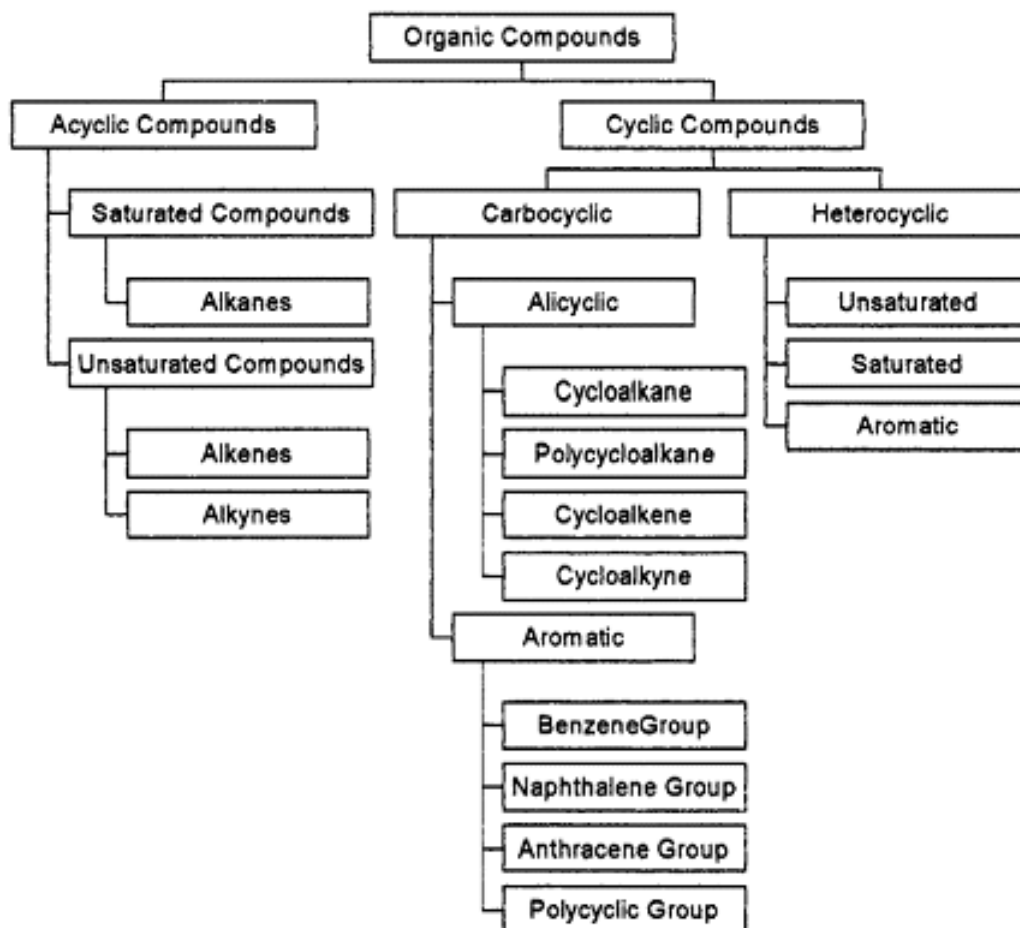**1. Classification and nomenclature of organic compounds.**
2. Reaction mechanism
3. Saturated hydrocarbons (alkanes and cycloalkanes).

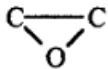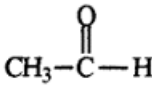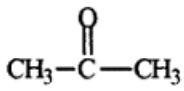TEST - Alkanes and Cycloalkanes
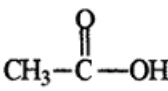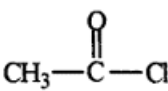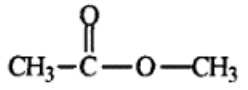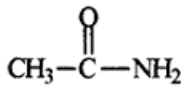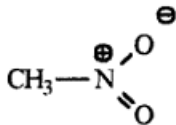
1. Classification and nomenclature of organic compounds.

General Classification of Organic compounds

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                          ┌─────────────────────┐
                          │  Organic Compounds  │
                          └─────────────────────┘
              ┌──────────────────────┴──────────────────────┐
   ┌─────────────────────┐                        ┌─────────────────────┐
   │  Acyclic Compounds  │                        │  Cyclic Compounds   │
   └─────────────────────┘                        └─────────────────────┘
        │                                    ┌──────────┴──────────┐
   ┌─────────────────────┐          ┌─────────────────┐   ┌─────────────────┐
   │ Saturated Compounds │          │   Carbocyclic   │   │   Heterocyclic  │
   └─────────────────────┘          └─────────────────┘   └─────────────────┘
        │                                │                       │
   ┌──────────────┐            ┌─────────────────┐       ┌─────────────────┐
   │   Alkanes    │            │    Alicyclic    │       │   Unsaturated   │
   └──────────────┘            └─────────────────┘       └─────────────────┘
   ┌─────────────────────┐        │                      ┌─────────────────┐
   │Unsaturated Compounds│     ┌───────────────┐         │    Saturated    │
   └─────────────────────┘     │  Cycloalkane  │         └─────────────────┘
        │                      └───────────────┘         ┌─────────────────┐
   ┌──────────────┐            ┌───────────────┐         │    Aromatic     │
   │   Alkenes    │            │Polycycloalkane│         └─────────────────┘
   └──────────────┘            └───────────────┘
   ┌──────────────┐            ┌───────────────┐
   │   Alkynes    │            │  Cycloalkene  │
   └──────────────┘            └───────────────┘
                               ┌───────────────┐
                               │  Cycloalkyne  │
                               └───────────────┘
                            ┌─────────────────┐
                            │    Aromatic     │
                            └─────────────────┘
                               ┌──────────────────┐
                               │   BenzeneGroup   │
                               └──────────────────┘
                               ┌──────────────────┐
                               │ Naphthalene Group│
                               └──────────────────┘
                               ┌──────────────────┐
                               │ Anthracene Group │
                               └──────────────────┘
                               ┌──────────────────┐
                               │  Polycyclic Group│
                               └──────────────────┘
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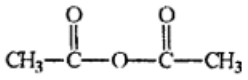
Classification by functional group

Type	Functional Group	Example	Name
Alkane	R-H	$CH_3CH_2CH_3$	propane
Alkene	R=R	$CH_2=CHCH_3$	propene
Diene	R=R-R=R	$CH_2=CH-CH=CH_2$	1,4-butene
Alkyne	R≡R	CH≡CH	ethyne
Halide	R-X	CH_3CH_2-Br	bromoethane
Alcohol	R-OH	CH_3CH_2-OH	ethanol
Ether	R-O-R	$CH_3CH_2-O-CH_2CH_3$	ethoxyether

Type	Functional Group	Example	Name
Epoxide	C—C with O bridge	CH_2—CH_2 with O bridge	ethylene oxide
Aldehyde	R-CHO	$CH_3-\overset{\overset{O}{\|\|}}{C}-H$	ethanal
Ketone	R-CO-R	$CH_3-\overset{\overset{O}{\|\|}}{C}-CH_3$	2-propanone
Carboxylic Acid	$R-CO_2H$	$CH_3-\overset{\overset{O}{\|\|}}{C}-OH$	ethanoic acid
Acid Chloride	R-CO-Cl	$CH_3-\overset{\overset{O}{\|\|}}{C}-Cl$	acetyl chloride
Acid Anhydride	$(RCO)_2O$	$CH_3-\overset{\overset{O}{\|\|}}{C}-O-\overset{\overset{O}{\|\|}}{C}-CH_3$	acetic anhydride
Ester	$R-CO_2R$	$CH_3-\overset{\overset{O}{\|\|}}{C}-O-CH_3$	methyl ethanoate
Amide	$R-CONH_2$	$CH_3-\overset{\overset{O}{\|\|}}{C}-NH_2$	ethanamide
Amine 1°	$R-NH_2$	$CH_3CH_2-NH_2$	ethaneamine
Amine 2°	R-NH-R	$CH_3CH_2-NH-CH_2CH_3$	diethaneamine
Amine 3°	R_3-N	$(CH_3CH_2)_3-N$	triethaneamine
Nitro Compound	$R-NO_2$	$CH_3-N^{\oplus}(O^{\ominus})(=O)$	nitromethane
Nitrile	R-C≡N	$CH_3C≡N$	ethanenitrile
Thiol	R-SH	CH_3CH_2-SH	ethanethiol

Base Name or Hydrocarbon name

Chain	Primary suffix	Generic name
C–C	–ane	Alkane
C=C	–ene	Alkene
C≡C	–yne	Alkyne

If the parent chain contains two, three or more double or triple bonds, then the following suffixes are used :

Bond	Two	Three
Double bond	–diene	–triene
Triple bond	–diyne	–triyne

The **root word** and the **primary suffix** together are known as **Base Name** or **Hydrocarbon name.**

Formula	IUPAC name(Base name)
CH_4	Methane (Meth+ane)
$CH_3(CH_2)_3CH_3$	Pentane (Pent+ane)
$CH_3(CH_2)_{23}CH_3$	Pentacosane (Pentacos+ane)
$CH_2 = CH_2$	Ethene (Eth+ene)
$CH_3CH_2CH = CH_2$	Butene (But + ene)
$CH_3CH_2CH=CH_2$	Butene (But+ene)
$CH_3(CH_2)_{12}CH=CH_2$	Pentadecene (Pentadec+ene)
$CH≡CH$	Ethyne (Eth+yne)
$CH_3(CH_2)_6C≡CH$	Nonyne (Non+yne)
$CH_3C≡CH$	Propyne (Prop+yne)

2. Reaction mechanism

CATEGORIES OF ORGANIC REACTIONS

Virtually all organic reactions fall into one of four categories: They are either **substitutions, additions (cycloaddition), eliminations, or rearrangements, Ox/Red**.

(S)
Substitutions are the characteristic reactions of saturated compounds such as alkanes and alkyl halides, and of aromatic compounds (even though they are unsaturated). In a substitution, one group replaces another. For example, methyl chloride reacts with sodiumhydroxide to produce methyl alcohol and sodium chloride:

$$H_3C - Cl + Na^+OH^- \xrightarrow{H_2O} H_3C - OH + Na^+Cl^-$$

A substitution reaction
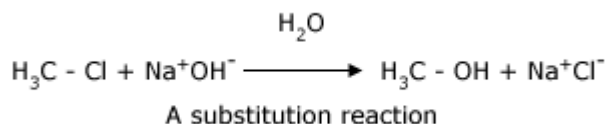
In this reaction a hydroxide ion from sodium hydroxide replaces the chlorine of methyl chloride.

(A)
Additions are characteristic of compounds with multiple bonds. Ethene, for example, reacts with bromine by an addition. In an addition all parts of the adding reagent appear in the product; two molecules become one.

An addition reaction
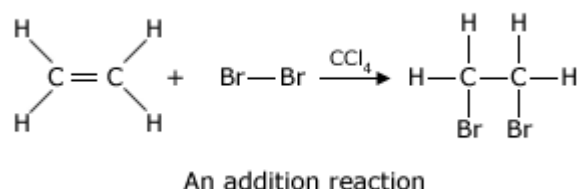
(E)
Eliminations are the opposite of additions. In elimination one molecule loses the elements of another small molecule. Elimination reactions give us a method for preparing compounds with double and triple bonds.

Eg: Dehydrohalogenation, a reaction that is used to prepare alkenes. In dehydrohalogenation, as the word suggests, the elements of a hydrogen halide are eliminated. An alkyl halide becomes an alkene:

An elimination reaction
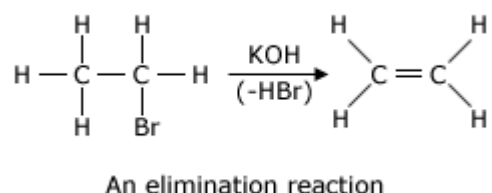
In a **Rearrangement** a molecule undergoes a reorganization of its constituent parts. For example, heating the following alkene with a strong acid causes the formation of another isomeric alkene.
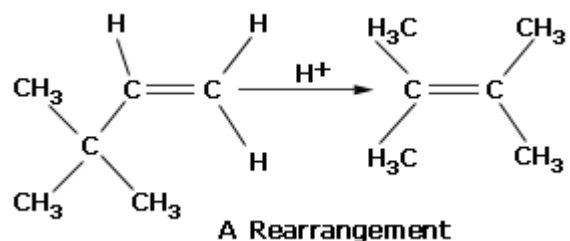
A Rearrangement

In this rearrangement not only have the positions of the double bond and a hydrogen atom changed but a methyl group has moved from one carbon to another. Now we'll learn some of the principles that explain how these kinds of reactions take place.

How these kind of reactions take place?

HOMOLYSIS AND HETEROLYSIS

Reactions of organic compounds always involve the making and breaking of covalent bonds. A covalent bond may break in two fundamentally different ways. The bond may break so that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital. This kind of cleavage, called **heterolysis** (In Greek, hetero–, different, + lysis, loosening or cleavage), produces **charged fragments** or **ions**. The bond is said to have broken heterolytically. The other possibility is that the bond breaks so that each fragment takes away one of the electrons of the bond. This process, called **homolysis** (Gr. **homo**–, the same), produces fragments with unpaired electrons called **radicals**

HOMOLYSIS

When a covalent bond (a nonionic chemical bond formed by shared electrons) is made up of two electrons, each of which is supplied by a different atom, the process is called colligation; the reverse process, in which the electrons of a covalent bond are split between two atoms, is known as **HOMOLYSIS**. These reactions are shown schematically by the equation

$$A\cdot \, + B\cdot \underset{\text{homolysis}}{\overset{\text{colligation}}{\rightleftharpoons}} \; A:B$$
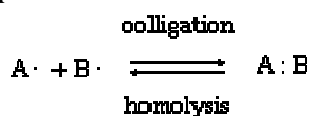
in which A and B represent the separate atoms (or groups), the single dots represent electrons, and the double dots represent the electron pair that makes up the bond. The products of a homolysis reaction are called radicals.

HETEROLYSIS

The cleavage of a covalent bond so that both bonding electrons remain with one of the two fragments between which the bond is broken, e.g.

$$A:B \longrightarrow \underset{\text{Ions}}{\underbrace{A^+ \, + \, :B^-}} \quad \text{Heterolytic bond cleavage}$$
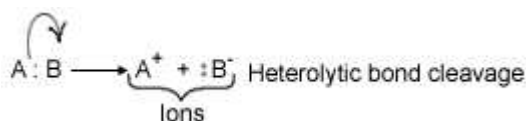
Heterolytic bond fission is a feature of many bimolecular reactions in solution (e.g. electrophilic substitution, nucleophilic substitution).
The products of a homolysis reaction of carbon compound could be carbo-anions or carbo-cation.
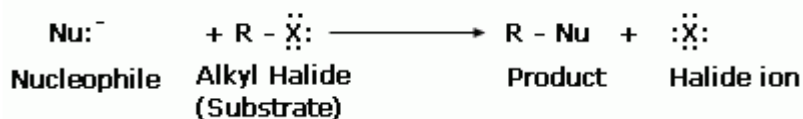
MECHANISM TYPES

Reaction mechanisms attempt to describe how reactions occur. This provides important information about what affects reaction rates and directions and thus ultimately what products will be formed under specific conditions. The advantages for synthetic chemistry should be obvious; the correct conditions can be specified to maximize the yield of a specific product. The basic mechanism types are:
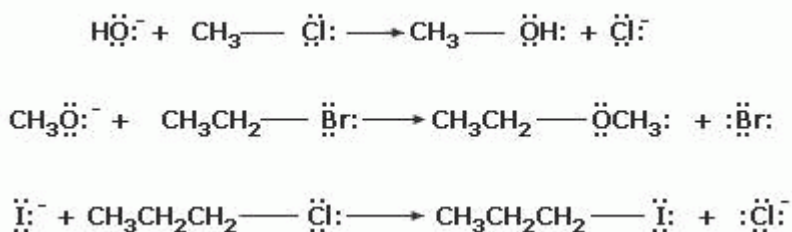
- Nucleophilic substitution Reactions (S_N)

- Electrophilic substitution Reactions (S_E)

- Nucleophilic addition Reactions (A_N)

- Electrophilic addition Reactions (A_E)

- Elimination Reactions (**E**)

- Radicals substitution Reactions (S_R)

Nucleophilic Substitution Reactions (S_N)

There are many reactions (mostly biomolecular) of the general type shown here.

$$Nu:^- \quad + R - \ddot{X}: \longrightarrow R - Nu \quad + \quad :\ddot{X}:^-$$

Nucleophile   Alkyl Halide   Product   Halide ion
(Substrate)

Following are some examples:

$$H\ddot{O}:^- + CH_3 - \ddot{C}l: \longrightarrow CH_3 - \ddot{O}H: + \ddot{C}l:^-$$

$$CH_3\ddot{O}:^- + CH_3CH_2 - \ddot{B}r: \longrightarrow CH_3CH_2 - \ddot{O}CH_3: + :\ddot{B}r:$$

$$\ddot{I}:^- + CH_3CH_2CH_2 - \ddot{C}l: \longrightarrow CH_3CH_2CH_2 - \ddot{I}: + :\ddot{C}l:^-$$

In this type of reaction a nucleophile, a species with an unshared electron pair, reacts with an alkyl halide (called the substrate) by replacing the halogen substituent. A substitution reaction takes place and the halogen substituent, called the leaving group, departs as a halide ion. Because the substitution reaction is initiated by a nucleophile, it is called a nucleophilic substitution reaction.

In nucleophilic substitution reactions the carbon–halogen bond of the substrate undergoes heterolysis, and the unshared pair of the nucleophile is used to form a new bond to the carbon atom:

Leaving group

$$Nu:^- + R \,|\, :\ddot{X}: \longrightarrow Nu: R + :\ddot{X}:^-$$

Nucleophile   Heterolysis
occurs here
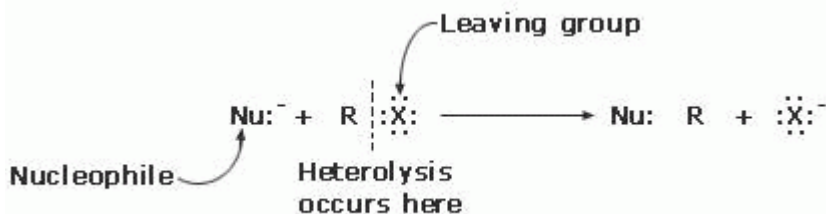
Elimination reactions (E):

Reaction involving the removal of substituents and the formation of a double bond:

$$(CH_3)_3 CCl + H_2O \longrightarrow CH_2 = C(CH_3)_2 + H_3O^+ + Cl^-$$
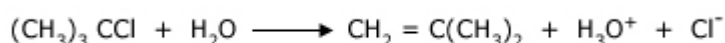
In these eliminations, as in S_N reactions, there is a leaving group and an attracting particle (the base) that possesses an electron pair.

Mechanism of E reaction

For elimination to occur it is necessary for the carbon to be bonded at least to one hydrogen.

$$\begin{array}{ccc} & H & R \\ & | & | \\ H - & C - & C^+ \quad :X^- \\ & | & | \\ & H & R' \end{array}$$
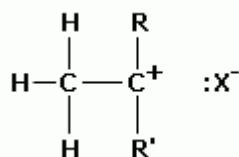
The first step is the slow step it is the rate–determining step. Thus this reaction is unimolecular. In the first step of the reaction, the compound ionizes and becomes a carbocation and a halide ion. The halide separates from the compound bringing with it the electron pair from the carbon–halide bond. It can sustain this negative charge due to its high electronegativity. The first step in an **E** reaction is identical to the first step in an **S_N** reaction. This is a problem because it leads to a mixture of products.

The spontaneous formation of the carbocation is the slow step in both reactions. Once formed, the carbocation reacts rapidly following either the **S_N** or the **E** path.

The **R** groups should be substituents able to donate electron density to help stabilize the carbocation.
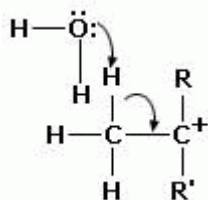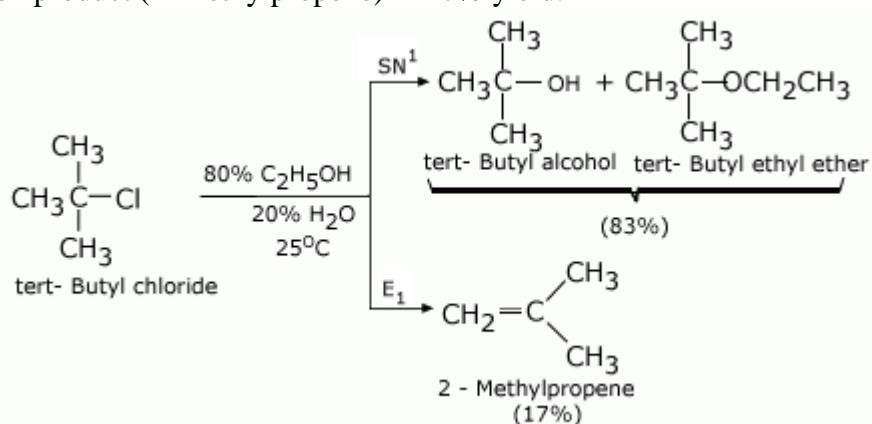
Carbocation rapidly transfers a proton to a molecule of water producing an alkene (double bond).
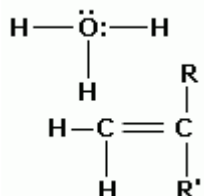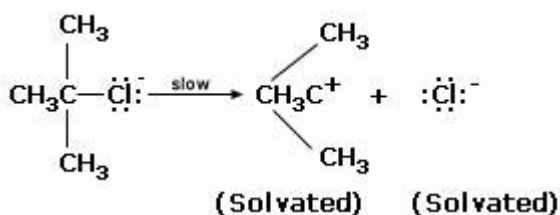

EXAMPLE

Treating tert–butyl chloride with 80% aqueous ethanol at 25°C, for example, gives substitution products in 83% yield and an elimination product (2–methylpropene) in 17% yield.


The initial step for both reactions is the formation of a tert–butyl cation. This is also the rate–determining step for both reactions; thus both reactions are unimolecular.

Whether for substitution or elimination to take place, it depends on the next step (the fast step). If a solvent molecule reacts as a nucleophile at the positive carbon atom of the tert–butyl cation, the product is tert–butyl alcohol or tert–butyl ethyl ether and the reaction is S_N
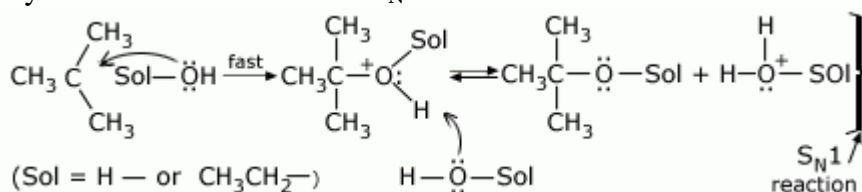

If, however, a solvent molecule acts as a base and abstracts one of the b hydrogen atoms as a proton, the product is 2–methylpropene and the reaction is **E**. E_1 reactions almost always accompany S_N reactions:
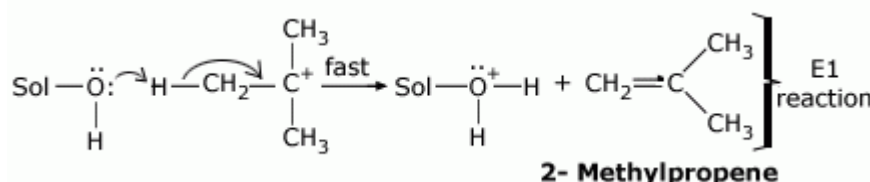
Radicals substitution Reactions (S_R) – the characteristic feature of alkanes

Reactions with halogens:

The alkanes react with the halogens, though only with an input of energy in the form of light. For example, hexane reacts with bromine in the vapour phase, decolorising it. A **substitution** reaction takes place, with bromine atoms substituting for the hydrogen atoms in the hexane molecule. This decolorisation does not occur in the dark – the reaction only takes place in the light.

$$CH_3CH_2CH_2CH_2CH_2CH_3(g) + Br_2(g) \xrightarrow{\text{light}} CH_3CH_2CH_2CH_2CH_2CH_2Br(g) + HBr(g)$$
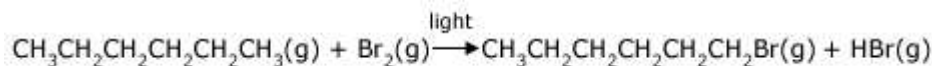
Similarly, methane and chlorine do not react in the dark, but in sunlight they react explosively to produce chloromethane and hydrogen chloride. This, combined with the very rapid reaction that follows, suggests that the reaction takes place by a radical mechanism, and this is indeed the case. This is another example of a substitution reaction, with chlorine atoms substituting for the hydrogen atoms in the methane molecule.

How does light cause chlorine to react with methane? As the following data show, the Cl – Cl bond is easier to break than the C – H bond. Light provides the energy needed to split the chlorine molecules into atoms – in other words, to **initiate** the reaction.

$$Cl_2 \longrightarrow Cl\bullet + Cl\bullet \qquad \Delta H^{\phi}_m = + 243 \text{ KJ mol}^{-1}$$
$$CH_4 \longrightarrow CH_3\bullet + H\bullet \qquad \Delta H^{\phi}_m = + 435 \text{ KJ mol}^{-1}$$
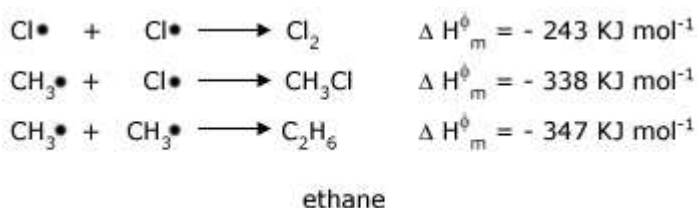
The chlorine atoms formed by this homolytic fission are radicals, and so are extremely reactive. The chlorine radicals react with methane molecules, combining with one of the hydrogen atoms to form HCl and another radical:

$$CH_4 + Cl\bullet \longrightarrow CH_3\bullet + HCl \qquad \Delta H^{\phi}_m = + 4 \text{ KJ mol}^{-1}$$
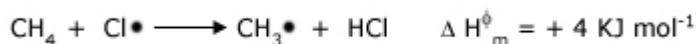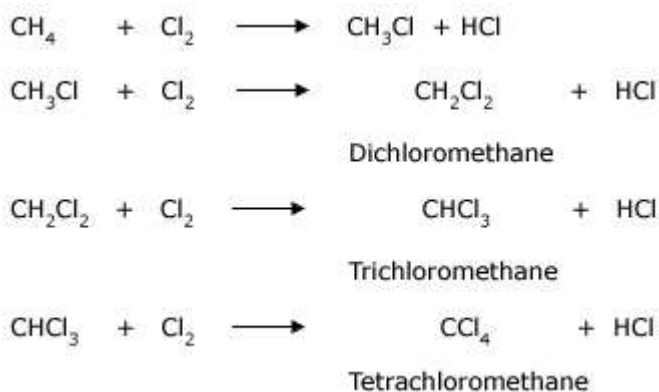
The methyl radical then reacts with another chlorine molecule to form chloromethane and a chlorine radical. This is a propagation step, as it produces another radical. The process is then repeated hundreds of times, which makes the reaction explosive:

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet \qquad \Delta H^{\phi}_m = - 97 \text{ KJ mol}^{-1}$$
$$\text{Chloromethane}$$
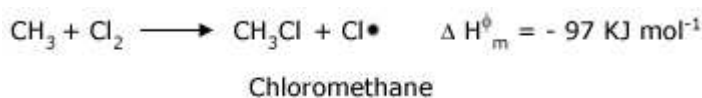
The propagating steps of this reaction continue until there is a termination step. This is the name given to the reaction between two radicals – a very exothermic process.

$$Cl\bullet + Cl\bullet \longrightarrow Cl_2 \qquad \Delta H^{\phi}_m = - 243 \text{ KJ mol}^{-1}$$
$$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl \qquad \Delta H^{\phi}_m = - 338 \text{ KJ mol}^{-1}$$
$$CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6 \qquad \Delta H^{\phi}_m = - 347 \text{ KJ mol}^{-1}$$
$$\text{ethane}$$

If the supply of chlorine is limited, the net result of this reaction is lots of chloromethane and hydrogen chloride and little ethane. However, if there is a plentiful supply of chlorine, then further substitutions of the methane will take place to give di–, tri– and tetrachloromethane as follows:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$
Dichloromethane

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
Trichloromethane

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$
Tetrachloromethane

Trichloromethane or chloroform was one of the first anaesthetics to be used for surgical operations and to ease the pain of childbirth, whilst tetrachloromethane was widely used as a solvent until its carcinogenic (cancer–producing substance) properties were recognised. With chlorine and bromine, an input of energy is needed to overcome the activation energy and so initiate the reactions. With fluorine, a vigorous reaction occurs even without an input of energy – a mixture of fluorine and a hydrocarbon will explode at room temperature even in the dark. Radicals also play an important part in the reaction of the alkanes with oxygen, and in both cracking and reforming hydrocarbon molecules.

3. Saturated hydrocarbons (alkanes and cycloalkanes).

ALKANES

PREPARETION OF ALKANES	REACTIONS OF ALKANES
1. Wurtz Reaction $$2\,R{-}X \xrightarrow{\;Na\;} R{-}R$$ **2. Grignard Reduction** $$RX + Mg \longrightarrow RMgX \xrightarrow{\;H_2O\;} RH$$ **3. Reduction** $$RX + Zn + H^+ \longrightarrow RH + ZnX_2$$ $$RX + LiAlH_4 \xrightarrow{\;dry\ ether\;} RH + LiX + AlX_3$$ **4. Kolbe Reaction** $$R{-}COO^{\ominus} \xrightarrow[-\,e^{\ominus}]{} R{-}R$$ **5. Hydrogenation** $$R{-}C{\equiv}C{-}R' \xrightarrow{\;H_2\;} RCH_2CH_2R'$$	**1. Combustion** $$R + O_2 \longrightarrow CO_2 + H_2O$$ **2. Halogenation (S_R)** $$R + X_2 \xrightarrow[light]{heat\ or} RX + HCl$$ Reactivity $\quad$ X: $Cl_2 > Br_2$ H: $3° > 2° > 1° > CH_3\text{-}H$ **3. Free radical substitution (S_R)** $$X_2 \xrightarrow{heat\ or\ light} 2\,X\cdot$$ $$R{-}H + X\cdot \longrightarrow R\cdot + HX$$ $$R\cdot + X_2 \longrightarrow R{-}X + X\cdot$$

Cycloalkanes:

Whilst many of the alkanes present in crude oil are aliphatic, having straight–or branched–chain molecules, some of them form rings – they are **alicyclic**. These compounds are denoted as cycloalkanes. These **cycloalkanes** have the general formula C_nH_{2n} instead of C_nH_{2n+2} for the chain molecules. Cycloalkanes behave very similarly to the other alkanes, but they tend to have higher melting and boiling points. They have the same name as the corresponding straight–chain molecule, but with the prefix 'cyclo–'. These ring molecules are not aromatic compounds – the aromatic ring structure is based on the benzene ring.

Because of the restricted movement available to a cyclic compound, it undergoes a number of different types of strain. The smallest cycloalkane is cyclopropane, which forms a triangular molecule which is much more reactive than straight–chain propane. Cyclobutane forms a square molecule, which is less reactive than cyclopropane, but is more reactive than butane. Cyclopentane and higher cycloalkanes have a similar reactivity to their straight–chain equivalents. The structures of these cycloalkanes are shown below. A shortcut notation is used to represent the structure where only the bonds are shown and intersection of bonds represents carbon atoms. Because of the tremendous angle strain cyclopropane is very reactive.