

Class - U.G. sem - I

Paper - MJC - 1 (T)

Unit - 3

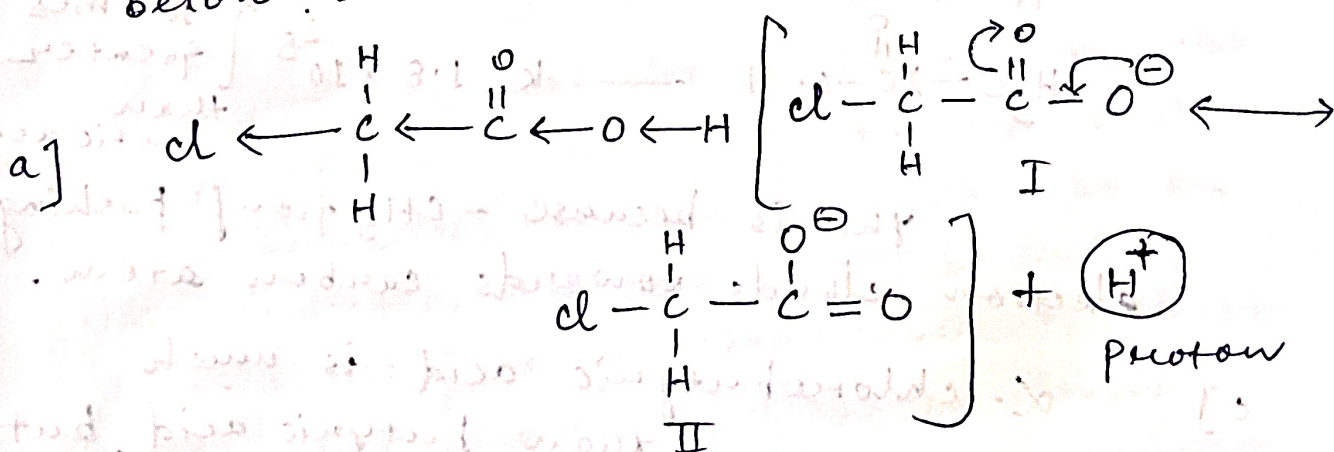
Topic - Inductive effect continued....

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Dept. of chemistry

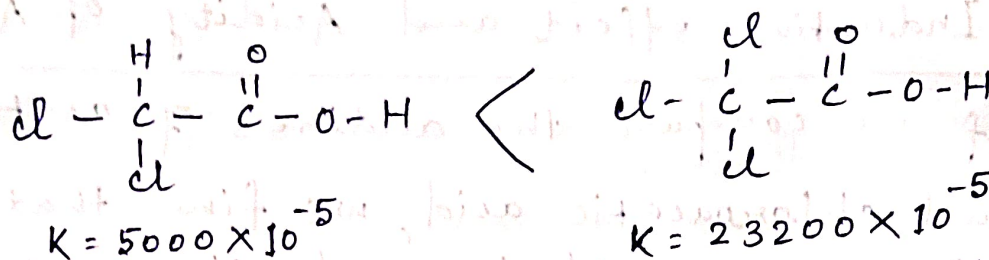
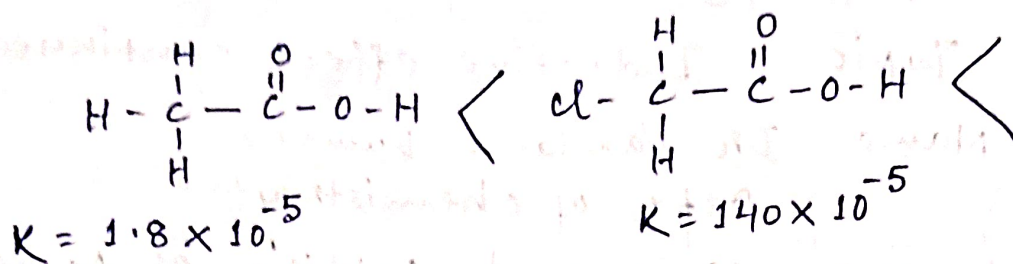
Inductive effect and Acidity of Acids:

If we compare the acidities of acetic acid and chloroacetic acid, we find that the chloroacetic acid is much stronger than the acetic acid. Cl has $-I$ effect and it decreases the electron-density on the carbon atom carrying chlorine. This decrease in electron density on the carbon of ClCH_2- sets up a relay of electrons away from $-\text{COOH}$ (and thereby facilitates the removal of the proton) as shown below: -



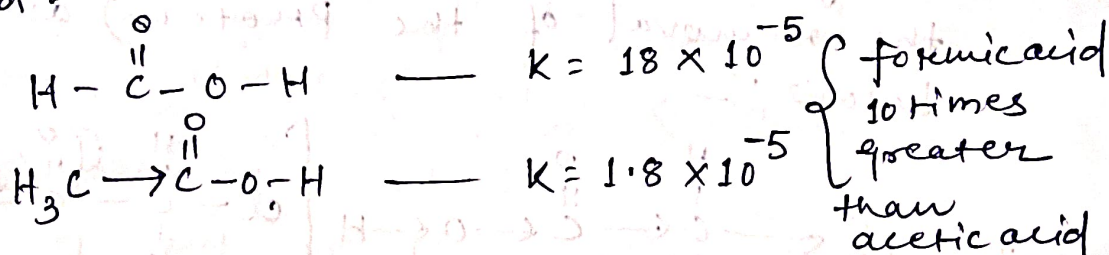
Thus greater the number of electronegative (chlorine) atoms in an acid molecule, the greater is the stability of carboxylate anion due to the greater electron-withdrawing Inductive effect of the electronegative (Cl) atom.

Dichloroacetic acid and trichloroacetic acid should be even stronger and this is actually so.



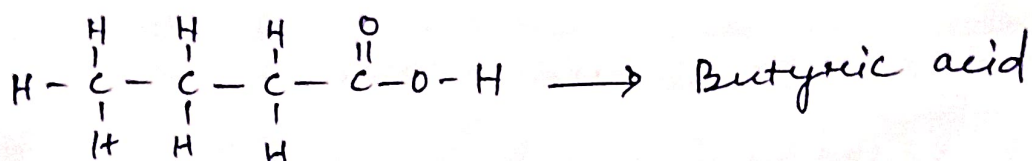
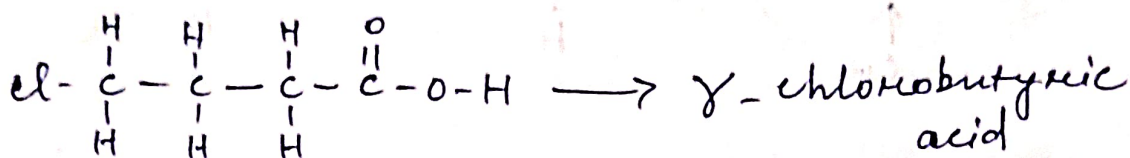
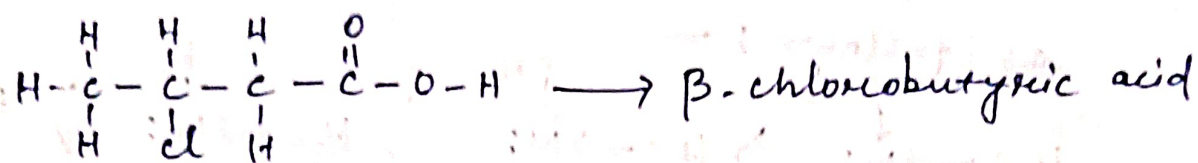
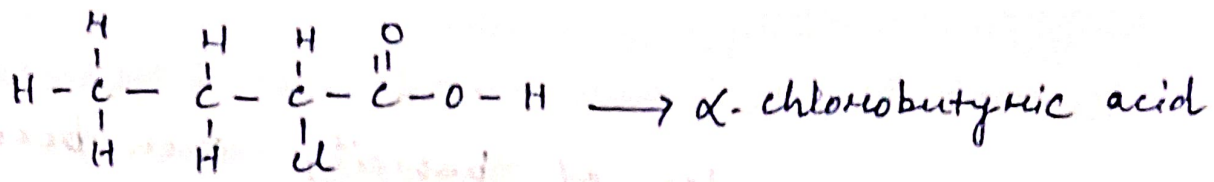
K = Dissociation constant for acid

b] Methyl group ($-\text{CH}_3$) on the other hand exhibits +I effect and as such acetic acid should be a weaker acid than formic acid this what we find:



this is because $-\text{CH}_3$ group pushing electron clouds towards carbon atom.

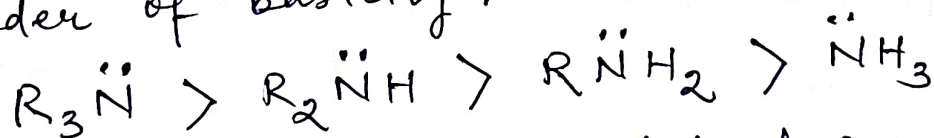
c] α -chlorobutyric acid is much stronger acid than butyric acid, but isomeric β and γ -chlorobutyric acid are only slightly stronger.



This is an agreement with the fact that the inductive effect diminishes rapidly with distance.

2.7 Tertiary amine is more basic than NH_3 , secondary and primary amines: —

The organic bases have the order of basicity:—



This order can be explained on the basis of +I effect of the group R. The more the number of R-groups on the nitrogen, the more will be the availability of its lone pair of electrons and hence more will be the basicity of the compound. This order of basicity of amine is disturbed if the alkyl group R, is bigger than C_2H_5 or CH_3 , because the steric hindrance which does not allow the lone pair to be readily available for donation to a proton.

the order of basicity then become

as follows : —

