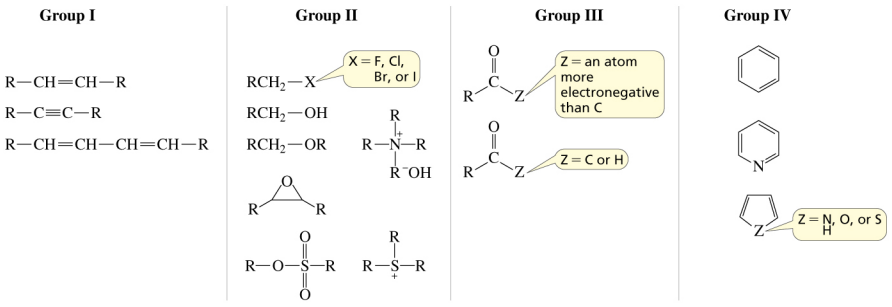
CHEM 109A
Organic Chemistry

https://labs.chem.ucsb.edu/zakarian/armen/courses.html

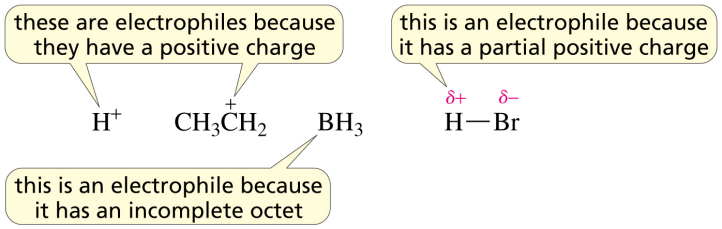
Chapter 5
Alkene: Introduction
Thermodynamics and Kinetics

Each Family of Organic Compounds Can Be Placed in One of Four Groups



The families in a group react in similar ways.

Electrophiles



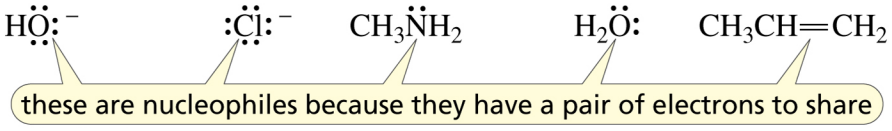
An electrophile has

a positive charge,

a partial positive charge,

or an incomplete octet.

Nucleophiles



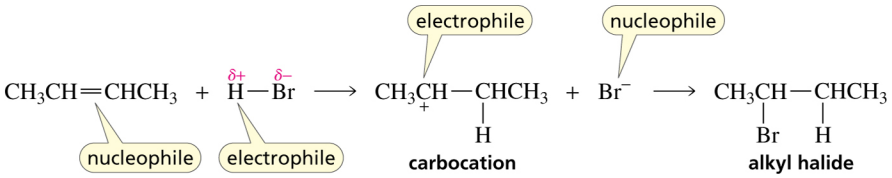
A nucleophile has

a negative charge,

a lone pair,

or a π bond.

A Nucleophile Reacts with an Electrophile

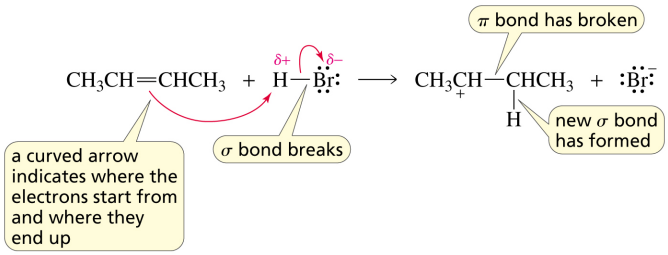


Your first organic reaction is a two-step reaction.

The Mechanism of the Reaction

The mechanism of a reaction is the step-by-step description of the process by which reactants are converted into products.

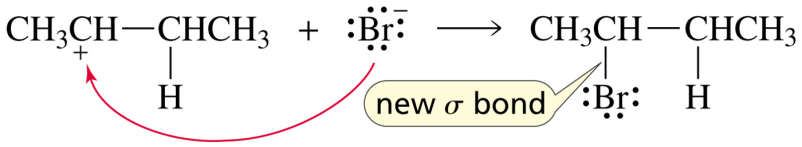
the mechanism for the first step of the reaction



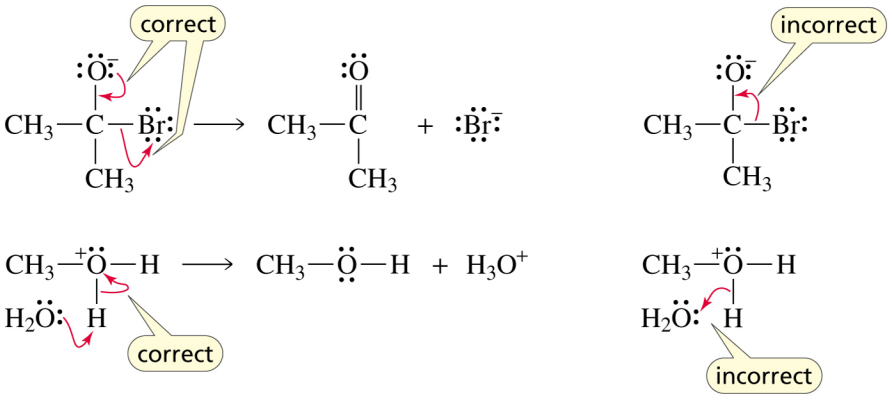
Curved arrows show where the electrons start from and where they end up.

The Mechanism of the Reaction (step 2)

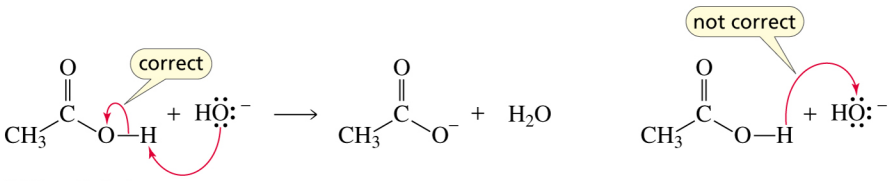
the mechanism for the second step of the reaction



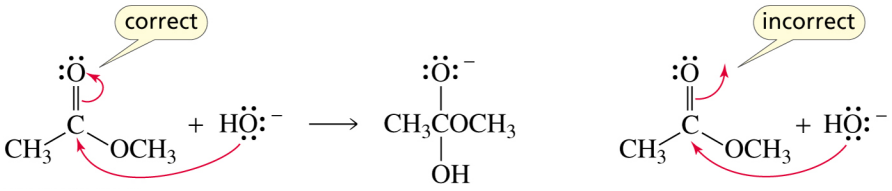
How to Draw Curved Arrows



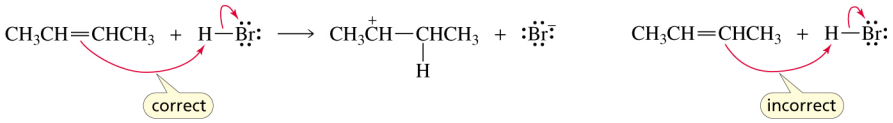
How to Draw Curved Arrows



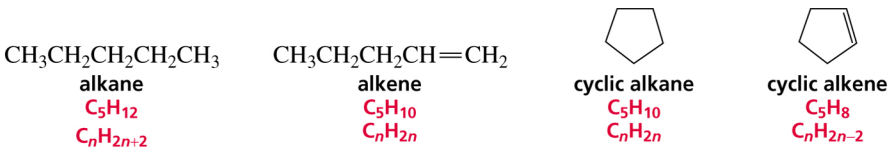
How to Draw Curved Arrows



How to Draw Curved Arrows



Molecular Formula and the Degree of Unsaturation



molecular formula =

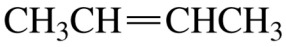
C_nH_{2n+2} – 2 hydrogens for every π bond or ring

degree of unsaturation =

the total numbers of π bonds and rings

Saturated and Unsaturated Hydrocarbons

alkane
a saturated hydrocarbon



alkene
an unsaturated hydrocarbon

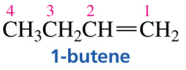
Saturated hydrocarbons have no double bonds.

Unsaturated hydrocarbons have one or more double bonds.

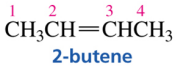
Nomenclature of Alkenes

Replace "ane" of alkane with "ene."

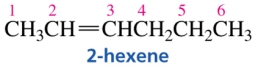
The functional group gets the lowest possible number.



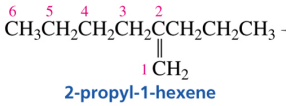
1-butene



2-butene



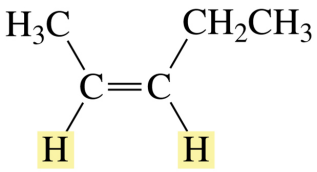
2-hexene



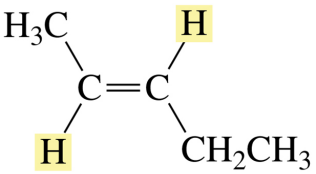
2-propyl-1-hexene

the longest continuous chain has 8 carbons, but the longest continuous chain containing the functional group has 6 carbons, so the parent name of the compound is hexene

Stereoisomers are Named Using a *cis* or *trans* (or *E* or *Z*) Prefix



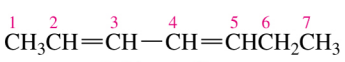
***cis*-2-pentene**
or
(*Z*)-2-pentene



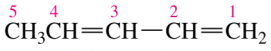
***trans*-2-pentene**
or
(*E*)-2-pentene

Nomenclature of Dienes

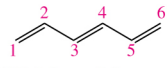
two double bonds = diene



2,4-heptadiene



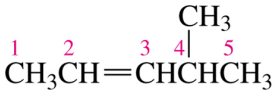
1,3-pentadiene



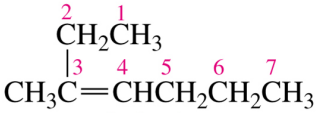
1,3,5-hexatriene

Nomenclature of Alkenes

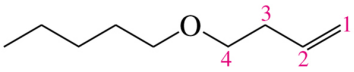
Number the chain in the direction that gives the double bond the lowest number.



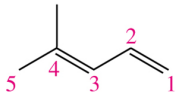
4-methyl-2-pentene



3-methyl-3-heptene



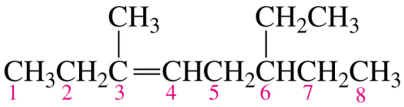
4-pentoxy-1-butene



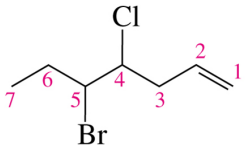
4-methyl-1,3-pentadiene

Nomenclature of Alkenes

Substituents are stated in alphabetical order.



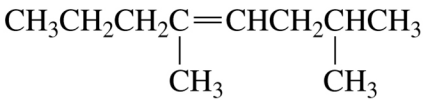
6-ethyl-3-methyl-3-octene



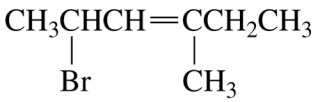
5-bromo-4-chloro-1-heptene

Nomenclature of Alkenes

If both directions give the same number for the double bond, the correct name has the lowest substituent number.



2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4

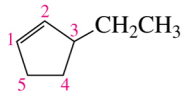


2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
because 2 < 3

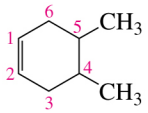
Nomenclature of Cyclic Alkenes

In a cyclic compound
A number is not needed to denote the position of the double bond:

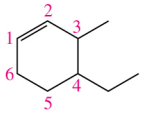
because it is always between C1 and C2.



3-ethylcyclopentene

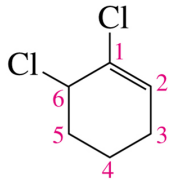


4,5-dimethylcyclohexene

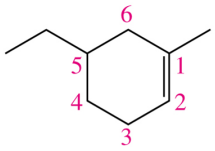


4-ethyl-3-methylcyclohexene

Nomenclature of Alkenes

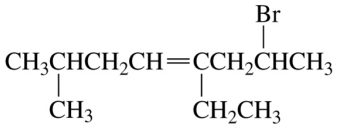


1,6-dichlorocyclohexene
not
2,3-dichlorocyclohexene
because 1 < 2

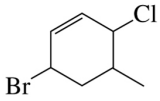


5-ethyl-1-methylcyclohexene
not
4-ethyl-2-methylcyclohexene
because 1 < 2

Nomenclature of Alkenes



2-bromo-4-ethyl-7-methyl-4-octene
not
7-bromo-5-ethyl-2-methyl-4-octene
because 4 < 5

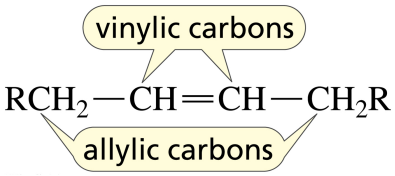


6-bromo-3-chloro-4-methylcyclohexene
not
3-bromo-6-chloro-5-methylcyclohexene
because 4 < 5

Vinylic and Allylic Carbons

vinylic carbon: the sp^2 carbon of an alkene

allylic carbon: a carbon adjacent to a vinylic carbon



Vinyl and Allyl Groups

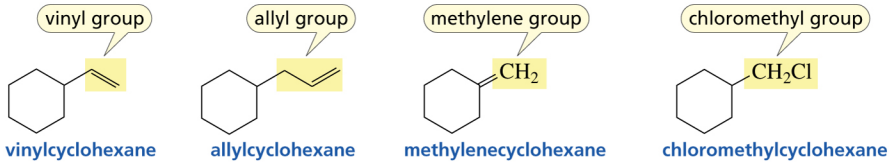
A vinyl group is the smallest group that contains a vinylic carbon.

An allyl group is the smallest group that contains an allylic carbon.

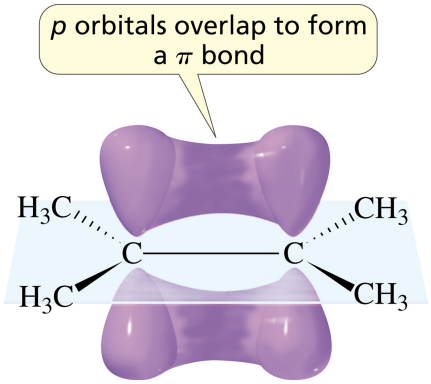
	$CH_2{=}CH-$	$CH_2{=}CHCH_2-$
	vinyl group	**allyl group**
	$CH_2{=}CHCl$	$CH_2{=}CHCH_2Br$
common name:	**vinyl chloride**	**allyl bromide**
systematic name:	**chloroethene**	**3-bromopropene**

The substituent is on the vinylic or allylic carbon.

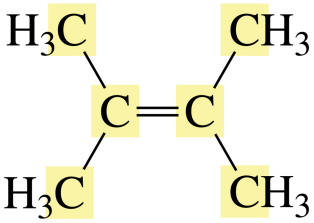
Substituent Names



The Structure of an Alkene

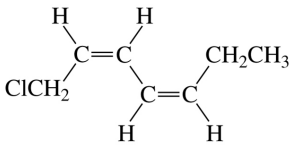


Six Atoms of an Alkene are in the Same Plane

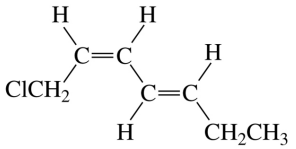


the six carbon atoms are in the same plane

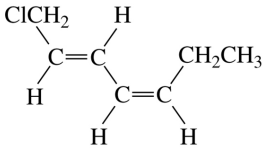
Stereoisomers for Compounds with Two Double Bonds



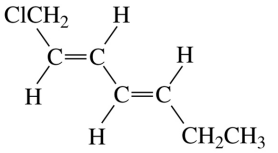
(2*Z*,4*Z*)-1-chloro-2,4-heptadiene



(2*Z*,4*E*)-1-chloro-2,4-heptadiene

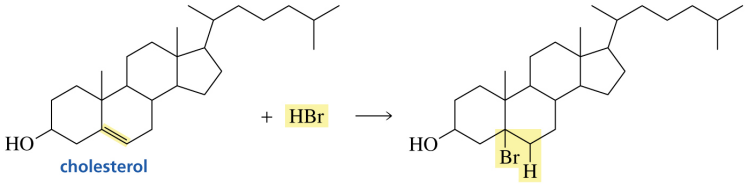


(2*E*,4*Z*)-1-chloro-2,4-heptadiene



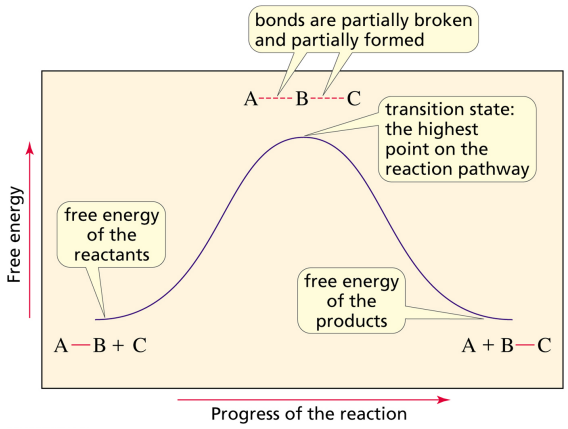
(2*E*,4*E*)-1-chloro-2,4-heptadiene

Reactions of Organic Compounds



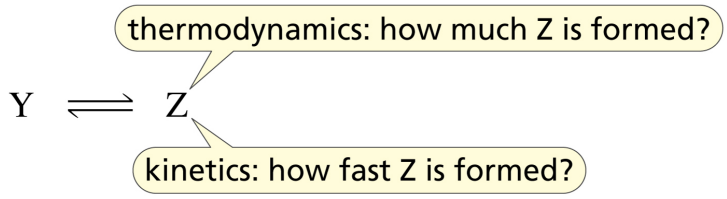
Organic compounds can be divided into families.
All members of a family react in the same way.
The family a compound belongs to depends on its functional group.

A Reaction Coordinate Diagram



A reaction coordinate diagram shows the energy changes that take place in each step of a reaction.

Thermodynamics and Kinetics



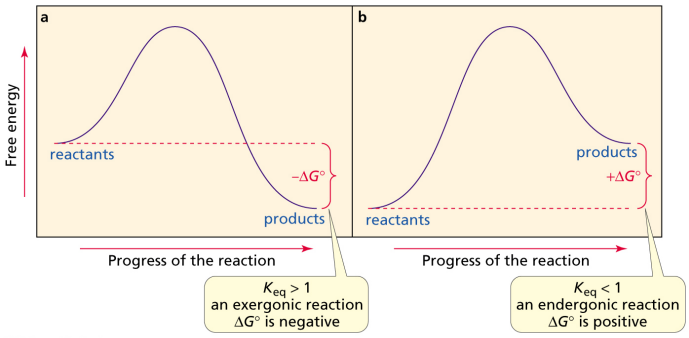
The Equilibrium Constant

The equilibrium constant gives the relative concentration of reactants and products at equilibrium.

$$\mathbf{A} + \mathbf{B} \rightleftharpoons \mathbf{C} + \mathbf{D}$$

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\mathbf{C}][\mathbf{D}]}{[\mathbf{A}][\mathbf{B}]}$$

Exergonic and Endergonic Reactions



$\Delta G°$ = free energy of the products - free energy of the reactants

the relationship between $\Delta G°$ and K_{eq}

$$\Delta G° = -RT \ln K_{eq}$$

Gibbs Free-Energy Change ($\Delta G°$)

$$\Delta G° = \Delta H° - T\Delta S°$$

$\Delta G°$ = (free energy of the products) − (free energy of the reactants)

$\Delta H°$ = (heat required to break bonds) − (heat released from breaking bonds)

$\Delta S°$ = (freedom of motion of the products) − (freedom of motion of the reactants)

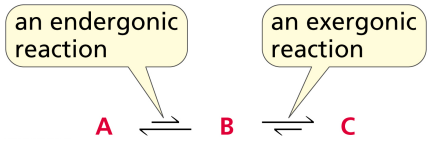
Increasing the Amount of a Product Formed in a Reaction

Le Chatelier's Principle: if an equilibrium is disturbed,
the system will adjust to offset the disturbance

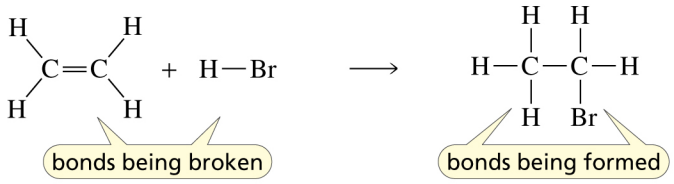
$$\mathbf{A} + \mathbf{B} \rightleftharpoons \mathbf{C} + \mathbf{D}$$

$$K_{eq} = \frac{[\mathbf{C}][\mathbf{D}]}{[\mathbf{A}][\mathbf{B}]}$$

Coupled Reactions: an endergonic reaction followed by an exergonic reaction



Calculating $\Delta H°$



π bond of ethene	DH = 62 kcal/mol	C—H	DH = 101 kcal/mol
H—Br	DH = 88 kcal/mol	C—Br	DH = 71 kcal/mol
	DH_{total} = 150 kcal/mol		DH_{total} = 172 kcal/mol

$\Delta H°$ for the reaction = DH for bonds being broken − DH for bonds being formed

= 150 kcal/mol − 172 kcal/mol

= −22 kcal/mol

Table 5.1 Experimental Bond Dissociation Enthalpies Y—Z → Y + Z

Bond	*DH* (kcal/mol)	Bond	*DH* (kcal/mol)
CH_3—H	105.0	H—H	104.2
CH_3CH_2—H	101.1	F—F	37.7
		Cl—Cl	58.0
$(CH_3)_2CH$—H	98.6	Br—Br	53.5
$(CH_3)_3C$—H	96.5	I—I	51.0
		H—F	136.3
CH_3—CH_3	90.2	H—Cl	103.2
CH_3CH_2—CH_3	89.1	H—Br	87.5
$(CH_3)_2CH$—CH_3	88.6	H—I	71.3
$(CH_3)_3C$—CH_3	87.5		
		CH_3—F	114.8
H_2C=CH_2	174.5	CH_3—Cl	83.6
HC≡CH	230.4	CH_3CH_2—Cl	84.7
		$(CH_3)_3C$—Br	70.7
H_2C=CH—H	110.7	CH_3—I	57.1
HC≡C—H	133.3	CH_3CH_2—I	56.3
		$(CH_3)_2CH$—Cl	85.1
HO—H	118.8	$(CH_3)_3C$—Cl	84.8
CH_3O—H	104.2	CH_3—Br	70.3
CH_3—OH	92.1	CH_3CH_2—Br	70.5
		$(CH_3)_2CH$—Br	72.0

S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, **2003,** *36*, 255.

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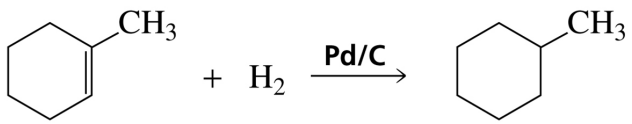
Catalytic Hydrogenation

$$CH_3CH{=}CHCH_3 + H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_3$$

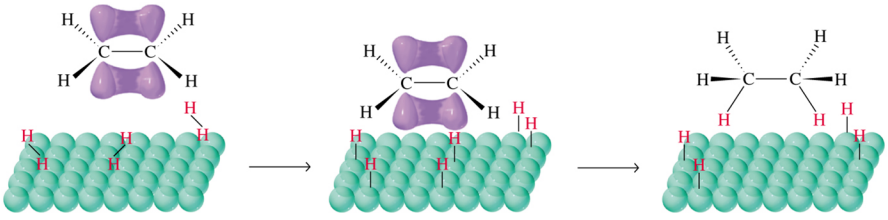
alkene → alkane



alkene → alkane

reduction reactions
(the number of C-H bonds increases)

Catalytic Hydrogenation



hydrogen molecules settle on the surface of the catalyst and interact with the metal atoms

the alkene approaches the surface of the catalyst

the π bond between the two carbons is replaced by two C—H σ bonds

$$CH_3CH{=}CHCH_3 \longrightarrow CH_3\dot{C}H{-}\dot{C}HCH_3 \longrightarrow CH_3CH(H){-}CH(H)CH_3$$

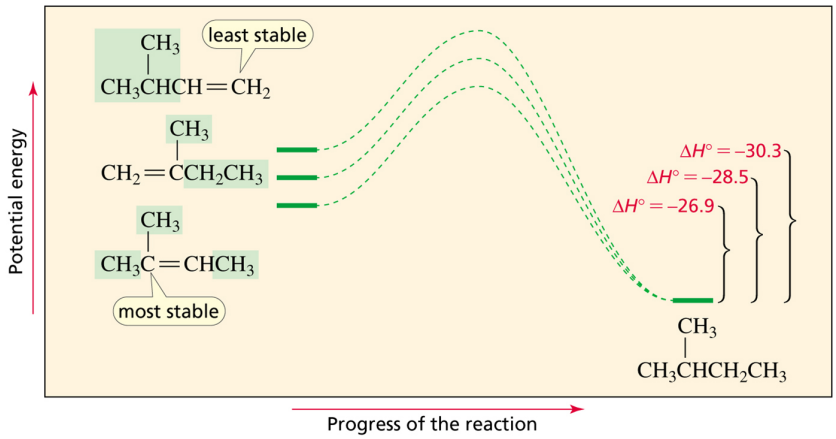
H—H H· ·H

Using $\Delta H°$ Values to Determine the Relative Stabilities of Alkenes

	$\Delta H°$ (kcal/mol)	heat of hydrogenation
$CH_3CH(CH_3){=}CHCH_3 + H_2 \xrightarrow{Pd/C} CH_3CH(CH_3)CH_2CH_3$	–26.9	26.9 kcal/mol
$CH_2{=}C(CH_3)CH_2CH_3 + H_2 \xrightarrow{Pd/C} CH_3CH(CH_3)CH_2CH_3$	–28.5	28.5 kcal/mol
$CH_3CH(CH_3){=}CH_2 + H_2 \xrightarrow{Pd/C} CH_3CH(CH_3)CH_2CH_3$	–30.3	30.3 kcal/mol

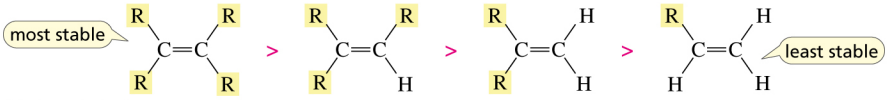
the product of each of the three reactions is 2-methylbutane

Using $\Delta H°$ Values to Determine the Relative Stabilities of Alkenes

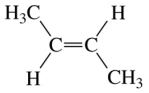
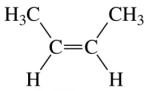


The Relative Stabilities of Alkenes

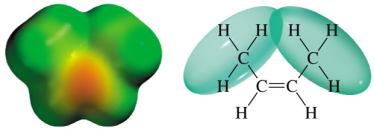
the more alkyl groups bonded to the sp^2 carbons, the more stable the alkene



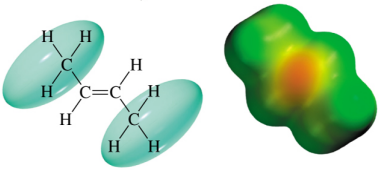
A Trans Alkene is More Stable Than a Cis Alkene

		$\Delta H°$ (kcal/mol)	heat of hydrogenation
 *trans*-2-butene	+ H_2 $\xrightarrow{Pd/C}$ $CH_3CH_2CH_2CH_3$	−27.6	27.6
 *cis*-2-butene	+ H_2 $\xrightarrow{Pd/C}$ $CH_3CH_2CH_2CH_3$	−28.6	28.6

the cis isomer has steric strain due to electron cloud overlap

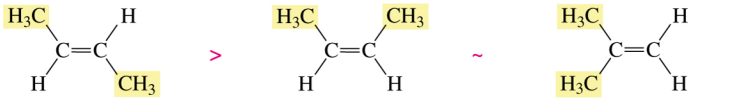


the trans isomer does not have steric strain



The Relative Stabilities of Alkenes

the relative stabilities of alkenes that have two alkyl groups bonded to the sp^2 carbons

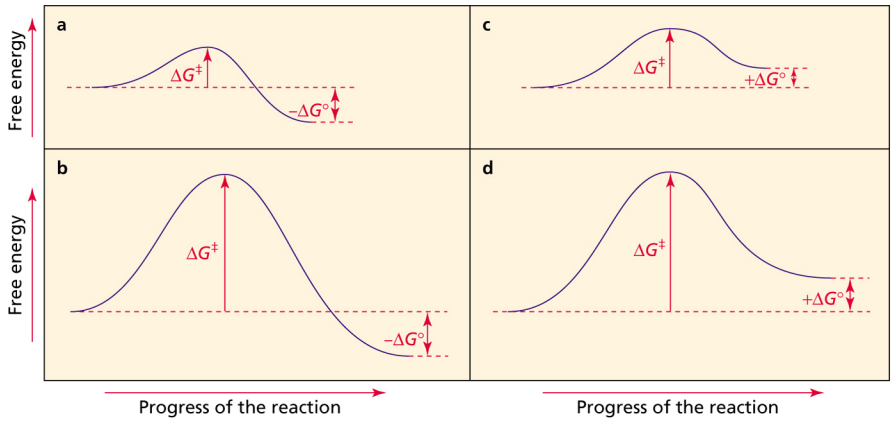


alkyl groups are on *opposite sides* of the double bond

alkyl groups are on the *same side* of the double bond

alkyl groups are on the same sp^2 carbon

Reaction Coordinate Diagrams for Fast and Slow Exergonic and Endergonic Reactions



Free Energy of Activation ($\Delta G^{\ddagger}$)

The free energy of activation is the energy barrier of the reaction.

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

$$\Delta H^{\ddagger} = (\text{enthalpy of the transition state}) - (\text{enthalpy of the reactants})$$

$$\Delta S^{\ddagger} = (\text{entropy of the transition state}) - (\text{entropy of the reactants})$$

Kinetic and Thermodynamic Stability

Kinetic Stability is indicated by $\Delta G^{\ddagger}$

If $\Delta G^{\ddagger}$ is large, the reactant is kinetically stable because it reacts slowly.

If $\Delta G^{\ddagger}$ is small, the reactant is kinetically unstable because it reacts rapidly.

Thermodynamic Stability is indicated by ΔG°

If ΔG° is negative,
the product is thermodynamically stable compared to the reactant.

If ΔG° is positive,
the product is thermodynamically unstable compared to the reactant.

Rate of a Reaction

$$\text{rate of a reaction} = \left(\begin{array}{c}\text{number of collisions}\\ \text{per unit of time}\end{array}\right) \times \left(\begin{array}{c}\text{fraction with}\\ \text{sufficient energy}\end{array}\right) \times \left(\begin{array}{c}\text{fraction with}\\ \text{proper orientation}\end{array}\right)$$

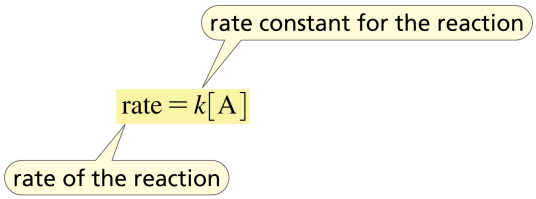
Increasing the concentration increases the rate.
Increasing the temperature increases the rate.

The rate can be increased by a catalyst.

The Rate of a Reaction *versus* the Rate Constant for a Reaction

$$\mathbf{A} \longrightarrow \mathbf{B}$$

$$\text{rate} \propto [\text{A}]$$



The Arrhenius Equation

$$k = Ae^{-E_a/RT}$$

The value of A pertains to
the frequency and orientation of collisions.

$$e^{-Ea/RT}$$

$e^{-Ea/RT}$ is the fraction of the collisions with
the minimum energy needed for a reaction.

How are Rate Constants Related to the Equilibrium Constant?

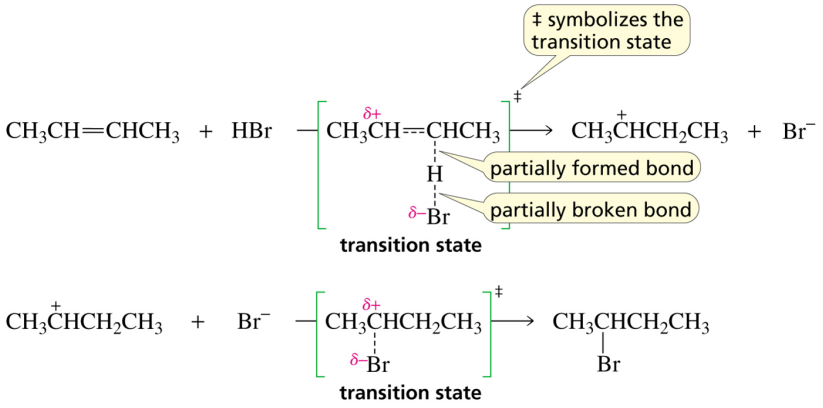
$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

$$\text{forward rate} = \text{reverse rate}$$

$$k_1[\mathrm{A}] = k_{-1}[\mathrm{B}]$$

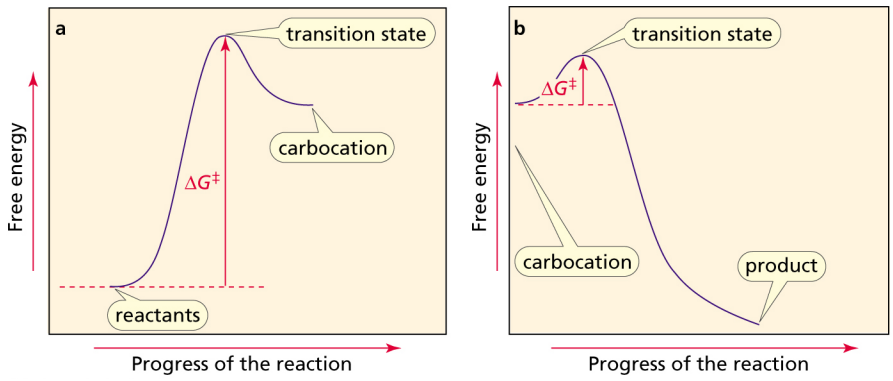
$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{B}]}{[\mathrm{A}]}$$

The Structure of the Transition State

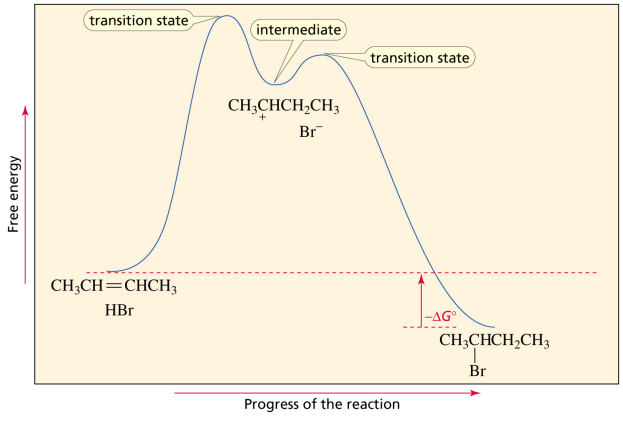


Transition states have partially formed bonds.

Reaction Coordinate Diagram for Each Step of the Addition of HBr to 2-Butene

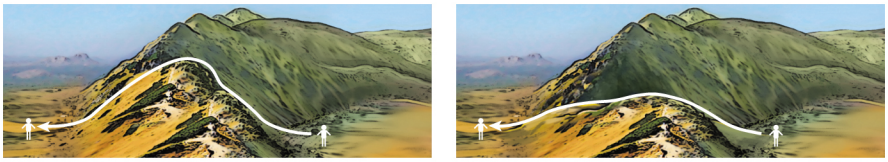


Reaction Coordinate Diagram for the Addition of HBr to 2-Butene



The rate-limiting step has its transition state at the highest point on the reaction coordinate diagram.

A Catalyst



A catalyst provides a pathway for a reaction with a lower energy barrier.

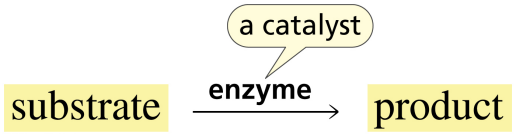
A catalyst does not change the energy of the starting point (the reactants) or the energy of the end point (the products).

Enzymes

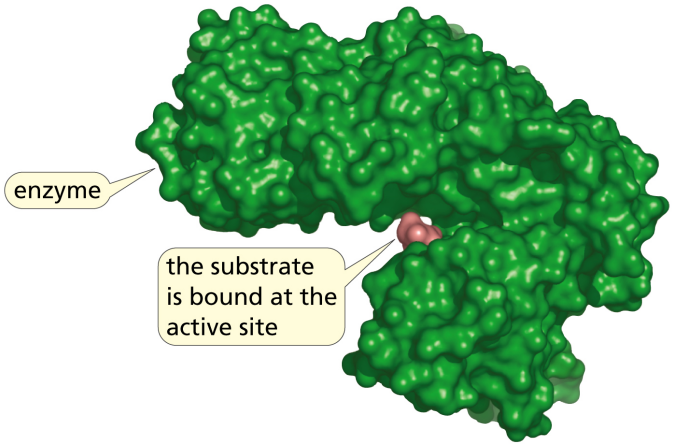
Most biological reactions require a catalyst.

Most biological catalysts are proteins called enzymes.

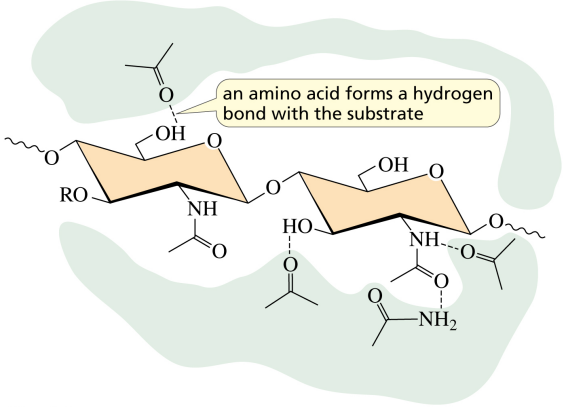
The reactant of a biological reaction is called a substrate.



The Active Site of an Enzyme

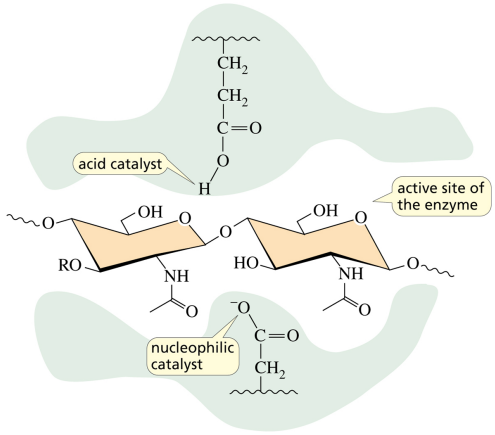


Enzyme Side Chains That Bind the Substrate



Enzyme side chains bind the substrate using hydrogen bonds, London dispersion forces, and dipole-dipole interactions.

Enzyme Side Chains That Catalyze the Reaction



Some enzyme side chains are acids, bases, and nucleophiles that catalyze the reaction.