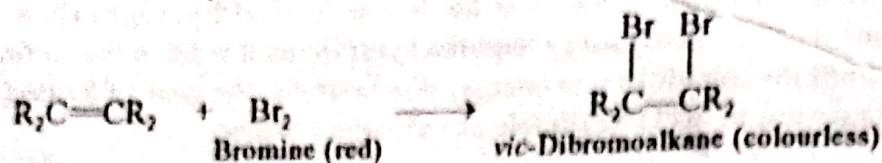
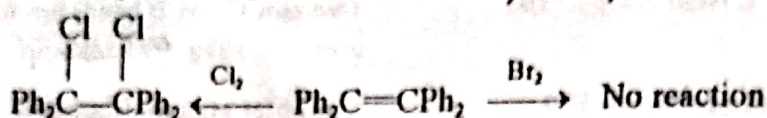


produces a *vicinal* dihalide. The process, known as halogen addition*, is used as a quick diagnostic test for the presence of a carbon-carbon double bond, since compounds bearing such group discharge the red colour of a dilute solution of bromine in an inert solvent to produce the colourless *vic*-dibromoalkane without the evolution of hydrogen bromide.



The order of reactivity for halogen addition is $Cl_2 > Br_2 > I_2$ and can be evidenced by the fact

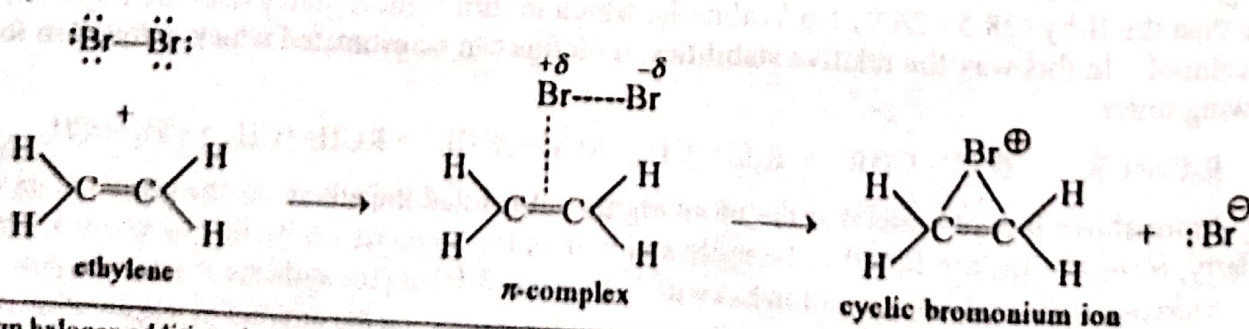


that the tetraphenylethylene adds up chlorine and not bromine because smaller size of the chlorine atom minimises the steric interference with the phenyl groups, while the large size of the bromine atom is not capable of doing this. The least reactive iodine can be added to the alkene by the use of its compounds *viz.* iodine monochloride, iodine bromide, etc.

Mechanism. Halogen addition to olefins can take place either by ionic or free-radical mechanism. Certain experimental facts are cited in favour of both mechanisms. Let us discuss one by one.

(A) Evidence in favour of ionic (polar) mechanism. The addition of halogen to olefins *via* the ionic mechanism is supported by the fact that when the reaction is carried out in presence of an ionising substance or solvent its velocity is increased, while it is decreased when the reaction is carried out in presence of non-ionising substance or solvent. Thus, Norrish in 1923 carried out the addition of bromine to ethylene in two vessels whose walls were coated either with paraffin wax (a non-ionising substance) or with stearic acid (an ionising substance) and observed that the rate of reaction was very less in the former vessel and very high in the latter. Similarly, the addition of halogens to olefins is found to be catalysed by inorganic halides, *viz.* HBr, $AlCl_3$, etc., which promote the ionisation of bromine. The mechanism of halogen addition to olefins is believed to be a two-step process. In the first-step, the π electrons of the olefin polarise the halogen molecule by repelling its electrons. Now the π electrons of the olefin attract the electrophilic end ($X^{\delta+}$) of the resulting halogen dipole to form a loose π complex, which then yields a bridged (non-classical) carbonium ion and a halide anion (Roberts *et al.*, 1937). It is important to note that as this is the slow step, it constitutes the rate determining step.

Step No. 1.

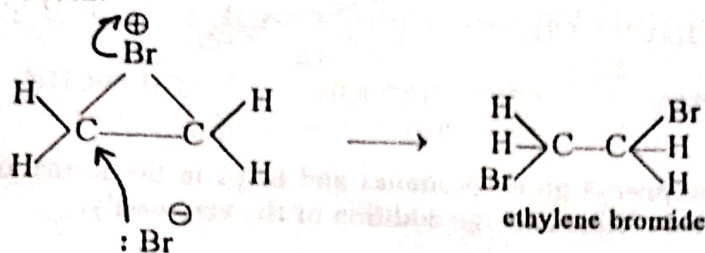


* The term halogen addition should be clearly distinguished from the term halogenation which is a substitution reaction and involves the replacement of a hydrogen atom by a halogen atom.

** It is interesting to note that during addition reaction, although chlorine is more reactive than bromine, the latter is frequently used owing to its ease of handling (as it is a liquid while chlorine is a gas).

Step No. 2.

Stage two of the reaction then involves attack by the negative bromide ion from the rear on the intermediate bromonium ion.



Rear attack by bromide ion is most probable because the bulky bromine atom in the bromonium ion hinders approach from the front.

The addition of halogens to olefins as a two stage process in which the two halogen atoms enter the molecule on opposite sides, *i.e.* the two-stage *trans* addition of halogens to olefins can be clearly evidenced from the following facts.

(i) The two stage mechanism explains the formation of three products when ethylene is treated with bromine water in presence of inorganic salts *viz.* NaCl, NaNO₃ or NaI, *e.g.*

