Acids and Bases: Factors Controlling Acid Strength (ARIO) — Study Guide

Memorized pKa values only get you so far. Exams ask you to rank acids you have never seen, explain why one proton is more acidic than another, and predict which site a base will attack. Every such question comes down to one idea: an acid is strong when its conjugate base is stable. Four structural factors control that stability, remembered as ARIO: Atom, Resonance, Induction, and Orbital.

Part of the A2 Acids and Bases series. Builds on pKa, Equilibrium, and Choosing a Base, and on the Resonance guide. pKa data from the CRC Handbook and standard compilations; ARIO framework as taught by Klein; concepts from Clayden, Wade, and McMurry.

Section	Topic
1	The Central Idea: Stabilise the Conjugate Base
2	A — The Atom Bearing the Charge
3	R — Resonance
4	I — Induction
5	O — Orbital Hybridization
6	Putting ARIO in Order (and Its Exceptions)
7	Solvation Effects
8	Using ARIO for Bases

1. The Central Idea: Stabilize the Conjugate Base

When HA loses a proton, the electron pair from the H–A bond stays on A as a negative charge (or a lone pair). Anything that stabilizes that charge makes the deprotonation easier and the acid stronger. So instead of asking "how acidic is this H?", ask "how happy is the conjugate base?"

> *Stronger acid = more stable conjugate base. Compare acids by drawing their conjugate bases and asking where the negative charge sits and how well it is stabilized.*

The Four Factors (ARIO)

Factor	Question to ask about the conjugate base	More stable when…
A — Atom	Which atom carries the negative charge?	It is more electronegative (same row) or larger (same group)
R — Resonance	Is the charge delocalised over several atoms?	More atoms share it, especially electronegative ones
I — Induction	Are there electron-withdrawing atoms nearby?	They are more electronegative, more numerous, and closer
O — Orbital	What orbital holds the lone pair?	It has more s-character (sp > sp^2 > sp^3)

A Fifth Factor: Charge

An acid that already carries a positive charge is far stronger than its neutral counterpart, because losing H^+ neutralizes the charge instead of creating a new negative one. Compare H_3O^+ (pKa −1.7) with H_2O (15.7), or NH_4^+ (9.2) with NH_3 (38). Some texts add this as the "C" in "CARDIO"; the logic is the same.

> Always draw the conjugate base, including its lone pairs and charge, before applying ARIO. Most ranking errors come from reasoning about the acid instead of the base.

2. A — The Atom Bearing the Charge (Size and Charge)

The identity of the atom holding the negative charge is usually the most important factor. Two periodic trends apply, and they point in different directions, which is the classic trap.

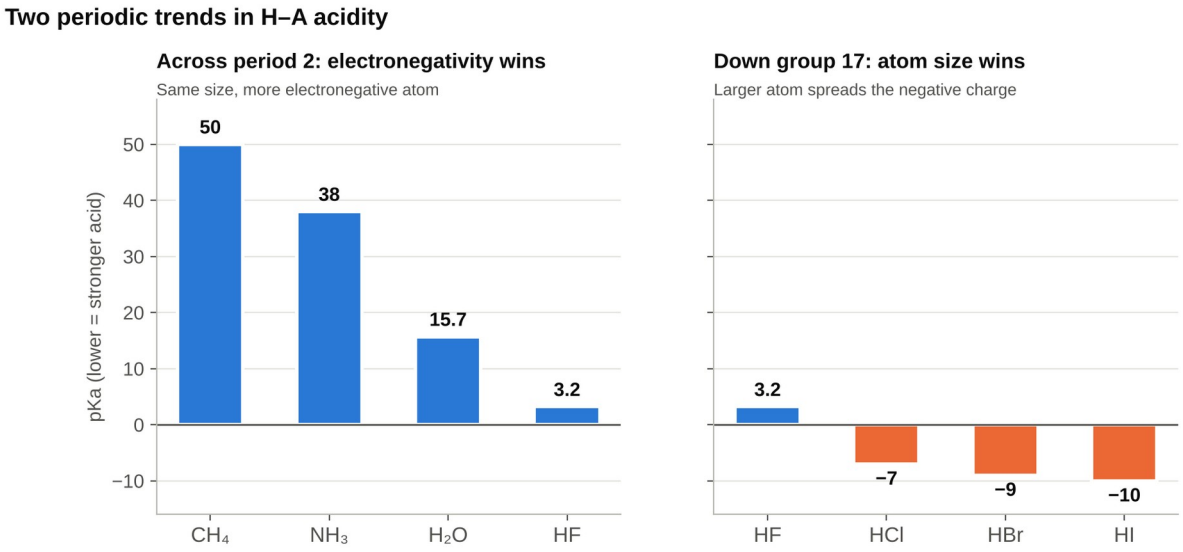
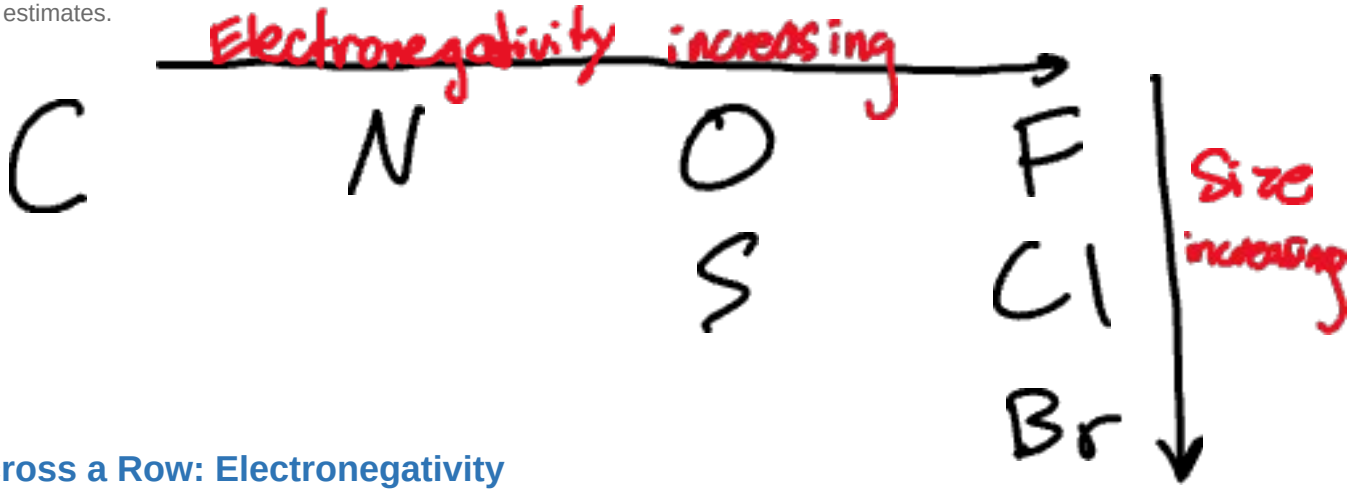


Figure 1. pKa of simple hydrides. Across period 2 (left), acidity rises 47 pKa units from CH_4 to HF as electronegativity increases. Down group 17 (right), acidity rises 13 units from HF to HI even though electronegativity decreases, because the larger atom spreads the negative charge over more volume. Source: pKa values from Klein, Ch. 3, and the CRC Handbook; values for CH_4, HCl, HBr, and HI are estimates.



Across a Row: Electronegativity

C, N, O, and F are similar in size, so the deciding factor is electronegativity. Fluorine (3.98) holds a negative charge far better than carbon (2.55). Acidity therefore increases across the row: $CH_4 < NH_3 < H_2O < HF$.

Overall: acidity goes up when electronegativity goes up!

Down a Group: Size

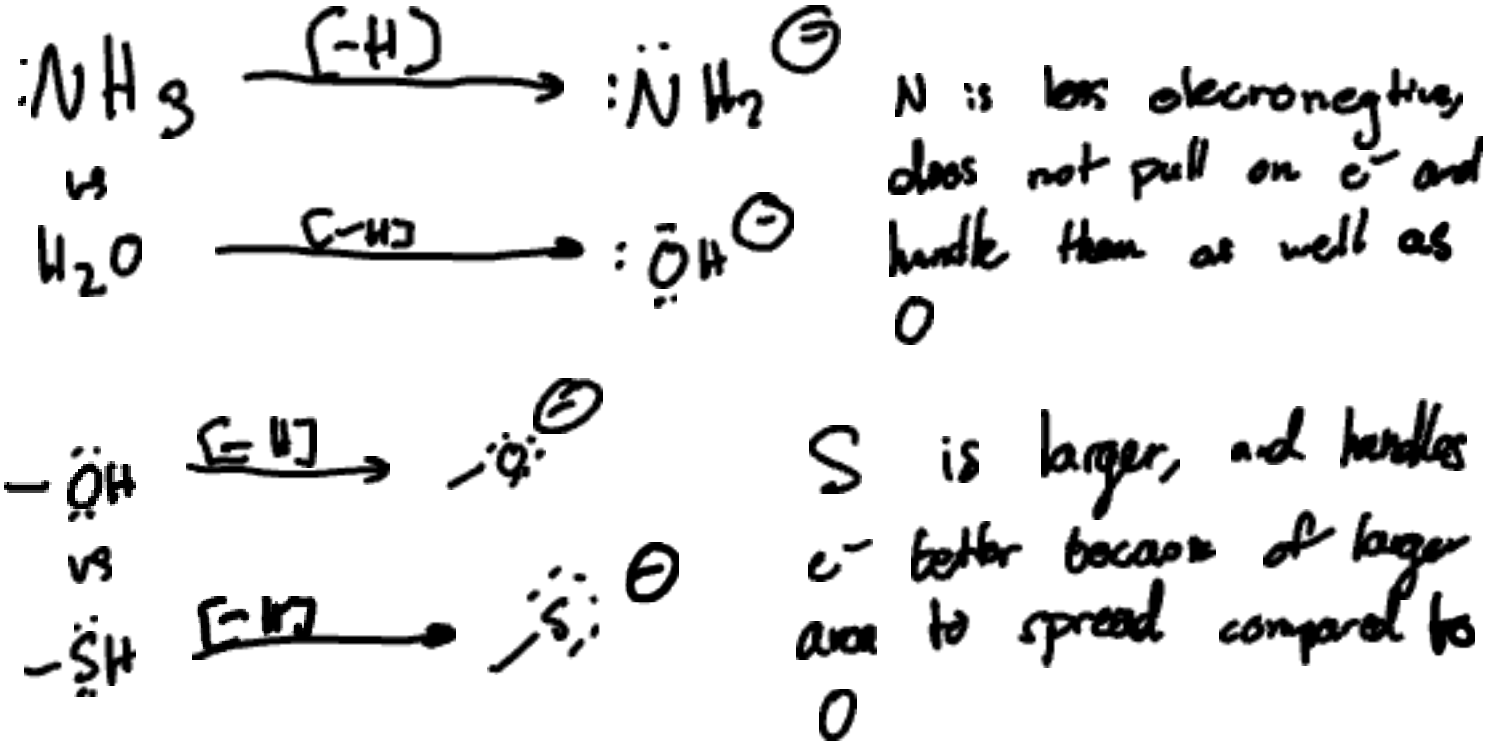
Going down a group, atoms get much larger. A negative charge spread over a larger volume is more stable (lower charge density), and the H–A bond is longer and weaker. Size wins over

electronegativity within a group: HF < HCl < HBr < HI in acidity. The same trend makes thiols much more acidic than alcohols (CH_3SH, pKa 10.3; CH_3OH, pKa 15.5).

Overall: acidity goes up when size goes up!

Comparison	Trend that decides	Result
NH_3 vs H_2O	Same row: electronegativity	H_2O more acidic (15.7 vs 38)
H_2O vs H_2S	Same group: size	H_2S more acidic (7.0 vs 15.7)
CH_3OH vs CH_3SH	Same group: size	CH_3SH more acidic (10.3 vs 15.5)
HF vs HCl	Same group: size	HCl more acidic (−7 vs 3.2)

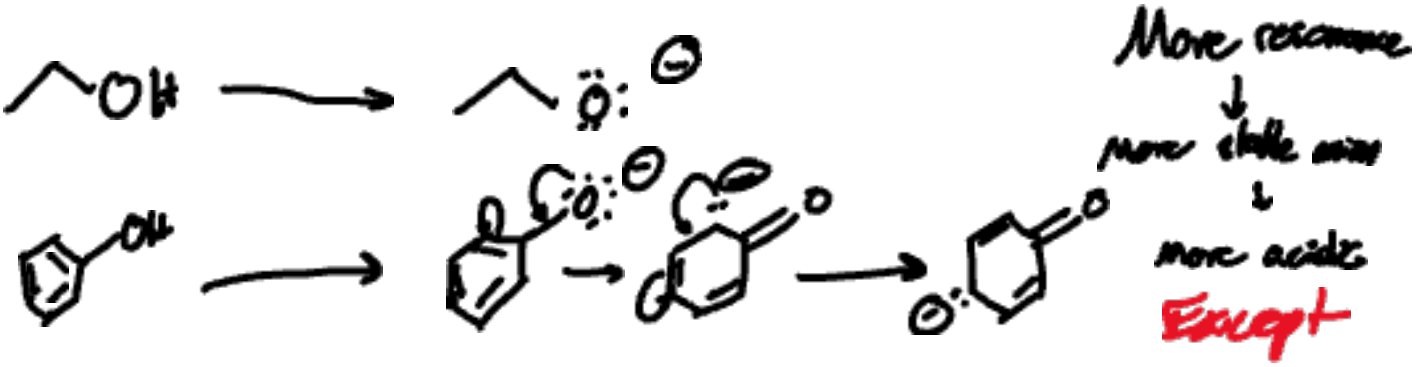
> Exam trap: "F is the most electronegative, so HF must be the strongest hydrohalic acid." Wrong. Within a group, size dominates; HF is a weak acid (pKa 3.2) while HCl, HBr, and HI are strong. Electronegativity only decides comparisons within a row.



3. R — Resonance

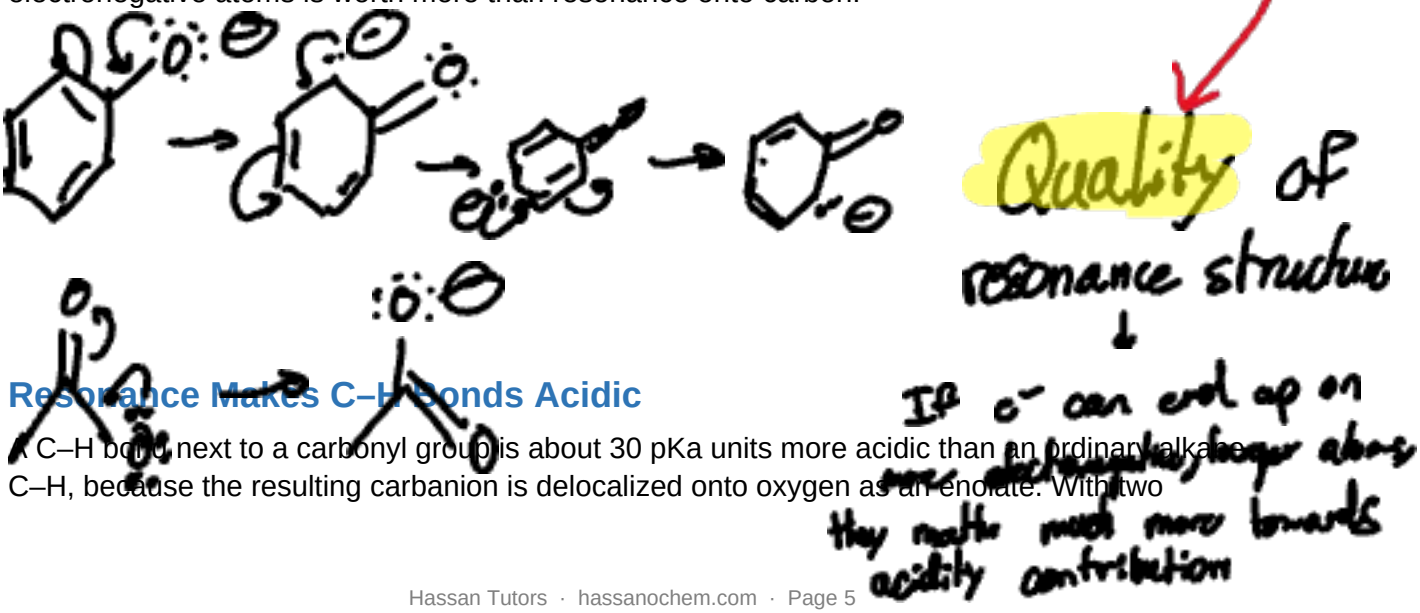
If the negative charge on the conjugate base can be delocalised by resonance, it is spread over two or more atoms and stabilised. Resonance is often worth many pKa units. The Resonance guide covers how to draw the contributors; here we focus on what resonance does to pKa.

Acid	Conjugate base	Delocalised over	pKa
Ethanol, CH_3CH_2OH	Ethoxide	One O (no resonance)	16
Phenol, C_6H_5OH	Phenoxide	O and three ring carbons	10
Acetic acid, CH_3COOH	Acetate	Two equivalent O atoms	4.76
Propane, $CH_3CH_2CH_3$	Propyl anion	One C	~50
Acetone, CH_3COCH_3 (α-H)	Enolate	C and O	19.2
2,4-Pentanedione (central CH_2)	Doubly stabilised enolate	One C and two O	9



Why Acetate Beats Phenoxide

Both conjugate bases are resonance-stabilised. In acetate the charge is shared equally by two oxygens, both highly electronegative. In phenoxide most of the charge stays on oxygen, and the rest is spread onto carbons, which hold negative charge poorly. Resonance onto electronegative atoms is worth more than resonance onto carbon.

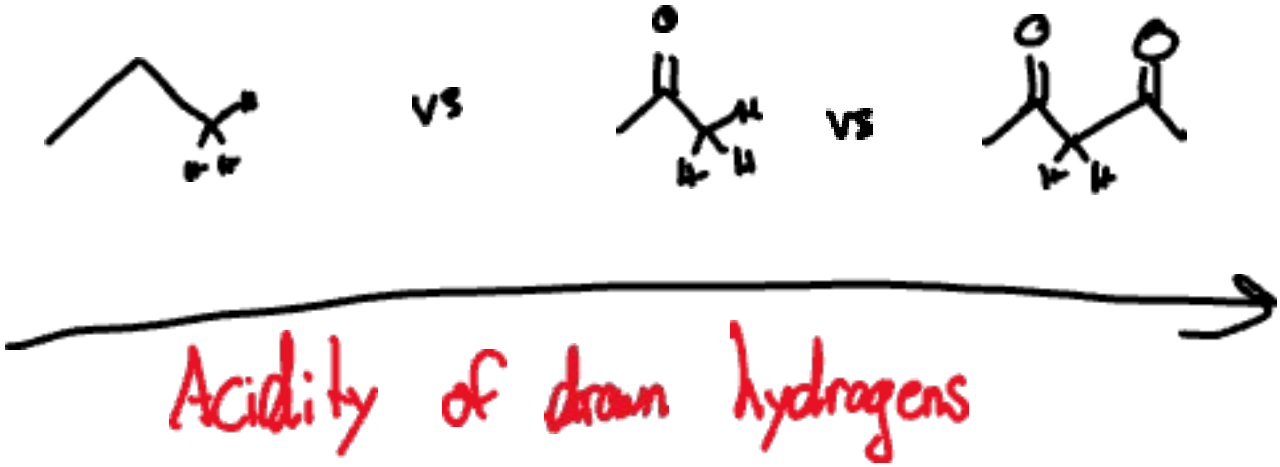


Resonance Makes C–H Bonds Acidic

A C–H bond next to a carbonyl group is about 30 pKa units more acidic than an ordinary alkane C–H, because the resulting carbanion is delocalized onto oxygen as an enolate. With two

carbonyls flanking the same CH_2 (2,4-pentanedione), the pKa drops to about 9, as acidic as a phenol. This is the foundation of enolate chemistry in Orgo 2.

> Resonance only counts if the charge can actually reach another atom through a continuous line of p orbitals. A carbonyl two carbons away from the charged atom, separated by an sp^3 carbon, provides induction only, not resonance.



4. I — Induction

Electronegative atoms near the acidic site pull electron density toward themselves through the σ bonds. This withdraws density from the negatively charged atom of the conjugate base and stabilises it. The inductive effect has three properties you can see directly in pKa data.

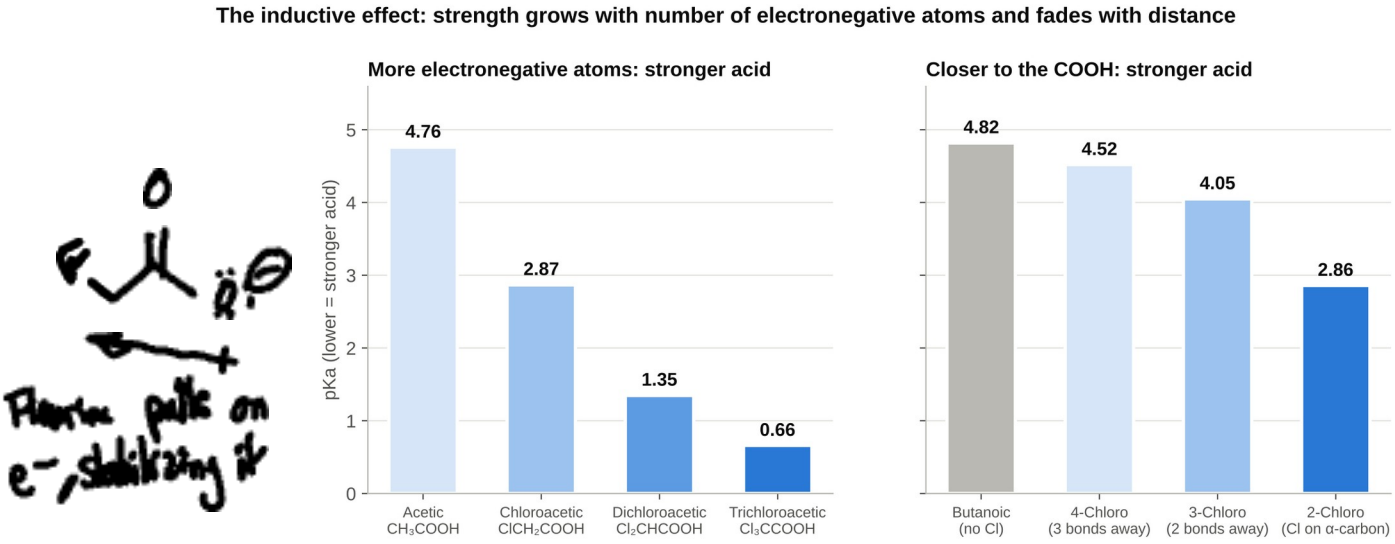


Figure 2. Left: each added chlorine on the α-carbon lowers the pKa of acetic acid; three chlorines make it about 10^4 times more acidic. Right: one chlorine has a large effect on the α-carbon, a modest effect one carbon further away, and almost none three bonds away. Source: pKa values in water at 25 °C from the CRC Handbook and standard compilations.

Three Rules of Induction

1. **More electronegative is stronger:** FCH_2COOH (2.59) < $ClCH_2COOH$ (2.87) < $BrCH_2COOH$ (2.90) < ICH_2COOH (3.18) in pKa.
2. **More withdrawing groups add up:** Cl_3CCOOH (0.66) is more acidic than $ClCH_2COOH$ (2.87).
3. **The effect falls off quickly with distance:** roughly halved or worse with each extra bond. By three or four bonds away it is nearly gone.



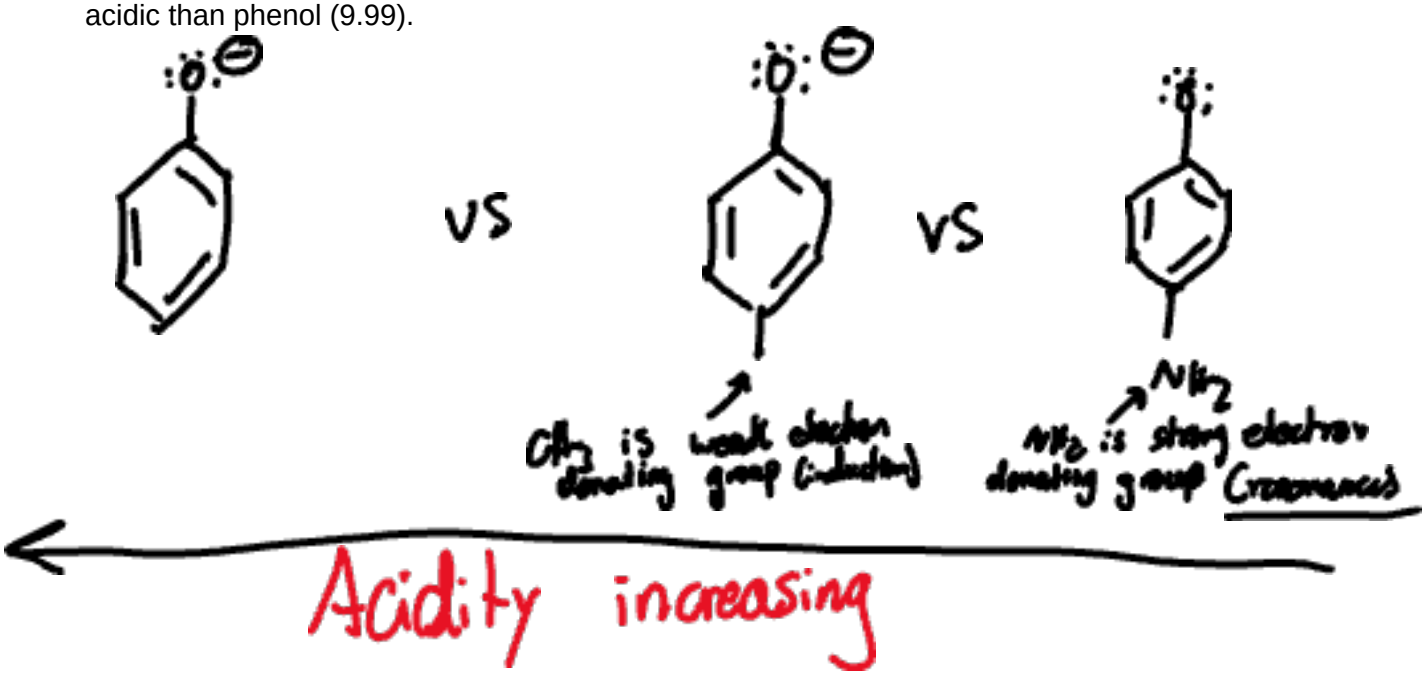


Induction in Alcohols

Alcohol	Withdrawing group	pKa
Ethanol, CH_3CH_2OH	None	16
2-Chloroethanol, $ClCH_2CH_2OH$	One Cl, two bonds from O	14.3
2,2,2-Trifluoroethanol, CF_3CH_2OH	Three F, two bonds from O	12.4

Electron-Donating Groups Work the Other Way

Alkyl groups are weakly electron-donating by induction and hyperconjugation. They slightly destabilize a negative charge, which is why p-cresol (p-methylphenol, pKa 10.26) is a little less acidic than phenol (9.99).



5. O — Orbital Hybridization

When the negative charge sits on the same atom in different molecules, the orbital that holds the lone pair matters. Orbitals with more s-character keep their electrons closer to the nucleus, where they are lower in energy and more stable.

Acid	Carbon hybridization	% s-character of the lone-pair orbital	pKa
Ethane, CH_3CH_3	sp^3	25	~50
Ethylene, $CH_2{=}CH_2$	sp^2	33	~44
Acetylene, HC≡CH	sp	50	~25

The sp effect is enormous: about 25 pKa units between ethane and acetylene, with no change in the atom, no resonance, and no induction. This is why terminal alkynes, unlike alkenes or alkanes, can be deprotonated by $NaNH_2$ and used as carbon nucleophiles (see the Alkyne guides and the Hybridization guide, Figure 3).

The Same Effect on Nitrogen Lone Pairs

Orbital effects also explain the basicity of nitrogen compounds. A lone pair in an orbital with more s-character is held more tightly and is less available to accept a proton.

Nitrogen compound	Lone pair in	pKa of conjugate acid	Basicity
Piperidine (cyclic amine)	sp^3	11.1	Strongest base
Pyridine (aromatic ring N)	sp^2	5.2	~10^6 times weaker
Acetonitrile, $CH_3C{\equiv}N$	sp	~ −10	Essentially non-basic

6. Putting ARIO in Order (and Its Exceptions)

When two acids differ in more than one factor, apply the factors in priority order. The general ranking, as taught by Klein, is Atom > Resonance > Induction > Orbital: compare the atom bearing the charge first; if it is the same, look for resonance; then induction; then orbital.

> *Priority: Atom > Resonance > Induction > Orbital. Use it as a starting rule, then check against the benchmark pKa values you know.*

The Important Exception

Compare acetylene (charge on carbon, pKa 25) with ammonia (charge on nitrogen, pKa 38). The Atom factor says nitrogen should win, yet acetylene is about 10^{13} times more acidic. Here the Orbital factor (an sp carbanion with 50% s-character versus an sp^3 nitrogen anion) overrides the Atom factor. This is why $NaNH_2$ deprotonates terminal alkynes. Memorize this exception; it is a favorite exam question.

Combining Resonance and Induction: Substituted Phenols

Substituents on a phenol ring change acidity through both effects at once. A nitro group withdraws electrons by induction from any position, but it can also accept the negative charge by resonance only when it is ortho or para to the O^-. That is why p-nitrophenol is more acidic than m-nitrophenol.

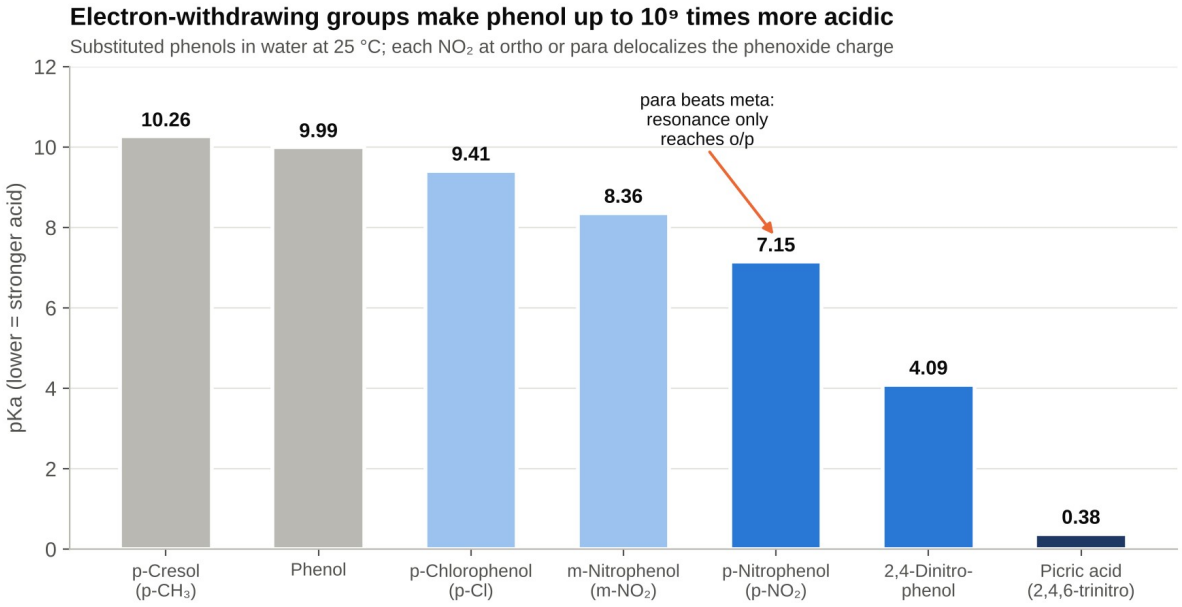
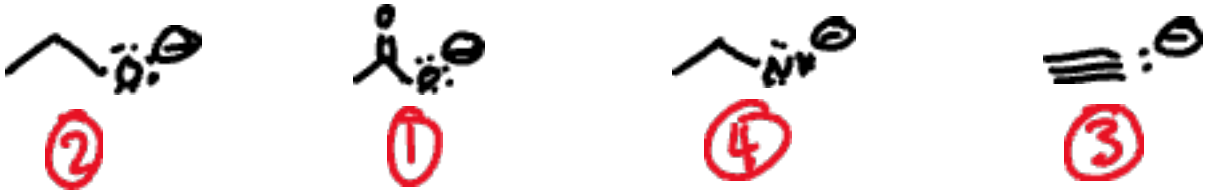


Figure 3. Acidity of substituted phenols. Electron-donating CH_3 slightly weakens the acid; electron-withdrawing Cl and NO_2 strengthen it. Three nitro groups (picric acid) bring the pKa down to 0.38, close to a strong mineral acid. Source: pKa values in water at 25 °C from the CRC Handbook and standard compilations.

Worked Ranking Problems

Problem A — Rank CH_3CH_2OH, CH_3COOH, $CH_3CH_2NH_2$, and $HC{\equiv}CH$ by acidity

First draw conjugate bases

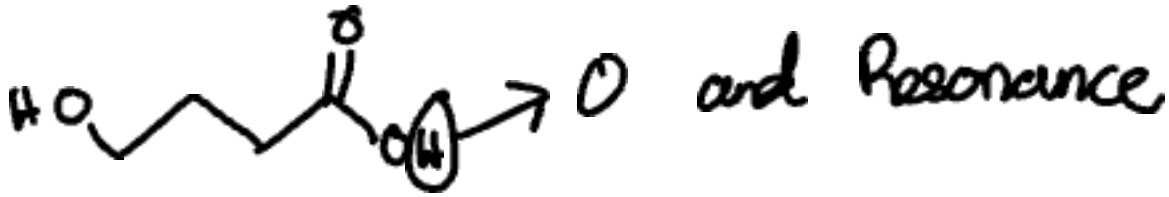


O is most relevant

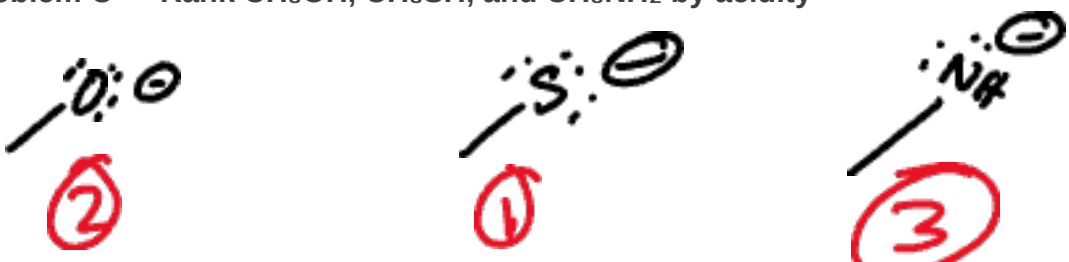
Resonance then puts acetic acid on top

N more acidic than C, but sp hybridization boosts it up

Problem B — Which proton in 4-hydroxybutanoic acid ($HOCH_2CH_2CH_2COOH$) is most acidic?



Problem C — Rank CH_3OH, CH_3SH, and CH_3NH_2 by acidity



N is least acidic because of least electronegative

S beats O because larger than O

7. Solvation Effects

ARIO describes the conjugate base in isolation. In solution, the solvent also stabilizes ions by surrounding them, and that can change the ranking among closely related acids. The clearest example is the series of simple alcohols.

Alcohol	pKa in water	Conjugate base	Solvation of the anion
Methanol, CH_3OH	15.5	CH_3O^- (small)	Best solvated
Ethanol, CH_3CH_2OH	16	$CH_3CH_2O^-$	Well solvated
2-Propanol, $(CH_3)_2CHOH$	17	$(CH_3)_2CHO^-$	Less solvated
tert-Butanol, $(CH_3)_3COH$	18	$(CH_3)_3CO^-$ (bulky)	Poorly solvated: methyl groups block water

Water molecules stabilize an alkoxide by hydrogen bonding to its oxygen. The three methyl groups of tert-butoxide crowd the oxygen and keep water away, so the anion is poorly solvated and less stable. In the gas phase, where there is no solvent, the order reverses: tert-butanol is more acidic than methanol, because larger alkyl groups are more polarizable and help stabilize the charge (Brauman and Blair, 1970).

8. Using ARIO for Bases

Basicity is the mirror image of acidity. A strong base has an unstable, available electron pair; a weak base has a stabilised one. Apply ARIO to the base itself: every factor that stabilises a lone pair makes that species a weaker base.

> *Stable lone pair = weak base. Compare bases by the pKa of their conjugate acids: higher conjugate-acid pKa = stronger base.*

Base	ARIO factor at work	pKa of conjugate acid	Relative basicity
$CH_3CH_2NH_2$ (alkylamine)	Localised sp^3 lone pair; alkyl group donates	10.7	Strongest of these
NH_3	Localised sp^3 lone pair	9.2	Strong
Pyridine	Orbital: sp^2 lone pair	5.2	Weaker
Aniline, $C_6H_5NH_2$	Resonance: lone pair delocalised into ring	4.6	Weaker
Acetamide, CH_3CONH_2	Resonance onto C=O oxygen	~ −0.5	Essentially non-basic at N

Halides and Other Anions

By the Atom factor, I^- is the most stable halide and therefore the weakest base; F^- is the strongest base of the four. The same reasoning ranks $HO^- > CH_3COO^-$ (resonance stabilises acetate) and $NH_2^- > HO^-$ (oxygen holds the charge better than nitrogen).

> Leaving-group ability follows the same logic: good leaving groups are weak, stable bases (I^-, Br^-, Cl^-, H_2O, TsO^-). Poor leaving groups are strong bases (HO^-, RO^-, NH_2^-). You will use this constantly in SN1, SN2, E1, and E2.

Quick Recap

Concept	Key fact
Central idea	Stronger acid = more stable conjugate base
Atom (row)	More electronegative atom holds charge better: CH_4 < NH_3 < H_2O < HF
Atom (group)	Larger atom holds charge better: HF < HCl < HBr < HI; ROH < RSH
Resonance	Delocalisation, especially onto O, lowers pKa by many units
Induction	Electronegative groups lower pKa; stronger with number, weaker with distance
Orbital	More s-character stabilises charge: sp (25) < sp^2 (44) < sp^3 (50)
Priority	A > R > I > O; key exception: HC≡CH (25) more acidic than NH_3 (38)
Solvation	Small anions are better solvated: CH_3OH more acidic than $(CH_3)_3COH$ in water
Bases	Same factors in reverse: a stabilised lone pair is a weak base

- ✓ Draw the conjugate base before ranking any set of acids
- ✓ Use electronegativity within a row and size within a group
- ✓ Look for resonance onto electronegative atoms first among same-atom acids
- ✓ Remember the alkyne vs ammonia exception
- ✓ Apply the same factors in reverse for bases and leaving groups
- × Do not call HF the strongest hydrohalic acid
- × Do not count a carbonyl separated by an sp^3 carbon as resonance; it is induction only
- × Do not ignore solvation when ranking simple alcohols in water

References & Further Reading

- Rumble, J. R., Ed. CRC Handbook of Chemistry and Physics, 104th ed.; CRC Press, 2023. Section 5: Dissociation Constants of Organic Acids and Bases (haloacetic acids, phenols, amines).
- Serjeant, E. P.; Dempsey, B. Ionisation Constants of Organic Acids in Aqueous Solution; IUPAC Chemical Data Series No. 23; Pergamon Press, 1979.
- Brauman, J. I.; Blair, L. K. Gas-Phase Acidities of Alcohols. J. Am. Chem. Soc. 1970, 92 (20), 5986–5992. DOI: 10.1021/ja00723a028
- Bordwell, F. G. Equilibrium Acidities in Dimethyl Sulfoxide Solution. Acc. Chem. Res. 1988, 21 (12), 456–463. DOI: 10.1021/ar00156a004
- Klein, D. R. Organic Chemistry, 4th ed.; Wiley, 2021. Chapter 3 (the ARIO framework and its priority order).
- Clayden, J.; Greeves, N.; Warren, S. Organic Chemistry, 2nd ed.; Oxford University Press, 2012. Chapter 8 (Acidity, Basicity, and pKa).
- Wade, L. G.; Simek, J. W. Organic Chemistry, 9th ed.; Pearson, 2017. Chapter 1.
- McMurry, J. Organic Chemistry, 9th ed.; Cengage Learning, 2016. Chapters 2 and 20 (substituent effects on carboxylic acid acidity).

- Chemistry LibreTexts: Structural Effects on Acidity and Basicity. https://chem.libretexts.org