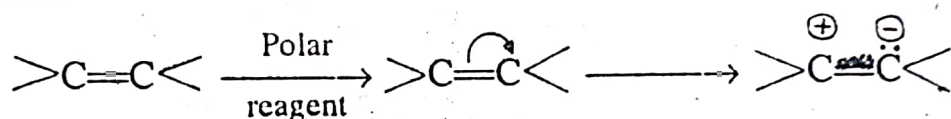


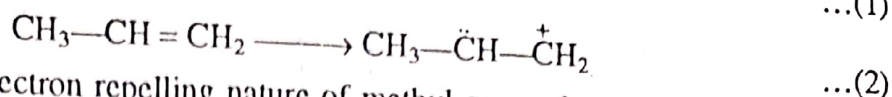
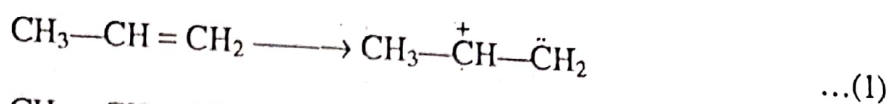
(iii) **Electromeric Effect.** It has been discussed earlier that a multiple bond consists of  $\sigma$  and  $\pi$  bonds. Due to the nature of  $\pi$  bonding the electrons involved in such a combination are loosely held and easily polarisable. Therefore, when a compound having double or triple bond is approached by a charged reagent, the electrons of the bond are completely polarised or displaced towards one of the constituent atoms due to electrostatic attraction or repulsion. Thus:



The atom that now acquires the electrons pair, becomes negatively charged while the other atom gets a positive charge.

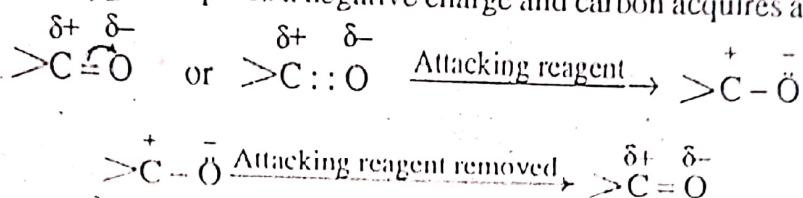
The effect, involving the complete transfer of a shared pair of electrons to one of the atoms joined by a double or triple bond at the requirement of attacking reagent, is known as *Electromeric effect* (E effect). It is a temporary effect and brought into play instantaneously at the demand of the attacking reagent. However, as soon as the attacking reagent is removed original electronic condition is restored.

Usually the electromeric effect precedes a polar or ionic addition reaction. In cases, where the constituent atoms linked by the multiple bond are similar, the direction of electromeric shift is not important. As displacement of electrons to either of the constituent atom will lead to similar structures. However, if one of the doubly bonded atom is linked to an electron withdrawing or electron releasing group, then the direction of electromeric shift is determined by the direction of the inductive influence of such a group. For example in propylene, the electromeric effect can be represented in two possible manners without considering the effect of methyl group.



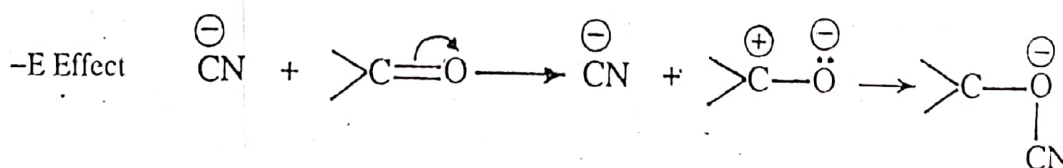
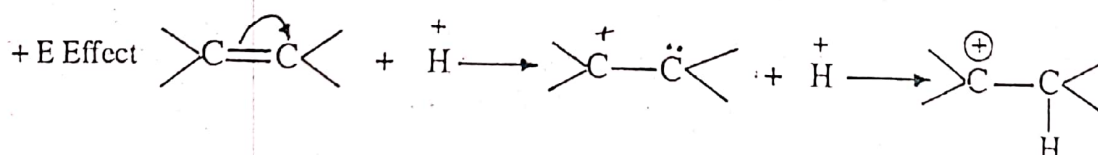
However, due to electron repelling nature of methyl group the electromeric shift will occur as in (1) and not as depicted in (2) because the latter type of shift opposes the electron releasing influence of methyl group. An opposite situation is encountered when an electron withdrawing group is present in place of electron releasing group.<sup>1</sup>

In case where one of the atoms involved in multiple bond is more electronegative, the electromeric shift of electrons is towards more electronegative atom. This effect may be best illustrated by taking the example of carbonyl group. Initially there is a small negative charge on oxygen and a small positive charge on carbon atom because of greater electronegativity of the oxygen. When a charged reagent approaches the carbonyl group one of the two shared pairs of electrons (in fact  $\pi$  electrons) is completely transferred to oxygen. As a result of this, oxygen acquires a negative charge and carbon acquires a positive charge.



Such a carbon atom (with a positive charge) may now react with a reagent rich in electrons and then oxygen may combine with an ion deficient in electrons resulting in addition to carbonyl group.

The electromeric effect is indicated by 'E' and represented by a curved arrow showing the direction of shifting of electron pair. When the transfer of electron pair takes place towards the attacking reagent (electrophile), the effect is called + E effect and when the transfer occurs away from the attacking reagent (nucleophile) the effect is called - E effect.



*In cases where inductive and electromeric effects operate simultaneously usually the electromeric effect predominates.*

### Applications of Electromeric Effect

Electromeric effect is very useful in explaining addition reactions of the compounds having double or triple bonds.

**1. Addition to Alkenes or  $>\text{C}=\text{C}<$ .** Simple examples are addition of bromine and hydrobromic acid to ethylene.

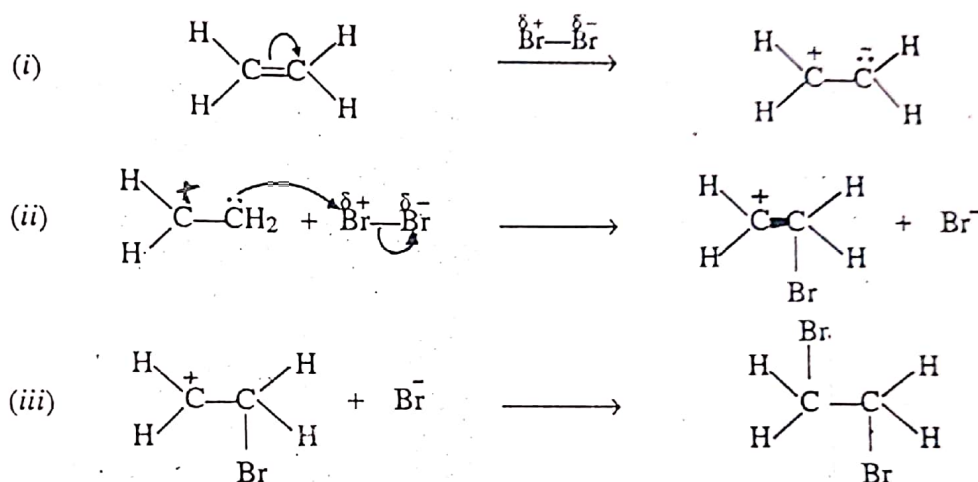
1. Usually electron withdrawing atoms and groups have lone pair of electrons. If the lone pair of electrons is conjugated (see later) with multiple bond, then conjugation effect is more important than electromeric effect and it may even reverse the direction of electron shift as in the case of vinyl halides (see later).



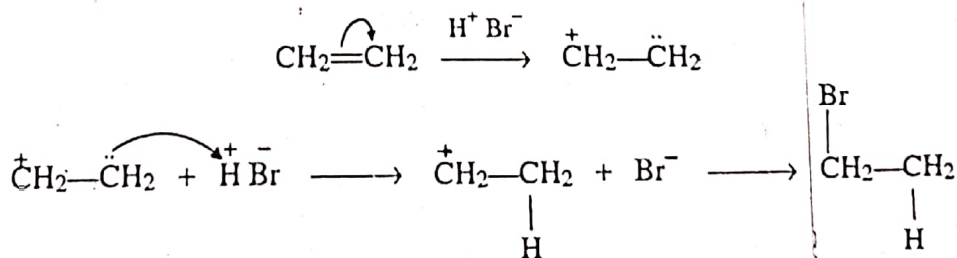
Ethylene molecule does not have an ionic character but at the requirement of the attacking reagent the normal distribution of electrons is disturbed. In the addition of bromine the symmetrical bromine molecule gets polarised on approaching the  $\pi$  electrons of ethylene molecule. This polarised bromine molecule ( $\delta^+ \text{Br} - \delta^- \text{Br}$ ) then causes the electromeric displacement of  $\pi$  electrons to one of the carbon atom constituting the double bond. Thus one carbon atom acquires a positive and the other one a negative charge.

The electrons then attack the electrophilic<sup>1</sup> (positively charged) end of the bromine molecule ( $\text{Br}^{\delta+}$ ) which combines with this carbon releasing the bromide ion and forming a carbonium ion.

Lastly the bromide ion combines with carbonium ion to complete the addition reaction.



In the addition of hydrobromic acid to ethylene, at first the ionised hydrobromic acid molecule ( $\text{H}^+ \text{Br}^-$ ) induces electromeric effect in ethylene molecule which then takes up  $\text{H}^+$  to form the carbonium ion. The carbonium ion in the final step combines with bromide ion to complete the addition reaction.



## 2. Addition to Carbonyl Group. ( $>\text{C}=\text{O}$ )

The carbonyl group undergoes addition at carbon to oxygen double bond. Let us consider the addition of HCN to carbonyl group of acetone. The carbonyl group is initially polarised with a slight negative charge on oxygen and a slight positive charge on carbon

$>\text{C}^{\delta+}=\text{O}^{\delta-}$ . The approaching ionised  $\text{H}^+ \text{CN}^-$  molecule then causes the transfer of  $\pi$  electrons towards the oxygen on account of its greater electronegativity (electromeric effect). Since the system having a positively charged carbon is less stable than the system having a negatively charged oxygen, the addition of the nucleophile to carbon precedes the addition of the electrophile on oxygen. (In alkenes the addition of electrophile precedes the addition

1. For definitions of terms 'electrophile' and 'nucleophile' see sections 7.4 and 7.5.

of nucleophile.) Therefore, in this addition  $\text{CN}^-$  will add at the carbon atom followed by  $\text{H}^+$  adding at oxygen.

