

Solutions to problems – Set 1: Acids and bases

ED: Electron donating / EW: electron withdrawing

Problem 1

Right order of acidity: $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{H}_2\text{S} < \text{HF} < \text{HBr}$

As moving across the period, electronegativity increases. A more electronegative atom better stabilize a negative charge. After dissociation of the acid, left with a negatively charged conjugate base, the more stabilized the conjugate base is, the more acidic.

	CH_4	$<$	NH_3	$<$	H_2O	$<$	HF
Electronegativity of main atom	2.55		3.04		3.44		3.98
pKa	50		34		15.7		3.2

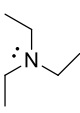
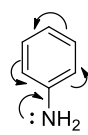
As moving down a column or group in the periodic table, we have an increase of the atomic radius. When dissociation occurs, the negative charge is left on the main atom. The more dispersed that charge is, the less destabilized the conjugate base. This argument will correlate to atomic radius and not to electronegativity.

	H_2O	$<$	H_2S	and	HF	$<$	HBr
Vdv radius	1.52		1.80		1.47		1.85
pKa	15.7		7.0		3.2		-9

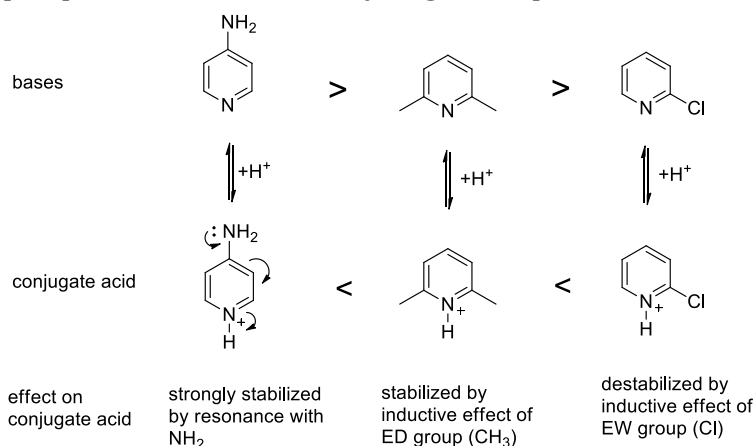
In comparison between H_2S and HF (both are more acidic than H_2O), F is more electronegative but S is a larger atom, so there is not similar explanation as mentioned above. As H_2S is larger than HF , more molecules of solvent can surround and solvate the acid stabilizing it. Then the corresponding base is stronger. It is noticed that the changing of acidity when moving across the period are much greater than one when moving down the period.

Problem 2

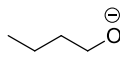
a) The basicity of pyridine, ammoniac, triethylamine and aniline originates from lone-pair electrons. If their density is higher, its basicity is stronger.

	:NH_3		
N at sp^2 hybridization, more s-character, more electronegative. (the lone-pair is closer to the nitrogen, less disponible)	none	inductive effect of ED groups (ethyl) increase density of electron	lone-pair electrons conjugated to aromatic ring, reducing density
3	2	1	4

b) If the conjugate acid is more acidic, then the base is less basic. It is less likely to accept a proton, and more likely to give it up.



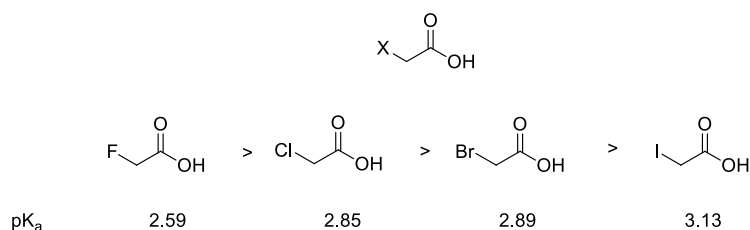
c) In this case, bases have negative charge. The more the negative charge is destabilized (by electron-donating group), the stronger base it is.

					
ED group	Ethyl	t-Butyl	none	n-Butyl	methyl
strength of ED group	3 rd	1 st	5 th	2 nd	4 th
basicity	3 rd	1 st	5 th	2 nd	4 th

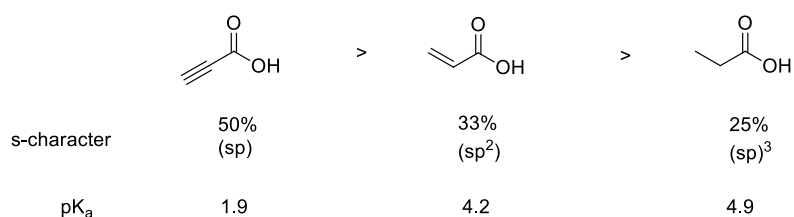
Problem 3

(a) Inductive effect

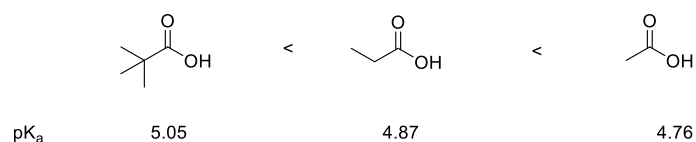
As X becomes more electronegative, electron density is pulled through sigma bond and the negative charge on the carboxylate is distributed more towards X. The conjugate base is stabilized and so the acid is more acidic.



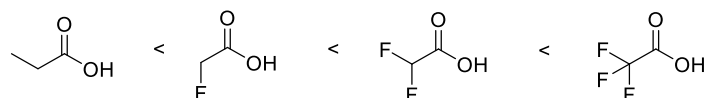
(b) This is again the inductive effect, but need to recognize that hybridization can alter the inductive electron withdrawing ability (c.f. electronegativity) of the carbon atom. Increasing the s character of a Carbon atom also increases its electron withdrawing ability. The reason for this is that the s-orbital - in the same valence shell - has a smaller effective radius than a p-orbital and is more dispersed. So then is closer to the nucleus and will better stabilize a negative charge.



(c) Here we need to consider that an alkyl is electron donating and so will then destabilize the negatively charged conjugate base. Hence the acid is less acidic.



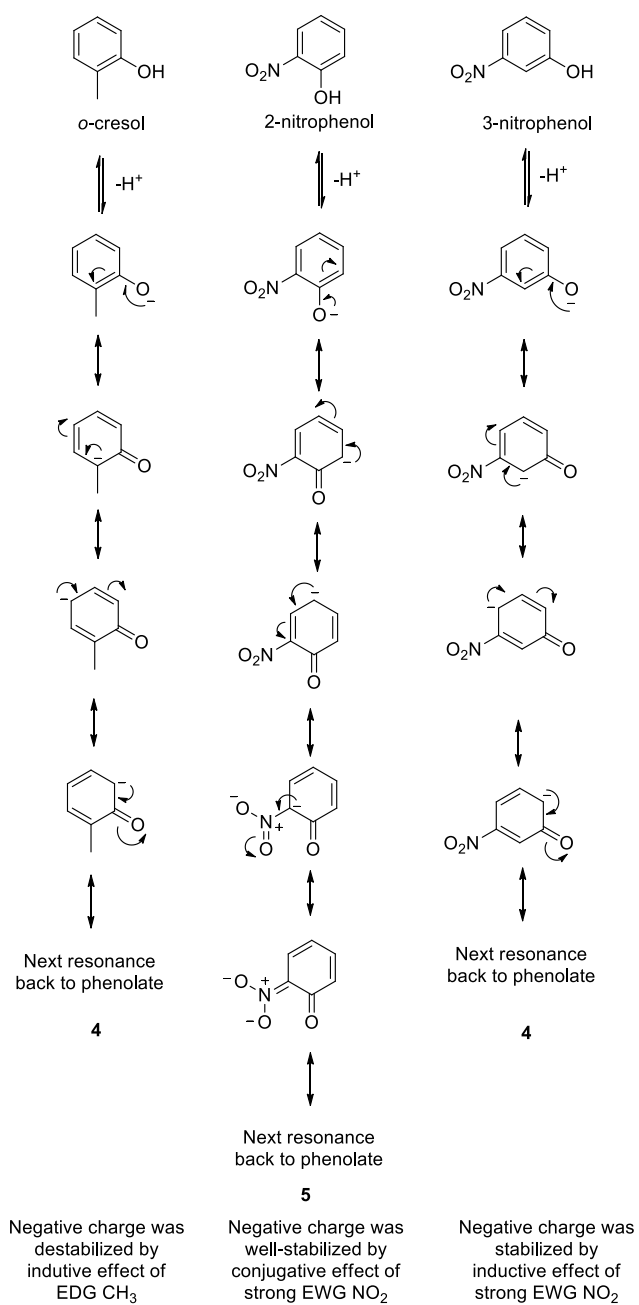
(d) This is again about the inductive effect. F is more electronegative than H so increasing number of F substituents will also better stabilize the conjugate base (c.f. electronegativities: F 3.98 and H 2.2).



Problem 4

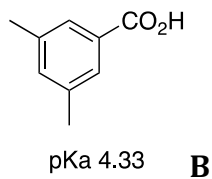
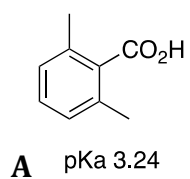
If the conjugate base is weaker, the acid is stronger. So 2-nitrophenol is the strongest acid, and 2-cresol is the weakest one.

The resonance structures of those compounds were shown below:



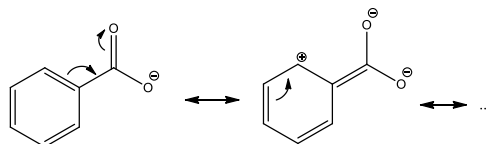
Problem 5

a)



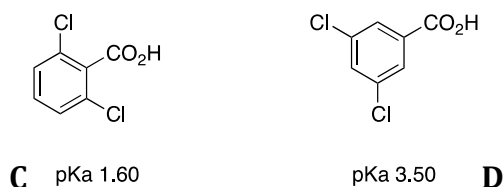
Answer : the ortho effect.

The phenyl ring (assuming there is no substituent) is electron donating to the carboxylate group (=conjugate base) by conjugation :



This destabilizes the conjugate base, making the acid less acidic. When there are substituents at the ortho positions (regardless of their donating or withdrawing nature), this conjugation is not possible because the molecule can't be "flat" (as it must be to allow conjugation through planar sp² carbons) because of the sterics of the substituents. As there is no conjugation, the conjugate base is less destabilized and the acid is therefore more acidic.

b)



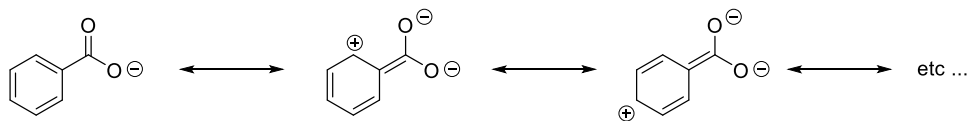
The same is true here: the compound bearing the substituents at the ortho positions is more acidic.

By comparing a) and b), one can observe that the compounds bearing the substituents at the ortho positions (**A** and **C**) are always more acidic than those with the substituents at the meta positions (**B** and **D**) : the inductive effect of the substituents (ie. Me=donating or Cl=withdrawing) is therefore not relevant because resonance effects dominate over inductive effects.

However, when comparing **A** vs. **C** and **B** vs. **D**, the inductive effects of the substituents are the key point : withdrawing groups (Cl) stabilize the conjugated base, making the acid more acidic -> **C** is more acidic than **A** and **D** is more acidic than **B**.

Quand aucun substituant sur le cycle aromatique:

Delocalisation possible car système π du carboxylate dans le même plan que celui du cycle aromatique



Phenyl: +M

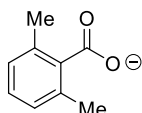
Dans le cas des fonctions carboxylates s'il y a délocalisation via effet mésomère des électrons du cycle aromatique (+M) dans le système π du carboxylate, on **déstabilise** la base conjuguée (Formation dans les formes mésomères de deux charges anioniques à côté l'une de l'autre). Donc si la base conjuguée est moins stable l'acide lui est **moins acide** (Plus stable).

Quand substituants en ortho sur le cycle aromatique:

Delocalisation impossible car l'encombrement stérique des substituants en ortho force le carboxylate a ne plus être dans le même plan



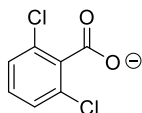
Du coup vu qu'il n'y a plus de délocalisation possible, la base conjuguée est **moins déstabilisée**, donc elle est plus stable donc l'acide lui devient **plus acide** (moins stable)



Les méthyls donnent des électrons par effet inductif +I au carboxylate.
Cela déstabilise la base conjuguée donc elle est moins stable et l'acide est donc moins acide.
pKa: 3.24

Me: Effet +I

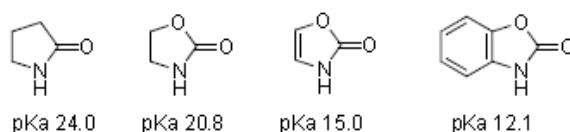
VS



Les Cl attirent les électrons par effet inductif -I.
Cela stabilise la base conjuguée donc elle est plus stable et l'acide est donc **plus acide**.
pKa 1.60

Me: Effet -I

c)



have replaced C with O
O is more electroneg, so
stabilizes the conjugate
base better.

increasing resonance, more stability
to conjugate base.