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ORGANIC

CH 04

General Organic Chemistry — Electronic Effects & Reactive Intermediates

Inductive, resonance and hyperconjugation effects, the stability of carbocations, carbanions and radicals, acidity and basicity orders, and aromaticity — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Rank groups by inductive and resonance effect, and decide which effect dominates
- Order carbocations, carbanions and free radicals by stability, with reasons
- Arrange acids (carboxylic acids, phenols) and bases (amines) by strength, step by step
- Use hyperconjugation for alkene and carbocation stability
- Decide whether a ring or ion is aromatic, antiaromatic or non-aromatic

INSIDE

A The big picture
B Bond fission and reagents
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D Resonance
E Hyperconjugation
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G Acidity
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I Aromaticity
J Exam trap gallery

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

One question behind every ranking: where does the charge go?

IN ONE LINE

Electrons are pushed or pulled through σ bonds (inductive) and through π systems (resonance, hyperconjugation). Anything that spreads a charge over more atoms stabilises it — and that stability decides acidity, basicity and which intermediate forms.

THINK OF IT LIKE THIS

A charge is like a crowd in a room. Crammed into one corner, it's unstable. Open more doors (resonance) or let people lean on the walls (inductive and hyperconjugative donation) and it settles down. Every ranking question asks: which structure gives the charge the most room?

KEY IDEA

Priority when effects compete: aromaticity > resonance > hyperconjugation > inductive. Use the strongest effect that applies, then break ties with the next one.

SECTION B

Bond fission and reagents

B

How bonds break decides what species you get.

Fission	What happens	Gives	Favoured by
Homolytic	Each atom keeps one electron	Free radicals (R•)	Light, heat, peroxides, non-polar conditions
Heterolytic	One atom keeps both electrons	Ions: carbocations (R^+) or carbanions (R^-)	Polar solvents, polar bonds

Electrophiles (electron-seeking)	Nucleophiles (nucleus-seeking)
H^+, NO_2^+, Br^+, R^+, carbonyl carbon, BF_3, $AlCl_3$ (neutral but electron-deficient)	OH^-, CN^-, RO^-, NH_3, H_2O, R–OH, R^- (lone pair or negative charge)

EXAM TRAP

Neutral species can be electrophiles or nucleophiles. BF_3 and $AlCl_3$ are electrophiles (empty orbital); NH_3 and H_2O are nucleophiles (lone pair). Don't decide by charge alone.

SECTION C

Inductive effect (I)

C

The σ-bond tug-of-war: permanent, but short-range.

- A permanent shift of σ electrons toward the more electronegative atom along a chain.
- **Fades fast with distance:** after about three bonds it is negligible.
- **-I (withdrawing):** $-NO_2$ > $-CN$ > $-COOH$ > $-F$ > $-Cl$ > $-Br$ > $-I$ > $-OH$ > $-OCH_3$ > $-C_6H_5$
- **+I (donating):** alkyl groups, $(CH_3)_3C-$ > $(CH_3)_2CH-$ > CH_3CH_2- > CH_3-; also $-COO^-$ and $-O^-$

SOLVED EXAMPLE 01 — INDUCTIVE EFFECT AND DISTANCE

Arrange in decreasing acid strength: 2-chlorobutanoic acid, 3-chlorobutanoic acid, 4-chlorobutanoic acid, butanoic acid.

SOLUTION

1. Each Cl withdraws electrons and stabilises the carboxylate ion (-I).
2. The effect weakens with every carbon between Cl and -COOH.

ANSWER 2-chloro > 3-chloro > 4-chloro > butanoic acid.

SECTION D

Resonance (mesomeric) effect, R or M

D

Electrons spread through π systems — long-range, but only through conjugation.

+R (donate into the π system)	-R (withdraw from the π system)
$-NH_2$, $-NHR$, $-OH$, $-OR$, $-NHCOR$, $-O^-$, halogens	$-NO_2$, $-CN$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$

Rules for valid resonance structures

1. Only electrons move (lone pairs and π electrons); atoms stay put.
2. Every structure has the same number of paired and unpaired electrons.
3. More covalent bonds, complete octets and negative charge on the more electronegative atom → more important structure.

KEY IDEA

Halogens are the exception. Their -I outweighs their +R, so chlorobenzene reacts **more slowly** than benzene in electrophilic substitution — yet +R still directs the new group to **ortho/para**.

SECTION E

Hyperconjugation

E

σ electrons from C–H bonds next door lend a hand.

Delocalisation of σ electrons from C–H bonds on the carbon **adjacent** (α) to a carbocation, a radical or a double bond. Also called "no-bond resonance". **More α-hydrogens → more stabilisation.**

Species	α-hydrogens	Stability
$(CH_3)_3C^+$	9	Highest
$(CH_3)_2CH^+$	6	
$CH_3CH_2^+$	3	
CH_3^+	0	Lowest

- **Alkene stability:** more substituted alkenes are more stable (lower heat of hydrogenation): tetrasubstituted > trisubstituted > disubstituted > monosubstituted. This is the basis of Saytzeff's rule.
- **Toluene:** hyperconjugation of the CH_3 group activates the ring and directs ortho/para.
- **Anomaly:** alkyl groups donate by hyperconjugation in the order CH_3- > CH_3CH_2- > $(CH_3)_2CH$- > $(CH_3)_3C$- (most α-H first) — the opposite of their +I order.

SECTION F

Reactive intermediates

F

The short-lived species that every mechanism passes through.

Intermediate	Carbon	Shape	Stability order
Carbocation	sp^2, 6 electrons	Planar	Benzyl ≈ allyl ≈ 3° > 2° > 1° > CH_3^+
Carbanion	sp^3, lone pair	Pyramidal	CH_3^- > 1° > 2° > 3° (reverse)
Free radical	sp^2, 7 electrons	Nearly planar	Benzyl ≈ allyl > 3° > 2° > 1° > CH_3•
Carbene	6 electrons, neutral	Bent (singlet) or linear (triplet)	Very reactive; e.g. :CCl_2 in Reimer–Tiemann

KEY IDEA

Carbanions are the mirror image. Alkyl groups push electrons onto a centre that already has too many, so they **destabilise** carbanions. Electron-withdrawing groups (-NO_2, -CN, C=O) and resonance stabilise them.

SOLVED EXAMPLE 02 — CARBOCATION STABILITY

Arrange: $CH_3CH_2^+$, $(CH_3)_3C^+$, $C_6H_5CH_2^+$, CH_3^+, $CH_2{=}CH{-}CH_2^+$.

SOLUTION

1. Benzyl and allyl: positive charge spread by resonance.
2. $(CH_3)_3C^+$: 9 α-H plus three +I groups.
3. Then ethyl (3 α-H), then methyl (none).

ANSWER $C_6H_5CH_2^+ \approx CH_2{=}CHCH_2^+ \approx (CH_3)_3C^+ > CH_3CH_2^+ > CH_3^+$. (Exam keys usually place benzyl first.)

CHECK YOURSELF

C1 Which is more stable: $(CH_3)_3C^-$ or CH_3^-? Why?

C2 Which is the most stable radical: $CH_3\bullet$, $(CH_3)_3C\bullet$, $C_6H_5CH_2\bullet$?

Answers at the end of the chapter.

SECTION G

Acidity

An acid is strong when its conjugate base is stable.

Acid	pKa	Reason
CH_3COOH	4.76	Reference
HCOOH	3.75	No +I alkyl group
ICH_2COOH	3.18	Weakest -I halogen
$BrCH_2COOH$	2.90	
$ClCH_2COOH$	2.86	
FCH_2COOH	2.59	Strongest -I halogen
$Cl_2CHCOOH$	1.29	Two -I groups
Cl_3CCOOH	0.65	Three -I groups

Phenols

- Phenol (pKa ≈ 10) is acidic because phenoxide is stabilised by resonance into the ring; ethanol (≈ 16) is not.
- **–NO_2 at ortho or para** increases acidity strongly (–R and –I); at meta only by –I. p-Nitrophenol (7.15) > o (7.23) > m (8.4) > phenol (10.0).
- **Electron donors decrease acidity:** p-cresol (10.2) and p-methoxyphenol are weaker than phenol.
- **2,4,6-Trinitrophenol (picric acid)** has pKa ≈ 0.4 — as strong as many mineral acids.

Benzoic acids and the ortho effect

Electron-withdrawing groups strengthen benzoic acid (p-nitrobenzoic, pKa 3.44, vs benzoic 4.20); donors weaken it. **Almost any group at the ortho position increases acidity**, even a donating CH_3 (o-toluic acid, 3.91), because it twists –COOH out of the ring's plane — the ortho effect.

$$\text{RCOOH} > \text{phenol} > H_2O > \text{ROH} > HC{\equiv}CH > NH_3 > \text{alkanes}$$

General order of acidity

SOLVED EXAMPLE 03 — SUBSTITUTED ACETIC ACIDS

Arrange: CH_3COOH, $ClCH_2COOH$, $Cl_2CHCOOH$, FCH_2COOH.

SOLUTION

1. More –I groups → more stable carboxylate.
2. Two Cl atoms withdraw more than one F.
3. F withdraws more than Cl.

ANSWER $Cl_2CHCOOH > FCH_2COOH > ClCH_2COOH > CH_3COOH$.

SOLVED EXAMPLE 04 — PHENOLS

Arrange: phenol, p-nitrophenol, m-nitrophenol, p-cresol.

SOLUTION

1. p-NO_2: –R and –I → most stabilised phenoxide.
2. m-NO_2: –I only.
3. p-CH_3: +I and hyperconjugation destabilise phenoxide.

ANSWER p-nitrophenol > m-nitrophenol > phenol > p-cresol.

SECTION H

Basicity of amines

H

A base is strong when its lone pair is available.

Amine	pKb (water)
$(C_2H_5)_2NH$	3.00
$(C_2H_5)_3N$	3.25
$(CH_3)_2NH$	3.27
$C_2H_5NH_2$	3.29
CH_3NH_2	3.38
$(CH_3)_3N$	4.22
NH_3	4.75
$C_6H_5NH_2$	9.38

- **Alkyl groups (+I)** raise basicity above NH_3.
- **In water, solvation also matters:** the protonated amine is stabilised by H bonds to water — best for 1° (three N–H), worst for 3° (one N–H). Combined with +I and steric effects:
- Methyl series: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.
- Ethyl series: $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.
- **In the gas phase** (no solvation): 3° > 2° > 1° > NH_3.
- **Aniline is much weaker:** its lone pair is delocalised into the ring. Amides are almost neutral: the lone pair is delocalised onto C=O.

SOLVED EXAMPLE 05 — BASICITY IN WATER

Arrange: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$.

SOLUTION

1. +I raises basicity above NH_3; solvation favours 1° and 2°.
2. 3° amine's cation is poorly solvated and crowded.
3. Aniline: lone pair in resonance.

ANSWER $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3 > C_6H_5NH_2$.

SECTION I

Aromaticity

I

Hückel's rule and the special stability it brings.

A species is **aromatic** if it is (1) cyclic, (2) planar, (3) fully conjugated (every ring atom sp^2 with a p orbital), and (4) has **$(4n + 2)$ π electrons**: 2, 6, 10, 14 …

Species	π electrons	Verdict
Benzene	6	Aromatic
Cyclopentadienyl anion	6	Aromatic
Tropylium (cycloheptatrienyl) cation	6	Aromatic
Cyclopropenyl cation	2	Aromatic
Pyridine, pyrrole, furan, thiophene	6	Aromatic
Naphthalene	10	Aromatic
Cyclobutadiene	4	Antiaromatic (4n, planar)
Cyclopentadienyl cation	4	Antiaromatic
Cyclooctatetraene	8	Non-aromatic (tub-shaped, not planar)
Cyclopentadiene	4 (one sp^3 C)	Non-aromatic

KEY IDEA

Aromaticity explains odd acidities: **cyclopentadiene (pKa ≈ 16) is far more acidic than other hydrocarbons** because losing H^+ gives an aromatic anion. Tropylium bromide is ionic for the same reason.

SOLVED EXAMPLE 06 — AROMATIC OR NOT?

Classify the cyclopentadienyl cation and anion.

SOLUTION

1. Both are planar, cyclic and fully conjugated.
2. Cation: 4 π electrons (4n, n = 1) → antiaromatic.
3. Anion: 6 π electrons (4n + 2, n = 1) → aromatic.

ANSWER **The anion forms easily; the cation is very unstable.**

CHECK YOURSELF

C3 Is pyrrole's N lone pair part of the aromatic sextet? What does that do to its basicity?

C4 Why is cyclooctatetraene not antiaromatic?

Answers at the end of the chapter.

SECTION J

Exam trap gallery

J

The rankings students get wrong most often.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Chlorobenzene is activated because Cl donates by resonance.	Chlorobenzene is **deactivated** (−I > +R) but still ortho/para-directing.

WHY Halogens are the exception to "resonance wins".

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Carbanion stability follows carbocation order: 3° > 2° > 1°.	Reversed: CH_3^- > 1° > 2° > 3°.

WHY Alkyl groups push electrons onto an already-rich centre.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Trimethylamine is the strongest base among methylamines in water.	$(CH_3)_2NH$ is strongest; $(CH_3)_3N$ is below CH_3NH_2.

WHY Poor solvation of the 3° ammonium ion.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
FCH_2COOH is stronger than $Cl_2CHCOOH$.	$Cl_2CHCOOH$ (1.29) is stronger than FCH_2COOH (2.59).

WHY Two −I groups beat one stronger one here.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
m-Nitrophenol is as acidic as p-nitrophenol.	p (7.15) is stronger than m (8.4).

WHY At meta, $-NO_2$ can't withdraw by resonance from the phenoxide oxygen.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Cyclooctatetraene is antiaromatic (8 π electrons).	It is non-aromatic: it folds into a tub.

WHY Aromaticity rules need planarity.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
+I order of alkyl groups = hyperconjugation order.	They're opposite: hyperconjugation is CH_3 > ethyl > isopropyl > tert-butyl.

WHY Hyperconjugation counts α-H atoms.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
BF_3 is a nucleophile because it has no charge.	BF_3 is an electrophile (empty p orbital).

WHY Electron-deficient, not charge, decides.

MEMORY HOOK

"**Spread the charge, gain the peace**" — delocalisation = stability.

"**Halogens: slow but ortho-para**" — deactivate, yet o/p direct.

"**Carbanions hate alkyls**" — reverse of carbocation order.

"**Two-ish in water**" — 2° amine is the strongest base in water.

"**4n + 2, flat and through**" — Hückel's checklist.

SECTION K

Practice MCQs

K

Levels: Easy, Moderate, Tough.

Q01 Which is an electrophile? [EASY]

(a) NH_3 (b) H_2O
(c) $AlCl_3$ (d) OH^-

Q02 Homolytic fission produces: [EASY]

(a) carbocations (b) carbanions
(c) free radicals (d) carbenes only

Q03 The most stable carbocation is: [EASY]

(a) CH_3^+ (b) $CH_3CH_2^+$
(c) $(CH_3)_2CH^+$ (d) $(CH_3)_3C^+$

Q04 Which group shows -R effect? [EASY]

(a) -OH (b) $-NH_2$
(c) $-NO_2$ (d) $-OCH_3$

Q05 Which is aromatic? [EASY]

(a) Cyclobutadiene (b) Cyclooctatetraene
(c) Cyclopentadienyl anion (d) Cyclopentadienyl cation

Q06 The strongest acid is: [MODERATE]

(a) CH_3COOH (b) $ClCH_2COOH$
(c) $Cl_2CHCOOH$ (d) FCH_2COOH

Q07 Which is the strongest base in water? [MODERATE]

(a) NH_3 (b) CH_3NH_2
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

Q08 The most acidic phenol is: [MODERATE]

(a) p-cresol (b) phenol
(c) m-nitrophenol (d) p-nitrophenol

Q09 The most stable carbanion is: [MODERATE]

(a) CH_3^- (b) $CH_3CH_2^-$
(c) $(CH_3)_2CH^-$ (d) $(CH_3)_3C^-$

Q10 Number of α-hydrogens available for hyperconjugation in $(CH_3)_2CH^+$ is: [MODERATE]

(a) 3 (b) 6
(c) 7 (d) 9

Q11 Chlorobenzene undergoes electrophilic substitution: [MODERATE]

(a) faster than benzene, ortho/para (b) slower than benzene, meta
(c) slower than benzene, ortho/para (d) faster than benzene, meta

Q12 o-Toluic acid is stronger than benzoic acid because of: [MODERATE]

(a) +I of CH_3 (b) hyperconjugation
(c) the ortho effect (d) resonance

Q13 Which is antiaromatic? [TOUGH]

(a) Tropylium cation (b) Cyclopropenyl cation
(c) Cyclopentadienyl cation (d) Benzene

Q14 In the gas phase, the basicity order of methylamines is: [TOUGH]

(a) 2° > 1° > 3° (b) 3° > 2° > 1°
(c) 1° > 2° > 3° (d) 2° > 3° > 1°

Q15 Which has the lowest heat of hydrogenation? [TOUGH]

(a) But-1-ene (b) cis-But-2-ene
(c) trans-But-2-ene (d) 2-Methylpropene

Answer key with explanations

Q01 **(c) $AlCl_3$** — Al has an empty orbital.

Q02 **(c) free radicals** — Each atom keeps one electron.

Q03 **(d) $(CH_3)_3C^+$** — Most +I and hyperconjugation (9 α-H).

Q04 **(c) $-NO_2$** — $-NO_2$ withdraws π electrons.

Q05 **(c) Cyclopentadienyl anion** — 6 π electrons, planar.

Q06 **(c) $Cl_2CHCOOH$** — pKa 1.29; two -I groups.

Q07 **(c) $(CH_3)_2NH$** — +I plus good solvation.

Q08 **(d) p-nitrophenol** — -R and -I of para NO_2.

Q09 **(a) CH_3^-** — No electron-donating groups.

Q10 **(b) 6** — Two CH_3 groups × 3.

Q11 **(c) slower than benzene, ortho/para** — -I deactivates; +R directs o/p.

Q12 **(c) the ortho effect** — Steric twisting of -COOH out of the ring plane.

Q13 **(c) Cyclopentadienyl cation** — 4 π electrons, planar, conjugated.

Q14 **(b) 3° > 2° > 1°** — No solvation: +I alone decides.

Q15 **(c) trans-But-2-ene** — trans-But-2-ene is the most stable of these (disubstituted, no steric strain between methyls); 2-methylpropene is also disubstituted but its heat of hydrogenation is slightly higher.

Check-yourself answers

C1 CH_3^-: the three +I methyl groups destabilise $(CH_3)_3C^-$.

C2 $C_6H_5CH_2\bullet$ (resonance with the ring).

C3 Yes: the lone pair is part of the six π electrons, so it isn't available for protonation; pyrrole is a very weak base.

C4 It isn't planar — it folds into a tub, so the p orbitals don't overlap all the way round.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Effects

- Priority: aromaticity > resonance > hyperconjugation > inductive
- −I: NO_2 > CN > COOH > F > Cl > Br > I
- +I: 3° alkyl > 2° > 1° > CH_3
- Inductive fades after ~3 bonds

Resonance

- +R: NH_2, OH, OR, halogens; −R: NO_2, CN, CHO, COOH
- Halogens: −I > +R → deactivate, o/p direct
- Only electrons move between structures

Intermediates

- Carbocation: benzyl ≈ allyl ≈ 3° > 2° > 1° > CH_3^+
- Carbanion: CH_3^- > 1° > 2° > 3°
- Radical: like carbocation
- Hyperconjugation counts α-H

Acidity

- Stable conjugate base = strong acid
- Cl_3CCOOH > $Cl_2CHCOOH$ > FCH_2COOH > $ClCH_2COOH$ > CH_3COOH
- p-NO_2 phenol > m > phenol > p-cresol
- Ortho effect strengthens benzoic acids

Basicity

- Water: 2° > 1° > 3° > NH_3 (methyl)
- Ethyl: 2° > 3° > 1° > NH_3
- Gas phase: 3° > 2° > 1°
- Aniline, amides weak: lone pair delocalised

Aromaticity

- Cyclic, planar, conjugated, 4n + 2 π e^-
- Cp^-, tropylium$^+$, cyclopropenyl$^+$ aromatic
- Cyclobutadiene, Cp^+ antiaromatic
- COT non-aromatic (tub)

END OF NOTES · RAMGOVINDYADAV.COM