

Effect of Structure on the relative strength of acids and bases

To explain the acidity and basicity order of several compounds we have to consider the stabilities of acids and their conjugate bases and the stabilities of bases and their conjugate acids.

Considering the position of acid-base equilibrium, if the equilibrium is more favorable towards right higher is the acidity of acids and higher is the basicity for bases.

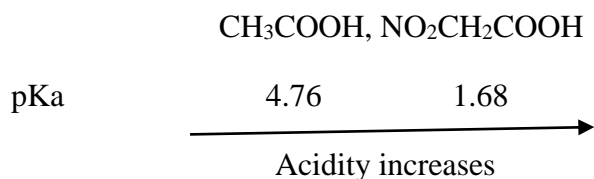
We can also explain the acidity order by considering the delocalization of electron density over the conjugated base (CB), higher the delocalization of negative charge density in the CB lower is the tendency to regain proton i.e., weaker the CB, higher is the acidity of corresponding acid.

Similarly basicity order is explained by considering the availability of lone pair of electrons of the base. If the availability is more, the basicity of the base is higher.

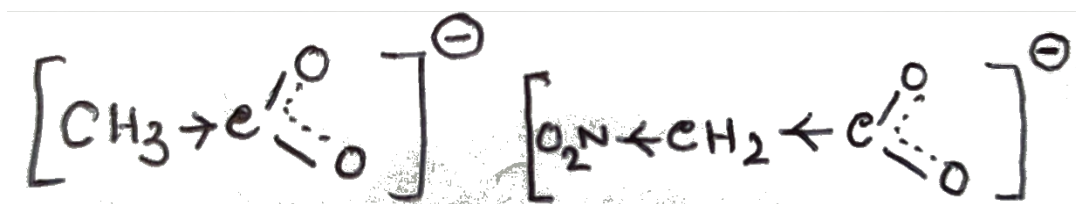
Inductive Effect

The presence of electron withdrawing substituents (-I effect) into the simple aliphatic acid increases the acidity, and the effect is increased with increasing the -I effect of the substituent.

- Let us compare the acidity of acetic acid and nitroacetic acid.



In case of CB of nitroacetic acid NO₂CH₂COO⁻, the negative charge over carboxylate ion is more dispersed due to the -I effect of NO₂ group.



So tendency of CB to regain proton is decreased compare to CB of acetic acid. Since higher the stability of CB higher is the acidity of corresponding acid thus nitroacetic acid is more acidic than acetic acid.

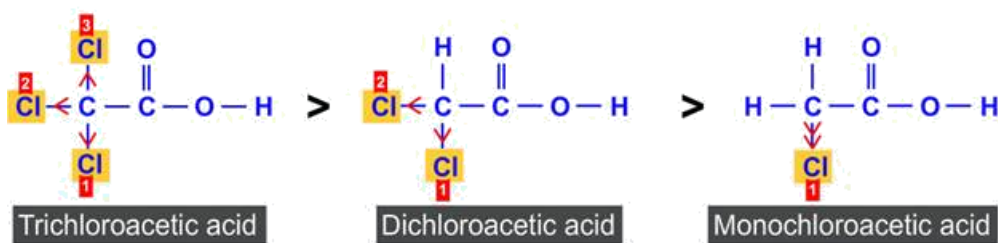
- Explain the acidity order



pKa	4.76	2.57	2.86	2.90	3.16
-----	------	------	------	------	------

Ans: With increasing $-I$ effect of substituents, the $-ve$ charge will be more dispersed in the CB of corresponding acids. As $-I$ effect of $\text{F} > \text{Cl} > \text{Br} > \text{I}$, so $-ve$ charge over carboxylate ion of fluoroacetic acid $\text{F-CH}_2\text{COO}^-$ is more dispersed than the other halogen substituted acid and therefore the acidity order is seen.

- Explain the acidity order of



Acidity of carboxylic acid increases with increasing the number of electron withdrawing group (Here Cl atom). This is because with increasing number of Cl atom, $-I$ effect will be increases and the negative charge over carboxylate ion will be more dispersed and CB will be more stabilized.

- Explain the acidity order of



pKa	2.84	4.06	4.52	4.82
-----	------	------	------	------

Ans: The introduction of halogen atom further away from the carboxyl group than the adjacent α - position has much less influence. Its inductive effect quickly dies away (decreases) down a saturated chain, with the result that the negative charge of carboxylate ion becomes progressively less dispersed i.e., more concentrated. Thus the acids behave like simple aliphatic acid.

- Explain the acidity order of

NO ₂ -CH ₂ -CO ₂ H, 1.68	Me ₃ N ⁽⁺⁾ -CH ₂ -CO ₂ H, 1.83	NC-CH ₂ -CO ₂ H, 2.47
EtO ₂ C-CH ₂ -CO ₂ H, 3.35	MeCO-CH ₂ -CO ₂ H, 3.58	MeO-CH ₂ -CO ₂ H, 3.53
HO-CH ₂ -CO ₂ H 3.83		

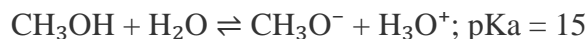
Higher the electron withdrawing effect (-I) of the substituent, it will pull the negative charge over carboxylate ion more i.e., the negative charge over carboxylate ion will be more dispersed, and acidity of corresponding acid will be increased.

As -I effect of NO₂ > Me₃N⁽⁺⁾ > NC > EtO₂C- > MeO- > MeCO- > HO. So acids follow the same order. Here +R effect of OMe and OH are not exerting in opposite direction to the -I effect.

Resonance effect

Resonance structures that stabilize a conjugate base will increase the acidity.

Consider the acidities of methanol and acetic acid.

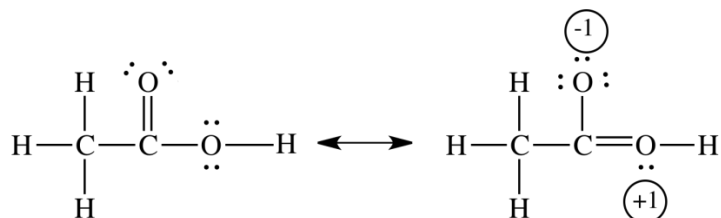


Why is acetic acid 10¹⁰ times as acidic as methanol?

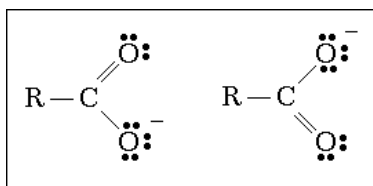
In methoxide ion, the negative charge is localized (concentrated) on the oxygen atom.

Resonance stabilizes both acetic acid and acetate ion,

In acetic acid, the stabilization is small because the resonance contribution involves separation of charge.



In acetate ion, there is no separation of charge.



Instead, the negative charge is delocalized (spread out) over three atoms. This delocalization produces a lower-energy state. **If the products of a reaction are more stable than the reactants, the position of equilibrium will lie to the right.**

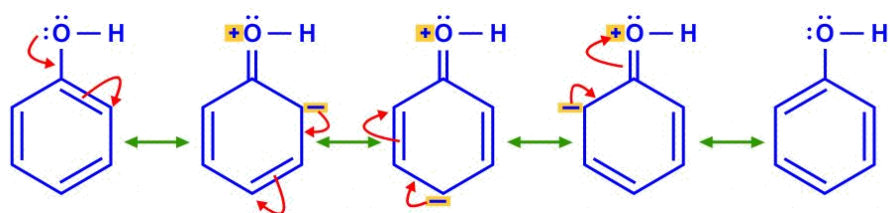
So, the resonance stabilization of acetate ion makes acetic acid more acidic than methanol.

In the same way, resonance makes phenol more acidic than ethanol

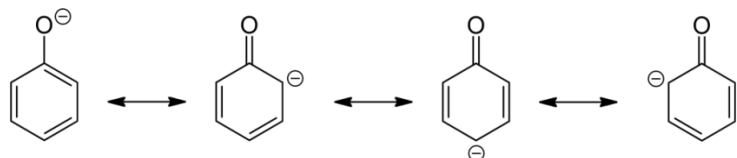
There is no resonance stabilization in the ethoxide ion.



Resonance stabilizes both phenol and phenoxide ion by delocalization of electrons into the ring. However, this delocalization in phenol involves separation of charge and makes the oxygen atom positive.



The same delocalization in phenoxide ion provides much more stabilization because there is no charge separation.

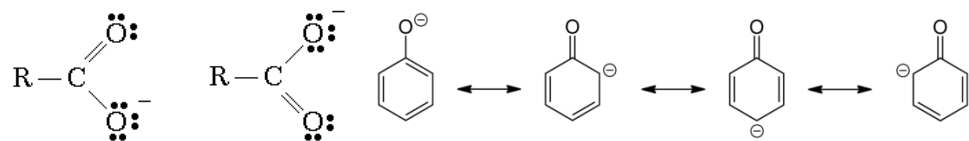


The position of equilibrium lies to the right. $\text{pK}_a=10$.

Thus, phenol is 10^7 times as acidic as ethanol because resonance stabilizes the phenoxide ion.

Why are carboxylic acids more acidic than phenol?

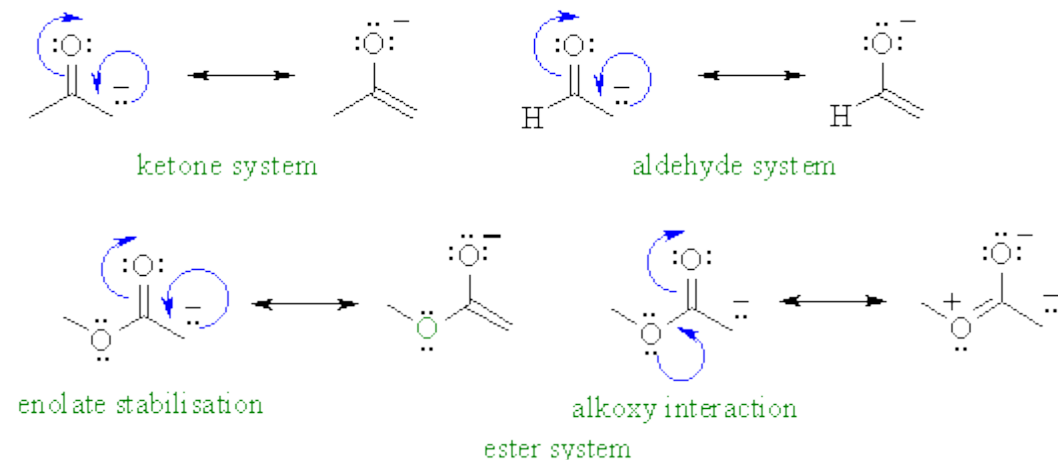
In carboxylate ion (CB of carboxylic acid) the two resonance canonicals are equivalent imparting greater stability to the anion, but this is not the case with phenoxide ion.



In case of canonical structures of carboxylate ion, the negative charge is on more electronegative oxygen but in case of phenoxide ion, the negative charge is present on less electronegative carbon (in 3 out of 4 structures). Thus carboxylate ion is more stable than phenoxide ion.

Again in case of carboxylate anion, there is also a strong $-I$ effect of the carbonyl carbon adjacent to the oxyanion centre, but in case of phenoxide this type of $-I$ effect of neighbouring sp^2 hybridised ring carbon is not so effective.

Compare pK_a of the common aldehyde $pK_a = 17$, ketone $pK_a = 19$ and an ester $pK_a = 25$



The aldehyde has a hydrogen attached to the common carbonyl, the ketone has an alkyl- group and the ester has an alkoxy- group attached to the common carbonyl.

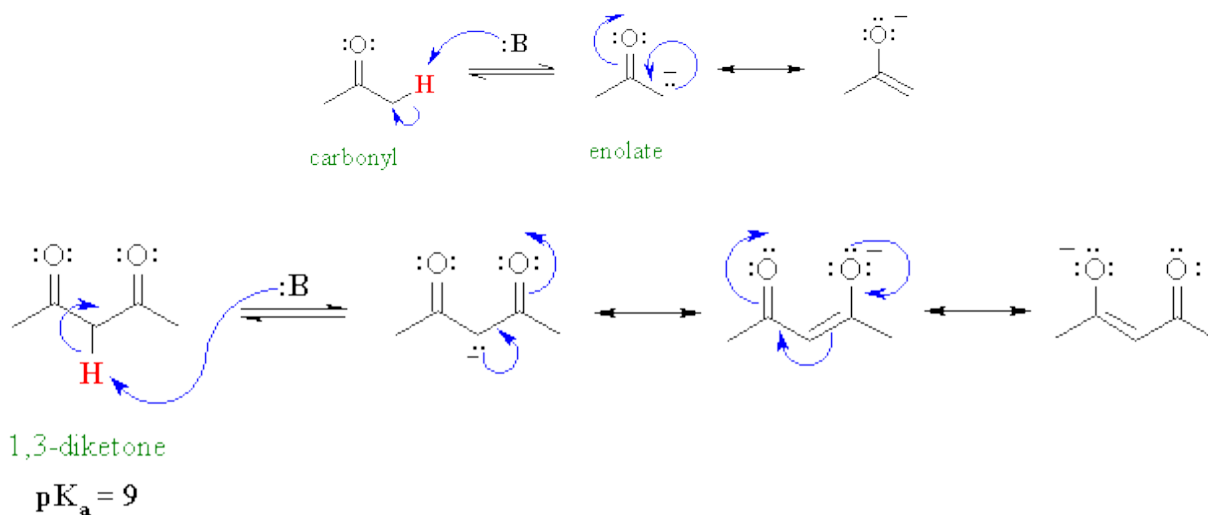
- H atoms are regarded as having no electronic effect : they don't withdraw or donate electrons.
- Alkyl groups are weakly electron donating, they tend to *destabilise* anions. This is because they will be "pushing" electrons towards a negative system which is *unfavourable* electrostatically. Hence, the anion of a ketone, where there are extra alkyl groups is *less stable* than that of an aldehyde, and so, a ketone is *less acidic*.
- In the ester, there is also a $+R$ effect from the alkoxy group towards the carbonyl that increases charge density of the enolate ion. This makes the ester enolate *less stable* than those of aldehydes and ketones so esters are even *less acidic*.

Compare the acidity of acetone and acetyl acetone

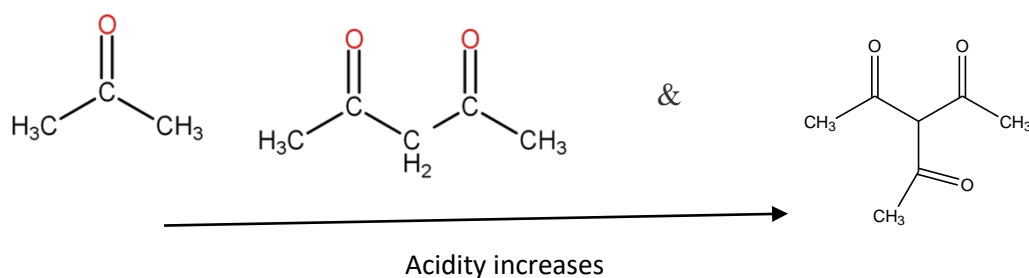


The more effective the resonance stabilisation of the negative charge, the more stable the conjugate base is and therefore the more acidic the parent system.

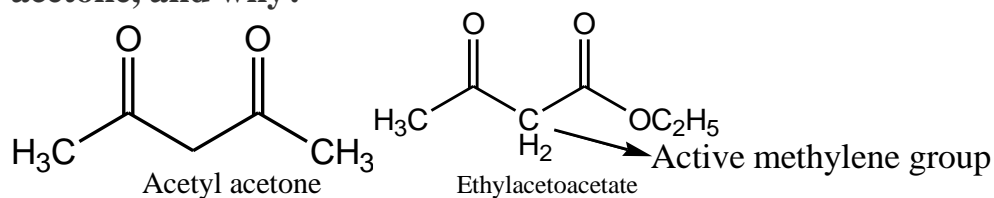
In acetylacetone, the middle hydrogens (on C3) are quite a bit more acidic than the hydrogens on acetone. In ketones, loss of H^+ from a carbon adjacent to the carbonyl group forms an enolate. In acetylacetone, there is an extra resonance structure as there are two adjacent carbonyl groups. This means that there is more resonance stabilisation of the anion since the charge can be delocalised to 2 electronegative oxygen atoms. This stabilizes this enolate more than an ordinary enolate, making the hydrogen more acidic.



Note: From the study it is clear that if we introduce more electron withdrawing group to the C3 carbon, the acidity of corresponding methylene group is expected to increase further, as the dispersion of negative charge on the CB will be higher through resonance. Greater the dispersion of negative charge over CB of an acid through resonance, higher is the acidity of the acid.

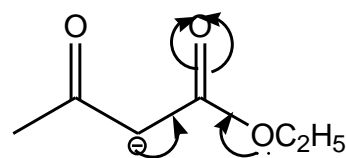
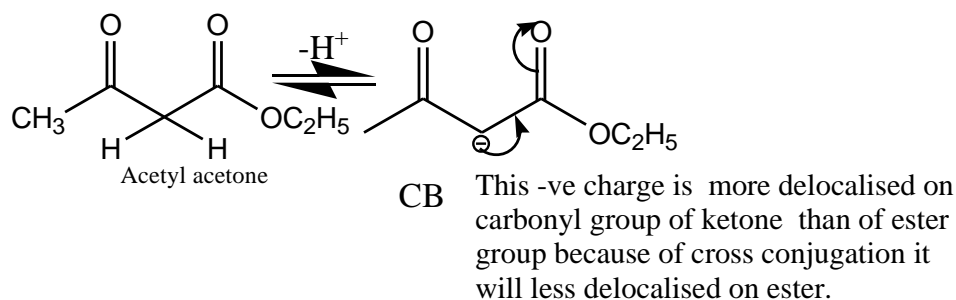
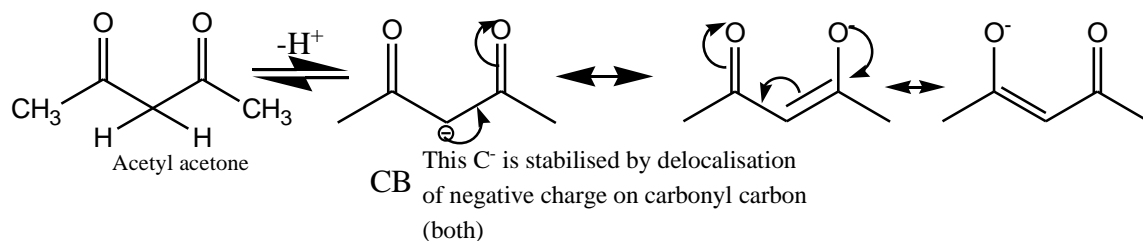


Which has the more acidic active methylene group, ethyl acetate or acetyl acetone, and why?



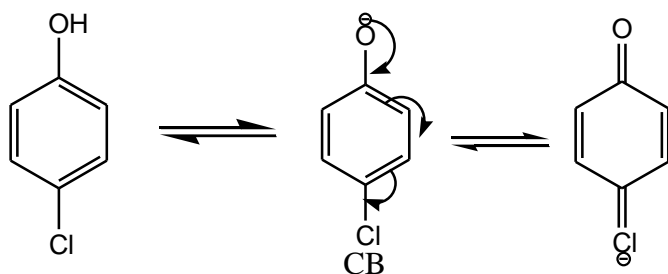
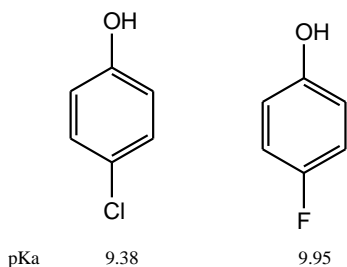
In the case of acetyl acetone (acac) the methylene group is flanked by two electron withdrawing carbonyl groups the removal of hydrogen become easier and the resulting anion is stabilised by resonance. These two driving force resulting in increasing the acidity.

Whereas in ethyl acetoacetate (EAA) the methylene group is flanked by a keto group and an ester group. Due to resonance (+R effect) of the ester carbonyl, the electron withdrawing power is reduced compared to acetyl acetone. In E.A.A two competitive resonance are present which act in opposite direction resulting in lower gain of resonance stabilisation of conjugate base of E.A.A

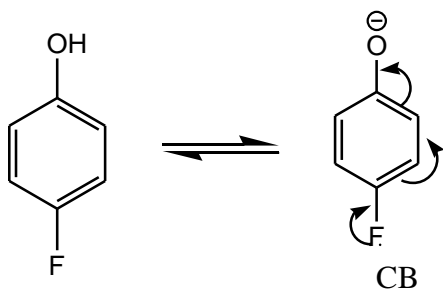


Ester enolate is cross conjugated
So -Ve charge is less delocalised over ester carbonyl.

• Account for the acidity difference:



In this CB the -ve charge is dispersed through resonance with benzene ring as well as low lying vacant d orbital of Cl. ($p_{\pi}C-d_{\pi}Cl$) bonding.

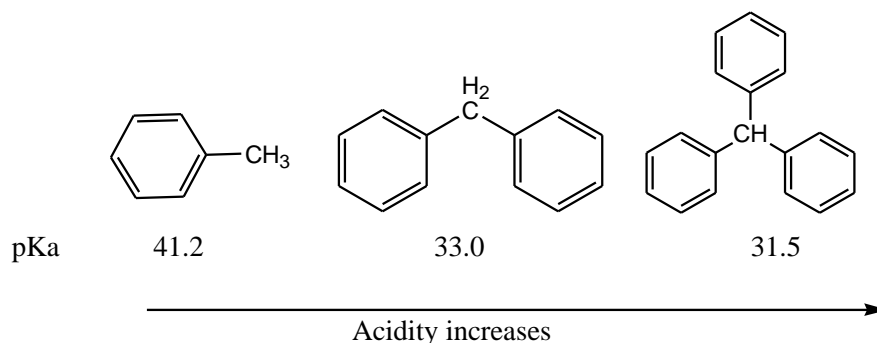


Here -ve charged is only dispersed through resonance with benzene ring. As F has not low lying vacant d orbital, so dispersion of -ve charge is less compared to the case of CB of p-chlororophenol.

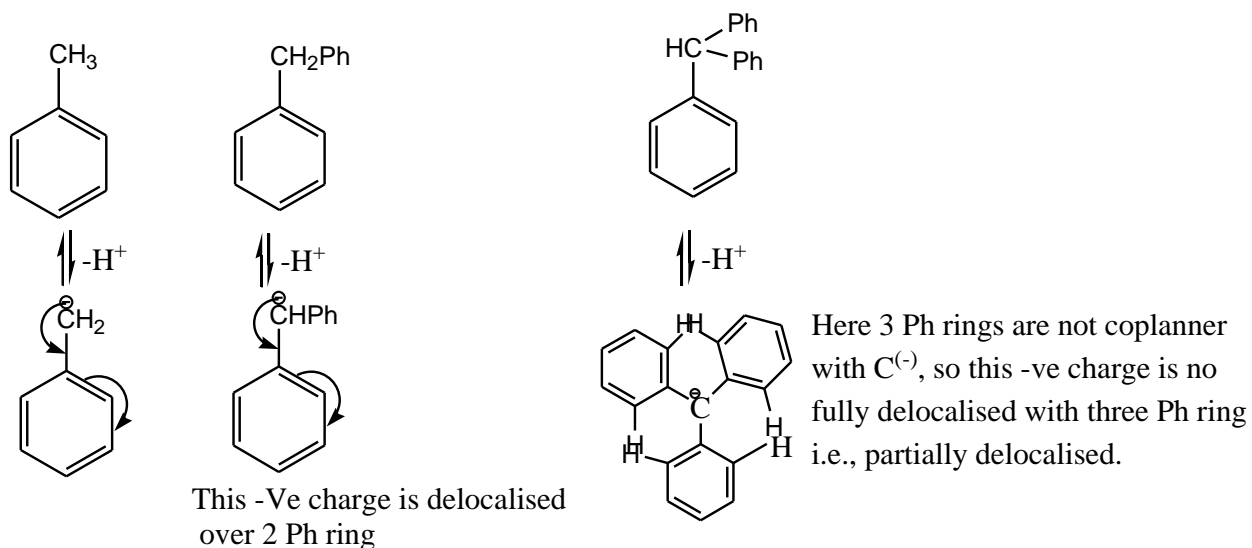
Since +R effect of F is more pronounced (2p-2p overlap) than +R effect of Cl (3p-2p overlap), so F increases charge density over its phenoxide ion than that of Cl. So tendency of regain proton increases in case of p-fluorophenoxide ion. Again -ve charge density is more dispersed in p-chlororophenoxide anion. So tendency of regain proton decreases in case of p-chlororophenoxide ion. Therefore p-chlororophenol is more acidic than p-fluorophenol.

Steric inhibition of resonance

Which of the mono-, di-, triphenyl methane is the most acidic- explain.



In monophenyl benzene i.e., toluene after removal of proton the CB become benzylic carbanion, in which the negative charge is delocalized by resonance with benzene ring. In this way the CB is stabilized. If second Ph ring is introduced the corresponding CB will be more stabilized due to additional resonance effect. So biphenyl methane is more acidic than toluene. However the third Ph ring has small effect because in this case due to steric effects between ortho hydrogens three Ph rings cannot be in same plane with the carbanion. So negative charge of CB cannot be in complete conjugation with three Ph ring and full resonance stabilization cannot be gained. So expected increase of acidity cannot be seen.



Similar Questions:

Explain the acidity order CH_3NO_2 , $\text{CH}_2(\text{NO}_2)_2$, $\text{CH}(\text{NO}_2)_3$

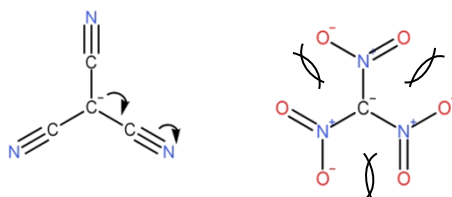
pKa 10.2 3.6 0.2

& CH_3CN , $\text{CH}_2(\text{CN})_2$, $\text{CH}(\text{CN})_3$

pKa 25 11.0 -5

We can see from the data that acidity of $\text{CH}_3\text{NO}_2 > \text{CH}_3\text{CN}$, As $-I$ effect of NO_2 group is greater than CN so in CB of CH_3NO_2 the negative charge is more delocalized than that in CB of CH_3CN . So acidity of $\text{CH}_3\text{NO}_2 > \text{CH}_3\text{CN}$.

But acidity of $\text{CH}(\text{NO}_2)_3 < \text{CH}(\text{CN})_3$, because in the CB from trinitro methane the three nitro group cannot all be coplanar with the anionic carbon as nitro group is trigonal planar in shape so negative charge is not fully delocalized with three nitro group. On the other hand three cyano groups are expected to be in the same plane with the anionic carbon as cyano groups are linear. So negative charge is fully delocalized with three CN groups. Now as dispersion of negative charge is greater for CB of $\text{CH}(\text{CN})_3$ than that of $\text{CH}(\text{NO}_2)_3$ so we see the acidity order $\text{CH}(\text{NO}_2)_3 < \text{CH}(\text{CN})_3$.



To be continued