ADVANCED CHEMISTRY BLOC

(ACIDIC STRENGTH, AN ANALYSIS)

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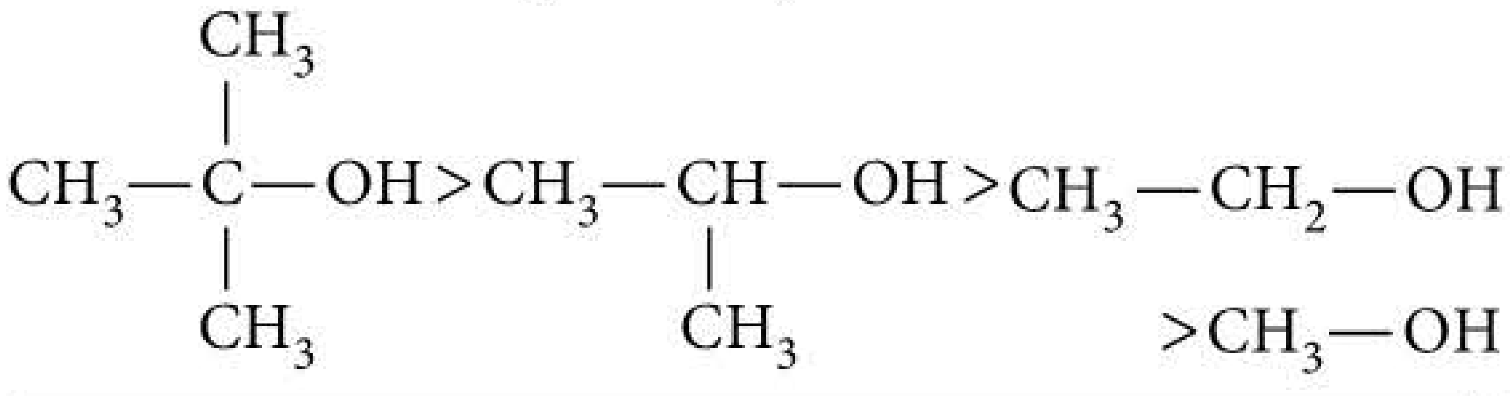
"An electronegative atom raises the acidity of carboxylic acids". It's a very common sentence. For example, $Cl-CH_2COOH$ is more acidic than CH_3COOH.

One quite interesting trend is that the interchange of atoms with different electronegativities does not necessarily yield the expected results. For example, examine the acidities of various halogenated acetic acids. The most acidic is iodoacetic acid $(I-CH_2-COOH)$ and the least acidic is fluoroacetic acid $(F-CH_2-COOH)$. Similarly, of the substituted methanes, the most acidic is iodomethane (CH_3I) and the least acidic is fluoromethane (CH_3F). This can be understood on the grounds that iodine is more polarisable than fluorine, being better able to accept and spread out the increase in electron density than the smaller harder fluorine in the absence of any solvent to mediate the charge. This happens to be gas phase acidity. Measurement of acidity in water, in many instances although show a very different order. In fact, although surprising at first glance, chloroform $(CHCl_3)$ is more acidic than fluoroform (CHF_3) in water by a factor of 10^7, again because of polarisable chlorine.

Another interesting and important trend is :



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH > CH_3-\underset{CH_3}{\underset{|}{CH}}-OH > CH_3-CH_2-OH > CH_3-OH$$

Acidity decreases in gas phase

Larger the size of the alkyl group, more is the acidity. Once again polarisation is found to be important. Larger the alkyl group, the better it can accept the increase in electron density upon heterolysis of the $O-H$ bond. Interestingly, the exact reverse order of acidity is found in solution, where methanol is the strongest acid.

Effect of solvents

Organic solvents generally lower acidity whereas polar solvents increase acidity.

Electrostatic interactions influence acidity

The second pK_a of a dicarboxylic acid is higher than the first pK_a due to formation of a dianion with the associated electrostatic repulsion.

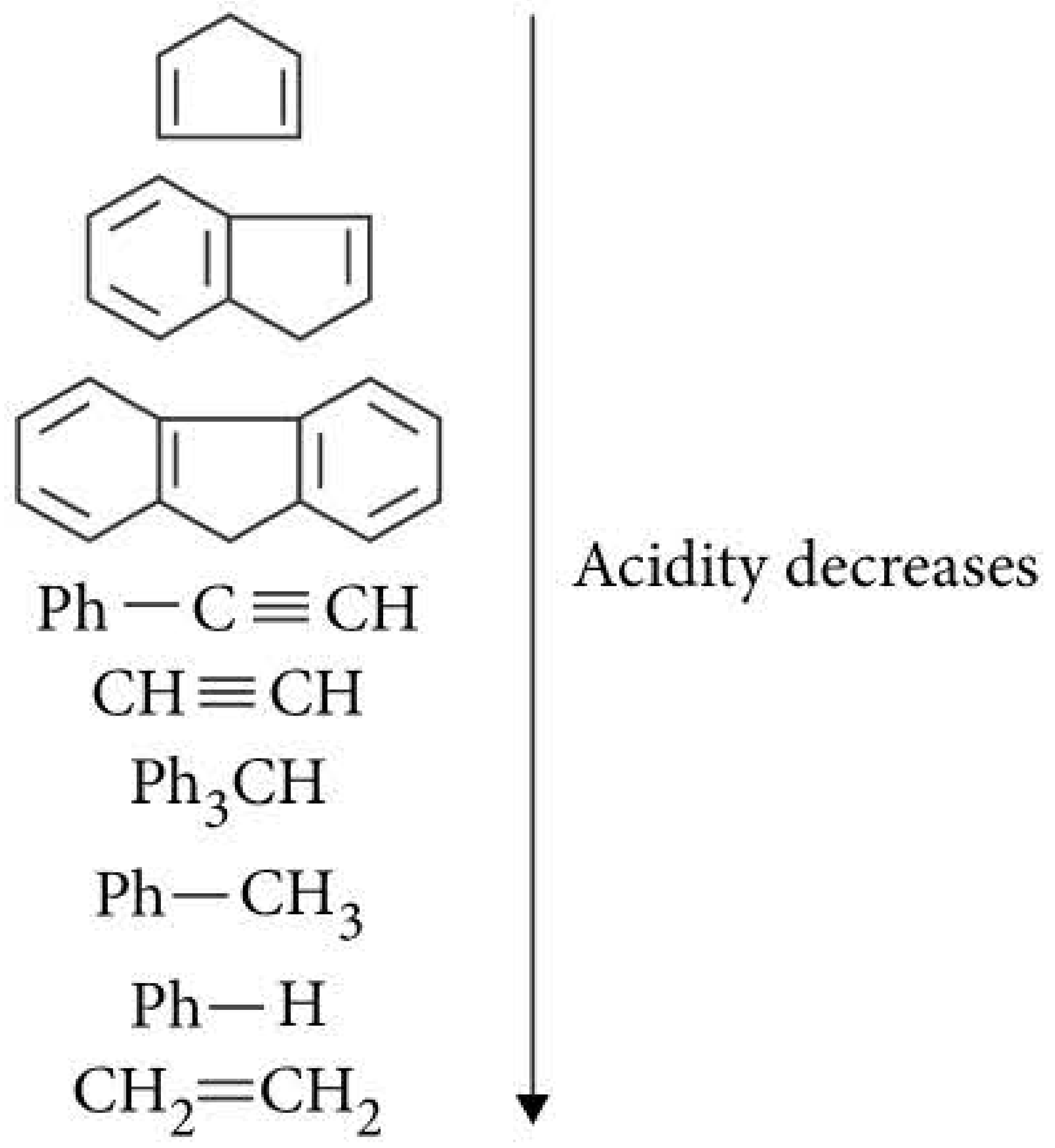
Dispersal of charge

As you have seen above, *t*-butyl alcohol is more acidic than ethanol in gas phase because the negative charge on the oxygen of corresponding alkoxide of *t*-butyl alcohol is easily dispersed on large number of alkyl groups. This explains the stability of conjugate base.

What if the acid itself is carrying charge? For example, NH_4^+, $CH_3\overset{+}{N}H_3$ and $(CH_3)_2\overset{+}{N}H_2$. In a same line of argument as you have seen for alkoxide, we expect the charge is more stabilised when we have more alkyl groups. That's what exactly we find. NH_4^+ is more acidic than $CH_3\overset{+}{N}H_3$ and which in turn is more acidic than $(CH_3)_2\overset{+}{N}H_2$. With more alkyl groups and more dispersal of charge, $(CH_3)_2\overset{+}{N}H_2$ does not feel like donating a proton.

Acidity of some hydrocarbons

Based on data,



$Ph-C\equiv CH$

$CH\equiv CH$

Ph_3CH

$Ph-CH_3$

$Ph-H$

$CH_2=CH_2$

Substituent effects on the strength of Bronsted acids

Based on data,

HF
*R*COOH
H_2CO_3
H_2S
ArSH
$RCOCH_2COR$
HCN
NH_4^+
ArOH
RCH_2NO_2
*R*SH
H_2O

*R*OH
$RCOCH_2R$

↓ Acidity decreases

Acid - Base equilibrium

As per Bronsted theory, equilibrium position of acid-base favours weaker acids and weaker bases.

For example,

$$\underset{\text{Acid-1}}{HCl} + \underset{\text{Base-1}}{H_2O} \rightleftharpoons \underset{\text{Acid-2}}{H_3O^+} + \underset{\text{Base-2}}{Cl^-}$$

If you see the reaction from the reverse side, H_3O^+ is the acid and Cl^- is the base. The equilibrium lies largely towards right as H_3O^+ is weaker acid than HCl and Cl^- is a weaker base than H_2O.

$$CH \equiv CH + 2NaOH \rightleftharpoons \overset{+}{Na}\overset{-}{C} \equiv \overset{-}{C}\overset{+}{Na} + 2H_2O$$

H_2O is a stronger acid than acetylene. Thermodynamics does not like to see strong acids are formed at the cost of weak acids in the medium. But

$$CH \equiv CH + AgNO_3 + NH_4OH \longrightarrow \underset{\text{ppt.}}{AgC \equiv CAg\downarrow} + NH_4NO_3 + H_2O$$

Don't you see this is a product favoured reaction; H_2O is formed at the expense of acetylene. This is because $AgC \equiv CAg$ is a precipitate. As it runs out of the medium, the reaction shifts towards right following Le Chatelier's principle.

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