

FEATURES OF AN ORGANIC REACTION

Mechanism: Describes the overall reaction using a series of simple steps.

Stoichiometry: Calculate reactant and product masses using the balanced equation and molar masses.

Kinetics: The study of the reaction rate and mechanism.

Theoretical yield: Mass of product given by a complete reaction.

%yield = 100% × product mass / theoretical yield

Equilibrium: Reaction does not proceed to completion, instead, it reaches a balanced state of forward and reverse reactions.

Major reaction types:

- Acid
- Base
- Oxidation-Reduction
- Condensation
- Substitution (SN1, SN2)
- Ionic Reaction
- Elimination (E1, E2)
- Cyclization
- Hydrolysis
- Radical reactions

Important named reactions:

- **Diels-Alder:** form cyclic alkenes
- **Friedel-Crafts:** add aryl or alkyl group
- **Kolbe:** add alkyl or aryl group
- **Wittig-Kricheldorf, Clemmensen:** reduce ketone to alkane
- **Wittig:** convert aldehyde/ketone to alkene

KINETICS AND REACTION MECHANISM



Transition state (TS): Maximum on the reaction coordinate curve; the least stable intermediate.

Activation Energy (E_a): Energy of the TS relative to the reactant. The change in enthalpy (ΔH) is < 0 for exothermic, > 0 for endothermic.

Hammond-Leffler postulate: The TS is more like the reactant or product that is closer in energy, exothermic TS is like the product, endothermic TS is like the reactant.

Kinetic vs. thermodynamic control: ΔG and ΔH describe Thermodynamic Stability.

- If ΔG is large and negative (irreversible), the product formation is likely controlled by "thermodynamics".
- Large K_{eq} corresponds to a large amount of product, relative to reactant.

- A large E_a may give rise to "kinetic" control; the energy of the TS controls the reaction, instead of the product-reactant thermodynamics.

Solvent effects: A solvent may stabilize an intermediate, decreasing E_a and increasing the rate of the reaction. Charged-complexes are stabilized by polar solvents.

ORGANIC ACID AND BASE

Acid:

- Electron-pair acceptor (Lewis acid)
- Proton donor (Brønsted-Lowry acid), example: carboxylic acid

Base:

- Electron-pair donor (Lewis base)
- Proton acceptor (Brønsted-Lowry base), example: amine

Factors enhancing acid strength (MAS):

- Weak H-A bond
- Greater electronegativity of "A"
- Inductive effect of substituents on "A" (electron withdrawal enhances acidity)
- More "s" character in hybrid orbital (sp hybrid is lower in energy than p-orbital)
- Resonance stabilized conjugate base (A⁻)

Factors enhancing base strength:

- Reverse of acid-strength guidelines
- A base is a nucleophile. Electron-donating groups shift electron density to the atom with the lone-pair, increasing base-strength.

ALKANE

Properties:

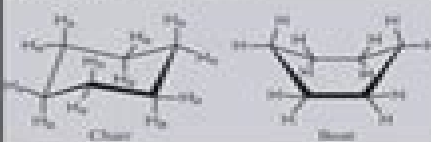
- Hydrocarbon
- Weak intermolecular forces
- Non-cyclic: general formula C_nH_{2n+2}
- Terminated C-C-C (109°)

Nomenclature:

- Add "ane" to prefix
- Locate substituent by position #
- Halohalide: substitute halide for H

Cycloalkane (C_nH_{2n}):

- Bicyclic: two fused or bridged rings
- $n = 1$: cyclopropane (slightly strained)
- $n = 4$: cyclobutane (some flexibility)
- $n = 5$: cyclopentane (slight puckering)
- $n = 6$: cyclohexane: chair = stable conformation; boat = less stable, axial position, "perpendicular" to ring, equatorial position, in ring "plane" (see H_a and H_e in chair diagram below)
- Cis = two substituents on up position
- Trans = one up and one down



Synthesis:

- Hydrogenate alkene or alkyne (H_2 , Pt catalyst)
- Free-radical reaction of alkene
- Radical halohalide (Br_2 , $h\nu$)
- Friedel-Crafts alkylation

Reactions:

- Combustion: alkane + $O_2 \rightarrow CO_2 + H_2O$
- Halogenation to halohalide (Cl_2/Br_2 , light or heat)

ALKENE $>C=C<$

Properties: Similar to alkane, non-polar, flammable

Nomenclature:

- Add "ene" to prefix, Use # to denote C=C position
- Isolated C-C=C-C-C-C, cumulated C-C=C-C
- Polyunsaturated fatty acid 2 or more C=C
- Alkene: adjacent C=C-C
- Vinyl group: $H_2C=CH-$
- Methylene group: $H_2C=$
- Allyl group: $H_2C=CHCH_2-$
- Vinyl halide: halide replaces H on $>C=C<$
- Conjugated: alternate C-C and C=C (resonance)
- Alkadiene, 2 conjugated C=C, example: butadiene, s-cis and s-trans (rotate about C-C bonds)
- Alkatriene, 3 conjugated C=C
- Aromatic: conjugated monocyclic compound, example: [4] p-orbitals = benzene
- Aromatic cyclic ions: cyclopentadienyl anion, cycloheptatrienyl cation (Hückel's rule)

Isomers: no free rotation of C=C



- E/Z, prioritize groups by atomic weight (Z = higher priority groups on the same side)
- For monocyclic: cis is less stable (steric hindrance), for cyclic, cis more stable
- **Hofmann Rule:** forms the least substituted alkene
- **Markovnikov Addition:** H adds to C with most H's
- **Zaitsev Elimination:** forms alkene with more substitution

Synthesis:

- Dehydration alcohol (H^+ , heat) (elimination)
- Dehydrohalogenate haloalkane (base, heat)
- Dehalogenate via dihalide (Zn , acetic acid)
- Hydrogenate alkyne:
 - syn, Z -isomer ($H_2/P-2$ catalyst)
 - anti, E -isomer (s.s., Hg^{2+} , $-N^+C$)
- Wittig, aldehyde/ketone + phosphorus ylide

Reactions:

- Combustion (O_2)
- Hydrate to 2°/3° alcohol (H^+ , H_2O , 1° from alkene, use rearrange (Markovnikov))
- Hydrate to alcohol, hydroboration/oxidation ($THF/H_2O_2/H_2O/CH_3OH$) (anti, anti-Markovnikov)
- Oxymercuration-demercuration to alcohol
- Hydrohalogenate (HX) (Markovnikov)
- Halogenate (Br_2/Cl_2), via dihalohalide (N_2/CH_2Cl_2 , anti)
- Halohydrin (N_2 , H_2O , anti-addition)
- Hydroboration to form a 1,2-diol ($KMnO_4$, acid OH^- , syn addition)
- Oxidize to carboxylic acid ($KMnO_4$, hot OH^-)
- Ozonolysis to ketone (O_3 , Zn , H_2O)
- Hydrogenate to alkane (H_2 , Pt, syn-addition)
- Free radical polymerization
- Alkylation Reaction
 - allylic halogenation (CH_3 heat)
 - Diels-Alder: cycloalkene from diene + alkene/alkyne

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William Swan Sonnenschein



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