Resonance — Study Guide

Some molecules cannot be described by a single Lewis structure. The two oxygens of acetate are identical, yet any one drawing shows one C=O and one C–O$^-$. Resonance is the tool for describing these molecules: we draw two or more contributing structures, and the real molecule is a hybrid of them. Resonance explains why carboxylic acids are acidic, why amides are flat and unreactive, why benzene is so stable, and why allylic and benzylic intermediates form easily.

Builds on Lewis Structures and Formal Charge, and Hybridization and Polarity. Drawing on Klein, Clayden, Wade, McMurry, crystallographic bond-length data, and Kistiakowsky's heats of hydrogenation.

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1	What Resonance Is (and What It Is Not)
2	Curved Arrows: The Rules for Drawing Resonance Structures
3	The Five Common Resonance Patterns
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1. What Resonance Is (and What It Is Not)

Resonance structures (also called resonance contributors) are two or more Lewis structures for the same molecule that differ only in where electrons are placed. The atoms stay exactly where they are. The real molecule is a single structure, the resonance hybrid, that is a weighted average of all the contributors.

> *The molecule does not flip back and forth between resonance structures. It exists at all times as one hybrid. Resonance structures are a limitation of our drawing system, not a description of motion.*

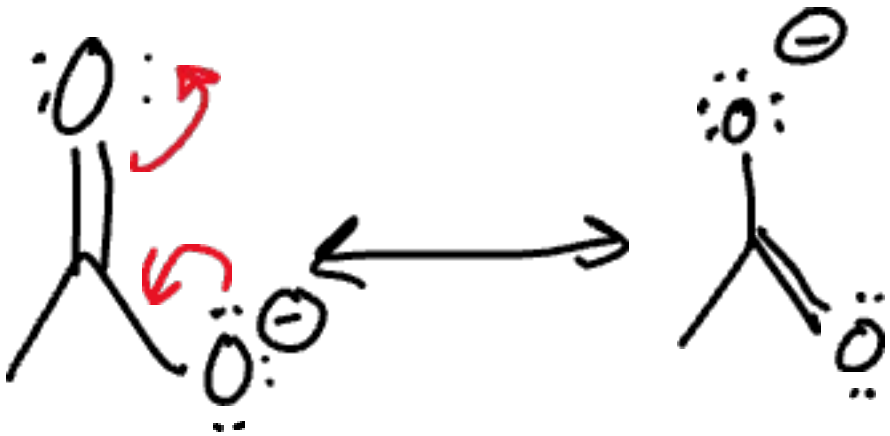
A classic textbook analogy: a rhinoceros is not a dragon one moment and a unicorn the next. If you had to describe a rhinoceros using only those two imaginary animals, you might say it is part of each, but the rhinoceros itself is a single, real animal. The resonance hybrid is the rhinoceros; the contributors are the imaginary descriptions.

Example — The Acetate Ion

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CH₃–C(=O)–O⁻      ↔      CH₃–C(–O⁻)=O
 contributor 1                  contributor 2
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Both contributors are equivalent, so they contribute equally. In the hybrid, each C–O bond is halfway between a single and a double bond (bond order 1.5), and each oxygen carries half of the negative charge (δ− of about −1/2). Experimentally, the two C–O bonds of acetate are the same length (Section 5).

> Use the double-headed arrow (↔) only between resonance structures. Equilibrium arrows (⇌) connect different molecules that interconvert. Using ⇌ between resonance structures is a common, penalised exam error.



2. Curved Arrows: The Rules for Drawing Resonance Structures

Curved arrows show how to get from one contributor to the next. Each arrow moves one pair of electrons. The tail starts at the electrons (a lone pair or a π bond) and the head points to where they go (a new bond position or a new lone-pair position).

The Two Commandments

1. **Never move atoms.** Only electrons move. If a hydrogen changes position, you have drawn a different molecule (a tautomer), not a resonance structure.
2. **Never break a single (σ) bond.** Only lone pairs and π bonds move in resonance.

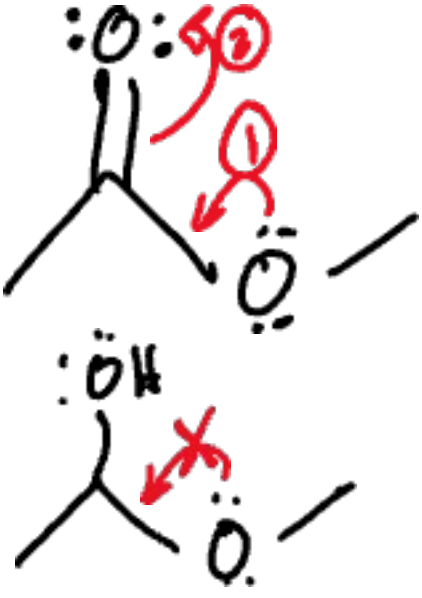
The Supporting Rules

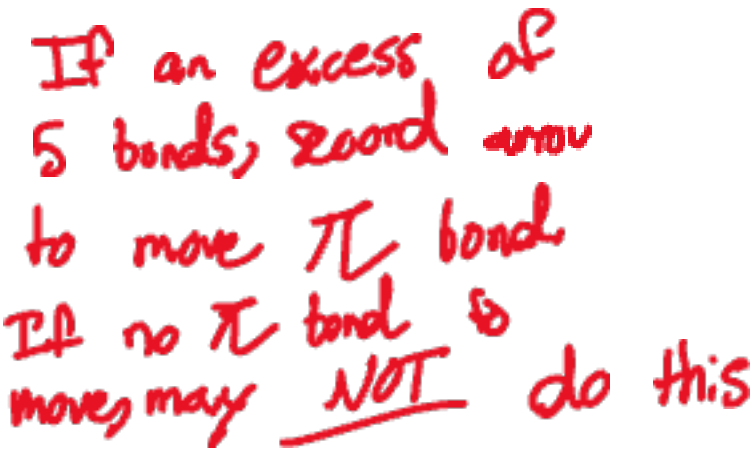
- Never exceed an octet on a second-row atom (C, N, O, F). Carbon may end up with six electrons (a carbocation) but never ten.
- The overall charge is the same in every contributor. Recalculate formal charges after each arrow.
- The number of unpaired electrons is the same in every contributor.
- Electrons generally flow toward an electronegative atom or toward a positive charge.

Two Legal Arrow Moves

Arrow starts at	Arrow ends at	Result
A lone pair	The bond to a neighbouring atom	The lone pair becomes a new π bond
A π bond	An atom of that bond, or the bond to the next atom	The π bond becomes a lone pair, or shifts one position over

> If an arrow would give an atom five bonds, a second arrow must take electrons away from that atom at the same time. This is why the acetate interconversion needs two arrows: the lone pair on O^- forms the new C=O, and the old C=O π bond moves onto the other oxygen.





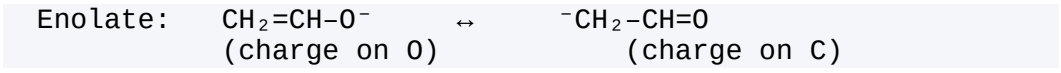
3. The Five Common Resonance Patterns

Almost every resonance structure you will need comes from five patterns (as organised by Klein). Learning to recognise them is far faster than pushing arrows by trial and error.

Pattern	What to look for	Arrows	Example
1. Allylic lone pair	A lone pair on an atom next to a π bond (X–C=C or X–C=O)	2	Acetate, enolates, amides
2. Allylic positive charge	A positive charge next to a π bond (C=C–C$^+$)	1	Allyl cation
3. Lone pair next to a positive charge	An atom with a lone pair bonded to a C$^+$	1	Oxocarbenium (protonated carbonyl)
4. π bond between atoms of different electronegativity	C=O, C=N	1	Carbonyl C$^+$–O$^-$ contributor
5. Conjugated π bonds in a ring	Alternating single and double bonds around a ring	3 (benzene)	Benzene and other aromatic rings

Pattern 1 — Allylic Lone Pair (Two Arrows)

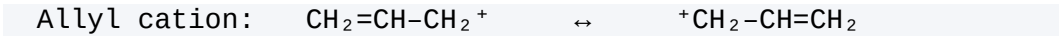
Arrow 1 turns the lone pair into a π bond to the neighbour. Arrow 2 pushes the existing π bond onto the far atom as a lone pair. The charge moves from the first atom to the third.

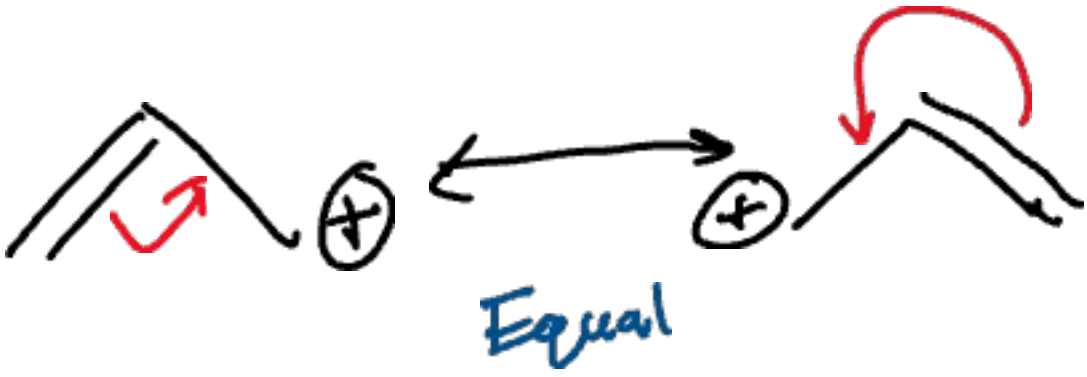




Pattern 2 — Allylic Positive Charge (One Arrow)

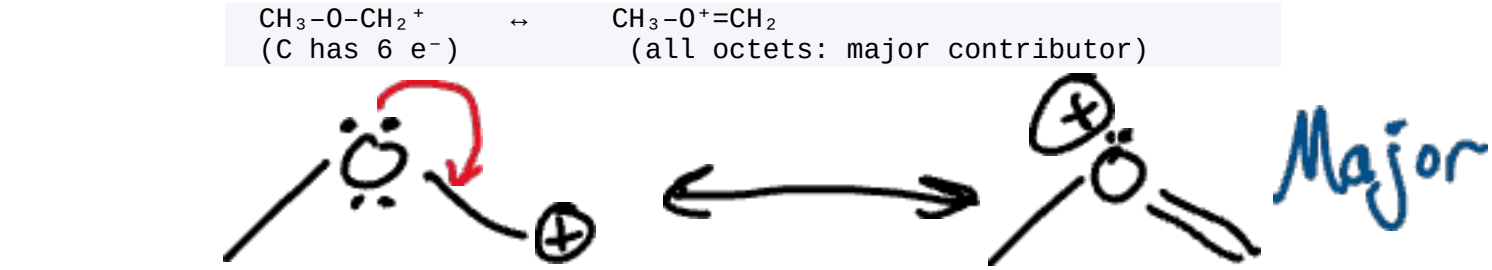
The π bond swings toward the positive carbon, forming a new π bond there and leaving the far carbon positive. The positive charge is shared by both end carbons, which is why the allyl cation is much more stable than a simple primary carbocation.





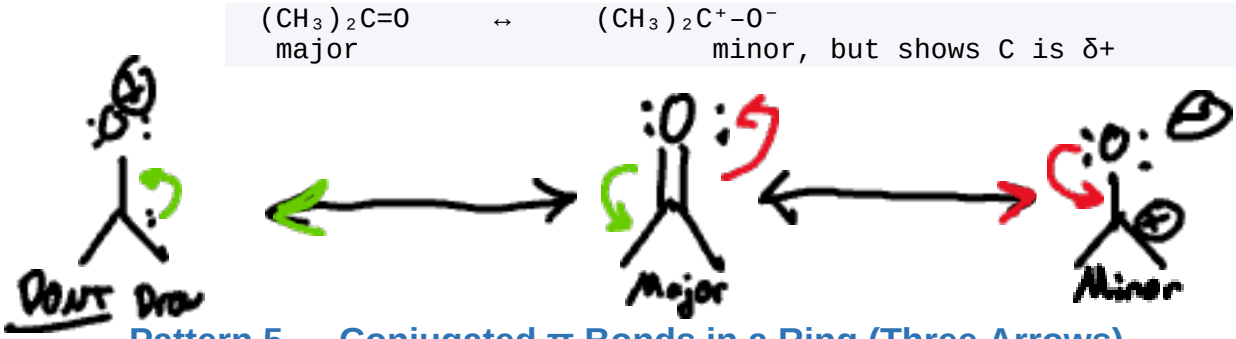
Pattern 3 — Lone Pair Next to a Positive Charge (One Arrow)

The lone pair forms a π bond to the positive carbon. The atom that donated the lone pair takes on the positive charge, but every atom now has an octet, so this contributor is often the more important one.



Pattern 4 — π Bond Between Atoms of Different Electronegativity (One Arrow)

The π electrons move entirely onto the more electronegative atom. This contributor is minor, because it separates charge and leaves carbon with six electrons, but it explains why the carbonyl carbon is electrophilic.



Pattern 5 — Conjugated π Bonds in a Ring (Three Arrows)

In benzene, three arrows shift every π bond one position around the ring, giving the second Kekulé structure. The two contributors are equivalent, so all six C–C bonds are identical in the hybrid. This is usually drawn as a hexagon with a circle inside.

> A fast check for Pattern 1: whenever you see a lone pair (or negative charge) one atom away from a π bond, there is a resonance structure. Look for this "X–C=Y" arrangement in every anion and every carbonyl compound you meet.

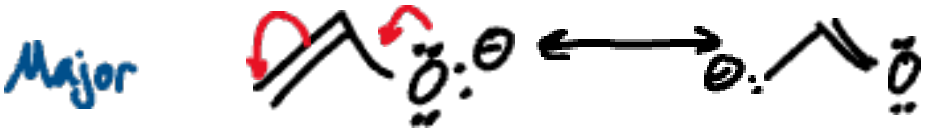
4. Ranking Resonance Contributors

Contributors are not all equal. The hybrid looks most like the most stable (major) contributor. Apply these rules in order; earlier rules outweigh later ones.

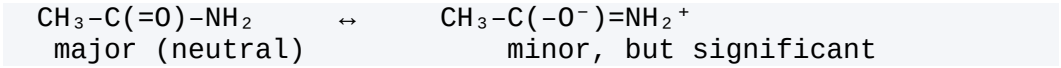
1. **Maximise octets.** A structure in which every second-row atom has an octet beats one with an electron-deficient atom.
2. **Minimise formal charges.** A neutral structure beats one with separated + and − charges.
3. **Put negative charge on the more electronegative atom** (and positive charge on the less electronegative atom).
4. **Equivalent structures contribute equally** and give especially strong stabilisation (acetate, benzene, the allyl cation).

Worked Example A — The Enolate Ion

Contributors: $CH_2{=}CH{-}O^-$ (charge on O) and $^-CH_2{-}CH{=}O$ (charge on C). Both have full octets and one formal charge, so Rules 1 and 2 tie. Rule 3 decides: oxygen (EN 3.44) holds negative charge better than carbon (2.55). The oxygen-anion contributor is major. Yet enolates usually react at carbon in alkylations and aldol reactions; the minor contributor tells you where the nucleophilic carbon is.



Worked Example B — The Amide



The neutral structure is major (Rule 2). The charge-separated contributor is still large, because both atoms keep their octets and the negative charge sits on oxygen. It gives the C–N bond partial double-bond character, which has three measurable consequences: amides are planar, rotation about the C–N bond is slow (barrier roughly 15–20 kcal/mol), and the C–N bond (~1.33 Å) is much shorter than an ordinary C–N single bond (~1.47 Å).

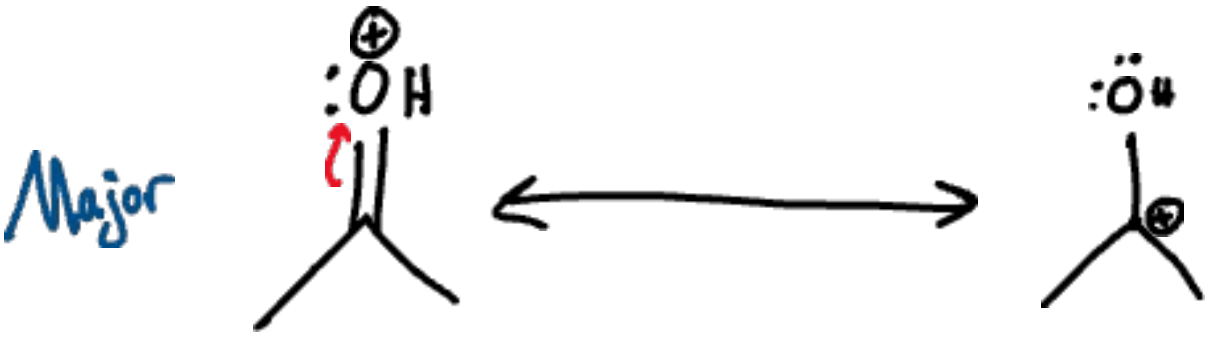


Worked Example C — Which Contributor of the Protonated Ketone Is Major?

Protonating acetone gives $(CH_3)_2C{=}OH^+ \leftrightarrow (CH_3)_2C^+{-}OH$. The first has positive charge on oxygen but full octets everywhere; the second puts positive charge on carbon, which has only

six electrons. Rule 1 (octets) outranks Rule 3, so the O^+ structure is major. The minor contributor still explains why acid makes the carbonyl carbon more electrophilic.

> Exam trap: students often pick the contributor with the negative charge on oxygen or the positive charge on carbon purely by electronegativity. Always check octets first. An oxygen with a positive charge and an octet beats a carbon with a positive charge and only six electrons.



5. Experimental Evidence for Resonance

Resonance is not just a drawing convention; it makes predictions that experiments confirm. Two of the clearest are bond lengths and energies.

Bond Lengths Are Intermediate

If acetate really had one C=O and one C–O⁻, X-ray crystallography would show one short and one long bond. Instead, both C–O bonds are identical and intermediate in length. Benzene behaves the same way: all six C–C bonds are 1.39 Å, between a C–C single (1.54 Å) and a C=C double bond (1.34 Å).

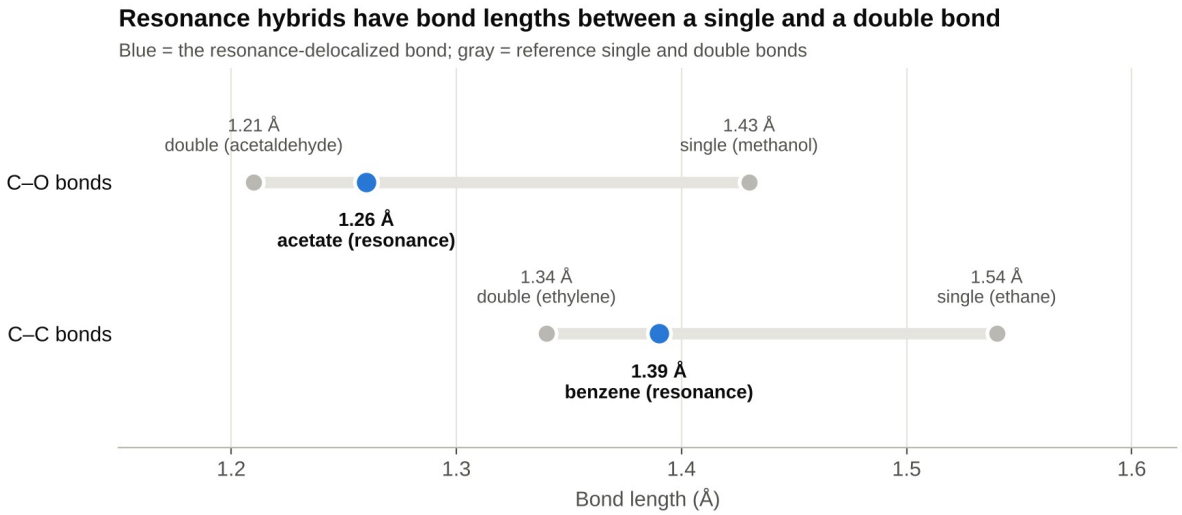


Figure 1. Resonance-delocalised bonds (blue) fall between the reference single and double bonds (gray). The acetate C–O bond length is a representative value from carboxylate crystal structures, which range from about 1.25 to 1.27 Å. Source: Allen et al., J. Chem. Soc. Perkin Trans. 2, 1987, S1–S19; benzene from gas-phase electron diffraction as tabulated in the CRC Handbook.

Resonance Lowers Energy: Benzene's Resonance Energy

Heats of hydrogenation give a direct measurement. Hydrogenating cyclohexene to cyclohexane releases 28.6 kcal/mol. A hypothetical "cyclohexatriene" with three isolated double bonds should release three times as much, 85.8 kcal/mol. Benzene actually releases only 49.8 kcal/mol. The missing 36 kcal/mol is benzene's resonance energy: it starts out that much lower in energy than a molecule with three localised double bonds.

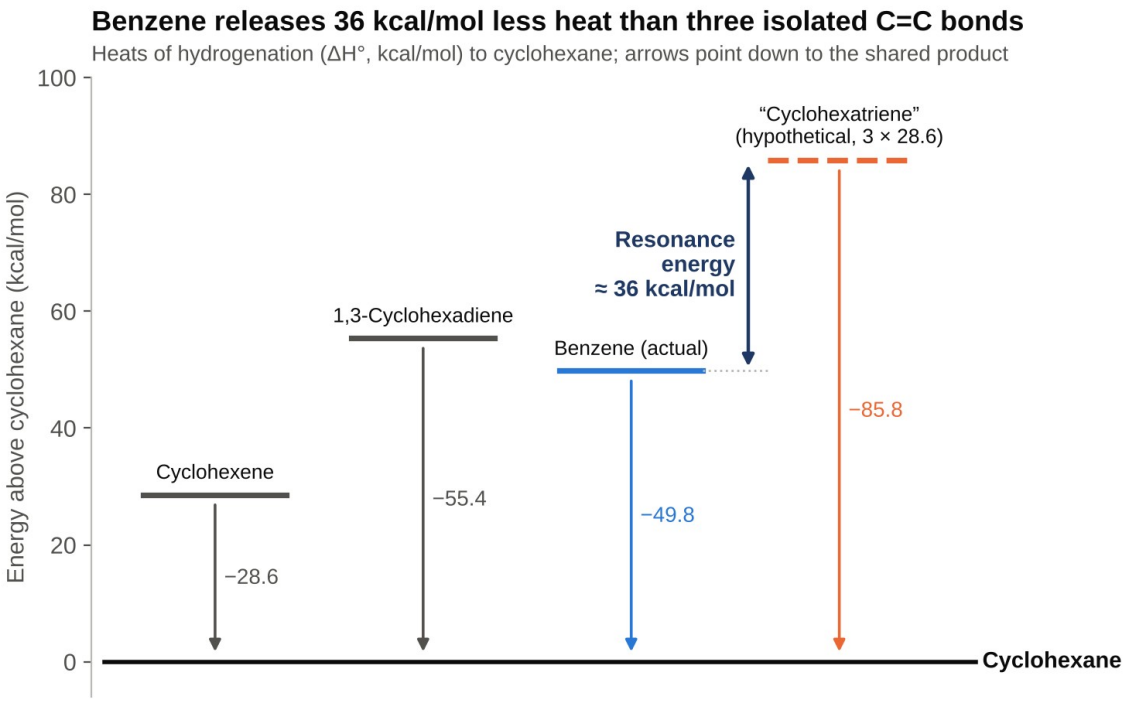


Figure 2. Heats of hydrogenation to cyclohexane. Each arrow's length is the heat released. Benzene (blue) releases 36 kcal/mol less than the hypothetical cyclohexatriene (dashed orange), so it is 36 kcal/mol more stable. Note that 1,3-cyclohexadiene releases slightly less than two cyclohexenes (55.4 vs 57.2), a small stabilisation from conjugation. Source: Kistiakowsky, G. B. et al., J. Am. Chem. Soc. 1936, 58, 146–153.

This is the same heat-of-hydrogenation logic used in the Alkene Oxidation and Reduction guide to rank alkene stability: a more stable starting material releases less heat because all routes end at the same product.

6. Consequences of Resonance: Acidity, Basicity, and Stability

Delocalising a charge over several atoms stabilises it. Any process that creates a resonance-stabilised species is therefore easier, and any process that destroys resonance is harder. This single principle explains a large share of organic reactivity.

Acidity: Resonance-Stabilised Conjugate Bases

An acid is strong if its conjugate base is stable. Compare three O–H acids. Ethoxide keeps its negative charge on one oxygen. Phenoxide spreads it onto three ring carbons. Acetate shares it equally between two oxygens, the best arrangement of all.

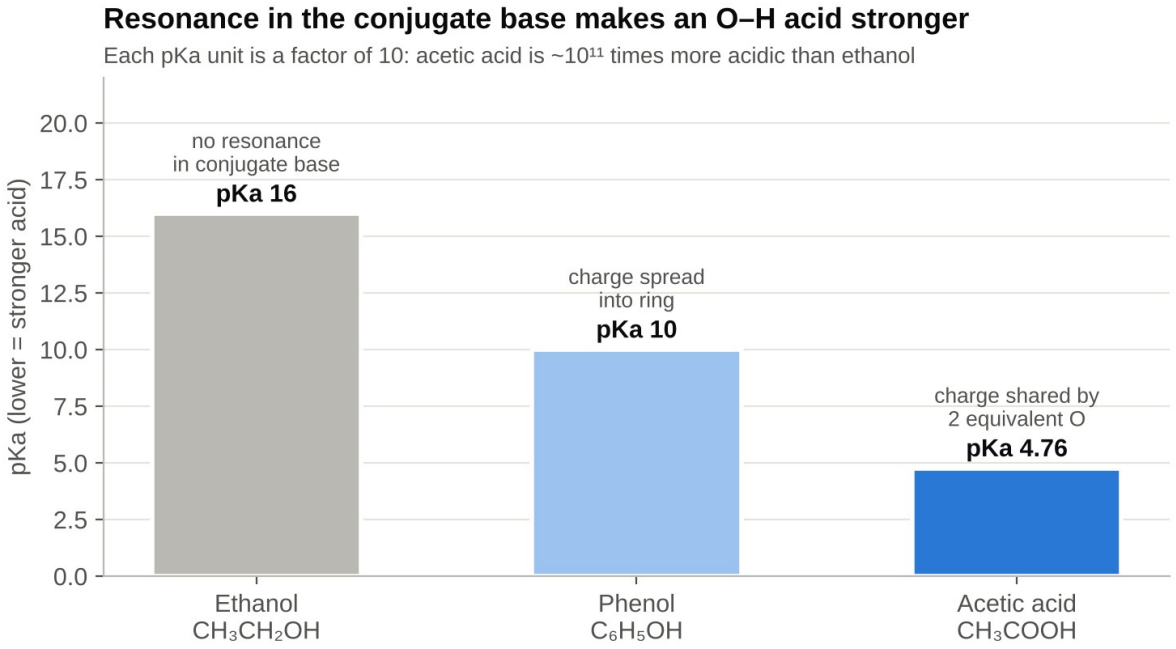


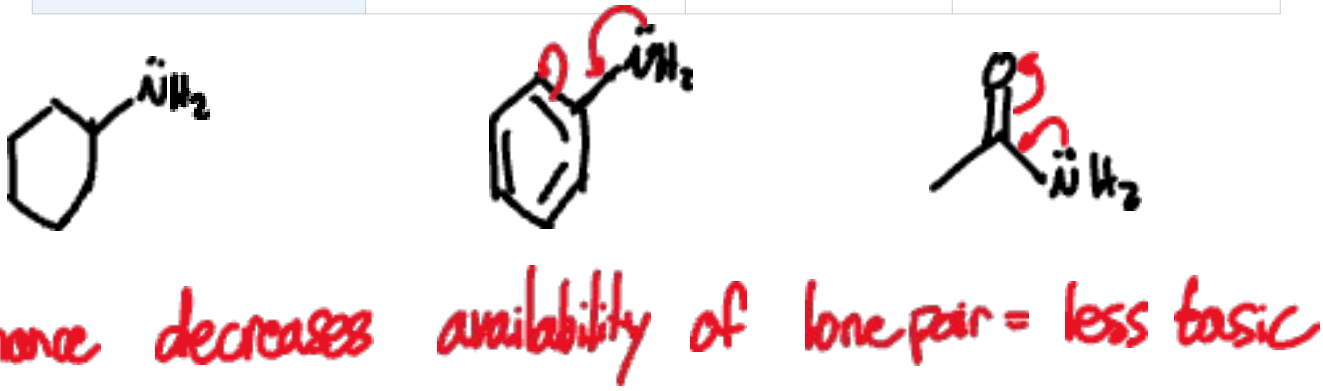
Figure 3. pKa of three O–H acids. More delocalisation of the conjugate base gives a stronger acid. Acetic acid (pKa 4.76) is about 10^{11} times more acidic than ethanol (pKa ≈ 16). Source: pKa values as tabulated in Klein, Ch. 3, and the CRC Handbook (acetic acid 4.76, phenol 9.99).



Basicity: Resonance Ties Up Lone Pairs

A lone pair that is delocalised by resonance is less available to accept a proton. This is why amides are not basic and aniline is a much weaker base than a typical alkylamine.

Compound	Lone pair	pKa of conjugate acid	Why
Cyclohexylamine (alkylamine)	Localised on N	~10.6	Lone pair fully available
Aniline	Delocalised into benzene ring	4.6	Protonation destroys resonance with the ring
Acetamide (amide)	Delocalised onto C=O oxygen	~ −0.5 (protonates on O)	Strong amide resonance; N is essentially non-basic



Stability of Reactive Intermediates

Carbocations, radicals, and carbanions next to a π system (allylic or benzylic) are stabilised by resonance. You have already used this: allylic and benzylic C–H bonds are weak (~88 kcal/mol) because the radical formed is delocalised (Radical Halogenation guide), and NBS brominates selectively at those positions. The same logic makes allylic and benzylic halides unusually reactive in both SN1 and SN2 reactions.

Intermediate	Stabilised by resonance?	Consequence
Allyl or benzyl cation	Yes (Pattern 2)	SN1 is fast even at primary allylic/benzylic carbons
Allyl or benzyl radical	Yes	Weak C–H bonds; selective NBS bromination
Enolate anion	Yes (Pattern 1)	α-C–H of ketones is acidic (pKa ~19–20)
Simple primary cation	No	Essentially never forms in solution

7. When Resonance Is Not Possible

Resonance requires a continuous line of p orbitals that can overlap: lone pairs, π bonds, empty p orbitals (carbocations), or radicals on adjacent atoms. An sp^3 carbon in the path breaks that line.

Three Quick Tests

1. **Is there an sp^3 atom in the way?** In $CH_2{=}CH{-}CH_2{-}CH_2^+$, the positive carbon is two atoms from the π bond, separated by an sp^3 CH_2. No resonance: this is an ordinary primary carbocation.
2. **Would any atom have to move?** Ketone and enol forms ($CH_3{-}CO{-}CH_3$ and $CH_2{=}C(OH){-}CH_3$) differ in where a hydrogen sits. They are tautomers, real and separate molecules in equilibrium, not resonance structures.
3. **Would a second-row atom exceed an octet?** Then that arrow is illegal and the structure does not exist.

Feature	Resonance structures	Tautomers
What changes	Only electron positions	Atom (usually H) positions
Real separate species?	No: one hybrid	Yes: separate molecules in equilibrium
Arrow used	↔ (double-headed)	⇌ (equilibrium)
Example	The two Kekulé structures of benzene	Acetone ⇌ its enol (keto–enol tautomerism)

> Keto–enol tautomerism is central to alkyne hydration (you have met it already) and to all of enolate chemistry in Orgo 2. Keeping tautomers and resonance structures separate in your mind now will save confusion later.

Quick Recap

Concept	Key fact
Resonance hybrid	One real structure; a weighted average of the contributors; no flipping
Arrow rules	Move electrons only; never break σ bonds; never exceed an octet on C, N, O
Five patterns	Allylic lone pair; allylic cation; lone pair next to C^+; C=O polarisation; conjugated ring
Ranking	Octets first, then fewest charges, then negative charge on the more electronegative atom
Evidence	Intermediate bond lengths (acetate 1.26 Å, benzene 1.39 Å); benzene resonance energy 36 kcal/mol
Acidity	Resonance-stabilised conjugate base = stronger acid (acetic 4.76 < phenol 10 < ethanol 16)
Basicity	Delocalised lone pair = weaker base (amide << aniline < alkylamine)
No resonance	An sp^3 atom in the path, or a moved atom (tautomer)

- ✓ Use ↔ between resonance structures and ⇌ between tautomers
- ✓ Recalculate formal charges after every arrow
- ✓ Rank contributors with octets first, then charges, then electronegativity
- ✓ Explain acidity and basicity differences by asking whether resonance is gained or lost
- × Do not move a hydrogen and call it resonance
- × Do not break a σ bond in a resonance arrow
- × Do not assume the electronegativity rule beats the octet rule

References & Further Reading

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