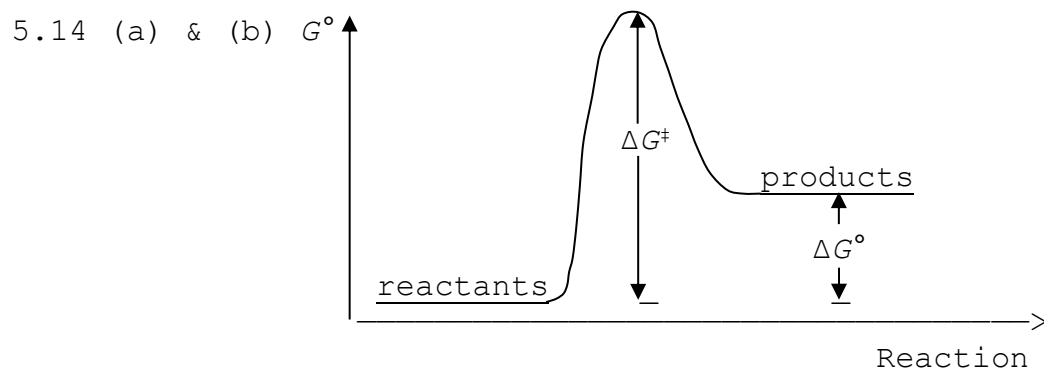
5.12 By binding reactants, an enzyme makes an intermolecular reaction an intramolecular one.

5.13 (a) $\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{ClCH}_2\text{CO}_2^-$

(b) Compare bases: in basicity: $\text{CH}_3\text{CH}_2\text{C}\overset{\delta-}{\text{O}}_2^- > \text{Cl}-\text{CH}_2\text{C}\overset{\delta-}{\text{O}}_2^-$
 because the $\delta+$ attracts & stabilizes the base e's. So the reactant base & acid are stronger.

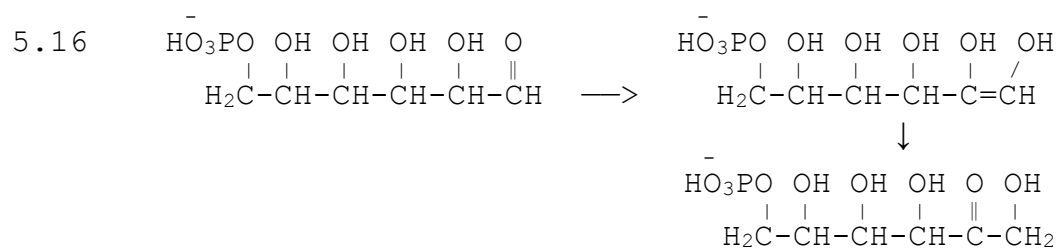


(d) The “downhill” equilibrium ($K > 1$) is favorable, and the kinetics of acid-base reactions are typically fast and favorable.

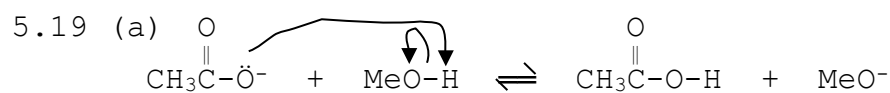
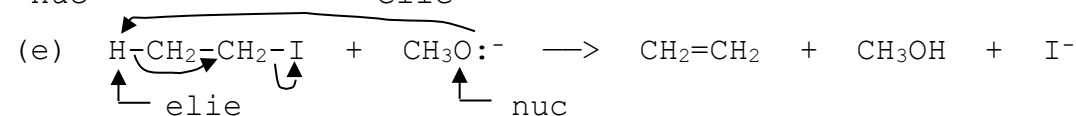
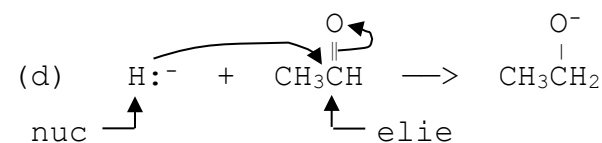
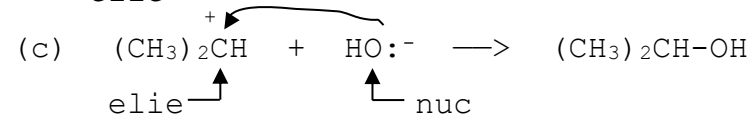
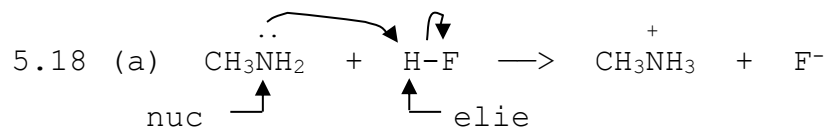


(c) Both equilibrium and kinetics are unfavorable.

5.15 Evidently a carbon-oxygen π bond is stronger than a carbon-carbon π bond to overcome the 50 kJ/mol disadvantage of propanone's extra, relatively weak carbon-hydrogen bond.



5.17 (a) 3 steps (3 TS's) (b) 2nd step (TS has highest G°) (c) 2nd step (TS has highest G°)



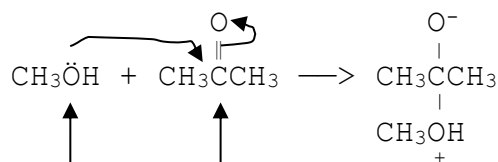
(b) $K = (3 \times 10^{-16}) / (2 \times 10^{-5}) = 1.5 \times 10^{-11}$

$\Delta G^\circ = -RT \ln K = -8.31(298)(\ln 1.5 \times 10^{-11}) = 61.5 \text{ kJ/mol}$

(c) $K = 1 / (1.5 \times 10^{-11}) = 6.7 \times 10^{10}$

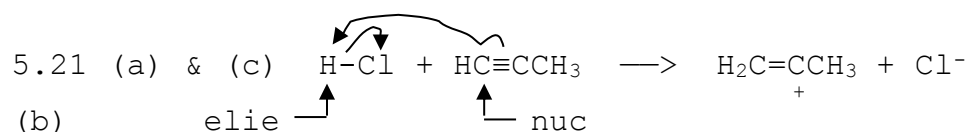
$\Delta G^\circ = -61.5 \text{ kJ/mol}$

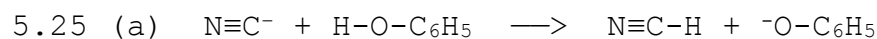
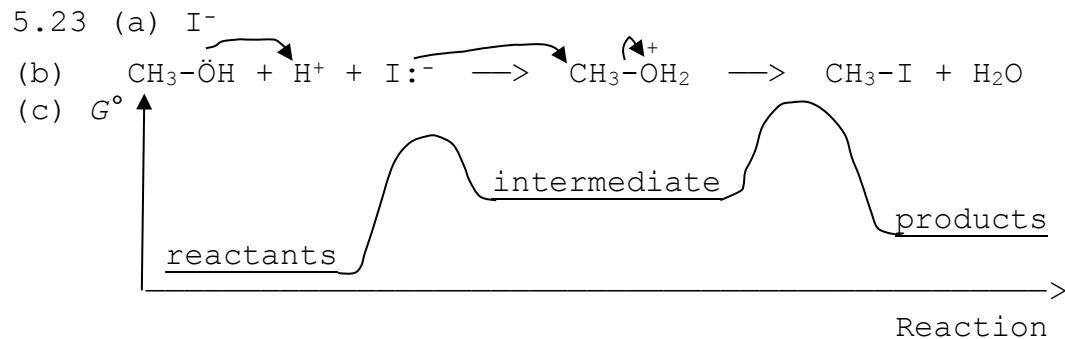
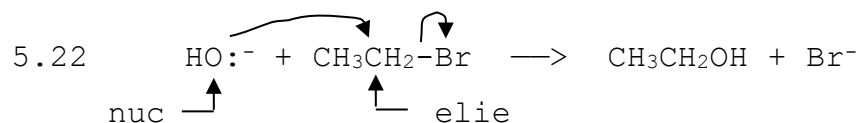
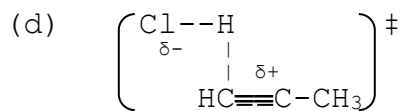
5.20 (a) & (c)



(b) nuc elie

(d) negative ΔS° : two molecules become one



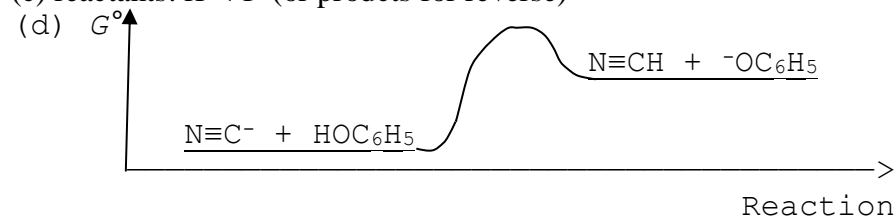


(or vice versa)

(b) $K = K_a(\text{HOC}_6\text{H}_5)/K_a(\text{N}\equiv\text{CH}) = 1 \times 10^{-10}/(6 \times 10^{-10}) = 0.17$

(or $K = 6$ for reverse)

(c) reactants: $K < 1$ (or products for reverse)



(e) yes, same TS

5.26 (a) reaction rate \uparrow (b) $k \uparrow$ (c) rate of reverse reaction \uparrow

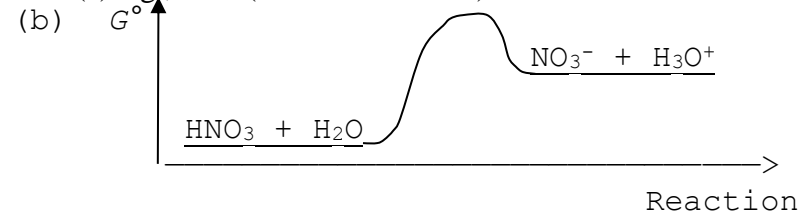
(d) equilibrium shifts toward side with more enthalpy

5.27 (a) reaction rate \uparrow (b) $k \uparrow$

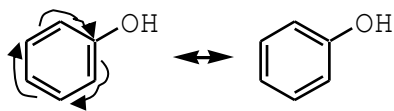
(c) adds $[\text{catalyst}]^x$ to the rate equation; may add or remove other concentrations or change exponents of concentrations

(d) rate \uparrow (e) no change in equilibrium

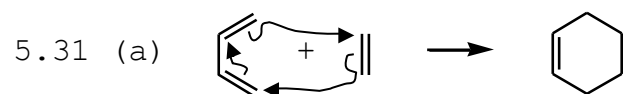
5.28 (a) e.g., H_2O (or less basic base)



5.29 The resonance of the benzene ring stabilizes the enol:



5.30 The rls converts the enolate ion to propanone. Its TS has the higher G° .



(b) ΔS° is negative and unfavorable, because 2 molecules become 1.

(c) ΔH° is negative and favorable: 2 weaker π bonds are broken but 2 stronger σ bonds are made.

(d) One can't predict the sign of K because one can't predict the sign of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ when both ΔH° and ΔS° are negative.

5.32 (a) $\text{HO}^- + \text{CH}_3\text{Br} \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$ is faster because CH_3Br is sterically more open than $(\text{CH}_3)_2\text{CHBr}$ to the nucleophile.

(b) $\text{HO}^- + \text{CH}_3\text{CH}_2\text{Cl} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Cl}^-$ is faster because the less bulky HO^- reacts with the electrophile more easily.

10/05