








# ORGANIC CHEMISTRY

## FUNDAMENTALS

### TYPES OF ORGANIC COMPOUNDS

HYDROCARBON	-O- ADDED	>C =O ADDED	>COO ADDED	NITROGEN ADDED	SULFUR ADDED
<b>ALKANE</b> $\text{C}-\text{H}$ • ethane: $\text{C}_2\text{H}_6$ • methyl (Me): $-\text{CH}_3$ • ethyl (Et): $-\text{C}_2\text{H}_5$ <b>ALKENE</b> $\text{C}=\text{C}$ • ethene: $\text{C}_2\text{H}_4$ • diene: two $\text{C}=\text{C}$ • triene: three $\text{C}=\text{C}$ <b>ALKYNE</b> $-\text{C}\equiv\text{C}-$ • ethyne: $\text{C}_2\text{H}_2$ <b>AROMATIC</b>  • benzene: $\text{C}_6\text{H}_6$ • arene: $\text{C}_6\text{H}_5$ (Ar-)	<b>ALCOHOL</b> $\text{R}-\text{OH}$ • methanol: Me-OH (methyl alcohol) • phenol: Ar-OH • diol/glycol: (2 -OH) • glycerol: (3 -OH) <b>ETHER</b> $\text{R}-\text{O}-\text{R}$ • ethoxyethane: Et-O-Et (diethyl ether) <b>EPOXY</b>  • cyclic ether <b>PEROXIDE</b> $\text{R}-\text{O}-\text{O}-\text{R}'$	<b>ALDEHYDE</b>  • methanal: $\text{H}_2\text{CO}$ (formaldehyde) • benzaldehyde: Ar-CHO <b>KETONE</b>  • 2-propanone: Me-CO-Me (dimethyl ketone, acetone) • diketone: R-CO-R''-CO-R'	<b>CARBOXYLIC ACID</b>  • ethanoic acid: Me-COOH (acetic acid) • acetate ion: Me-COO <sup>-</sup> • benzoic acid: Ar-COOH <b>Dicarboxylic acid</b> HOOC-R-COOH <b>ESTER</b>  • ethyl acetate: Me-CO-OEt, Other derivatives: • Peroxyacid: R-CO-OOH • Acid anhydride: RCO-O-CO-R'	<b>AMINE</b> $\text{R}-\text{N}-\text{R}$ • methyl amine: $\text{H}_3\text{C}-\text{NH}_2$ • phenylamine: Ar-NH <sub>2</sub> (aniline) • R-NH <sub>2</sub> (1°), RR'NH (2°), RR''N (3°) <b>NITRO</b> R-NO <sub>2</sub> <b>DIAZO</b> R-N≡N <b>NITRILE</b> $\text{R}-\text{C}\equiv\text{N}$ • methane nitrile: Me-CN <b>AMIDE</b>  • acetamide: Me-CO-NH <sub>2</sub>	• thiol: R-SH • thioether: R-S-R' • disulfide: R-S-S-R' • thiol ester: R-CO-SR' • sulfoxide: R-SO-R' • sulfone: R-SO <sub>2</sub> -R' • sulfonic acid: R-SO <sub>3</sub> H <b>HALOGEN ADDED</b> • haloalkane: R-X: Me-Cl chloromethane • halobenzene: Ar-X chlorobenzene: Ar-Cl • acyl halide: R-CO-X • aryl halide: Ar-X

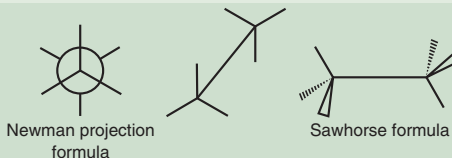
### FORMULAS AND ISOMERS

**Molecular formula:** elemental symbols with subscripts denote the composition of a compound

**Empirical formula:** subscripts denote the relative elemental composition

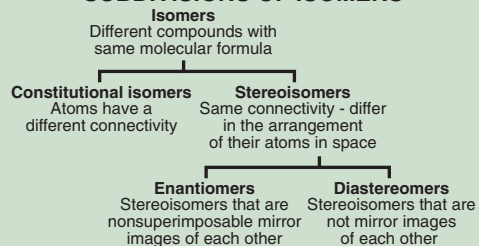
**Graphical depiction:**

- Dash formula: diagram all atoms, bonds as dashes
- Bond line formula: hide H, show carbon skeleton as lines, other atoms explicit



- Newman Projection: 2-d depiction
- 3-dimensional: wedges of sawhorse denote structure

### SUBDIVISIONS OF ISOMERS



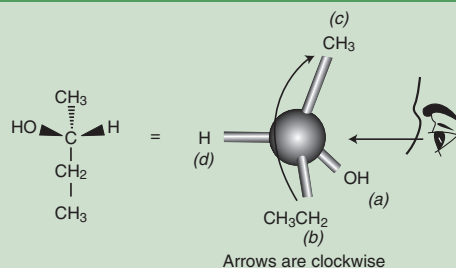
**constitutional isomers:** different bonding connectivity (ex. rings, bonds, branching, substituent positions)  
**tautomers:** easily interconverted structural isomers (ex. keto-enol for ketone)

**chiral:** not identical with mirror image  
**achiral:** has plane of symmetry (superimposable on mirror-image)  
**epimers:** a pair of diastereomers which differ only in the configuration of one atom

**More than 1 chiral center:**

- n chiral centers,  $\leq 2^n$  stereoisomers
- meso:** two chiral centers, 4 isomers: 3 stereoisomers, 1 achiral (mirror-plane)

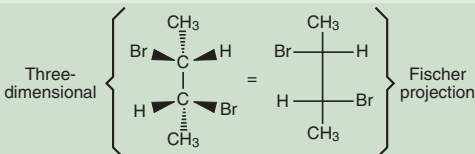
### FORMULAS AND ISOMERS



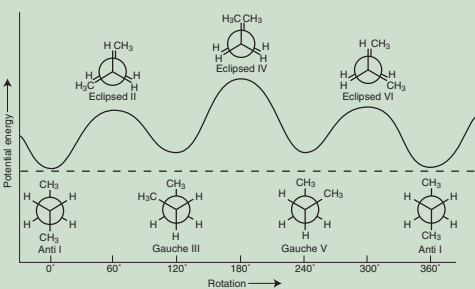
**R/S notation:** the four different atoms or groups attached to a central atom are ranked a,b,c,d, by molar mass. The lowest (d) is directed away from the viewer and the sequence of a-b-c produces clockwise (R) or counter-clockwise (S) configuration.

- chiral (optically active):** + or - rotation of plane polarized light. R/S: opposite effects
- racemic:** 50/50 mixture of stereoisomers (no net optical activity)
- nomenclature:** note R/S and +/- in the compound name; example: R (+) bromochloromethanol.

**Fisher-projection:** diagram depicts chiral/3-D structure  
**molecular conformations:** molecule exhibits structural variation due to free rotation about C-C single bond



**Newman-diagram:** depict rotation about a C-C bond;  
**eclipsed (high energy), anti (low energy), gauche (intermediate energy)**



### COMMON TERMS

- aliphatic:** non-aromatic
- aromatic:** benzene ring
- heterocyclic:** non-carbon atom in the ring structure
- hydrocarbon:** compound of H and C
- paraffin:** alkane
- olefin:** alkene
- saturated:** maximum # of H's (all C-C single bonds)
- unsaturated:** at least one C-C multiple bond

### NOMENCLATURE

**IUPAC** - standard guidelines for naming compounds  
**Nomenclature Strategy** - find longest carbon chain, identify and note location of functional groups and substituents by chain position number.  
**Classes of compounds** are defined by the functional group. There are many common names and functional group names. Multiple names are possible.

#### CARBON CHAIN PREFIXES

# of C's	Prefix	R-group
1	meth-	methyl
2	eth-	ethyl
3	prop-	propyl
4	but-	butyl
5	pent-	pentyl
6	hex-	hexyl
7	hept-	heptyl
8	oct-	octyl
9	non-	nonyl
10	dec-	decyl

**cyclo-:** ring structure; example: cyclopropane 3-carbon ring molecule

**iso-:** two methyl groups on the terminus of a chain

**n-:** normal straight chain

**t-:** tertiary alkyl group

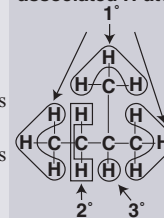
**vic (vicinal):** two substituents on adjacent carbons

**gem (geminal):** two substituents on the same carbon

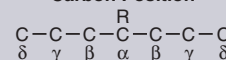
**alkene isomers:** cis or trans

**benzene substitution positions:** ortho (1,2), meta (1,3), para (1,4)

#### Carbon atoms & associated H-atoms



#### Carbon Position

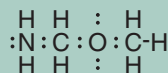


## CHEMICAL BONDING IN ORGANIC COMPOUNDS

Bonds are usually **polar covalent**. Polarity arises from **electronegativity** difference; the larger the difference, the more polar the bond. The more electronegative atom is the negative end of the bond.  
In  $>C=O$ , O is negative, C is positive.

### LEWIS STRUCTURE: SIMPLEST MODEL

- Assign valence electrons as bonding electrons and non-bonding lone pairs.
- Octet rule:** each atom is assigned 8 electrons; except H (2) and atoms with d-orbitals (the "filled-shell rule")



**Bond Order (BO):** # of bonds divided by the # of bonded neighbors. For a given pair of atoms, increased bond order reflects a stronger, shorter bond.

Example:	BO	Length (Å)	Energy (Kcal/mole)
C-C	1	1.53	90
C=C	2	1.33	173
C≡C	3	1.20	230

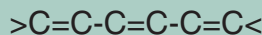
### Formal charge (effective atomic charge):

- = (# of non-bonded electrons) + (1/2 # of bonded electrons) - (# of atomic valence electrons)
- The ideal formal charge of each atom is zero. Otherwise, minimize magnitude of charge by shifting charge to the more electronegative atom (especially for ions).

### RESONANCE

The "average" of several Lewis structures provides a more accurate view of the bonding. Example:  $\text{CO}_3^-$  has 3 equal bonds, though each of 3 Lewis structures has 1 double bond and 2 single bonds.

- delocalization:** resonance lowers the energy; electrons are dispersed, diminishing electron-electron repulsion
- conjugated alkene:** has alternate single/double bonds:



- Hückel Rule:** A planar cyclic molecule with  $(4n+2)$   $\pi$ -electrons is aromatic.

Ex: Benzene



- antiaromatic:**  $4n$   $\pi$ -electrons: aromatic excited state.
  - heterocyclic:** heteroatom lone pairs join the planar  $\pi$  system
- Examples:



Pyridine



Pyrrole



Furan

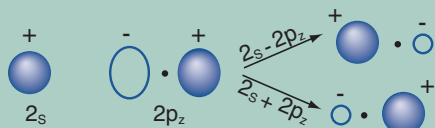


Thiophene

### REFINED MODEL: VALENCE BOND THEORY

Overlap of atomic orbitals (AO's) or hybrids allows electrons to pair up, forming a chemical bond.

**hybrid orbitals:** valence AO's mix to accommodate "equivalent" bonded neighbors. Non-hybridized orbitals form lone pairs or  $\pi$  bonds.



## MOLECULAR STRUCTURE AND HYBRID AO'S

**VSEPR** (Valence Shell Electron Pair Repulsion): bonding pairs (X) and lone pairs (E) define geometry of  $\text{AX}_n$ ; reflects hybridization of A

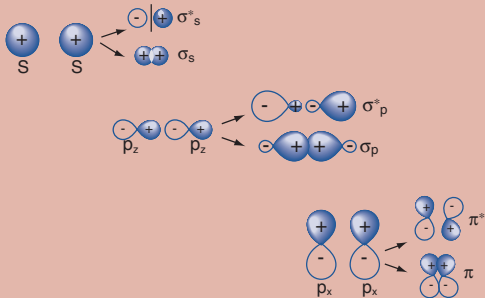
- $\text{sp}^3$  -  $\text{AX}_4$ : tetrahedral, bond angle of  $109.4^\circ$ ; alkane; lone-pair larger than bonded pair, distorts geometry  
Ex:  $\text{AX}_3\text{E}$  pyramidal; amines,  $\text{NR}_3$ , ammonia;  $\text{AX}_2\text{E}_2$  bent: water: alcohol:  $\text{R-O-H}$ , ether:  $\text{R-O-R}'$
- $\text{sp}^2$  -  $\text{AX}_3$  trigonal planar ( $120^\circ$ ); C-C-C in aromatic ring;  
Ex:  $\text{R-CO-R}$  in ketone, aldehyde, carboxylic acid
- $\text{sp}$  -  $\text{AX}_2$  linear;  
Ex: alkyne  $\text{-C}\equiv\text{C-}$ ; nitrile  $\text{R-C}\equiv\text{N}$

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## QUANTUM MECHANICAL MODEL: MO THEORY

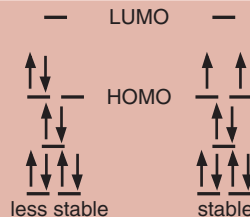
The **Schrodinger Equation:**  $\hat{H}\psi = e\psi$ , gives energy (e) and wavefunction ( $\psi$ );  $\hat{H}$ , Hamiltonian, the energy operator.  $\psi$  determines total energy, electron density and orbital energies.

- $\psi$  is given by a set of MO's (**molecular orbitals**) formed by combining AO's. Each MO creates an energy level for two electrons.
- Constructive overlap of AO's : **bonding** = stable
- Destructive overlap of AO's : **anti-bonding** = unstable
- On-bond-axis:  $\sigma$  bonding ;  $\sigma^*$  antibonding
- Off-bond-axis:  $\pi$  bonding ;  $\pi^*$  antibonding
- Organic compound: focus on s and p orbitals
- Transition-metal atom: focus on d orbitals



### MO'S AND ENERGY

- # of MO's = # of AO's
- bond order:** # of bonding electron-pairs - the # of antibonding electron-pairs
- Aufbau & Pauli Exclusion Principles:** MO's are filled from lower to higher energy; each level holds up to two electrons with paired spins
- HOMO:** Highest Occupied MO
- LUMO:** Lowest Unoccupied MO
- Hund's Rule:** For MO's of equal energy, maximize the total electron spin



### APPLICATIONS OF MO THEORY

**Chemical Reactivity:** The electrons in the **HOMO** are most likely to participate in nucleophilic attack (electron donor). These are the least stable (most reactive) valence electrons in the molecule.

- The **LUMO** is likely to represent an electrophilic site (electron acceptor). In photochemical processes electrons are excited to the LUMO.
- Molecules with **unpaired** electrons in MO levels exhibit a net electron spin which can be measured by **electron spin resonance spectroscopy (ESR)**.

## INTERMOLECULAR FORCES

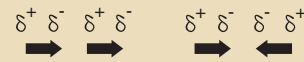
- ELECTROSTATIC INTERACTIONS:** strong forces between ions; for charges  $q_1$  and  $q_2$ ; separated by  $r_{12}$ , and solvent dielectric constant,  $\epsilon$

$$\text{Energy} = \frac{1}{\epsilon} \frac{q_1 \cdot q_2}{r_{12}}$$

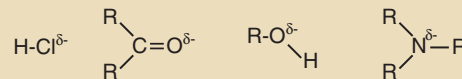
Solvent with large  $\epsilon$  stabilizes carbocation, carbanion  
**Solvents ( $\epsilon$ ):** water (80), ethanol (25), ethyl ether (4), methanol (33), acetone (21), hexane (1.9), benzene (2.2), toluene (2.4), phenol (9.8), aniline (6.9), pyridine (12),  $\text{CCl}_4$ (2)

- LONDON FORCES** (dispersion): attraction due to induced dipole moments; increases with  $\alpha$

**Polarizability,  $\alpha$ :** measures distortion of electron cloud by electric field of other nuclei and electrons  
**DIPOLE-DIPOLE INTERACTION:** the positive end of one dipole is attracted to the negative end of another dipole. Increases with  $\mu$ .

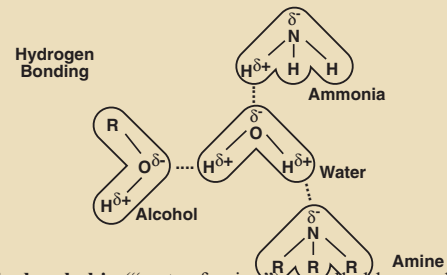


**Dipole moment,  $\mu$ :** asymmetric electron distribution; one end on a polar molecule or bond will have partial charge (alcohol, ketone, ether, amine, carboxylic acid)



### HYDROGEN BONDING

Enhanced dipole-dipole interaction between bonded H and the lone-pair of neighboring O, N or S. Can lead to dimer formation; gives "structure" to polar liquids.



**hydrophobic** ("water-fearing"), repelled by a polar group; attracted to "fat" or a nonpolar group

Examples: alkane or alkyl group, arene, alkene

**hydrophilic** ("water-loving"): attracted to a polar group; repelled by a nonpolar group

Examples: -OH of alcohol, -NH of amine, -COOH of carboxylic acid

### IMPACT ON SOLUBILITY

Ionic material tends to dissolve in **water**, as do polar organic compounds,  $\text{R-OH}$ ,  $\text{R-COOH}$ ,  $\text{R-NH}_2$ .

**Non-polar** compounds are usually **insoluble** in water, but tend to dissolve in non-polar solvents: alkanes, alkenes, alkynes, aromatics.

**solvation:** process in which solute is surrounded by solvent molecules, creating a more stable system

**miscible** (2 or more substances form 1 phase): liquids with similar molecular properties (polar+polar, non-polar+non-polar)

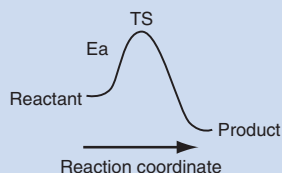
**immiscible** (separate phases): aqueous and organic layers do not mix

Compounds are partitioned between the layers based on chemical properties (acid/base, polar, nonpolar, ionic).

**partition coefficient:** the ratio of the solubility limits of a material in two immiscible phases

## ORGANIC REACTIONS

- Most reactions take place in several simple steps, producing an overall **mechanism**.
- Incomplete reactions may establish equilibria.
  - Each step passes through an energy barrier, characterized by an unstable configuration termed the **transition state (TS)**.
  - The height of the barrier is the **activation energy (Ea)**.
- The slowest step in the mechanism, the **rate-determining step**, limits the overall reaction rate.
- Key principle:** examine the reactants and identify the points of excess and deficit electrons; organic reactions are best understood by "following the electrons."
- The electron movement is often described using an **arrow** in the reaction mechanism.



## ACIDS AND BASES

Model Term	Acid	Base
Arrhenius	aqueous H <sub>3</sub> O <sup>+</sup>	aqueous OH <sup>-</sup>
Bronsted-Lowry	proton donor	proton acceptor
Lewis	electron-pr. acceptor electrophiles	electron-pr. donor nucleophiles

**Organic reactions:** use Bronsted-Lowry and Lewis models

Acid HA ⇌ H<sup>+</sup> + A<sup>-</sup>

- $K_a = \frac{[A^-][H^+]}{[HA]}$
- $pK_a = -\log_{10}(K_a)$
- strong acid:** full dissociation; examples HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>
- weak acid:**  $K_a \ll 1$ , large  $pK_a$ ; organic acid: RCOOH
- Examples ( $pK_a$ ): acetic (4.75), carbonic (6.37), HF (3.45), HCN (9.31), benzoic (4.19), citric (3.14), formic (3.75), oxalic (1.23)
- Proton donor:** acetylene (25), ethanol (16), phenol (9.9)

Base BOH ⇌ B<sup>-</sup> + OH<sup>-</sup>

- $K_b = \frac{[OH^-][B^-]}{[BOH]}$
- $pK_b = -\log_{10}(K_b)$
- strong base:** full dissociation; examples NaOH, KOH
- organic base:** R-NH<sub>2</sub>
- weak base:**  $K_b \ll 1$ , large  $pK_b$
- Examples: ( $pK_b$ ): NH<sub>3</sub> (4.74), CN<sup>-</sup> (4.7), hydrazine N<sub>2</sub>H<sub>4</sub> (5.77), hydroxylamine (7.97), aniline (4.63), pyridine (5.25)

**amphoteric:** material which can react as an acid or a base. Example: **amino acid**; amine (base) and carboxylic acid functionality

**zwitterion:** self-ionization of the amino acid; the "acid" donates a proton to the "base"

## OXIDATION-REDUCTION

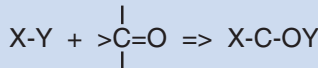
- oxidation:** loss of electrons; in organic reactions, add oxygen or remove hydrogen; examples: R ⇒ ROH ⇒ >C=O ⇒ RCOOH
- reduction:** gain of electrons; in organic reactions, add hydrogen or remove oxygen; examples: hydrogenation of alkene/alkyne to alkane

## ORGANIC REACTIONS

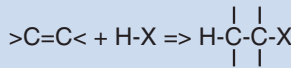
## ADDITION REACTIONS

Add groups to a pair of atoms joined by a multiple bond; Ex: hydrogenation, halogenation, hydrohalogenation, hydration, hydroxylation. Two major types:

- nucleophilic:** nucleophile attacks C of >C=O



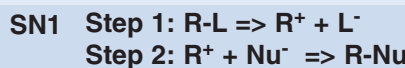
- electrophilic:** π electrons donated to electrophile; forms carbocation, which may rearrange



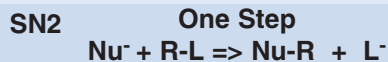
## SUBSTITUTION REACTIONS

Replace existing group on an alkane or aromatic compound.

- Nucleophilic substitution:** nucleophile (Nu<sup>-</sup>) seeks a "+" center (C of R group or >C=O), displaces leaving group -L. **SN1 and SN2 mechanisms**



**SN1:** Favored for sterically hindered R; carbocation is stabilized by polar solvent (3° > 2° > 1°), therefore carbocation may rearrange; racemic mixture; first-order kinetics (formation of R<sup>+</sup> determines the reaction rate).



**SN2:** Backside attack of C bonded to L (the leaving group), inversion of stereochemical configuration; second order kinetics (Nu attack sets rate).

- Nucleophilic aromatic substitution:**

Two possible mechanisms:

- elimination/addition via benzyne intermediate (dehydrobenzene), Ex.: Ar-Cl ⇒ Ar-OH
- addition/elimination (SNAr) mechanism; electron-withdrawing groups facilitate nucleophilic attack; ex: nitrochlorobenzene ⇒ nitrophenol

- Electrophilic aromatic substitution:**

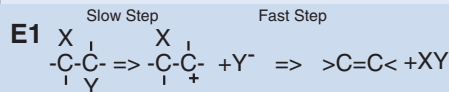
- Electrophile, E<sup>+</sup>, attacks π electrons on the benzene ring, form arenium cation (ring stabilizes positive charge)
- H leaves, -E is attached to the ring
- ex: alkylation, nitration, halogenation of benzene

## ELIMINATION REACTIONS

Reverse of addition, remove molecule "XY" from adjacent atoms, produces double bond.

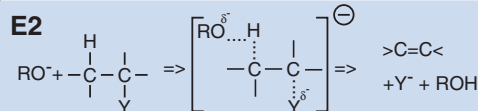
Example: dehydrogenation, dehydrohalogenation, dehydration

Two possible mechanisms: E1 and E2



**E1: slow step:** Y- leaves, forms a carbocation which may rearrange;

**fast step:** X leaves, giving alkene; 1st order kinetics



**E2:** Concerted reaction; base partially bonds to -H, weakens bond to Y, Y departs and H is removed by the base, producing alkene; 2nd order kinetics

## ORGANIC REACTIONS

## HYDROLYSIS REACTIONS

A type of solvolysis where water (the solvent) breaks a bond; adds -H and -OH to the molecule (or -H and -OR when solvent is alcohol).

Example: **saponification:** base-hydrolysis of ester

## CONDENSATION REACTIONS

Two reagents combine via bridging O or N, produce water or alcohol molecule;

Example: peptide bond (N-H + RCOOH), nylon synthesis, formation of polysaccharide

## REARRANGEMENTS

Change in bond connectivity; common with radical, carbocation and carbanion intermediates.

- Driving force:** Bonds are altered to shift charge to a more substituted carbon; ex: resonance stabilization
- Carbocation stability: Ar > 3° > 2° > 1° carbons

## IONIC REACTIONS

Heterolytic cleavage of X-Y ⇒ X<sup>+</sup> + Y<sup>-</sup>; ion pair, stabilized by resonance or polar solvent. Characteristic of ionic reactions involving nucleophiles and electrophiles.

## RADICAL REACTIONS

- Homolytic cleavage** of bond X-Y ⇒ X<sup>\*</sup> + Y<sup>\*</sup>
- radical:** Reactive species with unpaired electrons
- Reaction steps:** Initiation, propagation and termination. Radical geometries tend to be planar (sp<sup>2</sup> hybrid). Example: halogenation of alkane or alkene
- Radical stabilized by delocalization and rearrangement; relative stability: Ar-C<sup>\*</sup>H<sub>2</sub> > R<sub>2</sub>C=C<sup>\*</sup>H<sub>2</sub> > (CH<sub>3</sub>)<sub>3</sub>C<sup>\*</sup> > (CH<sub>3</sub>)<sub>2</sub>C<sup>\*</sup>H > CH<sub>3</sub>C<sup>\*</sup>H<sub>2</sub>

## EXAMPLES OF SPECIFIC REACTIONS

**acylation:** add RCO-

**alkylation:** add -R Ex: Grignard (RMgX)

**cyclization reaction:**

**Diels-Alder:** diene + alkene/alkyne

**decarboxylation:** lose CO<sub>2</sub> from a carboxylic acid

**hydroxylation:** add -OH

**nitration:** add -NO<sub>2</sub>

**pyrolysis:** anaerobic thermal decomposition

**sulfonation:** add -SO<sub>3</sub>H

**Wittig:** >C=O to >CH<sub>2</sub>

## MECHANISM TERMS

**anti addition:** add to opposite faces of substrate

**carbene:** divalent carbon; ethylene radical: H<sub>2</sub>C=

**carbocation:** trivalent carbon, positive formal charge

**carbanion:** negative formal charge on carbon

**electrophile:** a Lewis acid; attracted to the electron density found in a chemical bond or lone pair

**endo:** prefix for closed structure-type

**exo:** prefix for open structure-type

**nucleophile:** a Lewis base; attracted to the + charge of a nucleus or cation

**oxonium:** positively charged oxygen species

**syn addition:** add to the same face of a substrate

**ylide:** a neutral molecule with a formally-charged C<sup>-</sup> next to a P<sup>+</sup>, or an electropositive heteroatom

## SPECTROSCOPY AND INSTRUMENTAL METHODS

Chemical insight is gained by analyzing the interaction of matter and electromagnetic radiation (characterized by the wavelength,  $\lambda$  or frequency,  $\nu$ ).

### MEASUREMENT METHODS

core electrons (X-ray)    electronic transitions (UV/Vis)  
vibrations (IR)    nuclear spin (RF)

Energy of radiation is quantized in photons,  $e = h\nu$ ; one photon excites one molecule to a higher energy state.

### X-RAY

- **Structure determination:** x-ray  $\lambda$  is comparable to atomic-spacing, scattered x-rays give a diffraction pattern characteristic of a crystal structure
- **Photo-electron-spectroscopy (PES):** x-rays are energetic enough to dislodge core-electrons. Analysis of ejected electron energies gives MO and AO energies

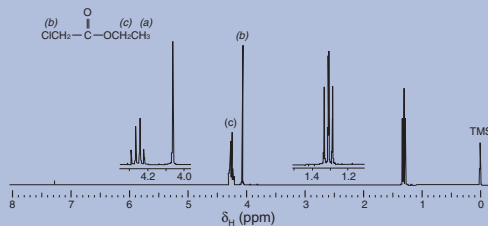
### ULTRAVIOLET/VISIBLE

- Probes electronic transitions; peaks are broadened by rotational, vibrational and solvent effects. The size of the peak depends on electronic energy spacing.
- For organic molecules, often corresponds to a transition from a  $\pi$ -type HOMO to a  $\pi^*$ -type LUMO.

### Colorimetry - Beer-Lambert Law: $A = abc$

Where **A** = absorbance; **a** = molar absorptivity (varies with  $\lambda$ ); **b** = sample path length; **c** = molar concentration. A is related to transmission (T) by the equation:  $A = -\log_{10}(T)$ .

### NUCLEAR MAGNETIC RESONANCE (NMR)



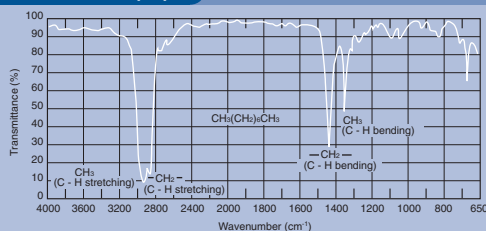
- **RF radiation** (radio waves) matches the spacing between nuclear-spin energy levels **artificially** split by a strong magnetic field.
- The **resonance** is characteristic of an atom's chemical environment; given as  $\delta$ , in ppm, the shift relative to a reference compound; for H-NMR, TMS (tetramethylsilane).
- **shielding:** resonance shifts to greater magnetic field (larger delta,  $\delta$ ) due to chemical environment of the atom. Proton NMR is most common, though isotopes of C, O, F, Si can be studied as well.

#### Shift ranges (in ppm)

R(1°)	R(2°,3°)	R-X	ether	H-C=C-	H-C C-	Ar-H
1	1-2	2-3	3.5	5	3	6-10
Ar-CH <sub>3</sub>	ket.	ald.	Ar-OH	R-OH	R-NH <sub>2</sub>	RCOOH
2.5	2.5	9.5	5-8	1-6	1-5	10-13

- **H-NMR splitting patterns:** peak split by spin-spin interactions between adjacent H-atoms; "n" H's, give "n+1" peaks; example: -CH<sub>2</sub>-CH<sub>3</sub> will have a quartet for the CH<sub>2</sub> and a triplet for the CH<sub>3</sub>
- **Quantifying H-NMR data:** The strength of the resonance signal, given by the area under the curve, is proportional to the number of H's producing the resonance. The relative peak-area gives the fraction of H-atoms in the compound associated with that peak. Temperature dependent NMR is used to explore fluxional distortions.

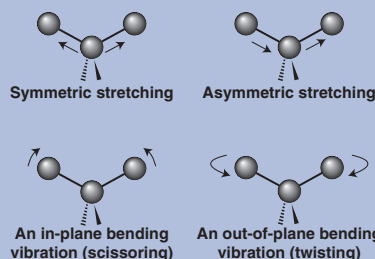
## INFRARED (IR)



- IR excites vibrations which change the molecular dipole moment.
- Vibrational frequencies are characteristic of functional groups and bond-types; typically given in wavenumbers ( $\nu$ ,  $\text{cm}^{-1}$ ),  $1/\lambda(\text{cm})$ .

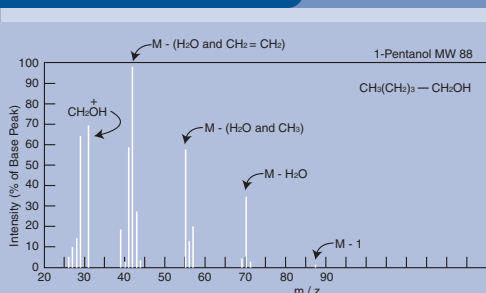
#### IR vibrational frequencies (wavenumber)

group	C=O	RO-H	R-OH	C-H	N-H
freq.	1700	3600	1200	2900	3400
group	H-Ar	>C=C<	-C≡C-	RC≡N	
freq.	3000	1650	2200	2250	



- **Isotope effects:** isotopic substitution changes the reduced mass (with little effect on spring constant), shifting the vibrational frequencies

## MASS SPECTROMETRY



- An electron-beam ionizes and fragments the molecules in a vacuum chamber. The molecular ions are sorted by mass/charge ( $M/z$ ) using a magnetic field.
- The observed spectrum is " $M/z$  vs. intensity."
- The fragmentation pattern gives the makeup of the molecule.
- Interpretation requires **isotope masses**, not **atomic weights**.

## CHROMATOGRAPHY

- Solubility and surface-interactions separate a mixture.
- The mobile phase carries the sample, which interacts with the stationary phase.
- The greater the interaction between a sample component and stationary phase, the longer the material stays on the column, giving a separation over time.

**paper chromatography:** liquid-solvent carries sample along a paper strip

**column chromatography:** sample passes through a high-surface-area matrix

**instrumental separation methods; HPLC (High Performance Liquid Chromatography):** sample carried by a liquid mobile phase, interacts with a solid column  
**gas chromatography (GC):** vaporized sample is carried by a flow of inert gas through a porous-packed solid or coated column

## THERMODYNAMICS

The study of the heat and work associated with a physical or chemical process.

### Key Thermodynamic Variables

#### Enthalpy (H):

$\Delta H$  = heat absorbed or produced by a process under constant pressure (normal lab conditions).  
 $\Delta H < 0$  for exothermic,  $\Delta H > 0$  for endothermic

#### Enthalpies of Formation, $\Delta H_f^\circ$ :

$$\Delta H = \sum \text{product } \Delta H_f^\circ - \sum \text{reactant } \Delta H_f^\circ$$

#### Entropy (S):

$\Delta S$  = change in thermodynamic disorder for a process

#### Standard Entropy, $S^\circ$ :

$$\Delta S = \sum \text{prod } S^\circ - \sum \text{react } S^\circ$$

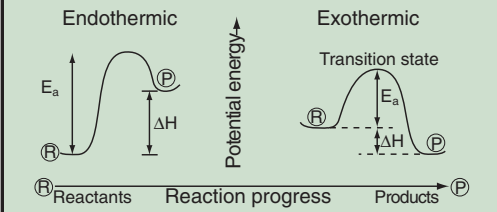
#### Gibbs Free Energy (G):

$\Delta G = \Delta H - T\Delta S$ .  $\Delta G$  is the capacity of the system to perform work.  $\Delta G = 0$  at equilibrium,  $\Delta G < 0$  for spontaneous (large  $K_{\text{eq}}$ ), for  $\Delta G > 0$ , the reverse process is spontaneous.

**Endergonic:**  $\Delta G > 0$ ; **Exergonic:**  $\Delta G < 0$ .  $\Delta G = -RT \ln(K_{\text{eq}})$

#### Free energy of formation, $\Delta G_f^\circ$ :

$$\Delta G = \sum \text{product } \Delta G_f^\circ - \sum \text{reactant } \Delta G_f^\circ$$



## KINETICS: RATE OF CHEMICAL REACTION

For a generic reaction,  $A+B \Rightarrow C$ , the reaction rate is defined as the rate of producing C (or consuming A or B); the rate law describes the mathematical dependence of the rate on [A].

### FIRST-ORDER:

#### Rate = $k_1[A]$

One species is involved in the rate determining step.

"ln [A] vs. time" is linear, the slope is the rate constant  $k_1$ .

- **Half-Life** ( $t_{1/2}$ ) characterizes the process. [A] decays exponentially with time;  $[A] = [A]_0 e^{-kt}$ .

Examples: radioactive decay, unimolecular decomposition, SN1, E1 (carbocation), molecular rearrangement

### SECOND ORDER:

#### Rate = $k_2[A]^2$ or $k_2[A][B]$

Two species in the rate determining step.

Examples: SN2, E2, acid-base

### MULTIPLE-STEP REACTION:

Complicated rate-law; focus on rate determining step. The intermediate formed at this step can be modeled using **transition-state-theory**. The **steady-state approximation** works for reactions with unstable intermediates.

### TEMPERATURE AND RATE CONSTANT (k)

Arrhenius Law:  $k = A e^{-E_a/RT}$

- $E_a$ : activation energy
- Plot of "ln(k) vs.  $1/T$ " is linear; slope is  $-E_a/R$ , intercept is  $\ln(A)$
- **T:** temperature in Kelvin (not °C)!
- **catalyst:** decreases  $E_a$  and accelerates the reaction

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Note: Due to the condensed nature of this chart, use as a quick reference guide, not as a replacement for assigned course work.

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