It is very important to note that the addition of hydrogen is always cis since the hydrogen molecule can attack only from one side of the alkene absorbed on the metallic surface.

Heat of hydrogenation. Since energy is liberated during hydrogenation, it is a potentially spontaneous process. The energy liberated during the process is known as heat of hydrogenation and may be calculated by subtracting the total amount of energy required to break the π bond of the olefin and σ bond of the hydrogen molecule from the total liberated energy. For example, the heat of hydrogenation of a tetrasubstituted ethylene comes out to be 31 kcal/mole as calcualted below.

It is important to note that the heats of hydrogenation of olefins depend upon their structure. For example, the following three branched olefins, although giving the common compound 2-methylbutane on hydrogenation, liberate different amount of energies, i.e. possess different heats of hydrogenation.

Since an olefin having lower heat of hydrogenation is more stable than that with higher heat of hydrogenation, that is, it is closer in energy to the corresponding alkane, the isomeric olefin III is more stable than the II by (28.5–26.9) 1.6 kcal/mole, which in turn is more stable than the I by (30.3 – 28.5) 1.8 kcal/mole. In this way the relative stabilities of olefins can be estimated which is found to follow the following order.

$$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2$$
, $RCH=CHR > RCH=CH_2 > CH_2=CH_2$

From above it is obvious that the more highly substituted the alkene is, the greater is its stability. Similarly, trans olefins are found to be more stable than the isomeric cis olefins by about 1 kcal/mole.

Stereospecific cis hydrogenation has widely been used during the sythesis of several types of natural products. Besides this, catalytic hydrogenation is used for estimating the amount of unsaturation in a given unsaturated compound.

2. Addition of halogens. When an alkene is treated at room temperature with chlorine or bromine in an inert solvent (usually CHCl₃ or CCl₄), the halogen adds rapidly to the double bond of the alkene and

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 $Cl_1 > Br_1 > l_2$ and can be evidenced by the fact

$$Cl Cl$$
 $Ph_2C-CPh_2 \longleftrightarrow Ph_2C-CPh_2 \xrightarrow{Br_2} No reaction$

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 nonionising 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, AlCl₃, 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.

^{*} 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 case 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.