

Inductive Effect

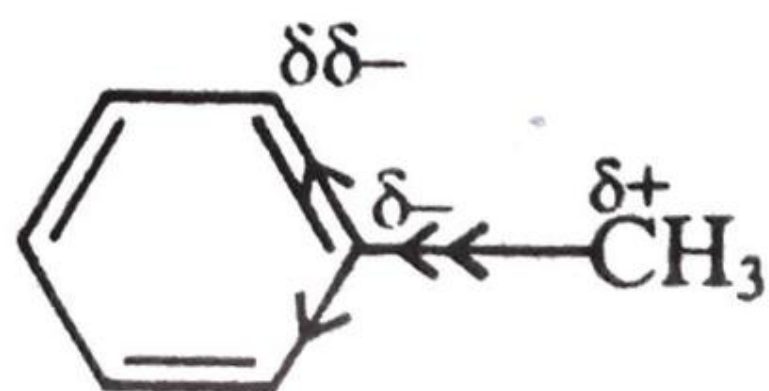
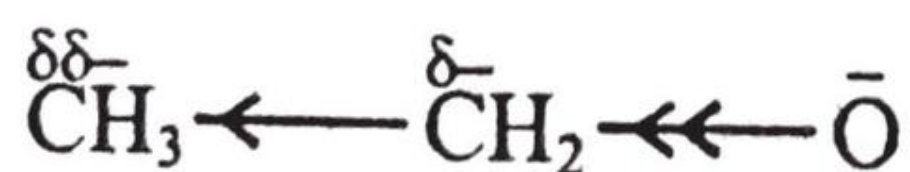
Electronegativity of chlorine atom makes carbon-chlorine bond in chloroethane polar, depriving the carbon atom of some of its electron density and producing a partial positive charge on it. This electron deficiency of carbon is partially compensated by drawing the electrons of the next bond closer to it, resulting in the polarization of this bond with a slight positive charge on the second carbon atom. However, this positive charge on the second carbon atom will be smaller than the positive charge of the first carbon atom.



This type of *polarization of a bond induced by an adjacent polar bond* is known as the **inductive effect**. Inductive effect may be induced by a dipole as explained above in the case of chloroethane or by a formal charge as in the case of ethyltrialkylammonium cation.



Similarly, inductive effect may operate in the opposite direction, depending on the nature of the functional group, e.g.,



Thus, the inductive effect can be considered as a dipole-dipole or a charge-dipole interaction. The inductive effect *operates through σ bonds* and is greatest for adjacent bonds decreasing rapidly with the distance so that in most cases it causes very little effect on a bond four bonds away.

The functional groups responsible for producing inductive effect, can be classified as with an electron-withdrawing inductive effect ($-I$) or with an electron-donating inductive

effect (+I), relative to hydrogen, depending on whether they are more electronegative or less electronegative than hydrogen. Some of the common -I and +I groups are listed below, approximately in the order of decreasing inductive effect.

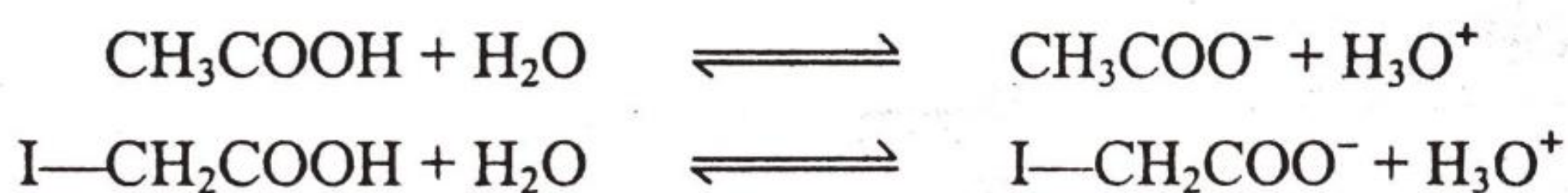
Electron-withdrawing groups (-I): $-\overset{+}{\text{N}}\text{R}_3$, $-\overset{+}{\text{N}}\text{H}_3$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CO}_2\text{H}$, $-\text{F}$,
 $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OAr}$, $-\text{CO}_2\text{R}$, $-\text{OR}$, $-\text{COR}$,
 $-\text{OH}$, $-\text{C}\equiv\text{CR}$, $-\text{Ar}$, $-\text{CH}=\text{CR}_2$.

Electron-donating groups (+I): $-\text{O}^-$, $-\text{CO}_2^-$, $-\text{CR}_3$, $-\text{CHR}_2$, $-\text{CH}_2\text{R}$, $-\text{CH}_3$,
 $-\text{D}$.

Alkyl groups are usually classified as weakly electron-donating, but in recent years there has been considerable evidence that their effect may be either -I or +I, relative to hydrogen, depending on the situation.

It may be emphasized that there is no actual withdrawal or donation of electrons; there is merely a difference in the position of electrons due to the difference in electronegativity between hydrogen and the functional group.

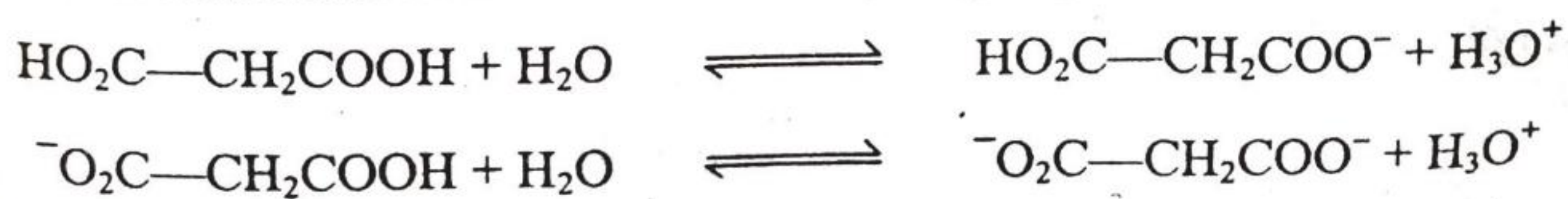
The concept of inductive effect is very useful in either explaining or predicting the behaviour of organic compounds. For example, iodoacetic acid is about 40 times more acidic than acetic acid (Table 1.9). This can be explained by the fact that iodine being electronegative with an -I effect, can stabilize the carboxylate ion which is produced after the ionization of the acid, by dispersing its negative charge. It, therefore, favours the ionization of the carboxylic acid and thus enhances its acidity.



Chlorine being more electronegative than iodine, is expected to further increase the acidity, and, in fact, chloroacetic acid is about twice as acidic as iodoacetic acid. Trichloroacetic acid is about 10^4 times more acidic than acetic acid. The pK_a values of 2-, 3- and 4-chlorobutanoic acids illustrate how the inductive effect decreases with distance.

On the other hand, the electron-donating groups (+I) destabilize the carboxylate ion relative to the carboxylic acid and thus decrease its acidity. Acetic acid is 10 times less acidic than formic acid due to the presence of methyl group which is generally regarded as electron-donating as compared to hydrogen.

Ionization of the first carboxylic group in a dicarboxylic acid is enhanced by the electron-withdrawing inductive effect of the second carboxylic group but the carboxylate ion thus produced having an electron-donating inductive effect, has an unfavourable influence on the ionization of the second carboxylic group.



Thus, the second ionization constant is usually less than that of a monocarboxylic acid. For example, compare the first and the second ionization constants of malonic acid with that of acetic acid (Table 1.9).