Mechanism of Organic Reactions

−I order $NR_3^+ > NO_2 > SO_2R > CN > COOH > F > Cl > Br > I > OR > COR > OH > C_6H_5 > CH{=}CH_2 > H$ **+I order** $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3 > D > H$

Intermediates carbocations, radicals: 3° > 2° > 1° > CH_3 · carbanions: CH_3 > 1° > 2° > 3° **Leaving groups** $I^- > Br^- > Cl^- > F^-$

1 Inductive Effect: −I and +I Groups

$\mu(CH_3I)$ = 1.64 D, $\mu(CH_3Br)$ = 1.79 D, $\mu(CH_3Cl)$ = 1.83 D

- −I: $NO_2 > CN > COOH > F > Cl > Br > I > OH > H$; +I: t-Bu > i-Pr > Et > Me > H. Fades after C_2.

2 Acid Strength: pKa and Carboxylic Acids

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$pK_b = -\log K_b$$

- Lower pK_a = stronger acid. −I (more, nearer halogens) strengthens; +I weakens; HCOOH > CH_3COOH.

3 Acidity of Alcohols and Hydrocarbons, Basicity of Amines

pK_b : $(CH_3)_2NH$ 3.23 < CH_3NH_2 3.32 < $(CH_3)_3N$ 4.2

- Phenol > H_2O > 1° > 2° > 3° ROH; HC≡CH > $CH_2{=}CH_2$ > C_2H_6. Methylamines (aq): 2° > 1° > 3° > NH_3.

4 Electromeric and Mesomeric (Resonance) Effects

- Electromeric: temporary, on demand. +M: OH, OR, NH_2, X; −M: NO_2, CN, CHO, COOH. M beats I.

5 Hyperconjugation and the Baker–Nathan Effect

>C=C< + H_2 ⟶ >CH−CH< + *E* (heat of hydrogenation)

C–C : 1.54 Å (propane) → 1.46 Å (propene)

μ : HCHO 2.27 D, CH_3CHO 2.72 D

- No-bond forms = number of α-H: more α-H, more stable alkene, cation, radical (3° > 2° > 1°).

6 Bond Fission and Free Radicals

- Homolysis → radicals (hv, heat, peroxide); heterolysis → ions. Radicals: allyl ≈ benzyl > 3° > 2° > 1° > $CH_3^{\cdot}$.

7 Carbocations: Structure and Stability

- R^+: 6 e, sp^2, planar. Benzyl ≈ allyl ≈ 3° > 2° > 1° > CH_3^+.

8 Carbanions: Structure and Stability

- R^-: 8 e, sp^3 pyramidal. CH_3^- > 1° > 2° > 3°; −I, C=O, CN, NO_2 stabilise.

9 Carbenes: Singlet, Triplet and Their Reactions

$$\text{Spin multiplicity} = 2\sum s + 1$$

singlet: $2\left(\frac{1}{2} - \frac{1}{2}\right) + 1 = 1$

triplet: $2\left(\frac{1}{2} + \frac{1}{2}\right) + 1 = 3$

- Carbene: 6 e. Singlet (bent, stereospecific addition) vs triplet (diradical, more stable); $CHCl_3$ + base → $:CCl_2$.

10 Nitrenes and Benzyne

- Nitrene R–N: from RN_3, + C=C → aziridine. Benzyne: ArX + $NaNH_2$ → cine-substitution.

11 Electrophiles, Nucleophiles and Ambident Reagents

- E^+ = Lewis acid, Nu = Lewis base. Protic: $I^- > Br^- > Cl^- > F^-$; ambident: CN^-, NO_2^-.

12 Types of Organic Reactions

- Substitution, addition, elimination (α → carbene, β → alkene), rearrangement.

13 Free Radical Substitution: Chlorination of Methane and NBS

$$\Delta H_{overall} = \Delta H_{step\ 1} + \Delta H_{step\ 2}$$

- Chain: initiation, 2 propagation steps, termination; F > Cl > Br > I. NBS: allylic bromination.

14 SN2 Reaction: Mechanism, Walden Inversion and Rates

$$\text{Rate} = k[RX][Nu^-]$$

- S_N2: one step, inversion; CH_3 > 1° > 2° > 3°; strong Nu, polar aprotic solvent.

15 SN1 Reaction: Carbocations, Racemisation and Rearrangement

$$\text{Rate} = k[RX]$$

- S_N1: R^+ (slow), racemisation, possible 1,2-shifts.

16 SN1 vs SN2: Substrate, Leaving Group and Solvent

- S_N1: 3°, weak Nu, polar protic. S_N2: CH_3/1°, strong Nu, aprotic.

17 Electrophilic Substitution: SE1 and SE2 in Benzene

- S_E2 (benzene): E^+ → arenium ion (slow) → $-H^+$ (fast).

18 Electrophilic Addition: Markovnikov's Rule and Rearrangements

- E^+ (slow) then Nu^-; Markovnikov = more stable cation; check 1,2-shifts.

19 Anti-Addition of Bromine and 1,4-Addition to Dienes

- Br_2 anti (bromonium): cis → racemic, trans → meso. Dienes: 1,2 (low T), 1,4 (high T).

20 Peroxide Effect: Anti-Markovnikov Addition

- HBr + peroxide: $Br^{\cdot}$ first → anti-Markovnikov. Only HBr.

21 Nucleophilic Addition to the Carbonyl Group

- Nu^- attacks C=O (slow); HCHO > CH_3CHO > CH_3COCH_3.

22 E1 and E1cB Eliminations: Saytzeff vs Hofmann

- E1: R^+ first; E1cB: carbanion first. Saytzeff; bulky base → Hofmann.

23 E2 Elimination and Anti-periplanar Geometry

$$\text{Rate} = k[RX][Base]$$

- E2: one step, H and X anti-periplanar; 2-bromobutane → trans-but-2-ene.