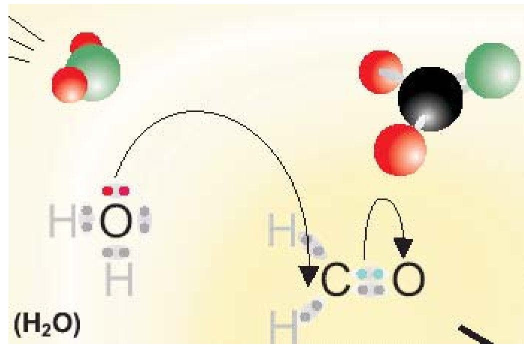
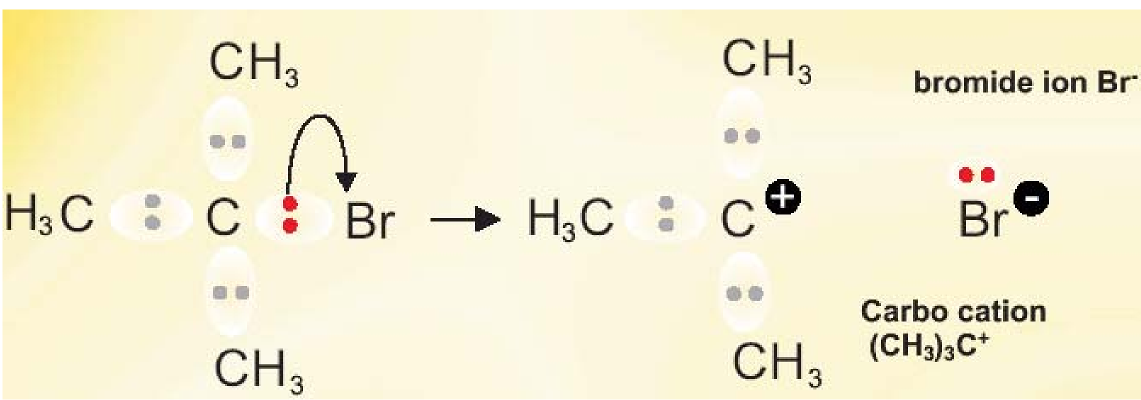
26:1a Homo and Heterolytic Fission

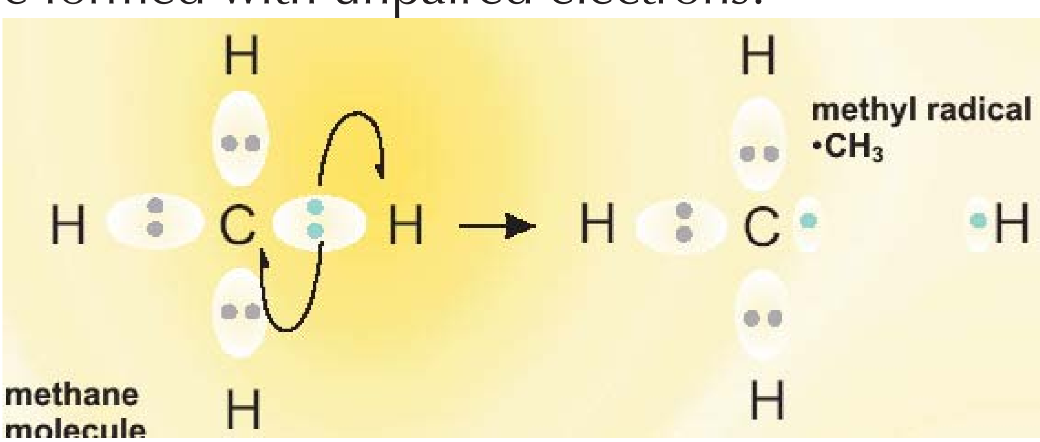
Making and breaking bonds can be illustrated by using 'curly arrows' to show what happens to electron pairs. The tail of the arrow shows where the electron pair comes from: the arrow head where they are going. An arrow with a 'full head' represents an electron pair; an arrow with a 'half head' a single electron.



When a bond breaks **HETEROLYTICALLY** two charged ions are formed:

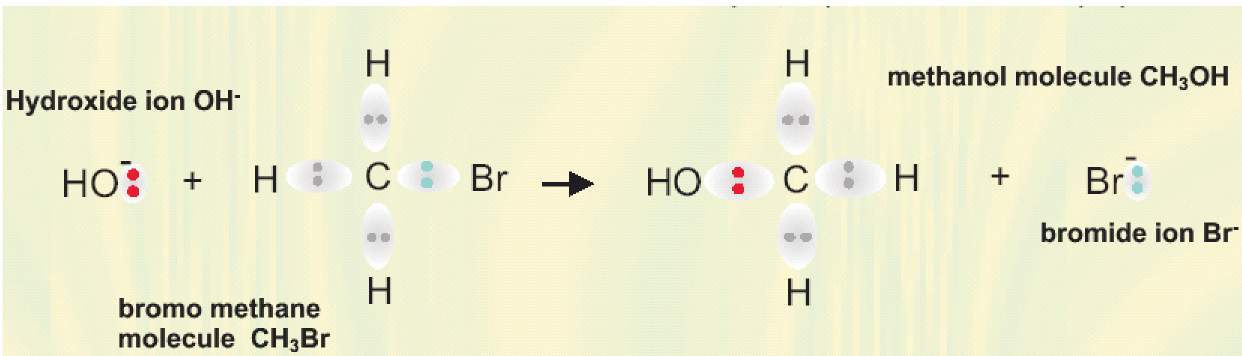


When a bond breaks **HOMOLYTICALLY** two 'radicals' are formed with unpaired electrons:

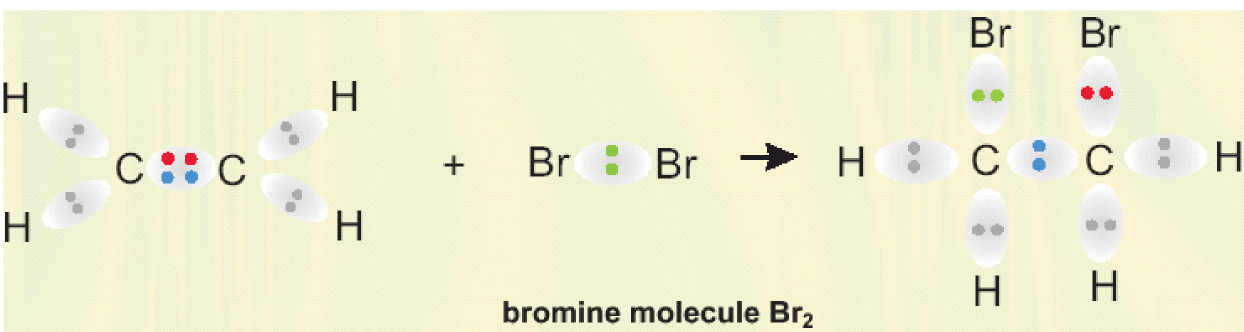


26:1b Types of Reaction

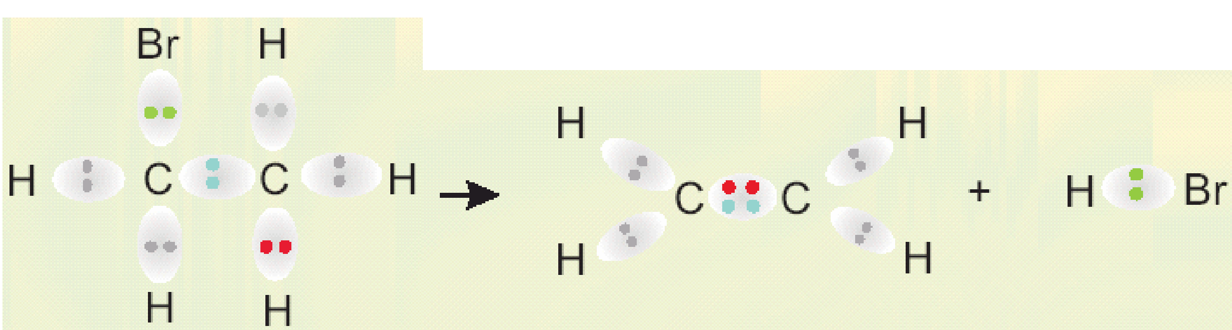
The reactions carbon compounds undergo can be classified as **substitution** ….



addition…

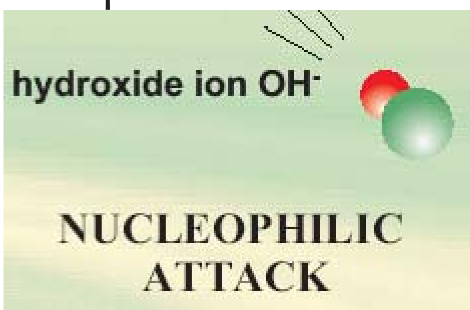


and **elimination.**



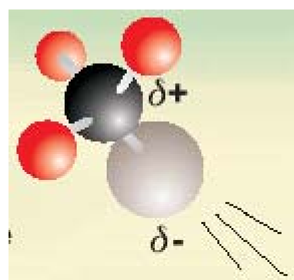
26:1c Reactive Sites

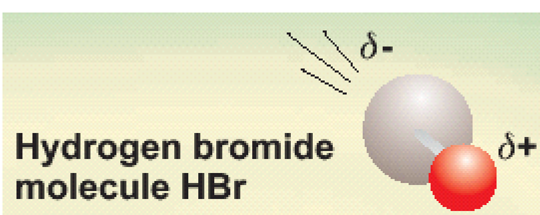
Molecules, exclusively made up of non polar C–C single bonds and C–H bonds, lack reactive sites. It is the presence of **polar bonds**, between carbon atoms and more electronegative non metals, or **multiple bonds**, between carbon atoms, that make carbon compounds **reactive**.



Nucleophiles, like hydroxide ions (OH^-), attack partially positive carbon atoms.

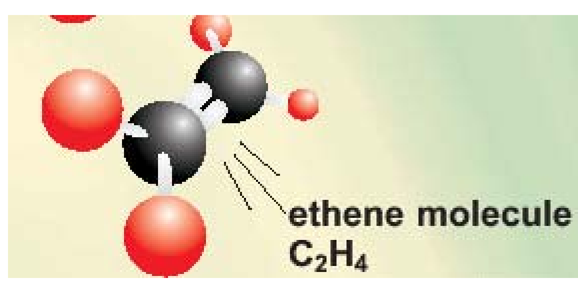
bromomethane molecule CH_3Br





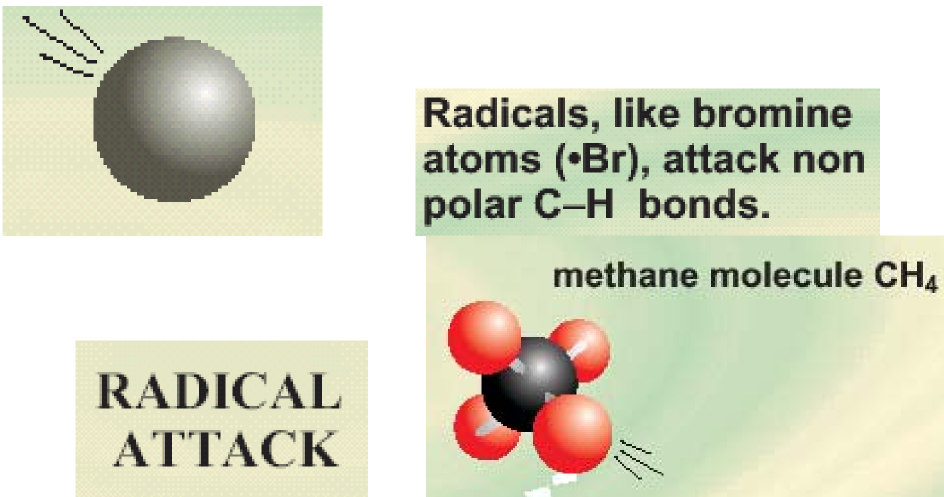
ELECTROPHILIC ATTACK

Electrophiles, like polar hydrogen bromide molecules (HBr), attack electron rich double bonds.



26:1d Attacking Non Polar Bonds

Immune to attack by nucleophiles and electrophiles, non polar C–H bonds can be attacked by the unpaired electron on **radicals**. This happens when the radical's desire to pair up with hydrogen exceeds that of carbon.



NUCLEOPHILES:
Reactants, like hydroxide ions (OH^-), that react by donating electrons are known as nucleophiles.

ELECTROPHILES:
Reactants, like polar hydrogen bromide molecules (HBr), that react by gaining electrons are known as electrophiles.

FREE RADICALS:
Reactants, like bromine atoms (Br), with an unpaired electron, are known as free radicals.

26.1e Nucleophilic Substitution

Compare the reaction of OH^- ions with C_6H_5OH molecules:

$C_6H_5OH + OH^- \;\Re\; C_6H_5O^- + H_2O$

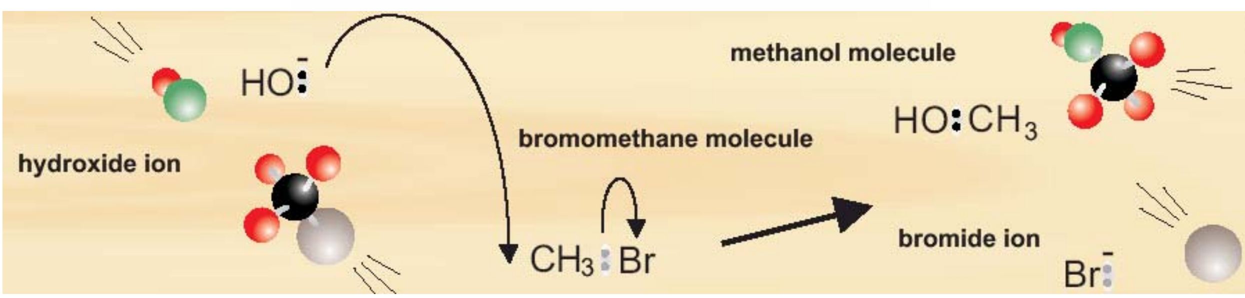
to that of CH_3Br molecules with OH^- ions

$CH_3Br + OH^- \;\Re\; CH_3OH + Br^-$

What is the difference in the 'reactive sites'?

Investigating the kinetics of the reaction between CH_3Br molecules and OH^- ions shows that it is 2nd order.

reaction rate $= \mathbf{k\,[CH_3Br]\,[OH^-]}$



Explain why the suggested mechanism is consistent with the reaction's kinetics?

This is an example of an S_N2 reaction mechanism: substitution, nucleophilic, bimolecular