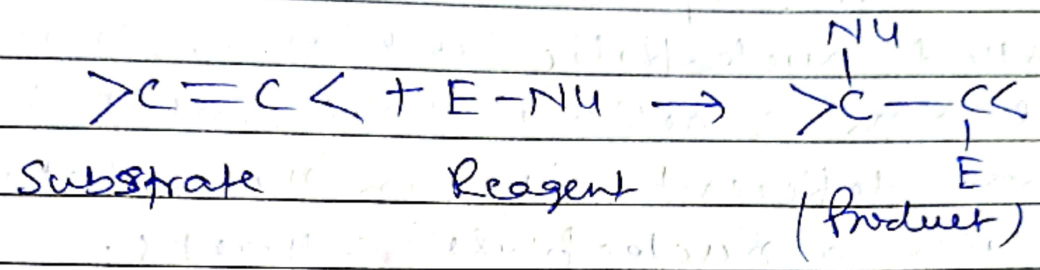
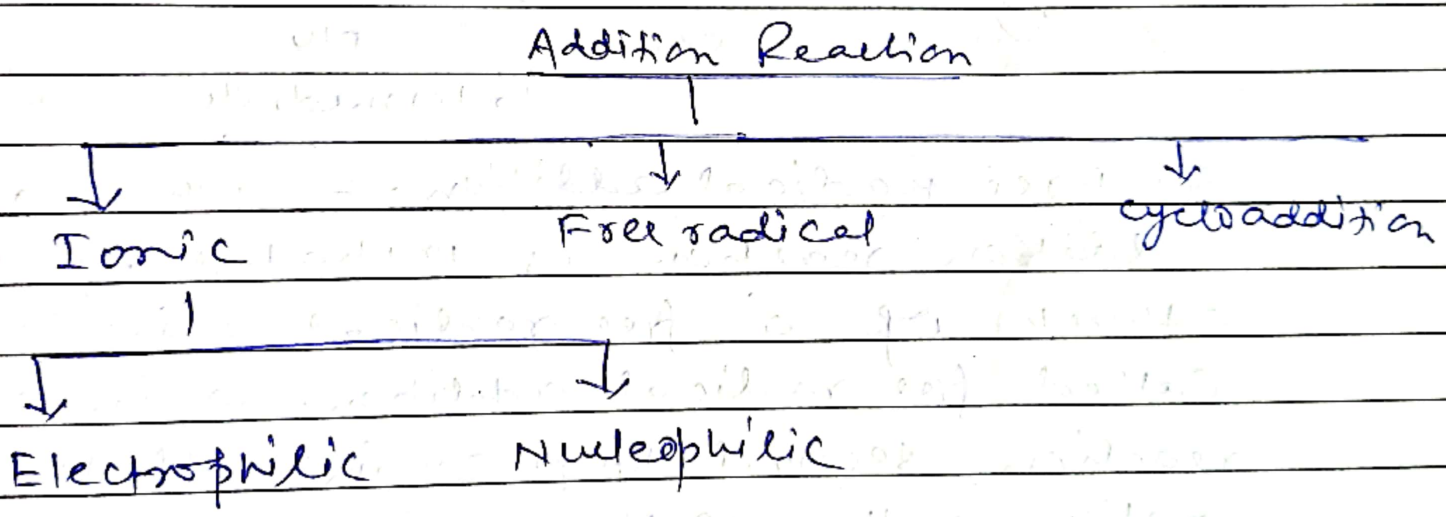


When a product is formed by the addition of a complete molecule of the reagent across a multiple bond of the substrate, then it is called addition product and the reaction is known as addition reaction. So in this reaction a weak π -bond is broken and two σ -bonds are formed, as a result it is energetically favourable.

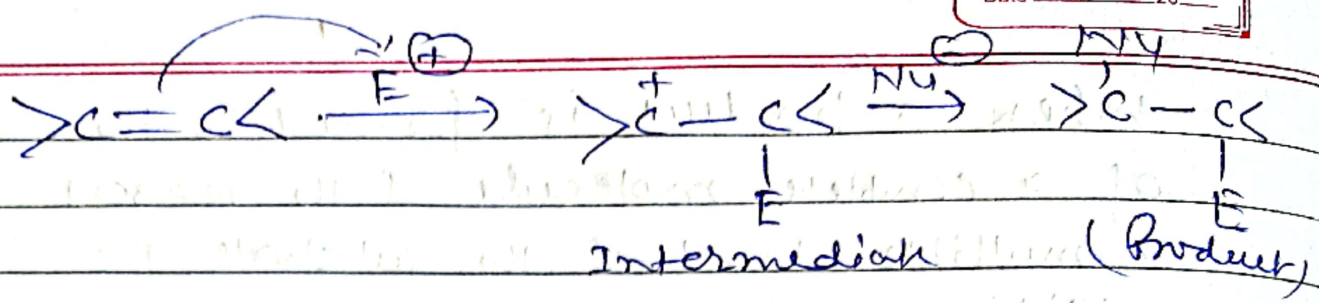


Types of Addition reactions:-



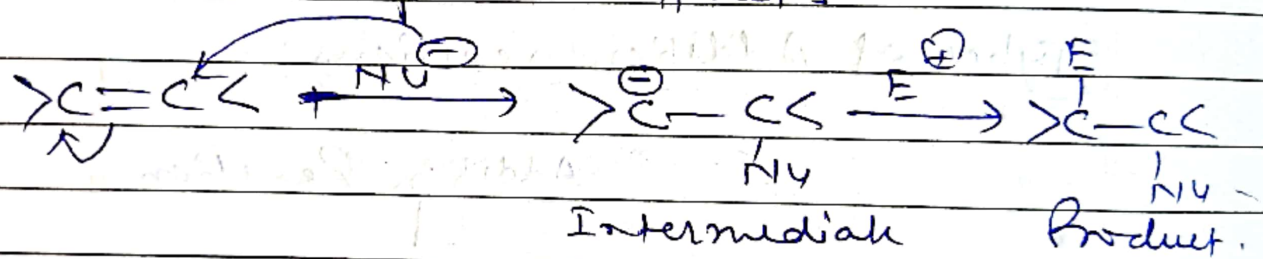
Ionic addition reactions generally take place in polar solvents, while free radical additions take place in non-polar solvents. All Ionic & free radical reactions take place by a two step mechanism.

(i) Electrophilic addition:- When an addition reaction is initiated by the attack of an electrophile, then it is called electrophilic addition. So in such reaction, second step consists of the combination of the resultant intermediate with a negative species (i.e. nucleophile) as shown below:-

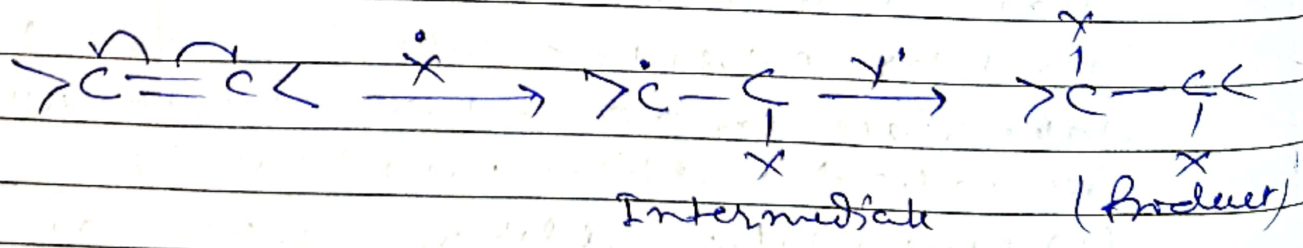


(ii) Nucleophilic addition:-

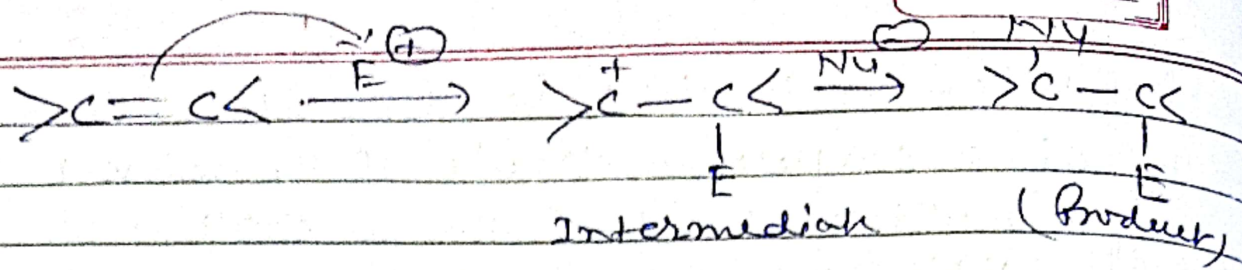
When an addition reaction is initiated by the attack of a nucleophile, then it is called nucleophilic addition. So in such addition reactions there must be an electron deficient site in the substrate, on which a nucleophile attacks.



(iii) Free Radical addition:- when an addition reaction is initiated by the attack of a free radical, then it is called free radical addition. So in such reactions, second step consists of the combination of the resultant intermediate with another radical.

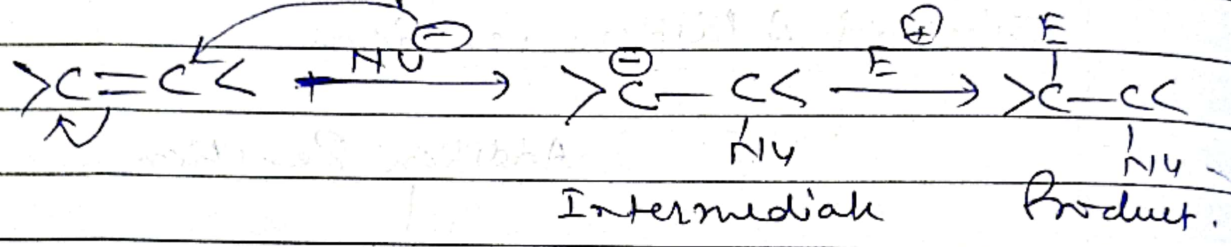


(iv) cycloaddition:- In such addition reactions, simultaneous attack of at both carbon atoms of multiple bond in the presence of a suitable reagent takes place, giving a cyclic product.

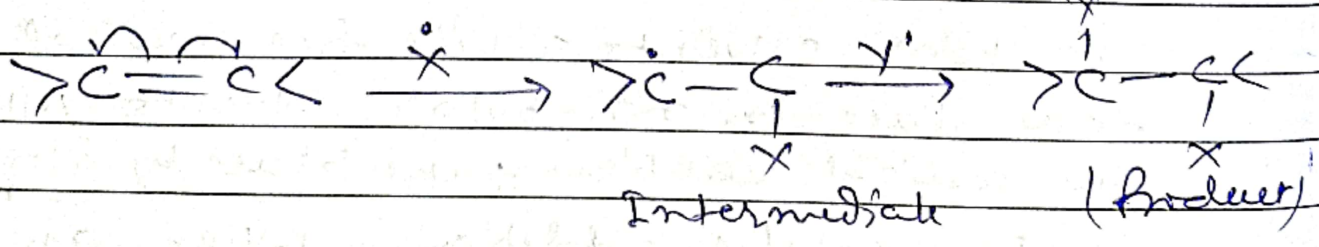


(ii) Nucleophilic addition:-

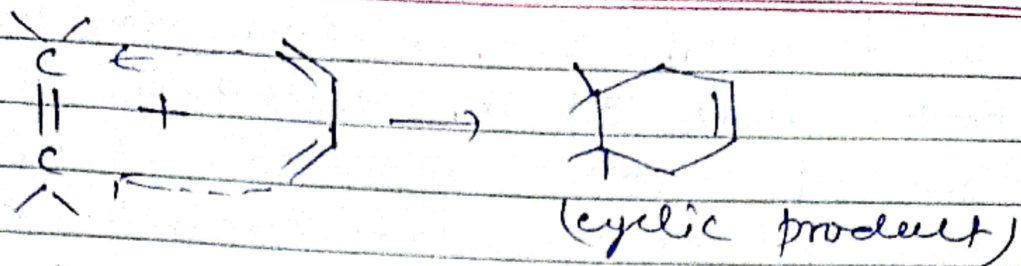
When an addition reaction is initiated by the attack of a nucleophile, then it is called nucleophilic addition. So in such addition reactions there must be an electrophilic site in the substrate, on which a nucleophile attacks.



(iii) Free Radical addition:- when an addition reaction is initiated by the attack of a free radical, then it is called free radical addition. So in such reactions, second step consists of the combination of the resultant intermediate with another radical.

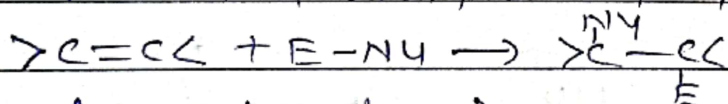


(iv) Cycloaddition:- In such addition reactions, simultaneous attack of at both carbon atoms of multiple bond in the presence of a suitable reagent takes place, giving a cyclic product.



Electrophilic Addition (Addition to C-C multiple bond) :-

Since a multiple-bonded carbon atoms consist of loosely held π -electron clouds, spread above & below the plane of the molecule, which are susceptible to electrophiles. So electrophilic addition is the characteristic reaction of alkenes/alkynes. The common electrophiles include: (i) positively charged species like, H^+ , helium ion (He^+), NO_2^+ --- etc (ii) neutral species like Cl_2 , Br_2 , $H-X$ ($X=O, Br, I$) --- etc (iii) Lewis acids like BF_3 , AlX_3 --- etc (iv) Metal ions having vacant d-orbitals like, Ag^+ , Hg^{2+} , Pt^{2+} --- etc.



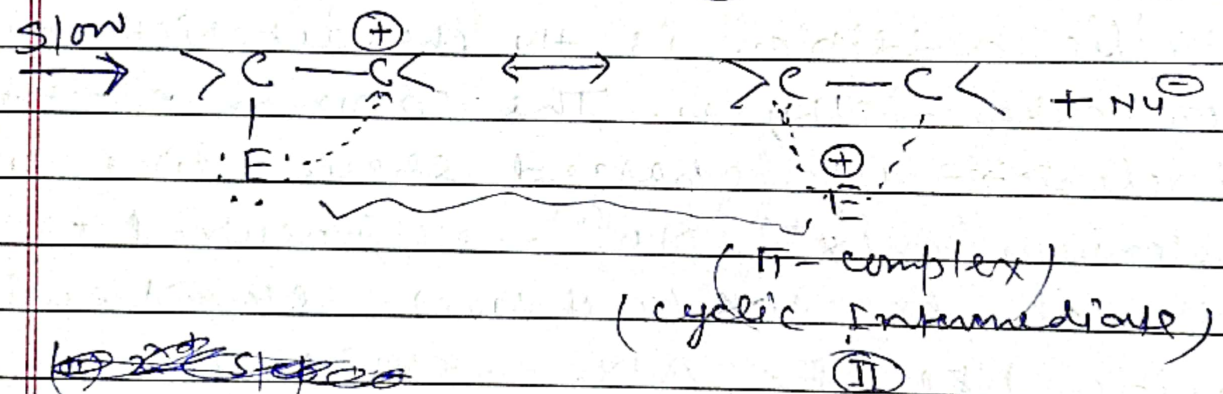
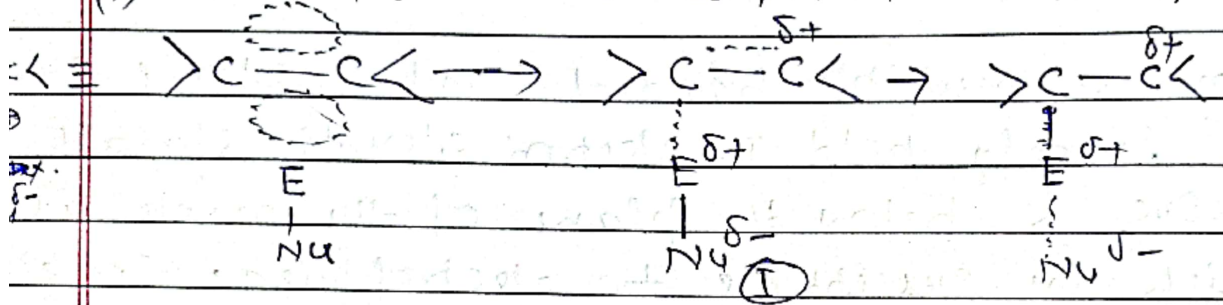
General Mechanism :-

Such addition reactions take place by a two step mechanism.

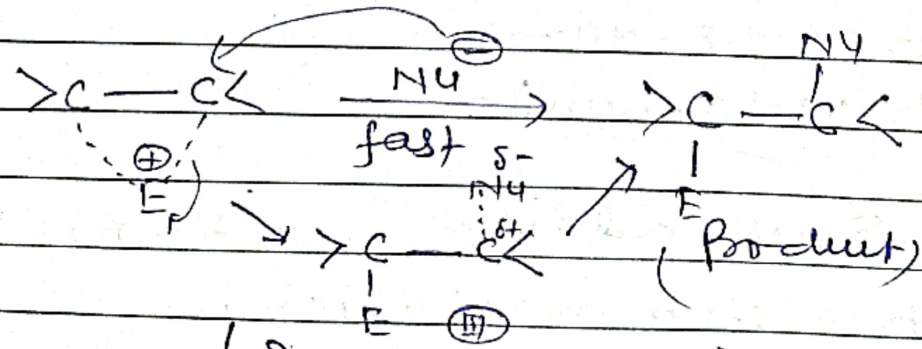
Spectroscopic and other evidences suggest that in the initial step a π -complex is formed by the attack of π -electron cloud on the vacant orbital of an electrophile, which does not involve actual bonding and may be regarded as an association in which electrophile gets embedded in one lobe of π -orbital of the double bond. This π -complex may change to a carbocation-

through the formation of a σ -bond between the electrophile and one of the doubly bonded carbon atoms. If the electrophile has a lone pair of electrons (as in case of Br^+ , Cl^+ etc) then a three membered cyclic cation is formed by the donation of one of these lone pairs to the other electron deficient C-atom and bearing a +ve charge on it (as shown below). This π -complex further reacts with the nucleophile

(i) - 1st step:- to complete the addition process.



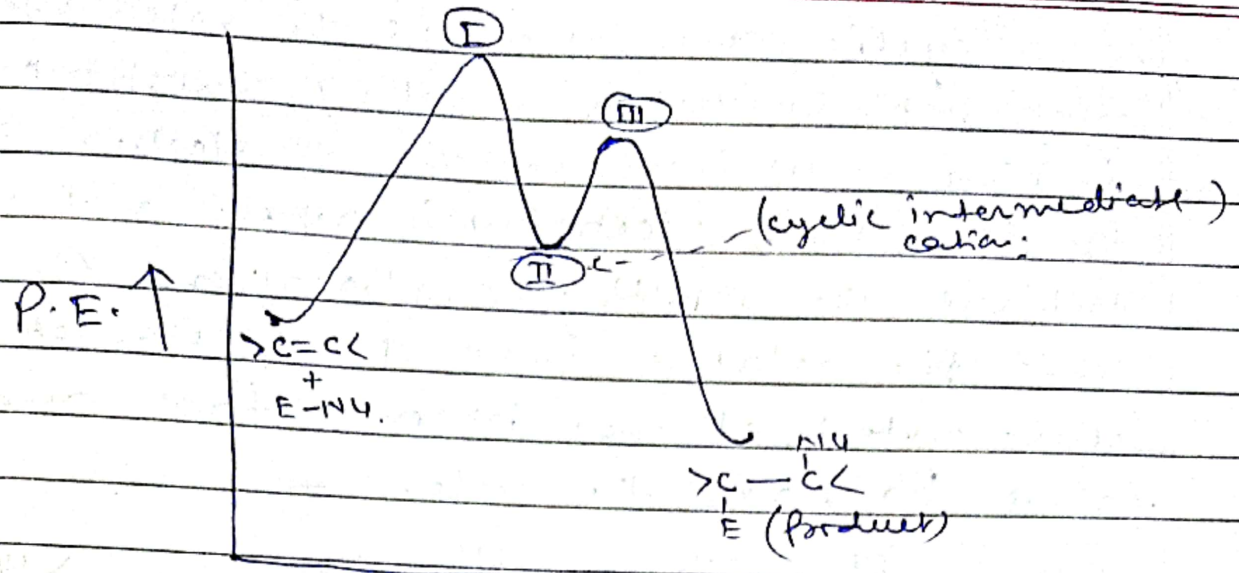
~~1st step~~
(ii) 2nd step:-



(In case of H^+ or a carbene or a nitrene, the electrophile has no lone pair, so a three membered ring intermediate is not formed.)

So the 1st step is slow & rate determining, while 2nd step is fast as in $\text{S}_{\text{N}}1$ -pathway.

Reaction may be shown as:-



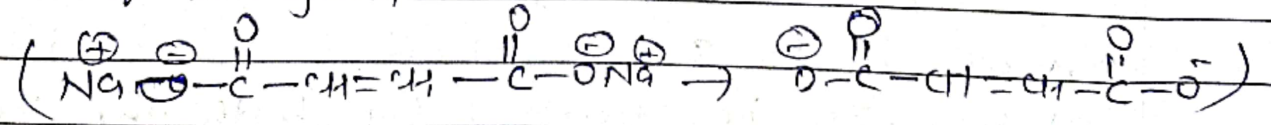
→ Reaction coordinate →

The reaction overall follows a 2nd order kinetics -
i.e., $r = k [\text{Alkene}] [\text{Reagent}]$
∴ order = 1 + 1 = 2

Evidence in favour of the proposed pathway:-

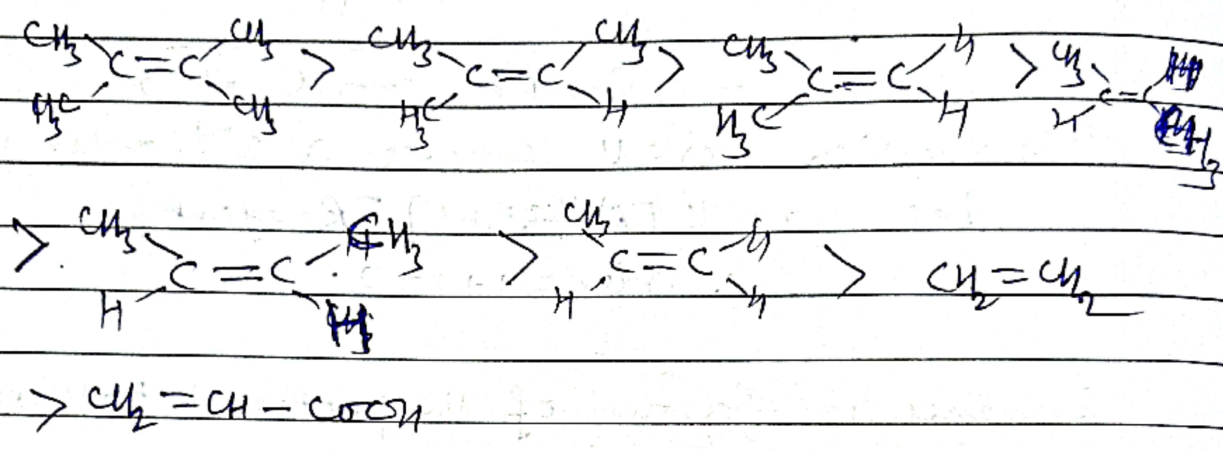
- (i) The rate of reaction becomes slow in case of non-polar solvents (like hexane), while fast in case of polar solvents (like H₂O, ~~acetone~~ ^{propyl alcohol}, etc).
- (ii) The rate of reaction becomes slow, when carried out with dry reagent and in dark, but in presence of light and moisture, which promotes ionisation, the rate becomes fast.

e.g., The reaction rate of Br₂ with maleic acid is very slow, but with sodium maleate it is quite fast.



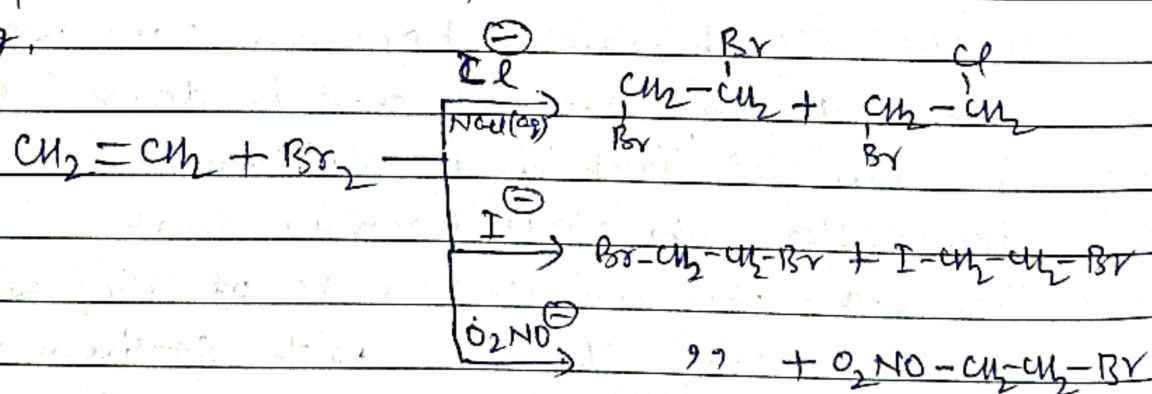
The electron releasing groups enhances the electron density polarisation of π-electrons, whereas electron pulling groups draws electron density from the double bond.

(iii) Since the formation of a free carbocation or a cyclic carbocation is the rate-determining step, so electron donating substituents (in place of H) increases the π -electron density for facile electrophilic attack and also stabilise the resulting carbocation. As a result the relative rate of addition of substituted alkenes becomes fast and found to have the order: -



(iv) When reaction is carried out in presence of an ~~an~~ auxiliary nucleophile, a mixture of products are obtained.

e.g.



Formation of mixture of products proves that carbocation is formed in the 1st step, which is attacked by both the nucleophiles Br^- (from Br_2) & X^- (from present in solution) in the second step.

All the above evidences show that the reaction is ionic in nature & occurs through the initial attack of electrophile.