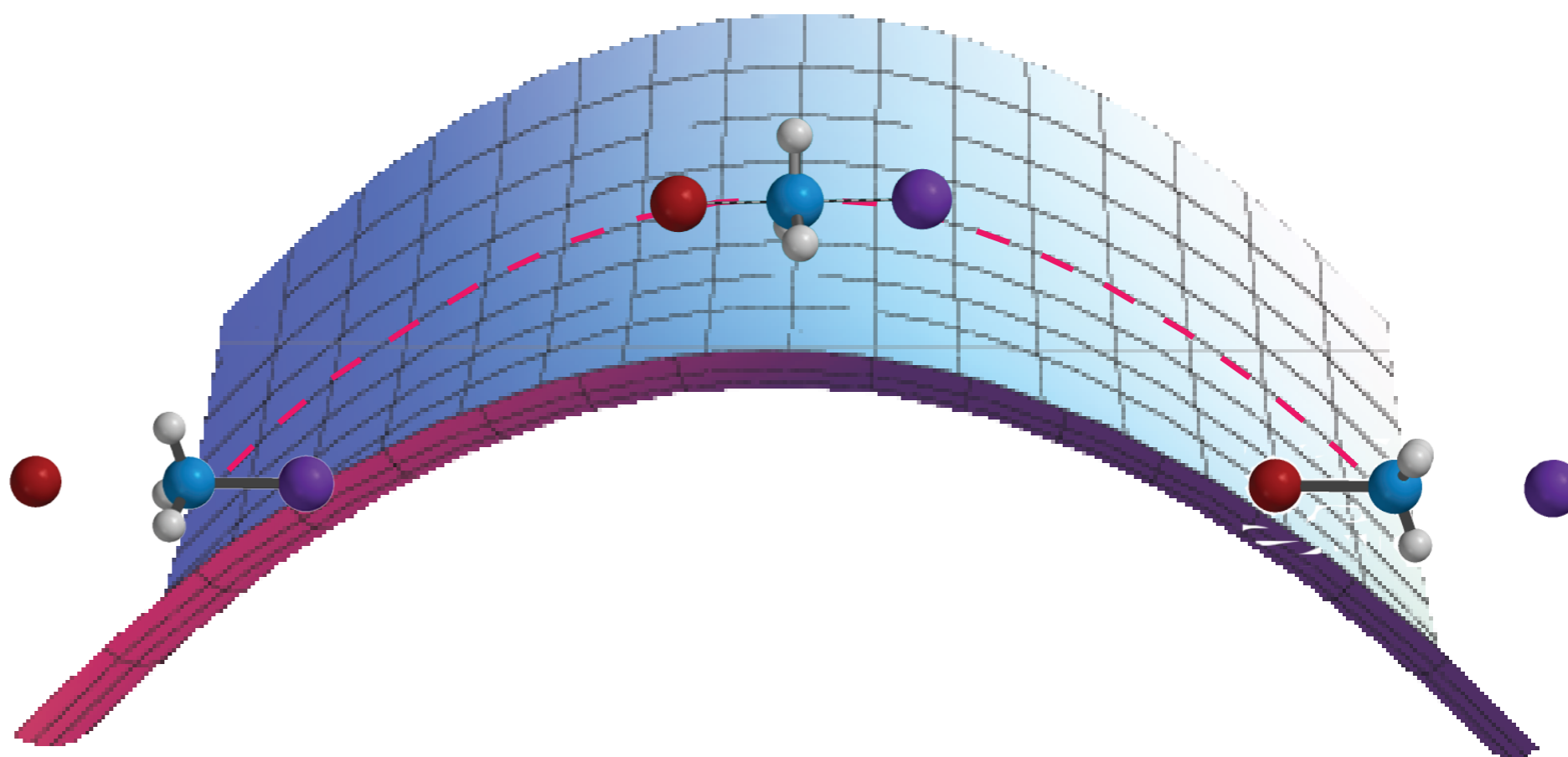


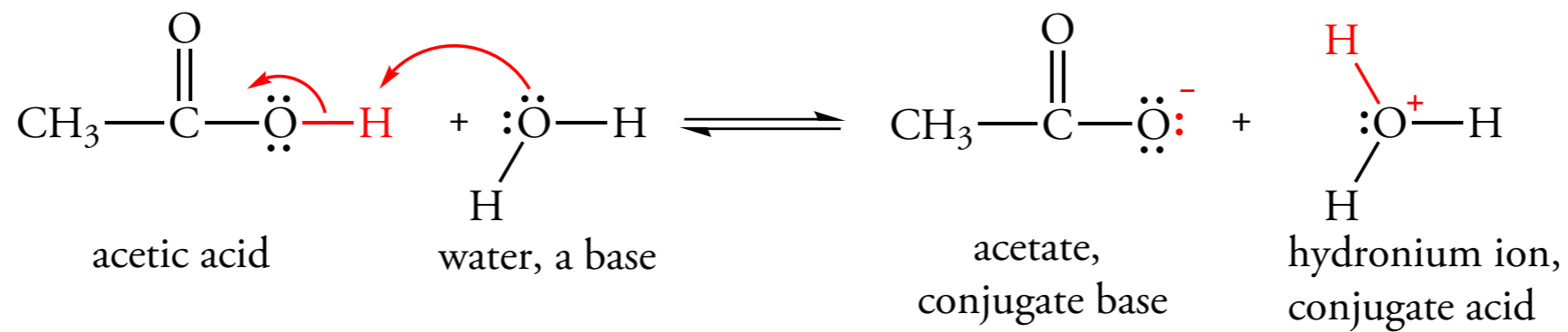
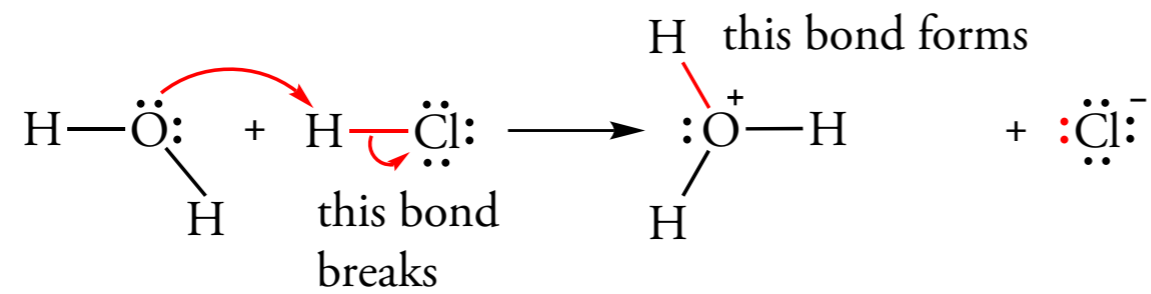
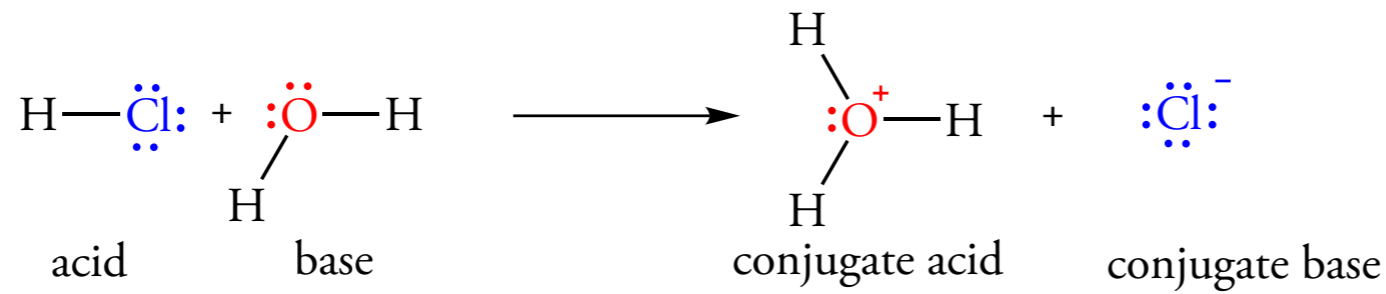
3

INTRODUCTION TO ORGANIC REACTION MECHANISMS



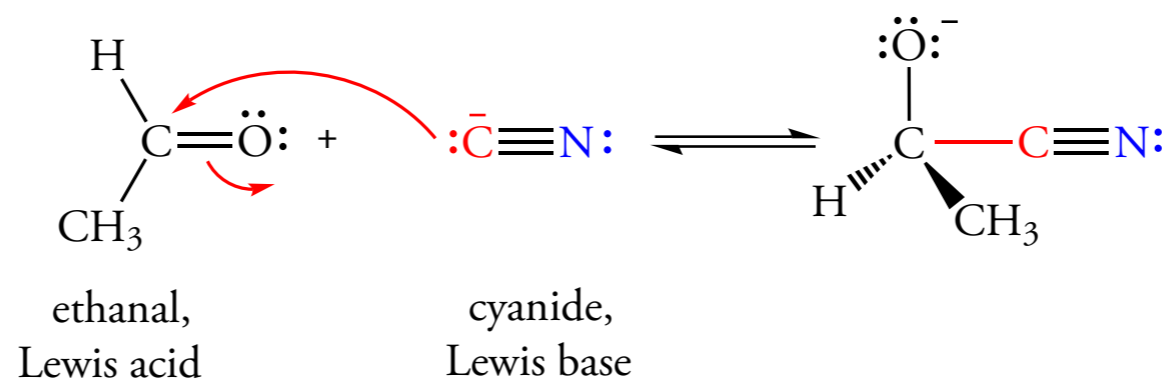
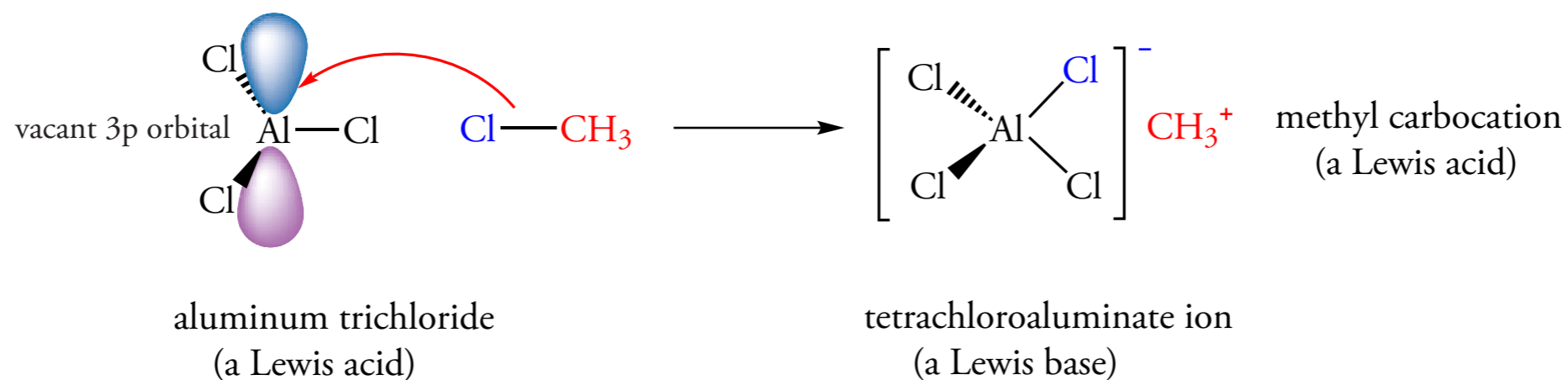
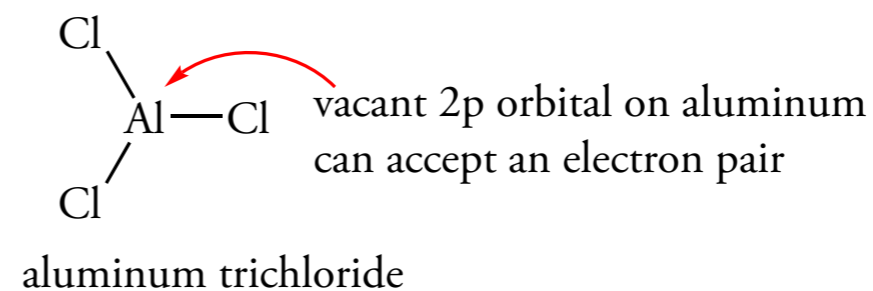
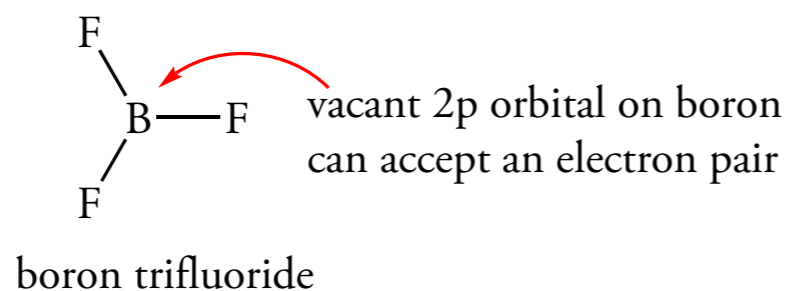
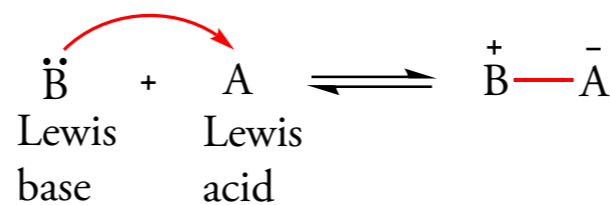
3.1 ACID-BASE REACTIONS

Brønsted-Lowry Acids and Bases

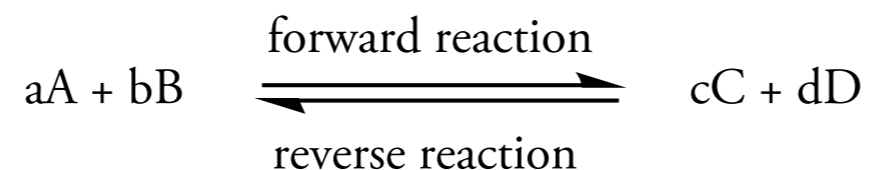


3.1 ACID-BASE REACTIONS

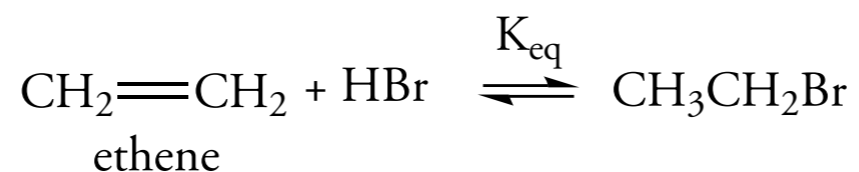
Lewis Acids



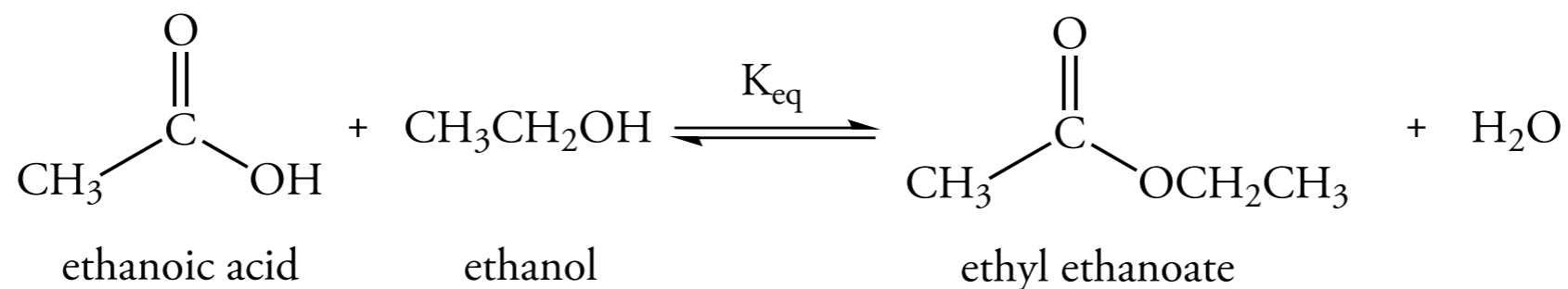
3.2 CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANTS



$$K_{\text{equilibrium}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



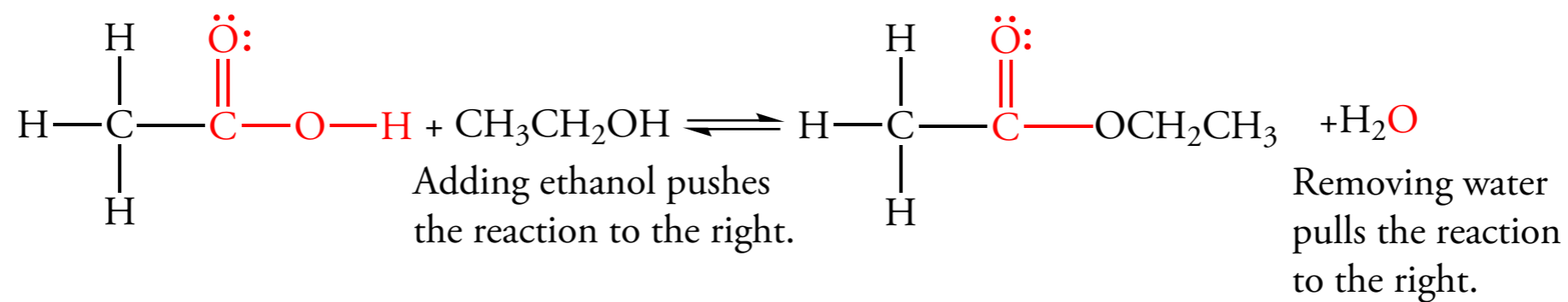
$$K_{\text{equilibrium}} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{CH}_2=\text{CH}_2][\text{HBr}]} = 10^8$$



$$K_{\text{equilibrium}} = \frac{[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3] [\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}] [\text{CH}_3\text{CH}_2\text{OH}]} = 4.0$$

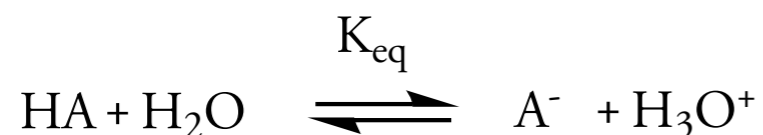
3.2 CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANTS

Le Chatelier's Principle



3.3 pH AND pK VALUES

K_a and pK_a



$$K_{\text{equilibrium}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

$$K_a = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

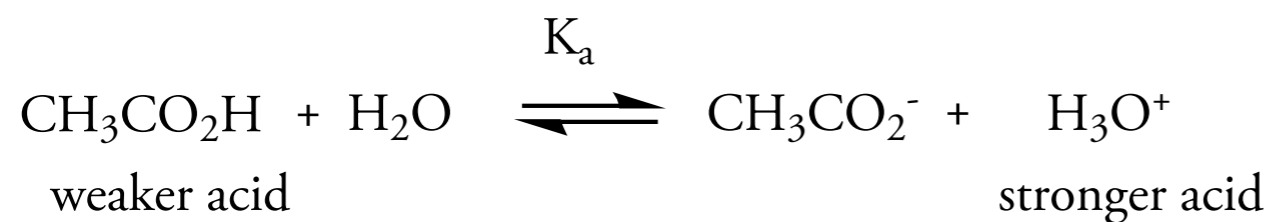


Table 3.1

K_a and pK_a Values of
Common Acids

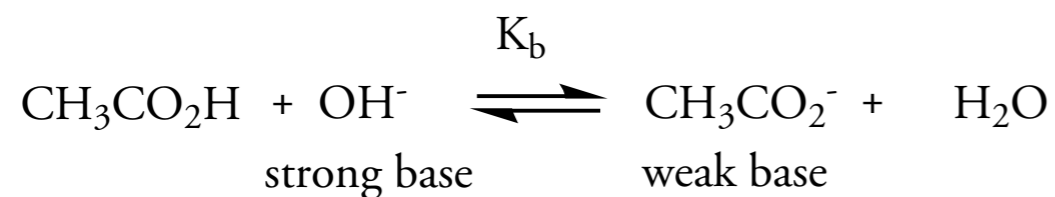
Acid	K_a	pK_a
HBr	10^9	-9
HCl	10^7	-7
H_2SO_4	10^5	-5
HNO_3	10^1	-1
HF	6×10^{-4}	3.2
$\text{CH}_3\text{CO}_2\text{H}$	2×10^{-5}	4.7
$(\text{CF}_3)_3\text{COH}$	2×10^{-5}	4.7
$\text{CH}_3\text{CH}_2\text{SH}$	3×10^{-11}	10.6
$\text{CF}_3\text{CH}_2\text{OH}$	4×10^{-13}	12.4
CH_3OH	3×10^{-16}	15.5
$(\text{CH}_3)_3\text{COH}$	1×10^{-18}	18
CCl_3H	10^{-25}	25
$\text{HC}\equiv\text{CH}$	10^{-25}	25
NH_3	10^{-36}	36
$\text{CH}_2=\text{CH}_2$	10^{-44}	44
CH_4	10^{-49}	49

3.3 pH AND pK VALUES

K_b and pK_b



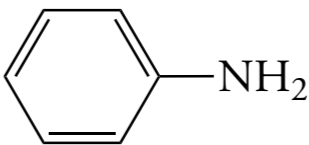
$$K_b = K_{eq}[H_2O] = \frac{[HA][OH^-]}{[A^-]}$$



$$K_b = K_{eq}[H_2O] = \frac{[HA][OH^-]}{[A^-]}$$

Table 3.2

K_b and pK_b Values of
Common Bases

Acid	K_b	pK_b
	4×10^{-10}	9.4
$CH_3CO_2^-$	5×10^{-10}	9.3
$C \equiv N^-$	1.6×10^{-5}	4.8
NH_3	1.7×10^{-5}	4.8
CH_3NH_2	4.3×10^{-4}	3.4
CH_3O^-	3×10^{-16}	-1.5

3.3 pH AND pK VALUES

K_b and pK_b

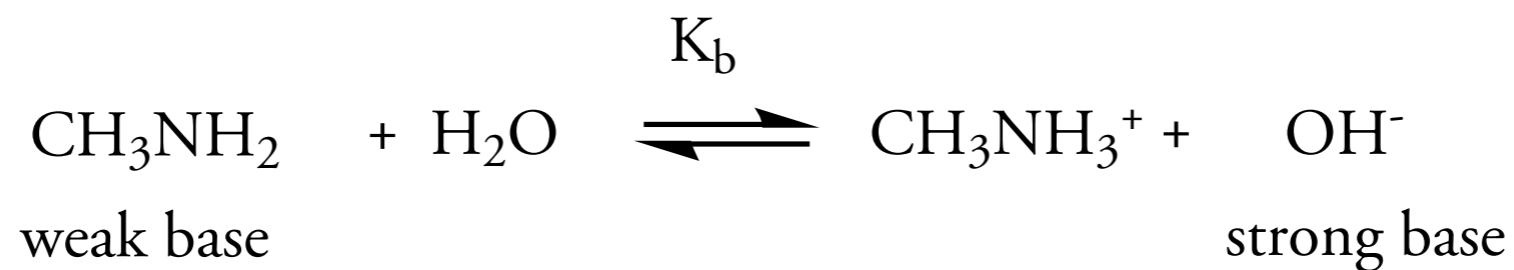


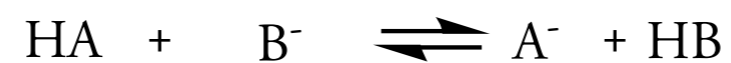
Table 3.3

K_b and K_a , and pK_a and pK_b Values of Amines and Ammonium Ions

Compound	K_b	K_a	pK_a	pK_b
NH_3	1.8×10^{-5}	5.5×10^{-10}	4.74	9.26
CH_3NH_2	4.6×10^{-4}	2.2×10^{-11}	3.34	10.7
$\text{CH}_3\text{CH}_2\text{NH}_2$	4.8×10^{-4}	2.1×10^{-11}	3.20	10.8
CH_3NHCH_3	4.7×10^{-4}	2.1×10^{-11}	3.20	10.8

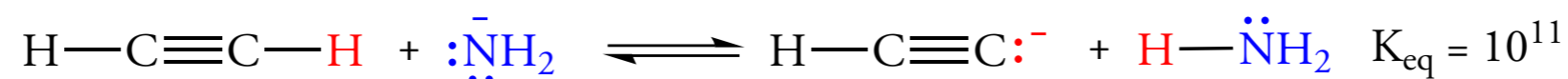
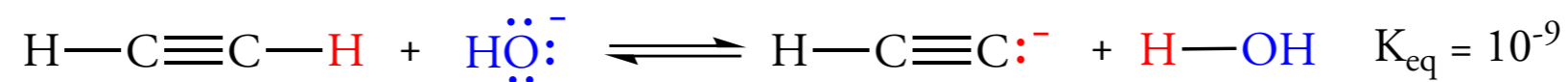
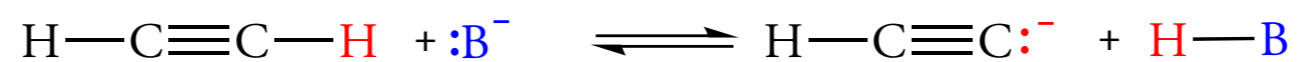
3.3 pH AND pK VALUES

Applying pK_a Values in Organic Acid-Base Reactions



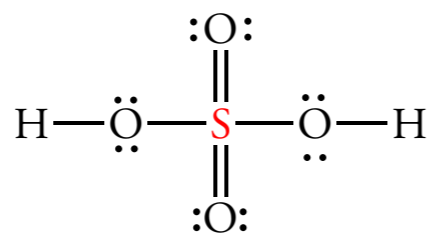
$$K_{\text{eq}} = \frac{K_{\text{HA}}}{K_{\text{HB}}}$$

$$pK_{\text{eq}} = pK_{\text{HA}} - pK_{\text{HB}}$$

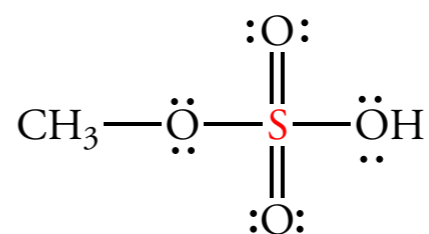


3.4 EFFECT OF STRUCTURE ON ACIDITY

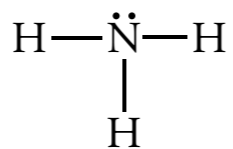
Effect of Periodic Trends on Acidity and Basicity



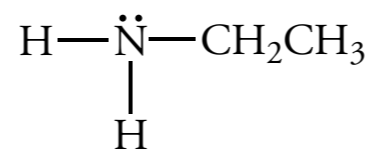
sulfuric acid,
a strong acid



methane sulfonic acid,
a strong acid



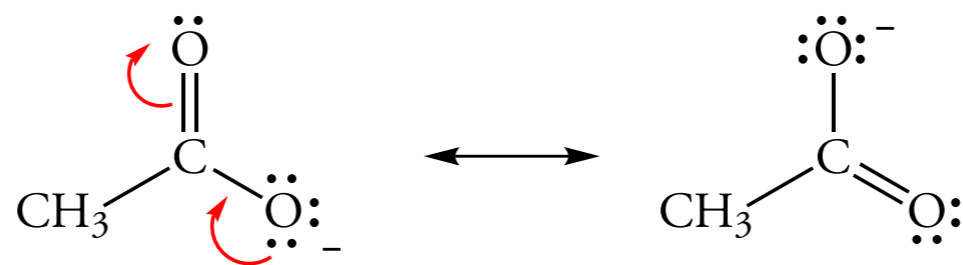
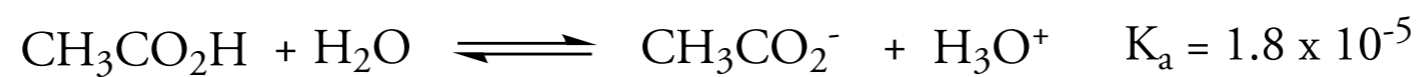
ammonia
pK_b 4.74
(weak base)



ethylamine
pK_b 3.25
(weak base)

3.4 EFFECT OF STRUCTURE ON ACIDITY

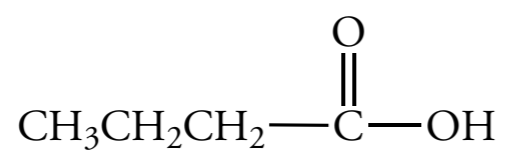
Effect of Resonance on Acidity and Basicity



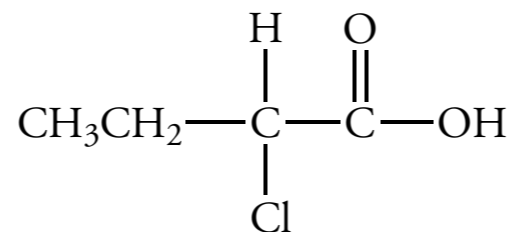
Ethanoate ion (acetate), is resonance stabilized, which increases K_a relative to ethanol.

3.4 EFFECT OF STRUCTURE ON ACIDITY

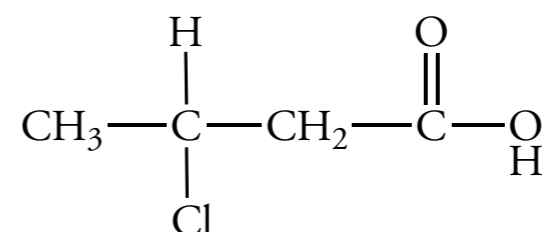
Inductive Effects



butanoic acid
 $\text{pK}_a = 4.82$



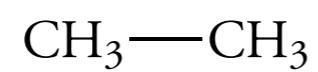
2-chlorobutanoic acid
 $\text{pK}_a = 2.86$



3-chlorobutanoic acid
 $\text{pK}_a = 4.02$

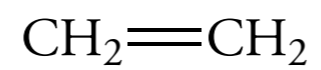
3.4 EFFECT OF STRUCTURE ON ACIDITY

Effect of Hybridization on Acidity



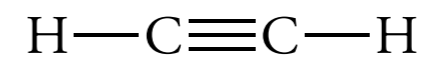
ethane

$$K_a = 10^{-49}$$



ethene

$$K_a = 10^{-44}$$



ethyne

$$K_a = 10^{-25}$$

3.5 STANDARD FREE ENERGY CHANGES IN CHEMICAL REACTIONS

The Standard Free Energy Change and the Equilibrium Constant

$$\Delta G_{\text{rxn}}^{\circ} = \Delta G_{\text{f}}^{\circ} (\text{products}) - \Delta G_{\text{f}}^{\circ} (\text{reactants})$$

$$\Delta G_{\text{rxn}}^{\circ} = -2.303RT \log K_{\text{eq}}$$

$$R = 8.314 \text{ kJ kelvin}^{-1} \text{ mole}^{-1} \text{ (1.987 cal kelvin}^{-1} \text{ mole}^{-1}\text{)}$$

$$T = \text{absolute temperature (kelvin)}$$

Table 3.4

Relation between ΔG° (kJ mole⁻¹) and K_{eq} at 25 °C

$X \rightleftharpoons Y$					
ΔG°	K_{eq}	% Y	ΔG°	K_{eq}	% Y
0.00	1.0	50	-4.3	5.67	85
-0.50	1.22	55	-5.45	9.00	90
-1.0	1.50	60	-7.30	19.0	95
-1.5	1.86	65	-9.65	49.0	98
-2.1	2.33	70	-11	99	99
-2.7	3.00	75	-17	999.9	99.9
-3.4	4.00	80	-22	9999.9	99.99

3.6 ENTHALPY CHANGES IN CHEMICAL REACTIONS



1. If heat flows out of the reaction into the surroundings, the reaction is *exothermic*, $\Delta H_{\text{rxn}}^{\circ} < 0$.
2. If heat flows into of the reaction from the surroundings, the reaction is *endothermic*, $\Delta H_{\text{rxn}}^{\circ} > 0$.

Standard conditions, ΔH° , refer to measurements made at 298 K and 1 atm.

1. The standard enthalpy of formation (ΔH_f°) of a compound is the enthalpy change when the compound is formed in its standard state from the elements in their standard states. The superscript ($^{\circ}$) indicates that the reaction occurs under standard conditions.
2. The standard state of any element or compound is its most stable form at 298 K and 1 atm pressure.
3. The standard enthalpy of formation of any element in its standard state is defined as 0 kJ mole^{-1} .

$$\Delta H_{\text{rxn}}^{\circ} = [p\Delta H_f^{\circ}(\text{X}) + q\Delta H_f^{\circ}(\text{Y})] - [m\Delta H_f^{\circ}(\text{A}) + n\Delta H_f^{\circ}(\text{B})]$$

3.7 BOND DISSOCIATION ENERGIES

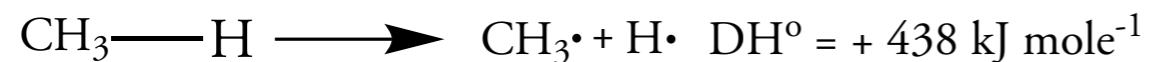
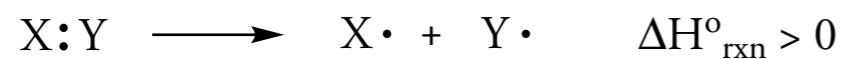
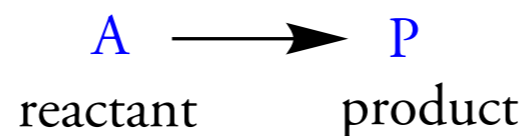


Table 3.5
Bond Dissociation Energies of Representative Compounds

<i>Bond</i>	<i>DH</i> ^o (<i>kJ mol</i> ⁻¹)	<i>Bond</i>	<i>DH</i> ^o (<i>kJ mol</i> ⁻¹)
H—H	435	CH ₃ —H	438
F—F	159	CH ₃ —F	451
Cl—Cl	242	CH ₃ —Cl	349
Br—Br	192	CH ₃ —Br	293
I—I	150	CH ₃ —I	234
		CH ₃ —OH	380
H—F	586		
H—Cl	431	CH ₃ CH ₂ —H	422
H—I	366	CH ₂ =CH—H	452
H—OH	297	HC≡C—H	523
		CH ₃ —CH ₃	368
		CH ₂ =CH ₂	610
		HC≡CH	830

3.8 INTRODUCTION TO REACTION MECHANISMS

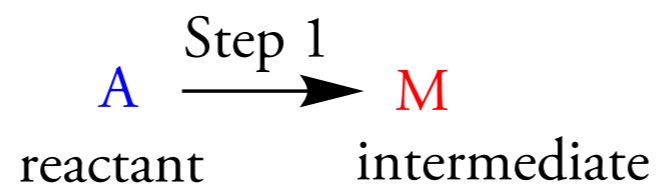
Concerted and Multistep Reactions



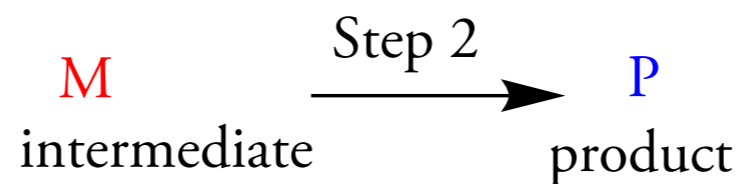
A one step, **concerted reaction**, has no reaction intermediates.

Multistep reaction.

Step 1. An intermediate forms.



Step 2. The intermediate is converted to product.



The slowest individual step, is the *rate-determining step*.

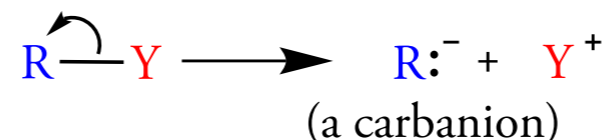
Types of Bond Cleavage



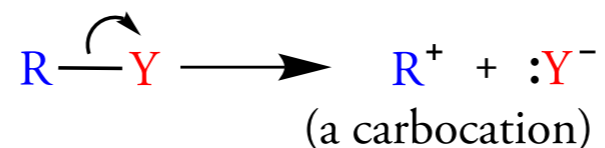
general reaction for homolytic bond cleavage



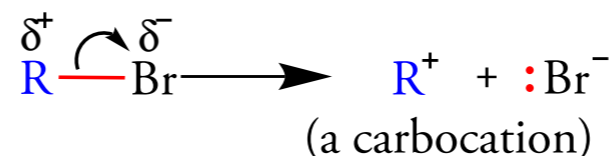
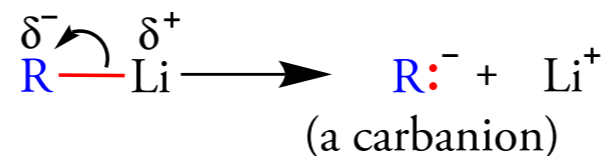
general reaction for heterolytic bond cleavage



A carbanion can act as a Lewis base or as a “nucleus loving” species called a **nucleophile**.



A carbocation can act as a Lewis acid or as a “electron loving” species called an **electrophile**.



1. If Y is a less electronegative element, such as a metal, the bond tends to break heterolytically to form a carbanion.
2. If Y is a nonelectronegative element other than carbon, a halogen atom, for example, the bond has the opposite polarity, and tends to break heterolytically to form a carbocation.

3.9 STRUCTURES AND STABILITIES OF CARBON RADICALS, CARBOCATIONS, AND CARBANIONS

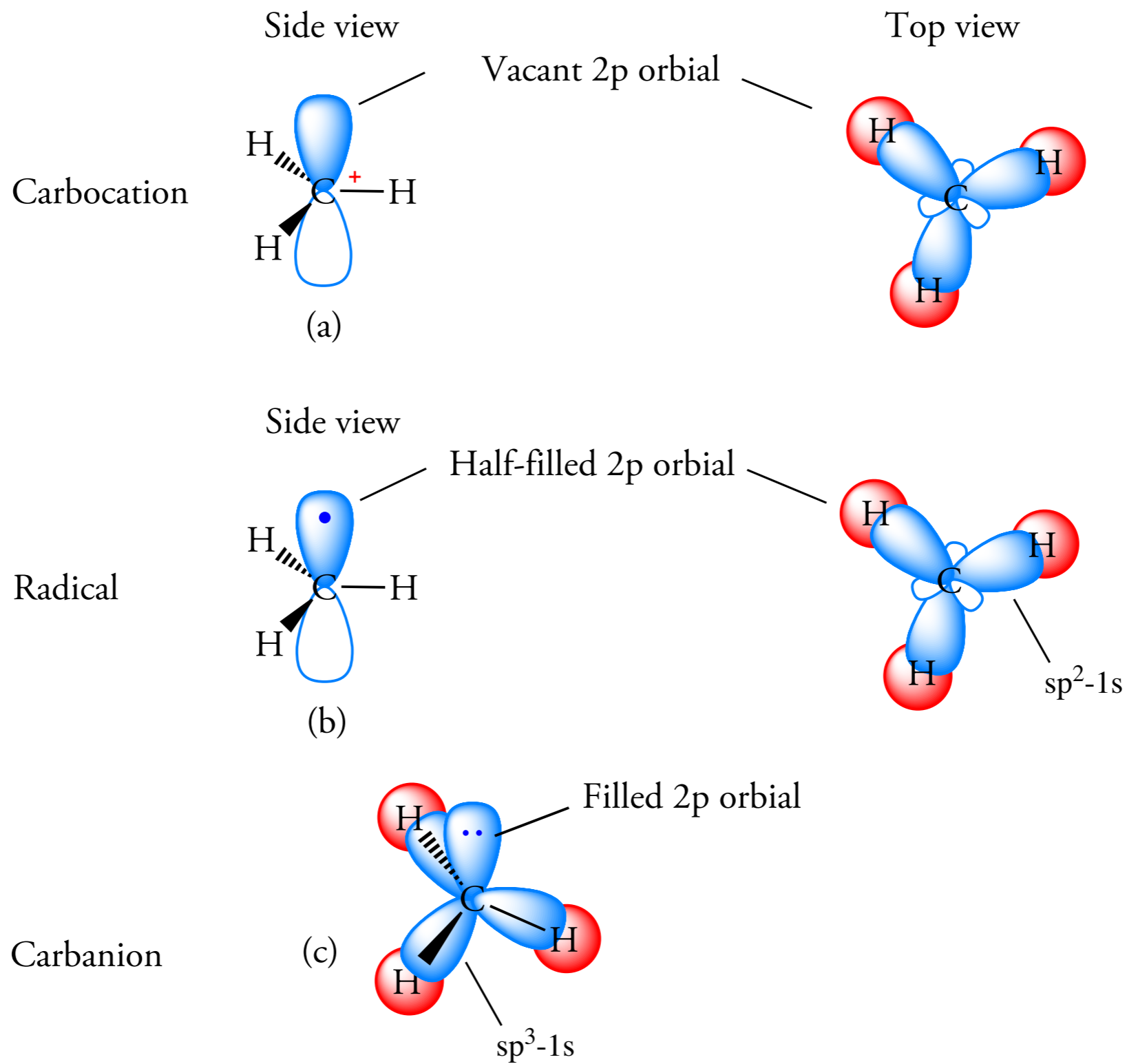
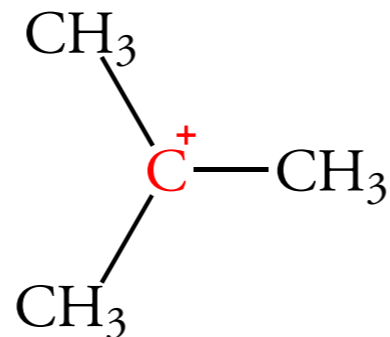
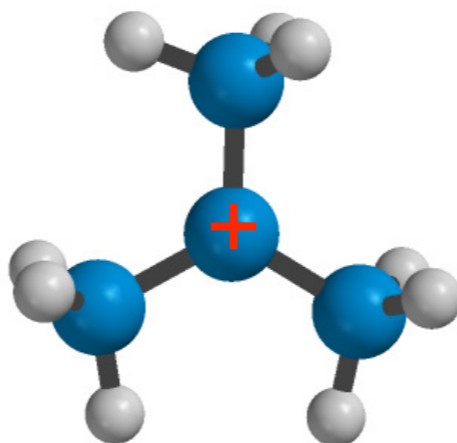


Figure 3.1 Structures of Reactive Carbon Intermediates

The *tert*-butyl Carbocation

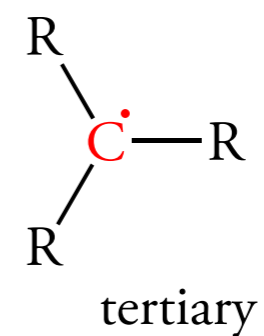
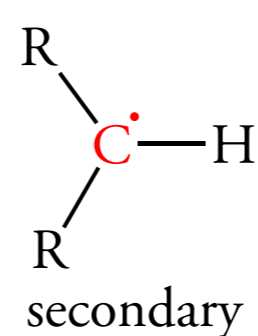
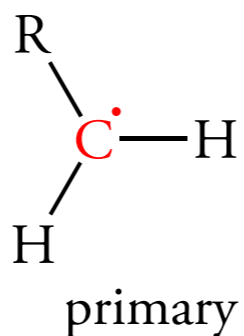
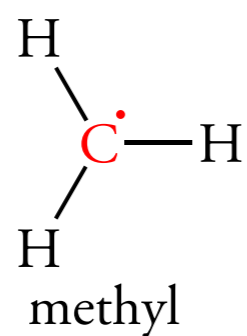


tert-butyl carbocation

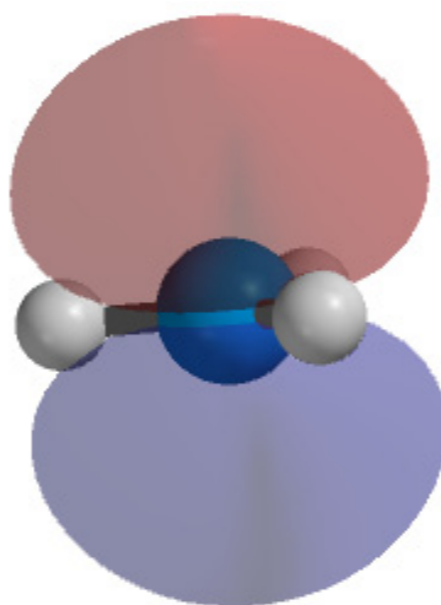


In a *tert*-butyl carbocation, the central carbon is sp^2 hybridized, and all four carbon atoms lie in the same plane.

Carbon Radicals



————— increasing stability —————>

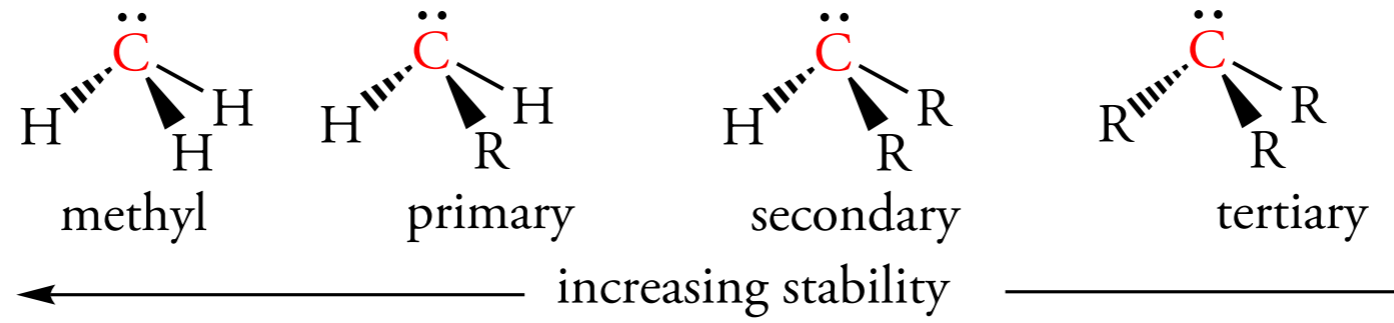
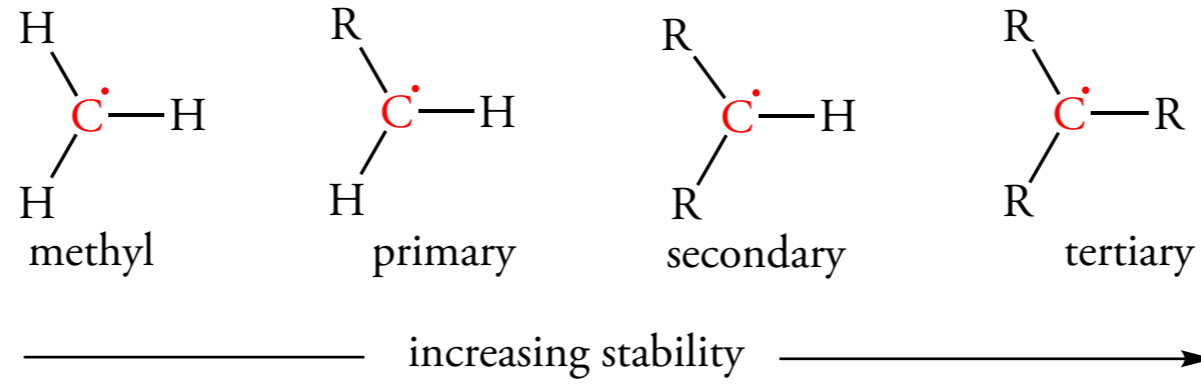


← half-filled 2p orbital

Methyl Radical

In a methyl radical (or any other), the central carbon is sp^2 hybridized, and the single, unpaired electron is in a 2p orbital orthogonal to the plane that contains the hydrogen atoms.

Carbanions

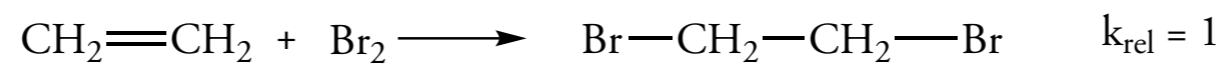


3.10 FACTORS THAT INFLUENCE REACTION RATES

Four major factors affect the rate of a reaction, and hence the rate constant for the reaction.

1. The structure of the reactants.
2. The concentration of reactants.
3. Temperature.
4. The presence of catalysts.

The Effect of Structure on Reactivity



The Effect of Reactant Concentration on Reaction Rates



$$v = k[\text{A}]^m[\text{B}]^n$$



$$\text{rate, } v = k [\text{CH}_3\text{Cl}][\text{OH}^-]$$

The Effect of Temperature on Reaction Rates

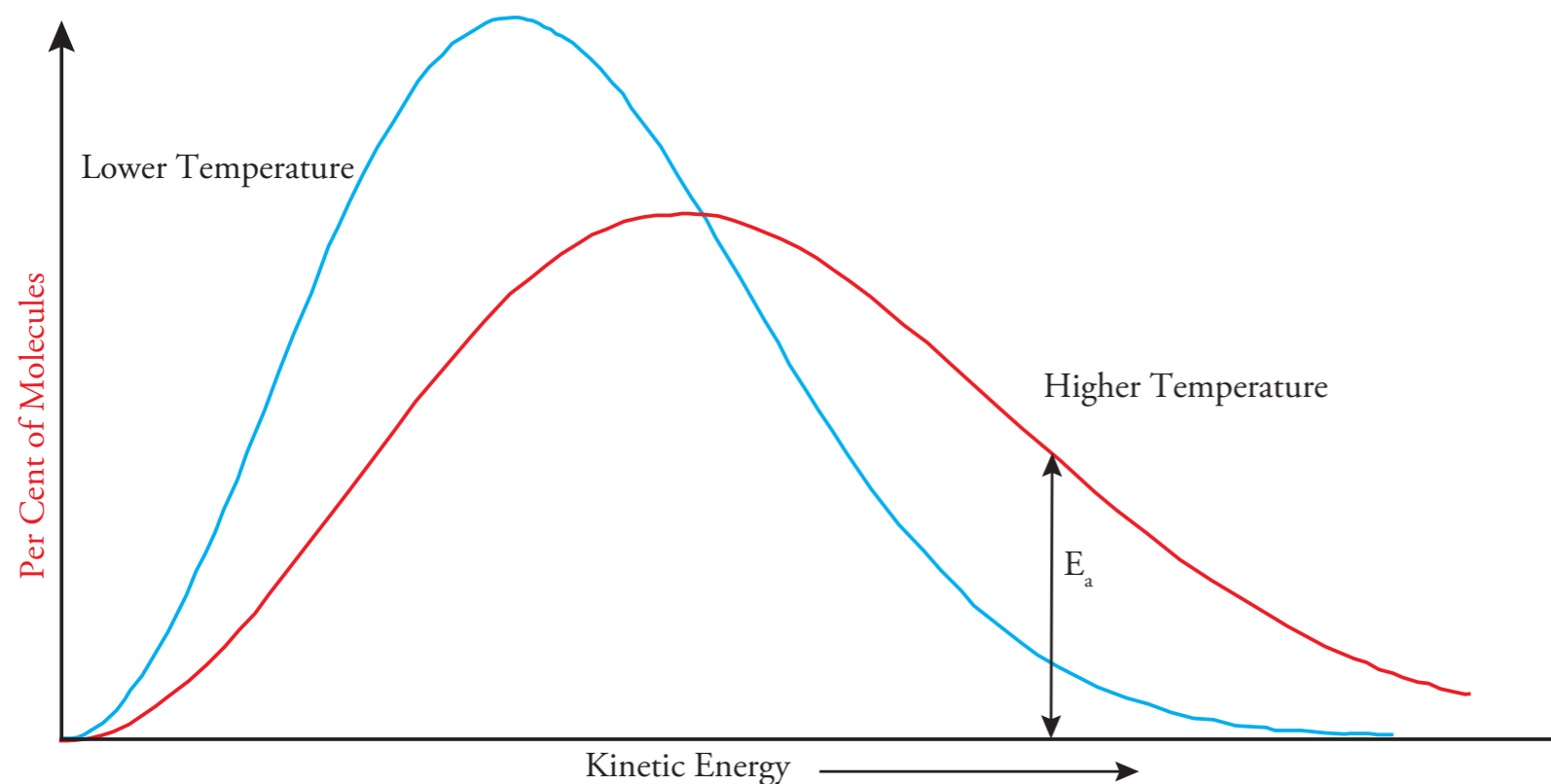


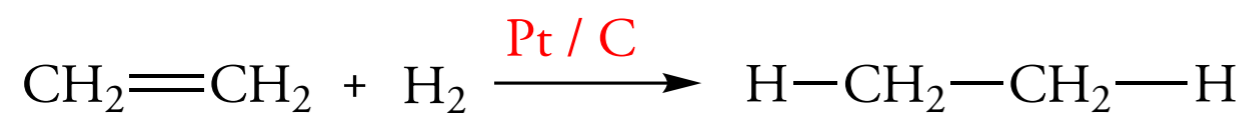
Figure 3.2 Distribution of Molecular Energies and Temperature

Table 3.6 Effect of Temperature on Rates of a Substitution Reaction¹

Temperature °C	Rate Constant (L mol ⁻¹ sec ⁻¹)
35	2.6 x 10 ⁻⁵
45	8.5 x 10 ⁻⁵
55	2.6 x 10 ⁻⁴
65	7.8 x 10 ⁻⁴

1. The rate increases by approximately a factor of 3 for each 10° C increase in temperature.

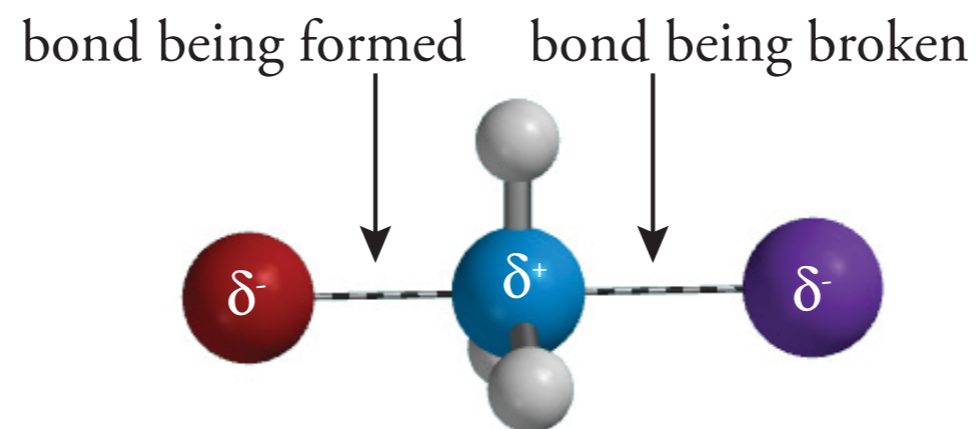
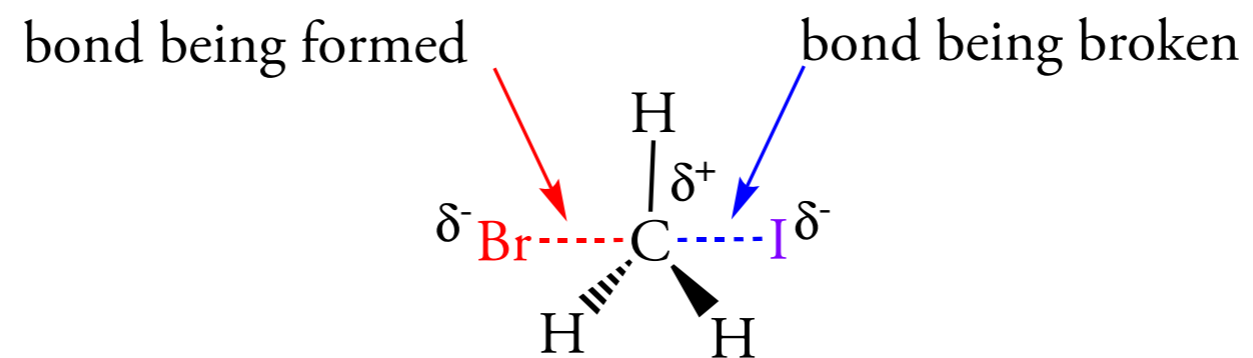
The Effect of Catalysts on Reaction Rates



The catalyst is not consumed, even though it does interact with the reactant during the reaction. Although a catalyst increases the rate of a reaction, it does not change the equilibrium constant for the reaction.

3.11 REACTION RATE THEORY

Transition States



Reaction Coordinate Diagrams

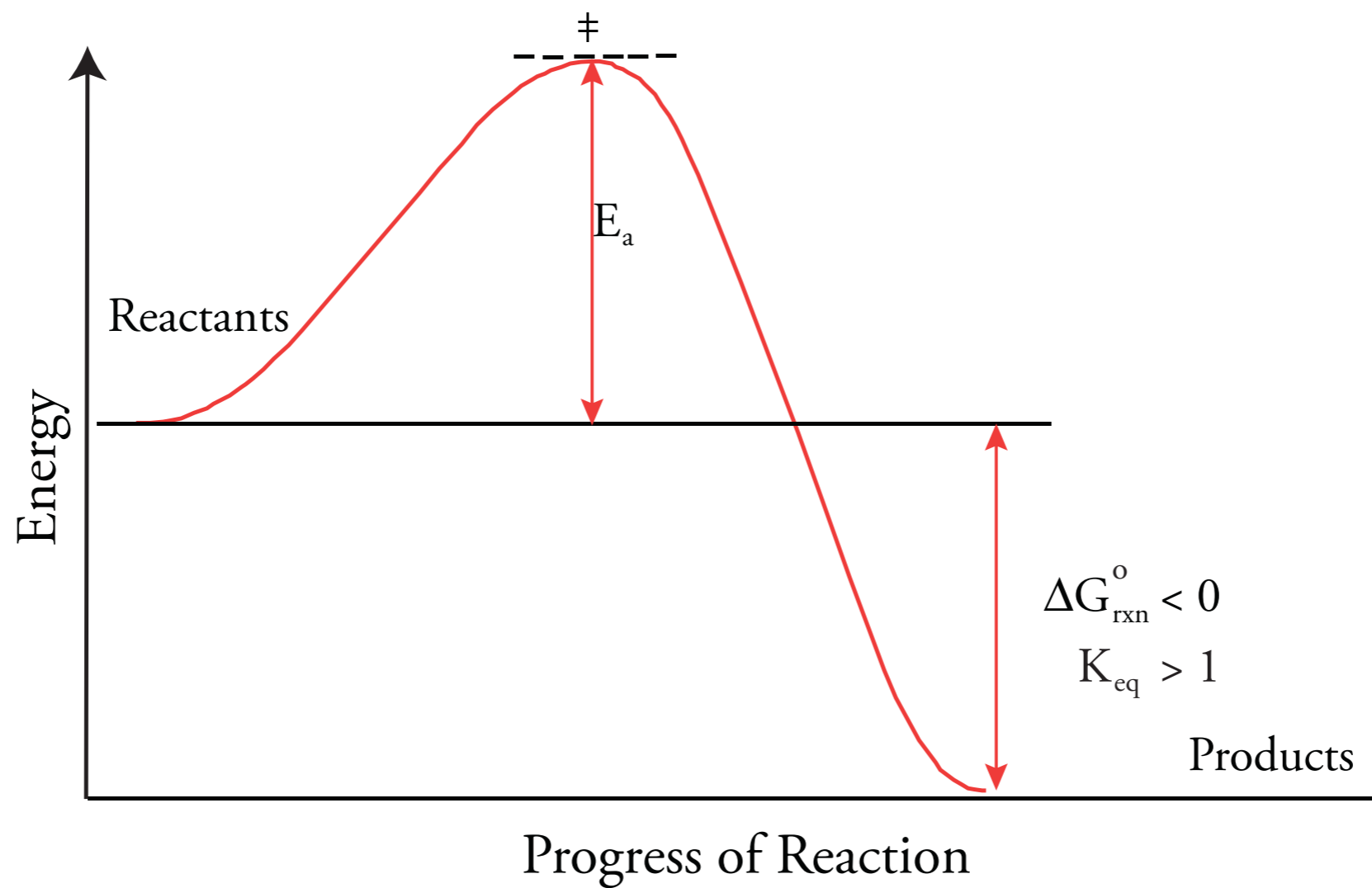


Figure 3.4 Reaction Coordinate Diagram For an Exergonic Reaction

Reaction Coordinate Diagrams and Reaction Mechanisms

Figure 3.5 Reaction Coordinate Diagram For a Substitution Reaction

(a) The reaction of iodomethane with bromide ion occurs in a single step. The activation energy reflects the stability of the transition state relative to the stability of the reactants.

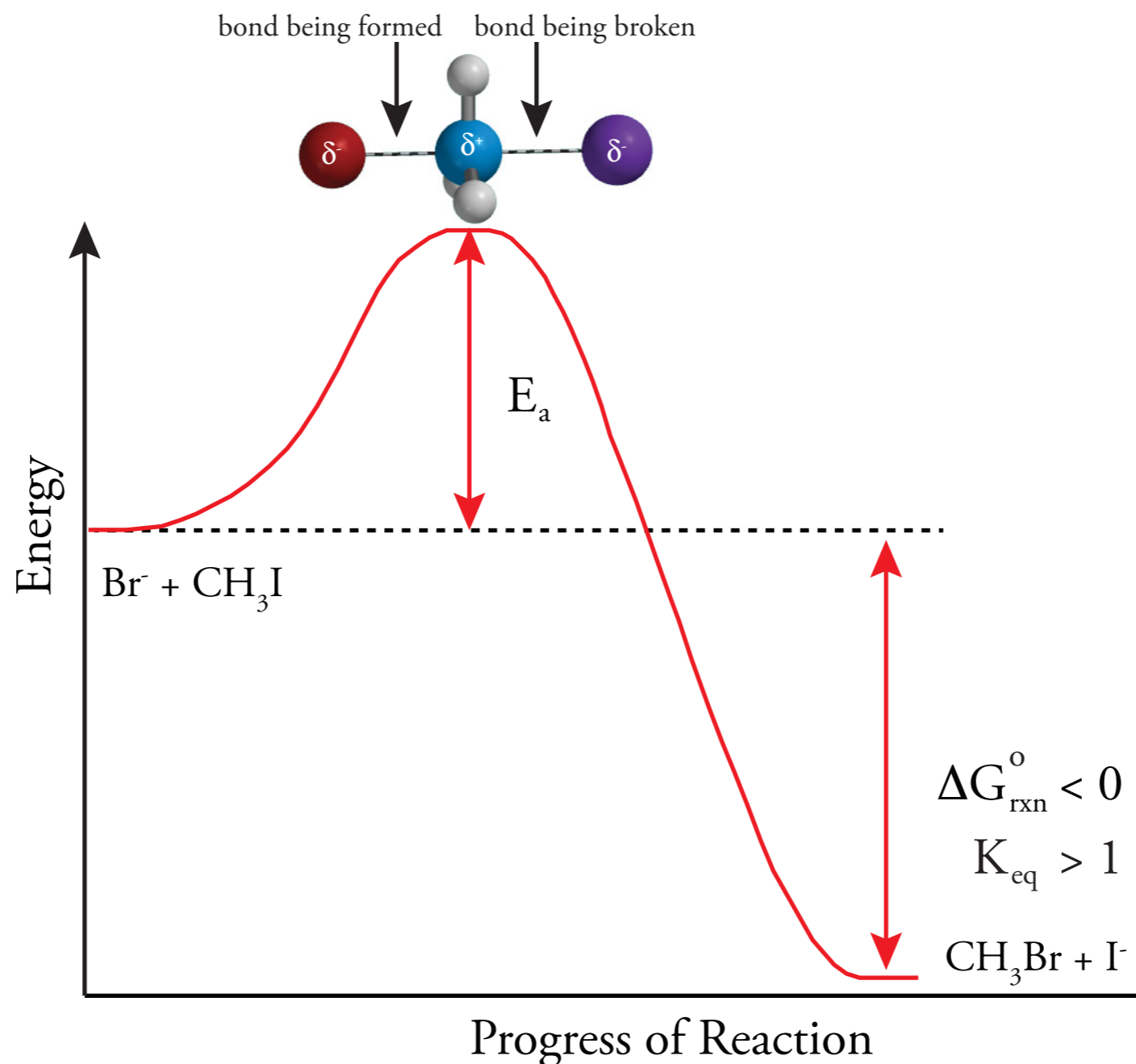


Figure 3.5 Reaction Coordinate Diagram For a Substitution Reaction

(b) The transition state occurs at the highest energy position on the pathway of minimum energy; it is at a saddle point.

(b)

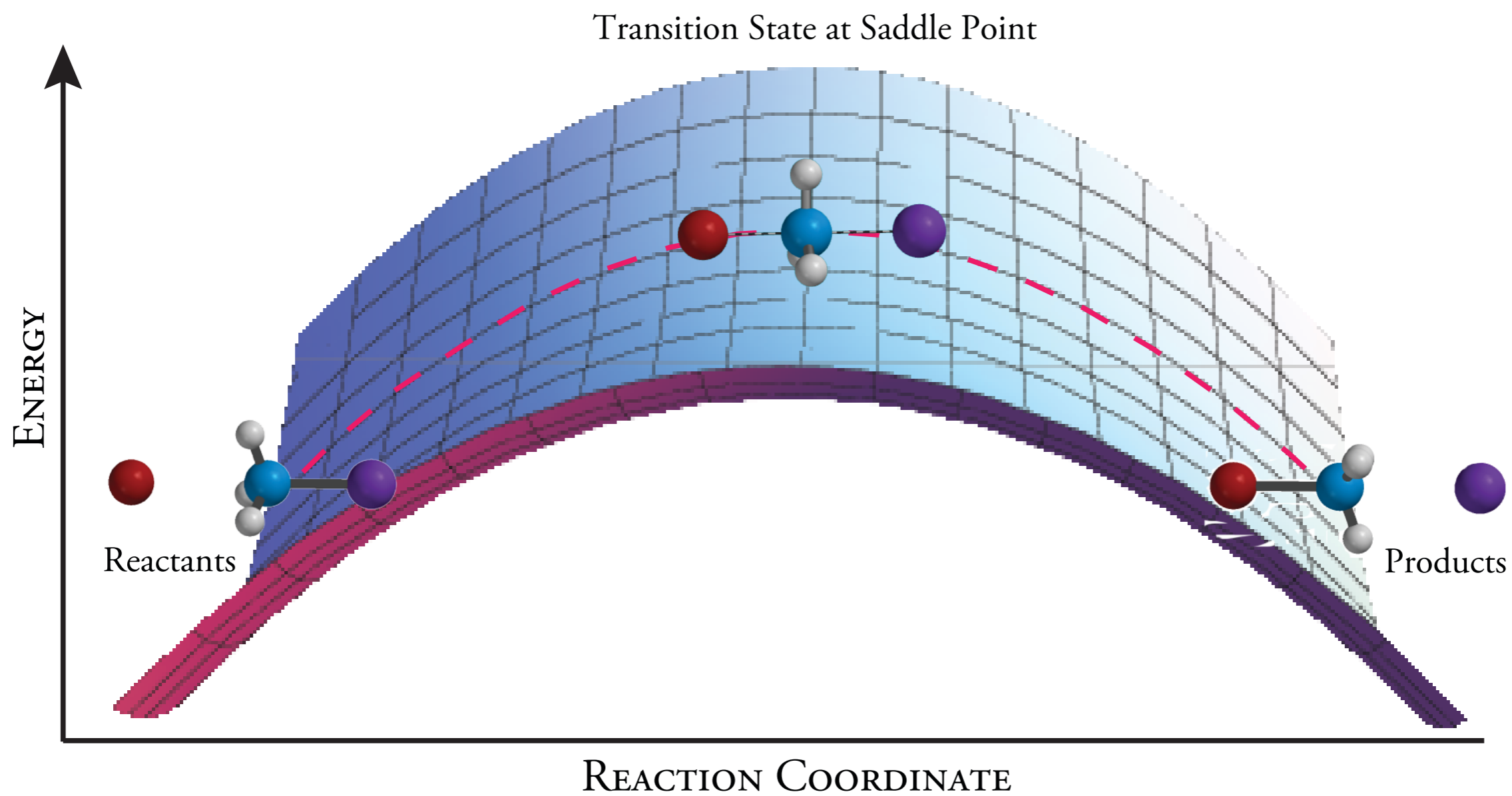
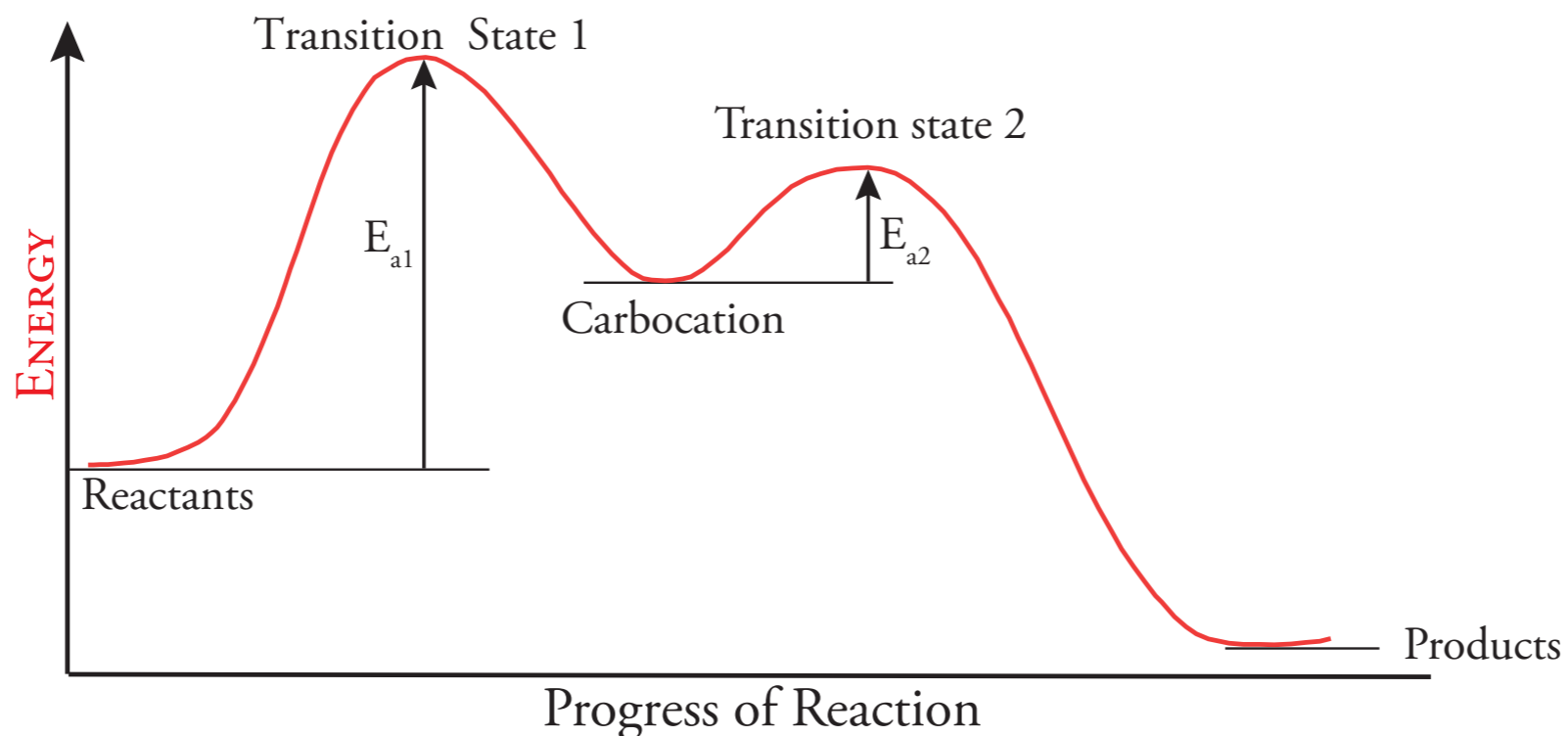
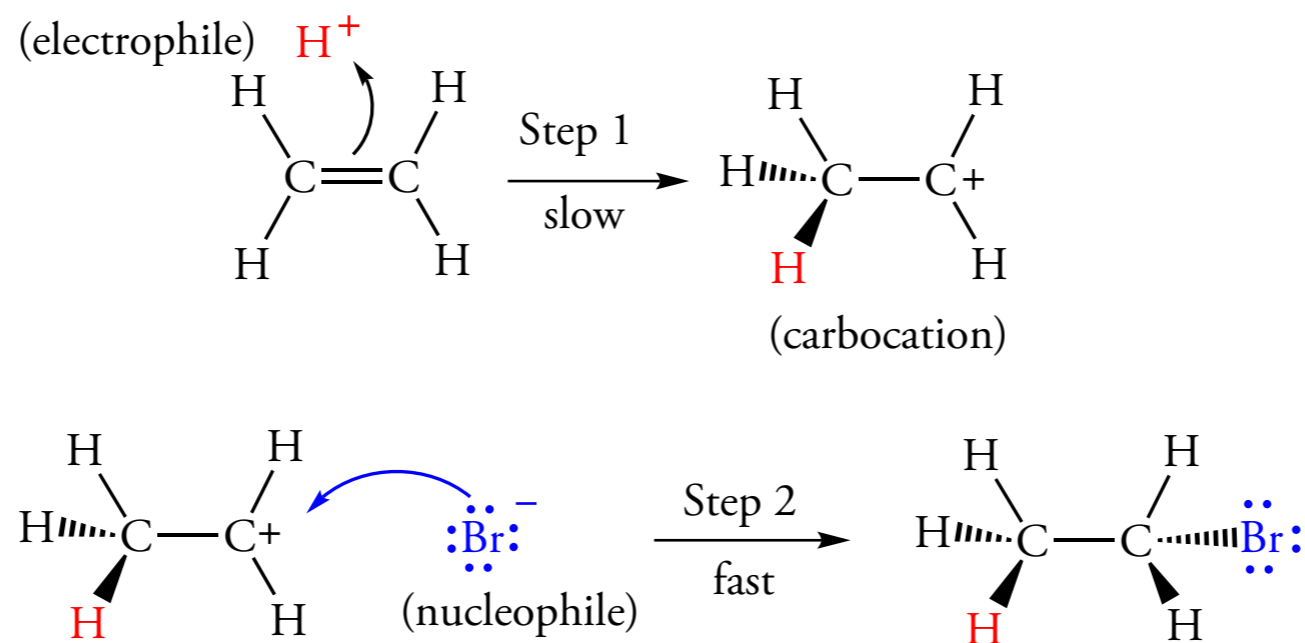


Figure 3.6 Energy Diagram for the Addition of HBr to an Alkene

The first, rate-determining step in the addition of HBr to ethene is the attack of the electrons of the double bond on a proton to give a carbocation. The second step occurs at a faster rate because the activation energy of the second step is lower than for the first step.

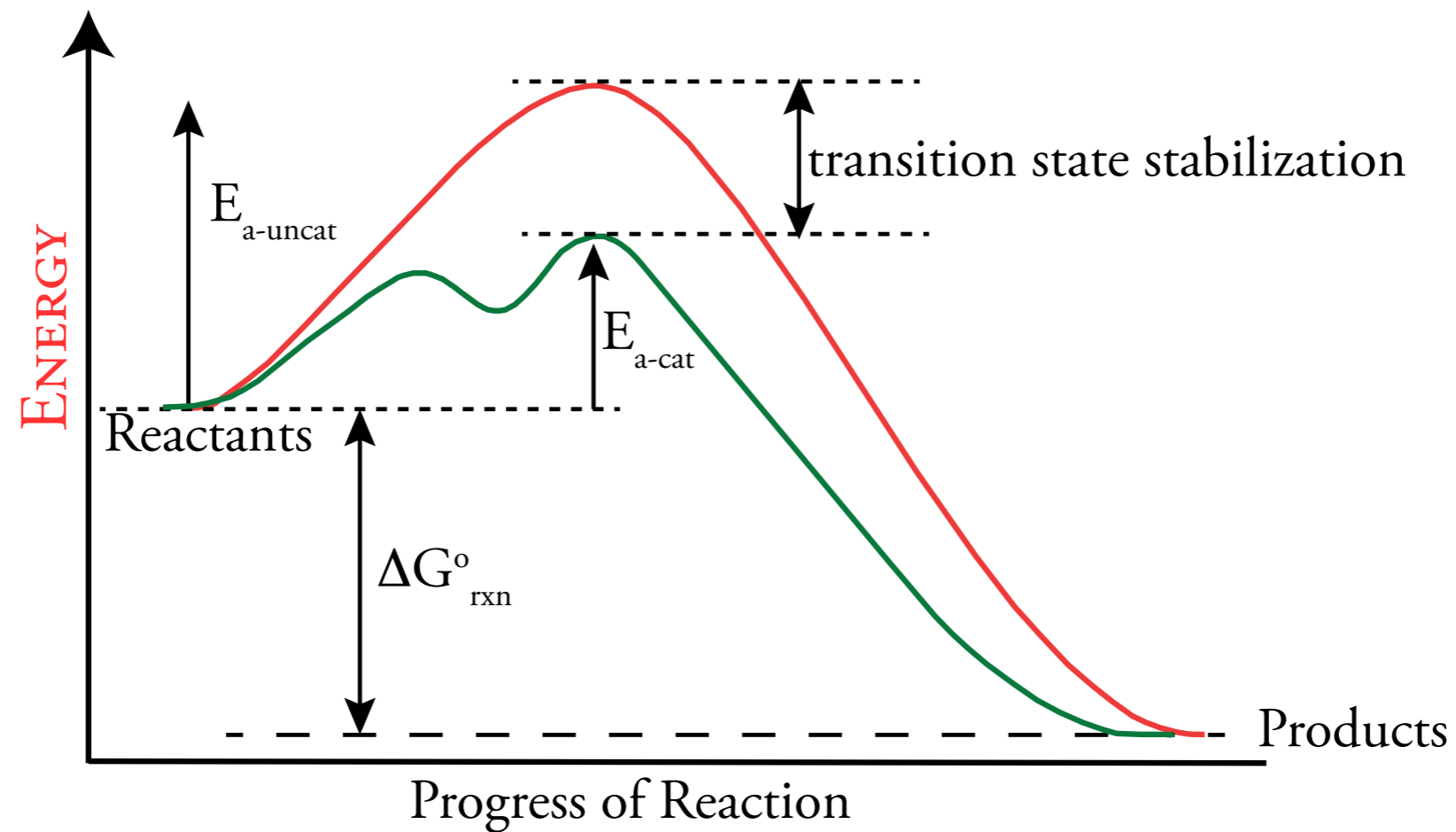


Catalysis



Figure 3.7 Energy Diagram for a Catalyzed and an Uncatalyzed Reaction

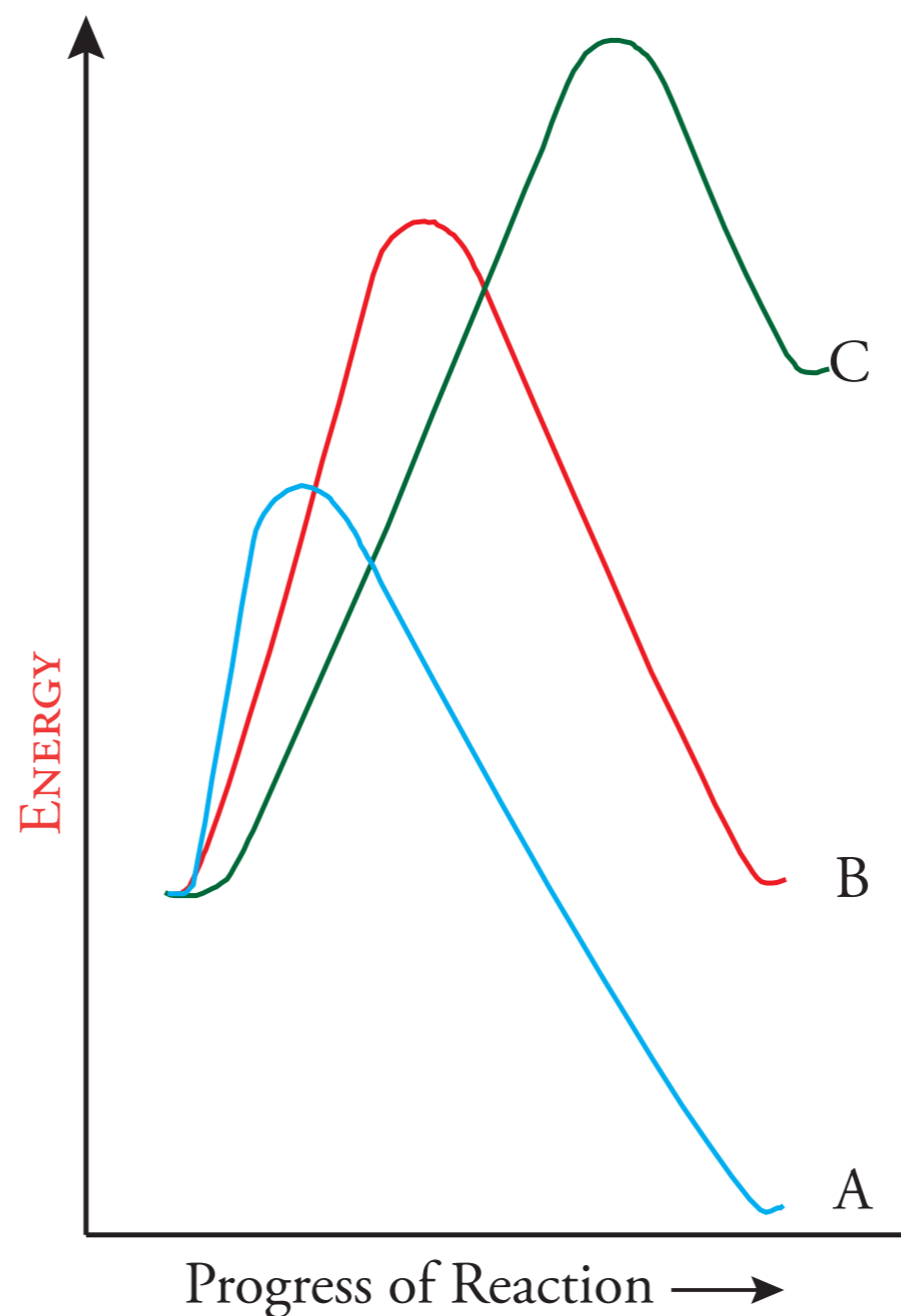
The activation energy for a catalyzed reaction is smaller than the activation energy for reaction in the absence of a catalyst. The catalyzed reaction may require a different number of steps than the uncatalyzed reaction.



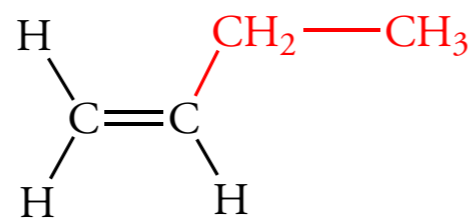
Transition State Structure: The Hammond Postulate

Figure 3.8 The Hammond Postulate

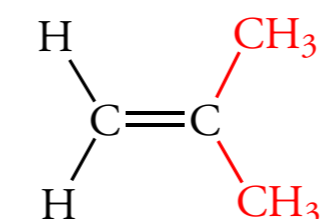
The location of the transition state along the reaction coordinate axis depends on the activation energy. Curve A for an exothermic process has an “early” transition state that is closer to the reactant side. Curve B is for a reaction with no difference in enthalpy between reactants and products. The transition state is in the middle. Curve C is for an endothermic process, which has a “late” transition state that is closer to the product side.



3.12 STABILITY AND REACTIVITY

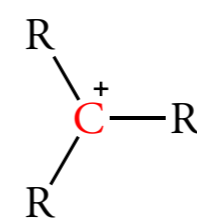
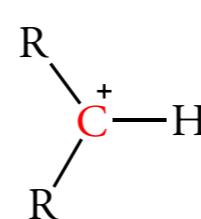
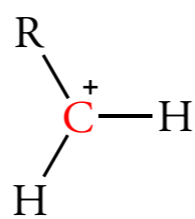
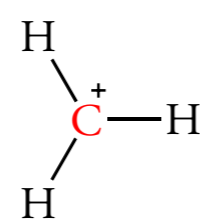


$$\Delta G_f^\circ = 70 \text{ kJ mole}^{-1}$$

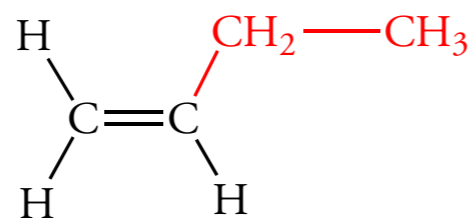


$$\Delta G_f^\circ = 58.6 \text{ kJ mole}^{-1}$$

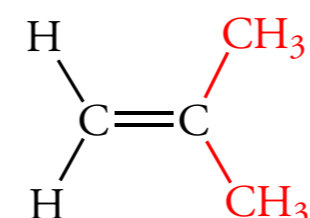
more stable



increasing stability



1-butene



2-methyl-1-propene

more reactive in addition of Br₂

more reactive in addition of H₂