

### Electrophiles:-

An electrophile is an electron deficient species. It may be an electron deficient positively charged species or an electron deficient neutral molecule. In reaction, the electrophiles get bonded to a site, which is rich in electron.

Positively electrophiles:  $H^+$ ,  $B^+$ ,  $Li^+$ ,  $NO_2^+$ ,  $R^+$ ,  $CH_3C^+=O$

Neutral electrophiles  $CO_2$ ,  $SO_3$ ,  $BF_3$ ,  $AlCl_3$ ,  $\ddot{C}Cl_2$

Nucleophiles:- They are electron rich species and in general any nucleophile bears atleast one lone pair of electrons. The nucleophiles may be negatively charged or neutral molecules. In a reaction, they always seek a site to which electrons can be donated, that is, nucleophiles get bonded to electron deficient centres.

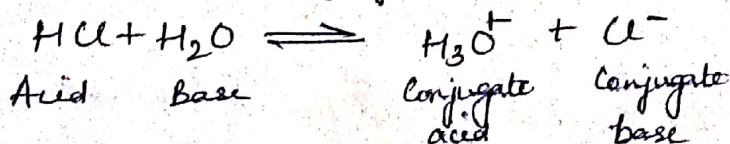
Negative Nucleophiles:-  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{SR}^-$ ,  $\text{H}^-$ ,  $\text{CN}^-$ ,  $\text{NH}_2^-$

Neutral Nucleophiles:-  $\text{NH}_3$ ,  $\text{R}-\ddot{\text{O}}-\text{R}$ ,  $\text{R}-\ddot{\text{O}}-\text{H}$ ,  $\text{R}-\ddot{\text{S}}-\text{H}$ ,  $\text{H}_2\ddot{\text{O}}$

## Acids & Bases

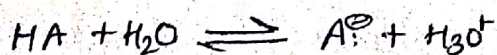
### Bronsted-Lowry Definition:-

An acid is defined as a proton donor and base as a proton acceptor. In a reaction, an acid loses a proton to form a conjugate base whereas a base gains a proton to form conjugate acid.



A strong acid has a weak conjugate base and weak acid has a strong conjugate base. Similarly, a strong base has a weak conjugate acid and a weak base has a strong conjugate acid.

⇒ The relative strength of acids or bases is expressed in terms of their dissociation constant values  $K_a$  &  $K_b$  or in terms of  $pK_a$  &  $pK_b$  values.



$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]}$$

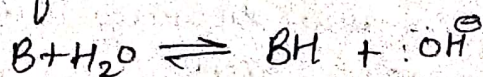
$\text{H}_2\text{O} = \text{Solvent}$

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

Larger the value of  $K_a$ , the stronger is the acid. that is,  $K_a \propto \text{acidic strength}$   
 $pK_a = -\log K_a$

Higher the value of  $pK_a$ , lower is strength of acid. This can be expressed as  $pK_a \propto \frac{1}{\text{acid strength}}$

in similar way for bases



(1)

$$K_b = \frac{[BH][OH^-]}{[B]}$$

\* Larger the value of  $K_b$ , stronger the base.

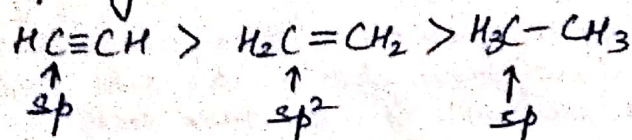
$$pK_b = -\log K_b$$

\* Higher the value of  $pK_b$ , lower is the strength of base.

According to Lewis definition, a base is a substance that can furnish an electron pair to form a covalent bond and acid is a substance that can take up an electron pair to form covalent bond. Thus an acid is an electron-pair acceptor and base is an electron pair donor.

\* A compound is acidic, if conjugate base can stabilise through resonance. Thus phenol ( $C_6H_5OH$ ) is acidic while ethanol is neutral,  $\therefore$  conjugate base of phenol ( $C_6H_5O^-$ ) can stabilise through resonance while that of alcohol ( $C_2H_5O^-$ ) can not. Similarly  $C_6H_5COOH$  is stronger acid than  $CH_3COOH$ .

\* H-atom attached to  $sp$ -hybridised carbon is more acidic than that on  $sp^2$  hybridised carbon, which in turn is more acidic than that on  $sp^3$  hybridised carbon atom



\*  $-I$  effect increases acidic strength whereas  $+I$  effect decreases.

\* Carboxylic acids are stronger acids than phenols.

~~Effect~~ Effect of substituents on acidic strength of carboxylic acid! —

① Effect of electron donating substituents alkyl group —



Methyl group present in acetic acid molecule has electron donating inductive effect ( $+I$  effect). This will increase the electron density in  $O-H$  bond. As a result, ~~the electron density in the  $O-H$  bond.~~ the release of  $H^+$  ions from acetic acid will be more difficult as compared to formic acid.

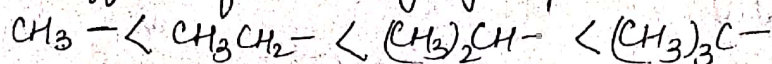


$+I$  effect of  $CH_3$ -group intensifies the negative charge on the carboxylate ion thereby making acetate ion less stable than formate ion

As a result, the result of  $H^+$  ion from acetic acid will become more difficult as compared to formic acid. Hence formic acid is a stronger acid than acetic acid.

\*  $Y \rightarrow C \begin{matrix} \nearrow O \\ \searrow O^- \end{matrix}$  { An electron releasing substituent  $\rightarrow$  release electron and destabilises anion, Acidity decreases }

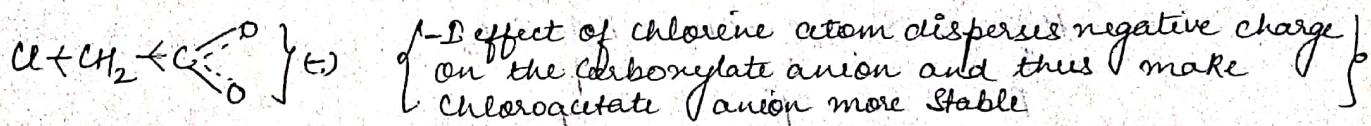
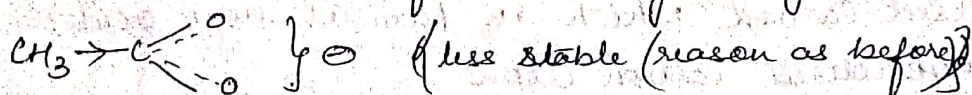
\* +I-effect of the alkyl groups increases in the order:



\* Effect of electron withdrawing substituent



The halogen atom (i.e. Cl) has electron withdrawing inductive effect. Chlorine atom withdraws electrons from the O-H bond. As a result, electron density in the O-H bond decreases. In other words, it facilitates the release of  $H^+$  ions by making the O-H bond weaker.



\* -I effect of halogen decreases in order  $F > Cl > Br > I$

\* Greater the number of electron withdrawing substituents, greater will be the dispersal of negative charge and hence stronger will be acid.

Ex- trichloroacetic acid is stronger acid than dichloroacetic acid

