Alkanes

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ALKANES

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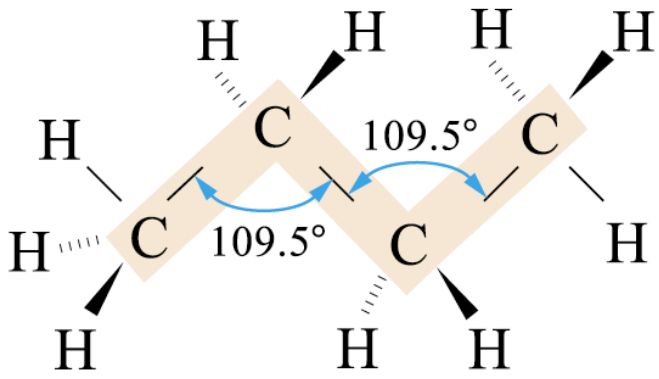
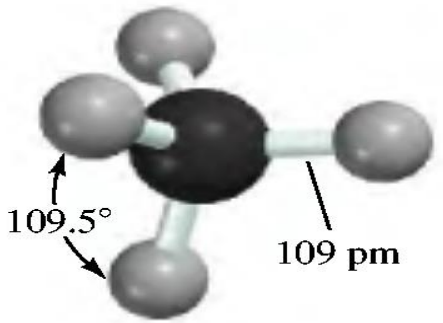
2 Nomenclature of Alkanes
3 Physical Properties of Alkanes
4 Preparation of Alkanes
5 Reactions of Alkanes

- Alkanes are the aliphatic hydrocarbons
- Alkanes are hydrocarbons in which all the bonds are single covalent bonds (σ-bonds).
- Alkanes are called saturated hydrocarbons.

- All carbon atoms are *sp3*-hybridized
- All bond angles are 109.5°





Methane

Alkyl groups

- Alkyl groups are formed by loss of a hydrogen atom from the corresponding alkane . General formula of alkyl group : CnH2n+1
- (e.g. CH_4 Methane – 1 H = -CH_3 Methyl group)
- Alkyl groups are named by dropping the -ane suffix of the alkanes and adding the suffix -yl. Methane becomes a methyl group, ethane an ethyl group, etc.

Unbranched alkyl groups

1. **Alkyl groups:** -ane ⇒ -yl (alkane ⇒ alkyl)

Alkane		Alkyl Group	Abbreviation
CH_3—H **Methane**	becomes	CH_3— **Methyl**	Me–
CH_3CH_2—H **Ethane**	becomes	CH_3CH_2— **Ethyl**	Et–
$CH_3CH_2CH_2$—H **Propane**	becomes	$CH_3CH_2CH_2$— **Propyl**	Pr–
$CH_3CH_2CH_2CH_2$—H **Butane**	becomes	$CH_3CH_2CH_2CH_2$— **Butyl**	Bu–

Table 4.4 The Unbranched Alkanes

Number of Carbons (n)	*Name*	*Formula* (C_nH_{2n+2})	*Number of Carbons (n)*	*Name*	*Formula* (C_nH_{2n+2})
1	Methane	CH_4	17	Heptadecane	$C_{17}H_{36}$
2	Ethane	C_2H_6	18	Octadecane	$C_{18}H_{38}$
3	Propane	C_3H_8	19	Nonadecane	$C_{19}H_{40}$
4	Butane	C_4H_{10}	20	Eicosane	$C_{20}H_{42}$
5	Pentane	C_5H_{12}	21	Henicosane	$C_{21}H_{44}$
6	Hexane	C_6H_{14}	22	Docosane	$C_{22}H_{46}$
7	Heptane	C_7H_{16}	23	Tricosane	$C_{23}H_{48}$
8	Octane	C_8H_{18}	30	Triacontane	$C_{30}H_{62}$
9	Nonane	C_9H_{20}	31	Hentriacontane	$C_{30}H_{62}$
10	Decane	$C_{10}H_{22}$	40	Tetracontane	$C_{40}H_{82}$
11	Undecane	$C_{11}H_{24}$	50	Pentacontane	$C_{50}H_{102}$
12	Dodecane	$C_{12}H_{26}$	60	Hexacontane	$C_{60}H_{122}$
13	Tridecane	$C_{13}H_{28}$	70	Heptacontane	$C_{70}H_{142}$
14	Tetradecane	$C_{14}H_{30}$	80	Octacontane	$C_{80}H_{162}$
15	Pentadecane	$C_{15}H_{32}$	90	Nonacontane	$C_{90}H_{182}$
16	Hexadecane	$C_{16}H_{34}$	100	Hectane	$C_{100}H_{202}$

Nomenclature of Alkanes

1. Select the longest possible straight chain; this gives the parent name for the alkane
2. Number the parent chain beginning with the end of the chain nearer the branched chain
3. Use the number obtained by application of rule 2 to designate the position of the branched chain
4. When two or more branched chains are present, give each branched chain a number corresponding to its position on the parent chain
5. When two or more branched chains are identical, indicate this by the use of the prefixes ‘di-’, ‘tri-’, ‘tetra-’, and so on

Physical Properties Of Alkanes and Cycloalkanes

1. A series of compounds, where each member differs from the next member by a constant unit, is called a **homologous series. Members of a homologous series** are called **homologs.**
2. At room temperature (25 °C) and 1 atm pressure, the **C1-C4 unbranched** alkanes are **gases; the C5-C17 unbranched alkanes are liquids; the unbranched** alkanes with **18 or more carbon atoms are solids.**

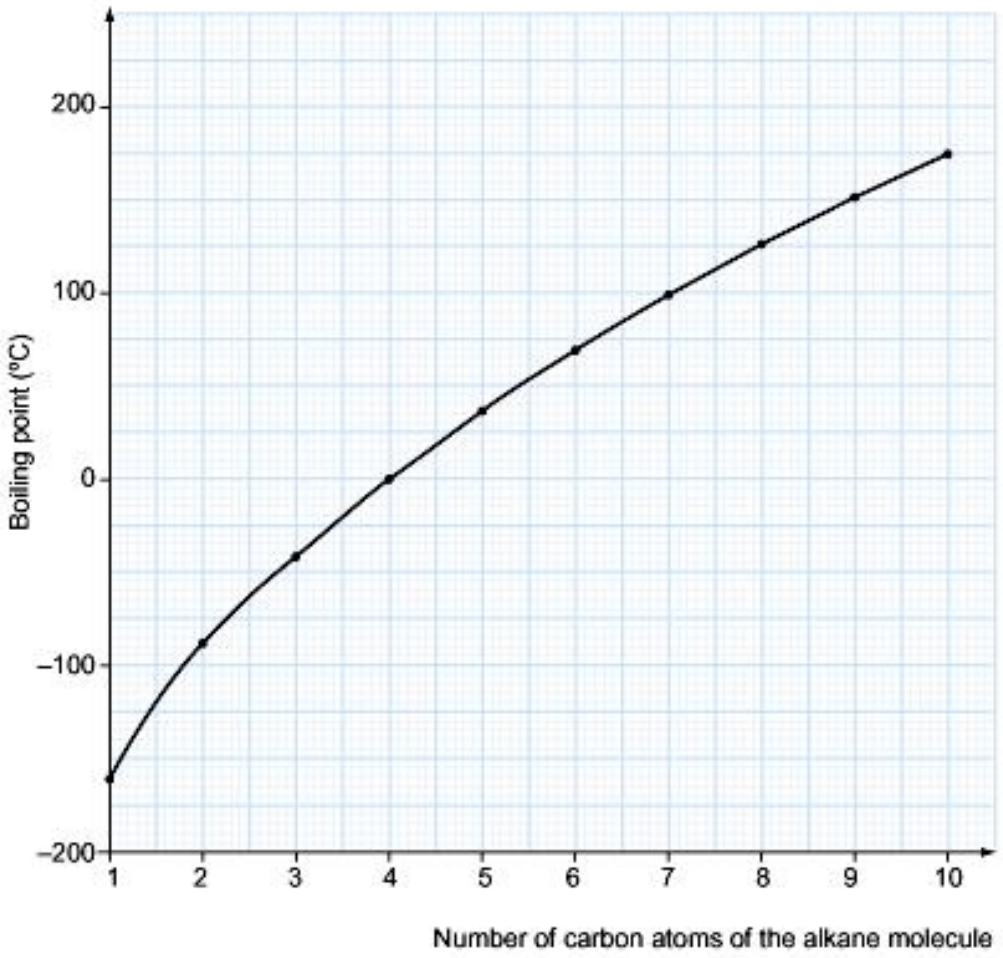
Physical Properties of Alkanes

Boiling Point

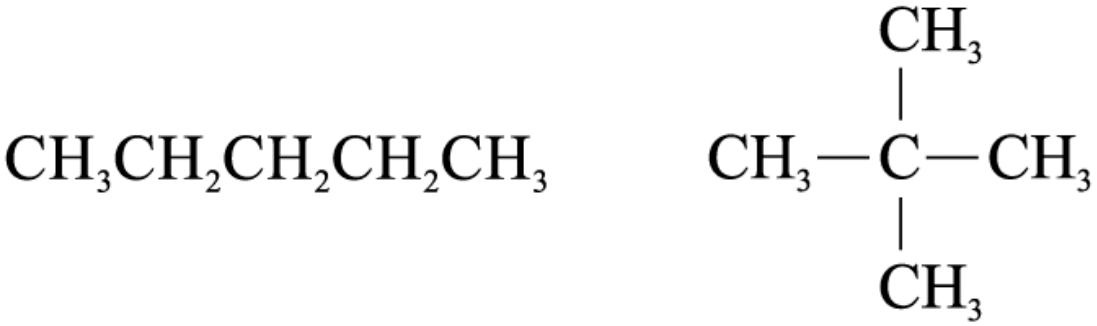
- Higher members have higher boiling points

Reason:

- Increase in molecular mass
- Increase in intermolecular force



Physical Properties of Alkanes



Pentane	Dimethylpropane
b.p. = 36°C	b.p. = 9.5°C
m.p. = −130°C	m.p. = −15.9°C

Branched-chain alkanes have lower boiling points than straight-chain alkanes

∵ molecule is more compact ⇒ surface area ↓

⇒ van der Waals' force ↓ ⇒ boiling point ↓

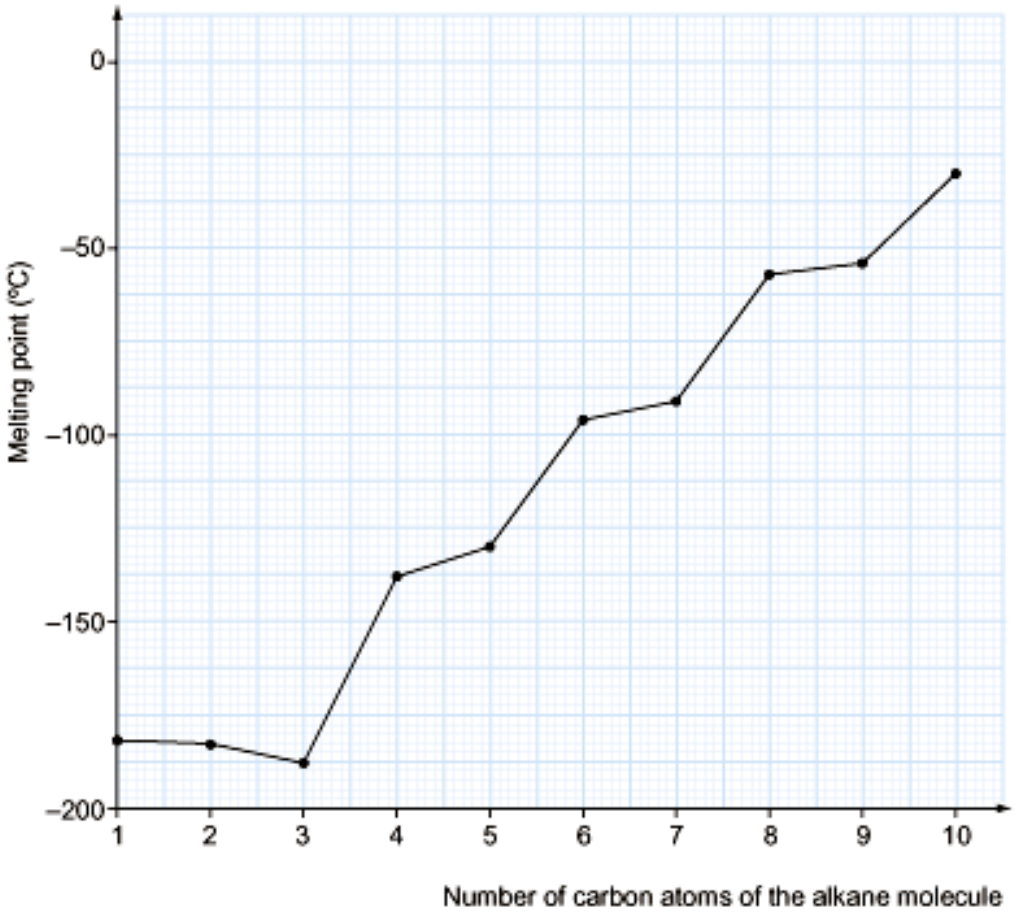
Physical Properties of Alkane

Melting Point

- Higher members have higher melting points

Reason:

- Increase in molecular mass
- Increase in intermolecular force



Physical Properties of Alkane

Solubility

- non-polar compounds
- insoluble in water and highly polar solvents
- soluble in non-polar solvents like benzene, 1,1,1-trichloroethane

Density

All alkanes and cycloalkanes have densities less than 1 g cm^{-3} at 20°C.

$\Rightarrow$ Petroleum floats on water surface

Alkanes are less dense than water and swim on top of water

Preparation of alkanes

From Alkyl Halides

- Wurtz Reaction
- Reduction
- Gringard reagent

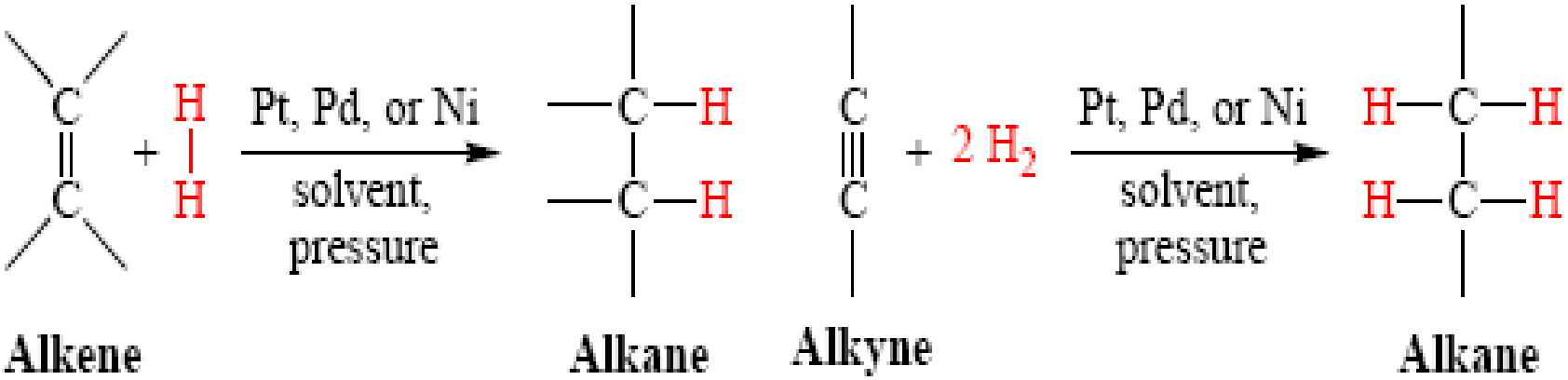
From Alkenes & Alkynes

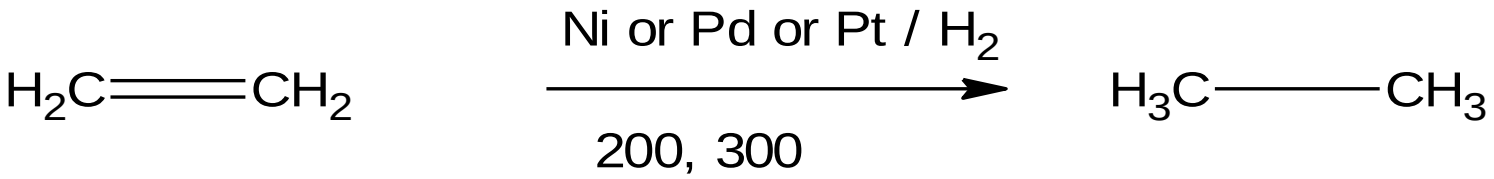
- Catalytic Hydrogenation

From Alkenes & Alkynes

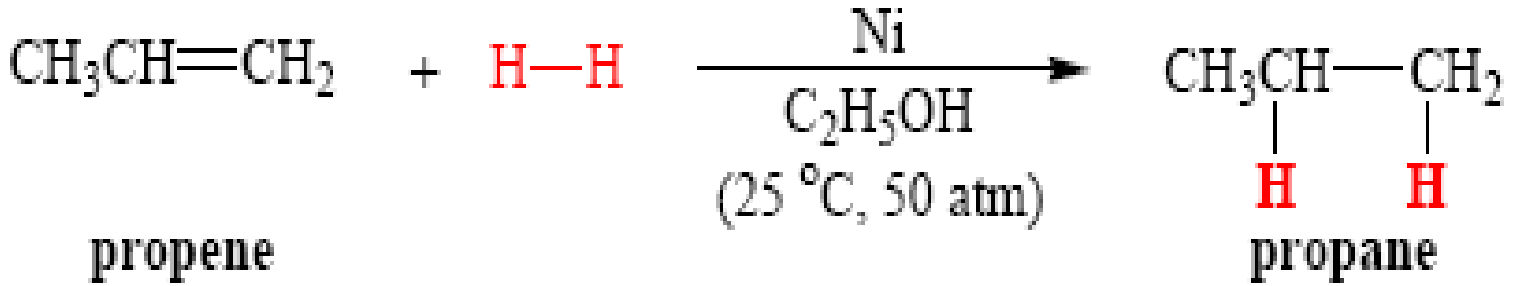
Hydrogenation of unsaturated hydrocarbon:

General Reaction

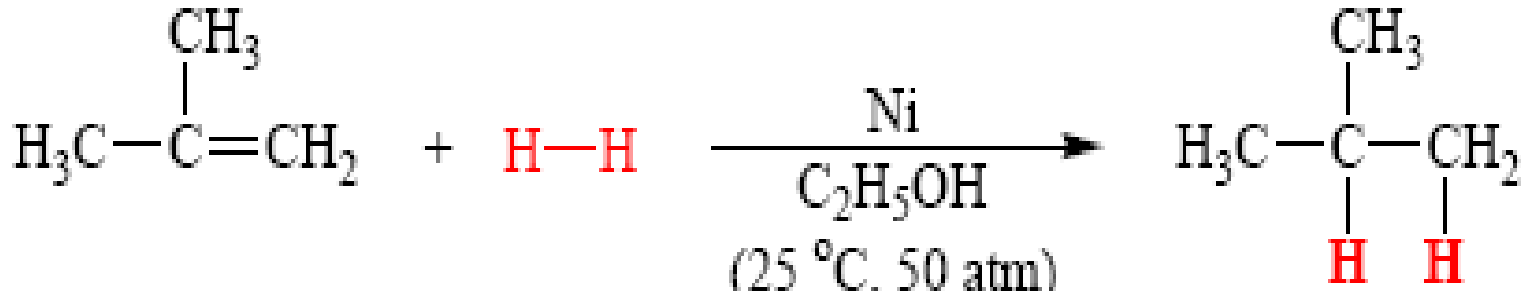




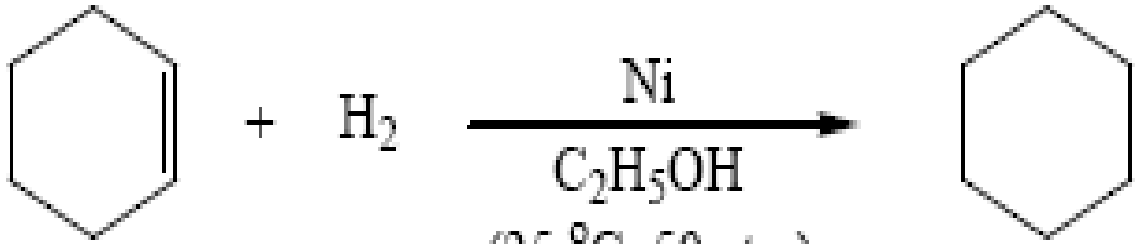
Specific Examples



propene **propane**



2-Methylpropene **Isobutane**

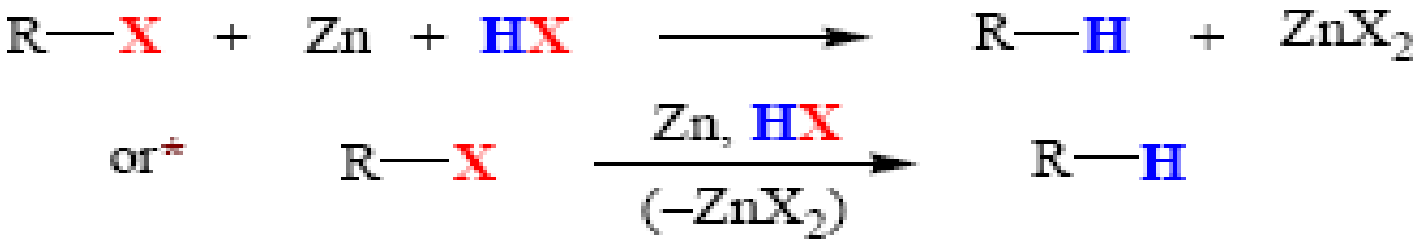


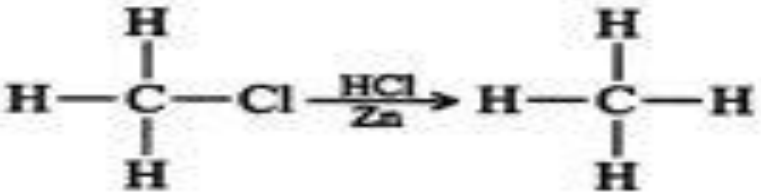
Cyclohexene **Cyclohexane**

From Alkyl Halides

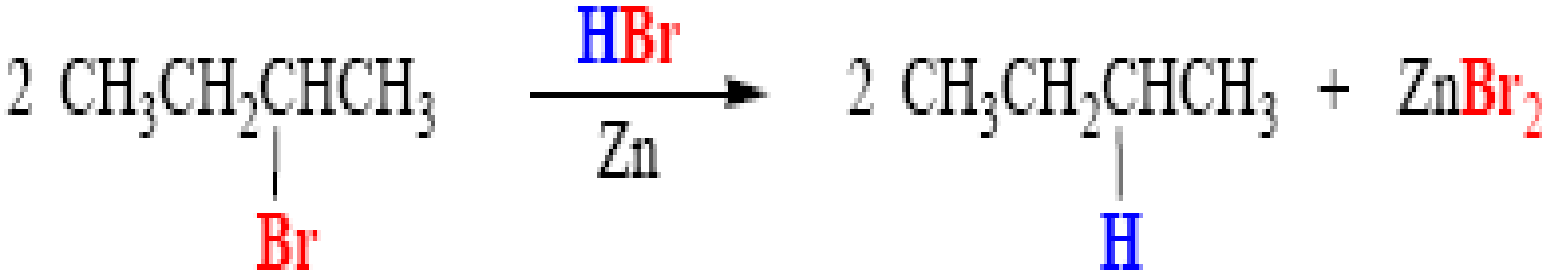
A) Reduction of alkyl halides

General Reaction



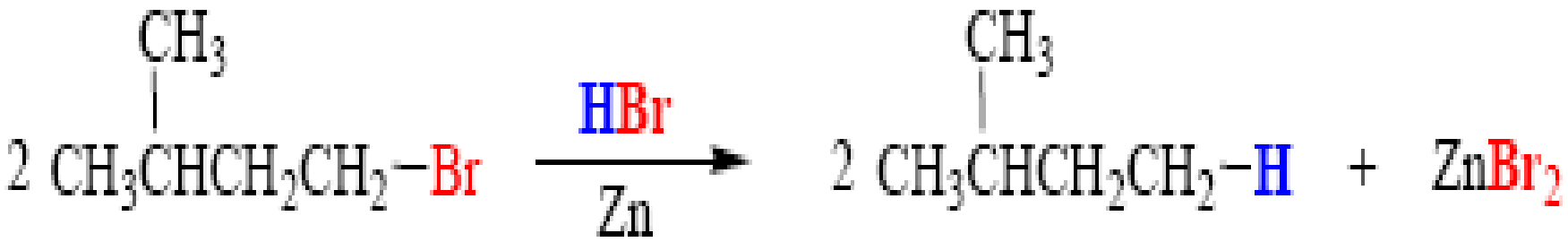


Specific Examples



sec-Butyl bromide
(2-bromobutane)

Butane



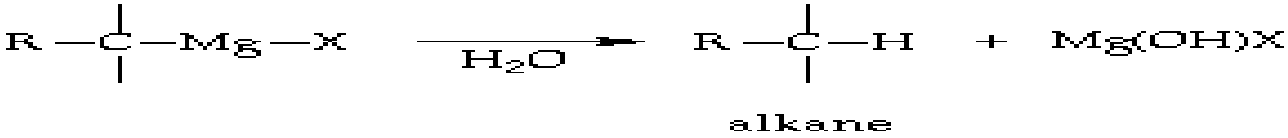
Isopentyl bromide
(1-bromo-3-methylbutane)

Isopentane
(2-methylbutane)

B) Hydrolysis of Grignard Reagent

Grignard reagent is an alkyl magnesium halide compound, R-Mg-X

The Grignard reagent is formed when a solution of an Alkyl Halide (R-X) is allowed to stand over a metallic magnesium in the presence of dry ether



$CH_3CH_2Br + Mg^{2+} \xrightarrow{\text{Dry ether}} CH_3CH_2MgBr$

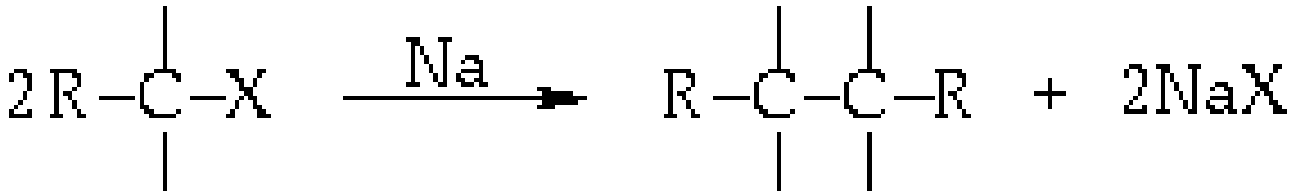
Grignard reagent

$CH_3CH_2MgBr \xrightarrow{H_3O^+} CH_3CH_3 + Mg(OH)Br$

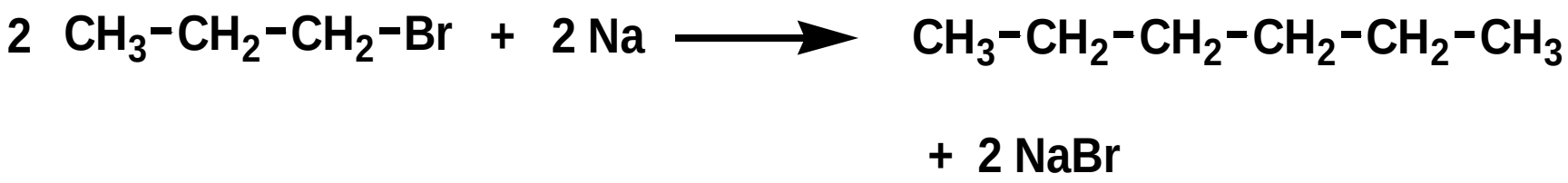
C) Wurtz Reaction

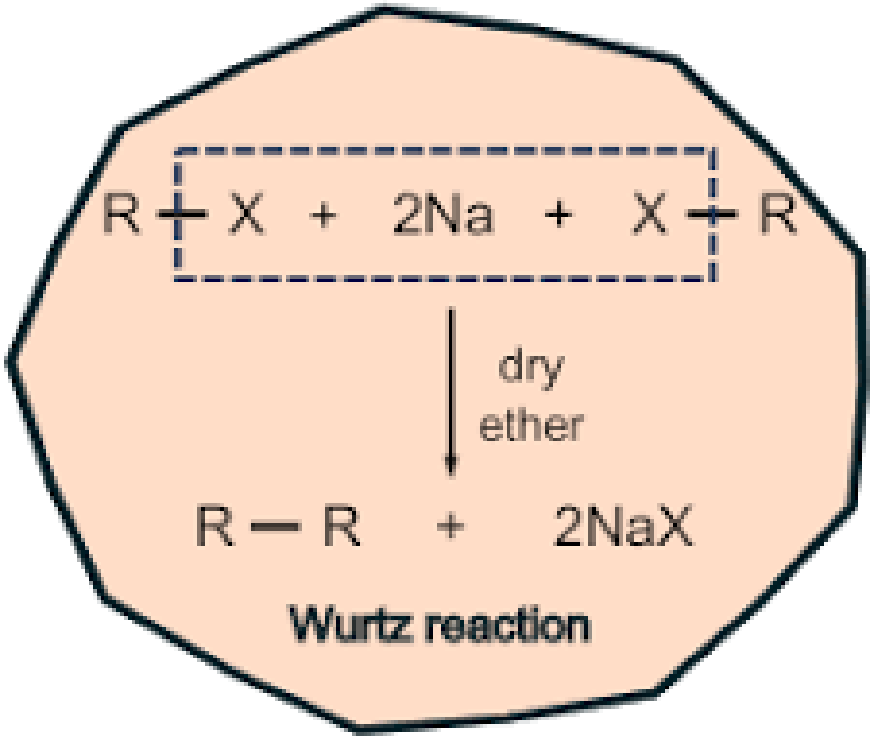
This is the reaction of two alkyl halides (R-X) with metallic sodium to give symmetrical alkanes.

The wurtz reaction is useful for the preparation of unsymmetrical alkanes



a symmetrical alkane





$RX + 2\,Na + RX \xrightarrow[\text{ether}]{\text{pure \& dry}} R - R + 2\,Na\,X$

$CH_3Cl + 2Na + Cl\,CH_3 \xrightarrow[\text{ether}]{\text{pure \& dry}} CH_3CH_3 + 2NaCl$

$2CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}} - Cl + 2Na \xrightarrow[\text{ether}]{\text{pure \& dry}} CH_3CH\,(\underset{\displaystyle CH_3}{\underset{|}{CH}})\,CH_3 + 2NaCl$

$RX + 2\,Na + XR' \xrightarrow[\text{ether}]{\text{pure \& dry}}$ Mixture of $R' - R' + R' - R + R - R$ (mixture of three)

$CH_3Cl + 2Na + Cl\,C_2H_5 \xrightarrow[\text{ether}]{\text{pure \& dry}} CH_3CH_3 + C_3H_8 + C_4H_{10}$

Reactions of Alkanes

Combustion

Complete combustion :

Alkanes react with sufficient oxygen to give carbon dioxide and water through a complex series of reaction with the release of a large amount of energy.

General formula:

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

Complete combustion

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Incomplete combustion

$$CH_3\text{-}CH_2\text{-}CH_3 + 4\ O_2 \longrightarrow CO_2 + 2\ CO + 4\ H_2O + \text{heat}$$

Chlorination

- Methane reacts with chlorine under diffuse sunlight or heating but not in dark
- A mixture of products (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) is formed with the replacement of hydrogen by one or more chlorine atom

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

$$CH_3Cl(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_2Cl_2(g) + HCl(g)$$

$$CH_2Cl_2(g) + Cl_2(g) \xrightarrow{\text{UV light}} CHCl_3(g) + HCl(g)$$

$$CHCl_3(g) + Cl_2(g) \xrightarrow{\text{UV light}} CCl_4(g) + HCl(g)$$

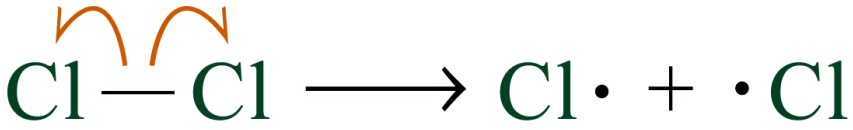
Reaction Mechanism: Free Radical Substitution Reaction

Mechanism of reaction :

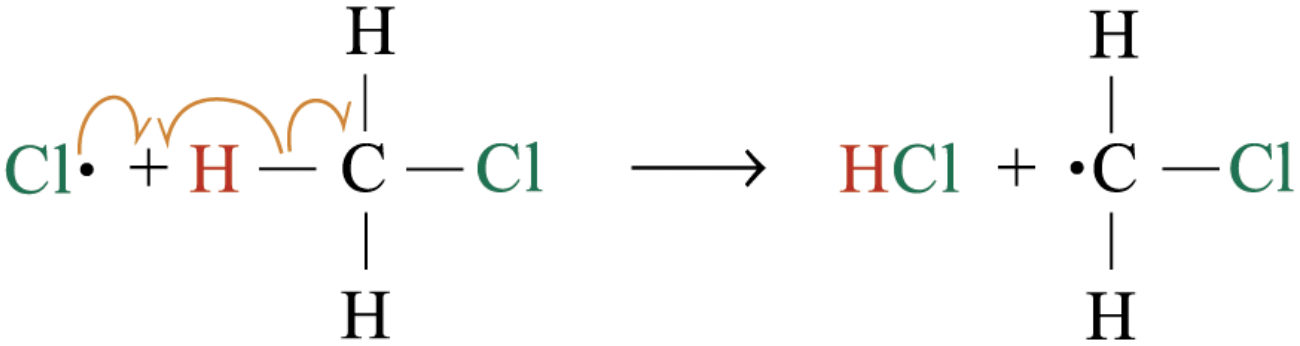
1. *Chain initiation*

- homolytic fission of chlorine molecules by heat or light into two chlorine radicals

  Step 1:

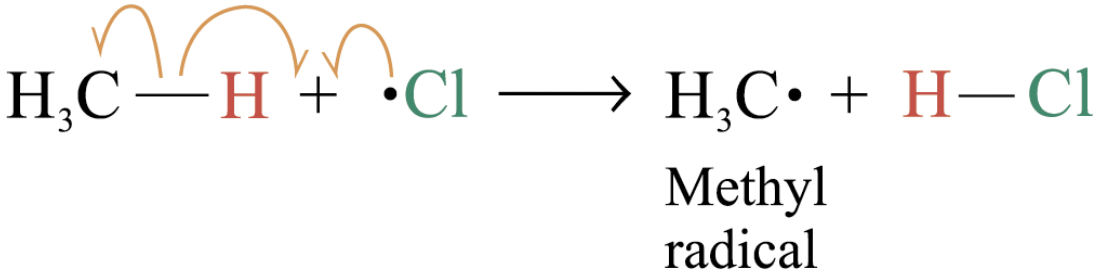


Further substitution occurs:

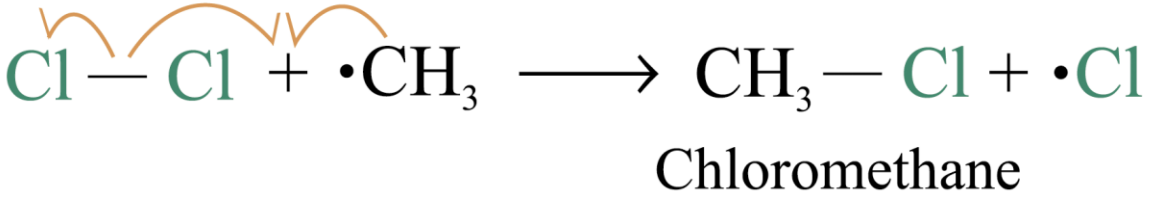


2. *Chain propagation*

Step 2:

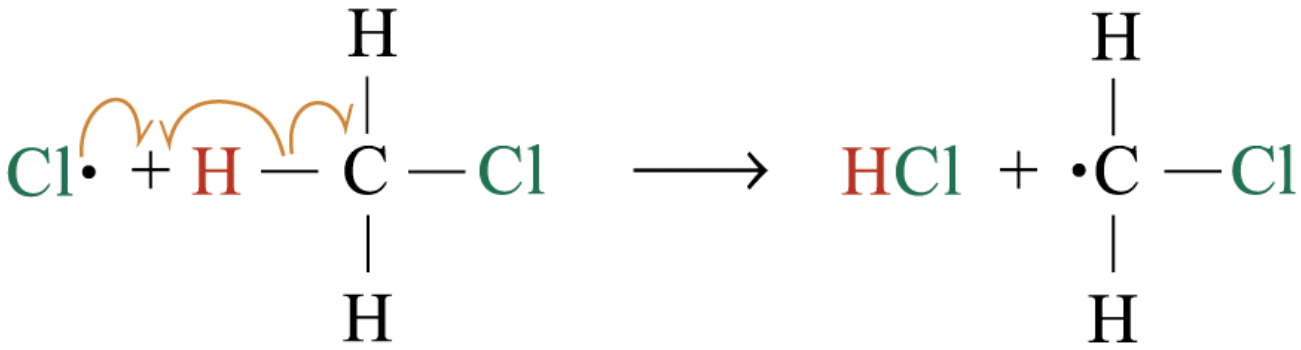


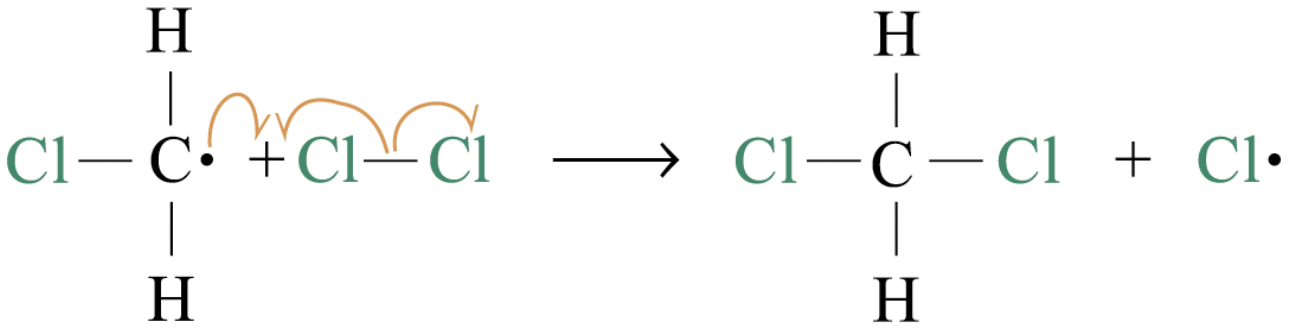
Step 3:



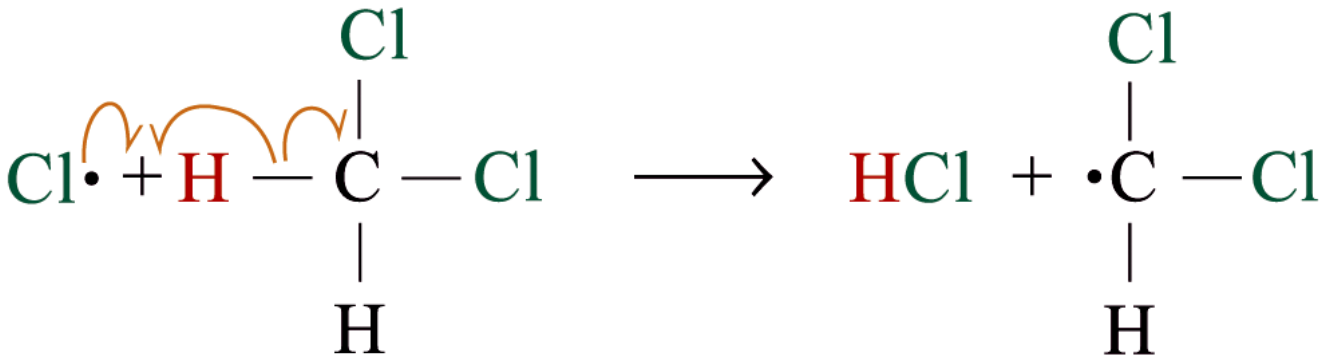
- steps 2 and 3 repeat hundreds or thousands of time due to formation of the reactive intermediate in each step
  ⇒ chain reaction

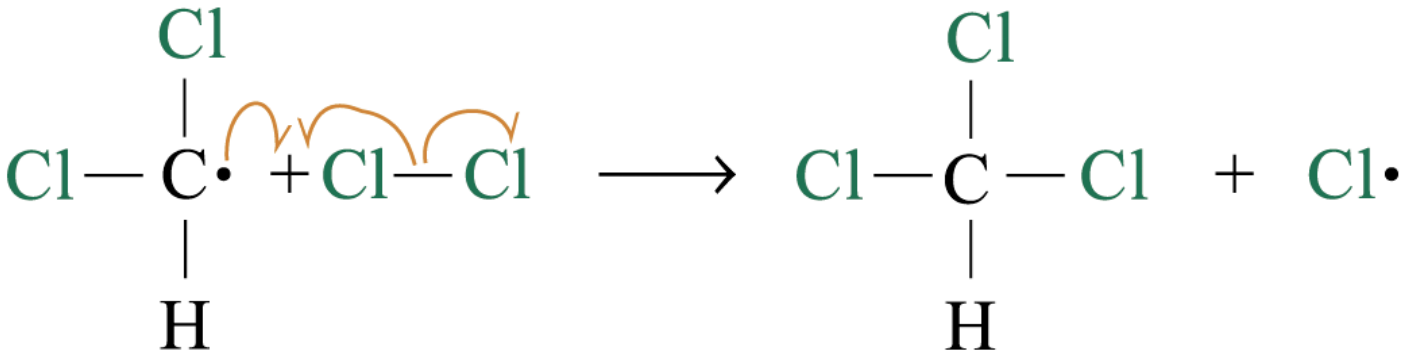
Further substitution occurs:



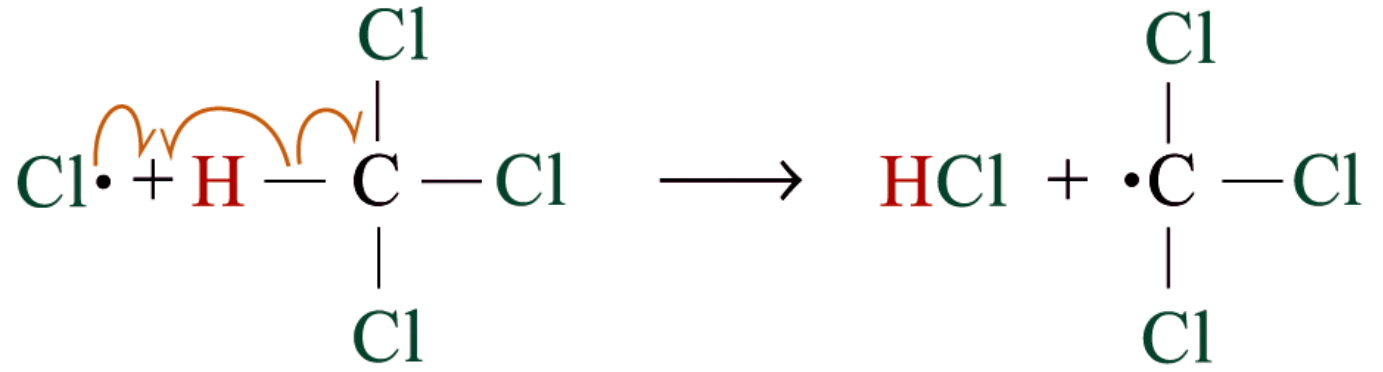


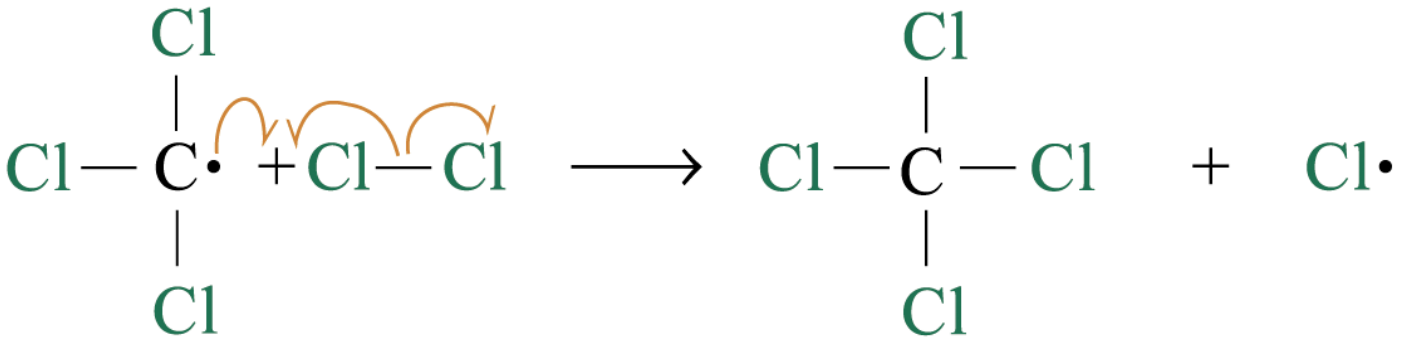
Dichloromethane





Trichloromethane

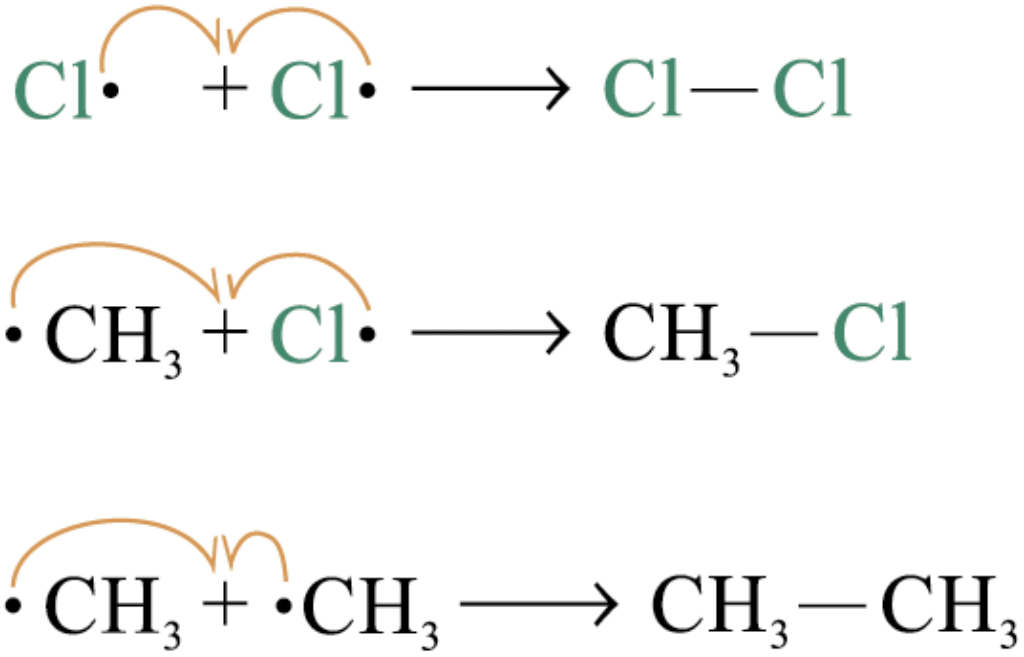




Tetrachloromethane

3. *Chain termination*

- two free radicals combine to form a neutral molecule
- the chain reaction is terminated



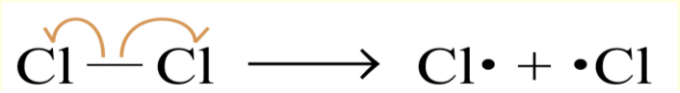
Example

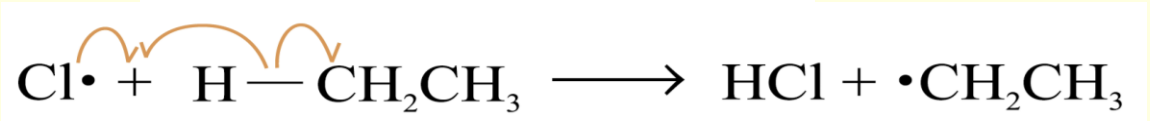
Write down the reaction mechanism involved in the chlorination of ethane in the presence of diffuse sunlight.

Solution:

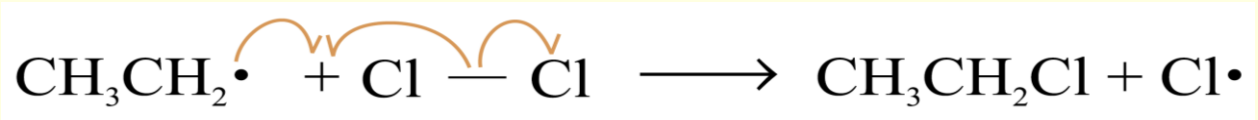
The reaction mechanism is shown as follows:

1. Chain initiation



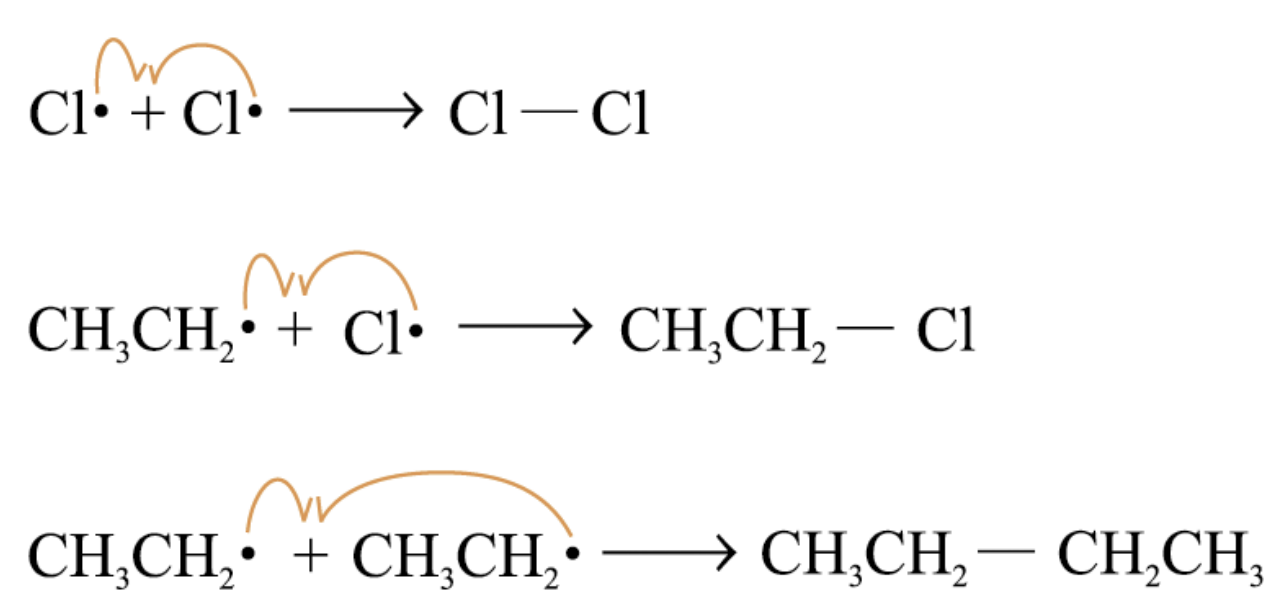


2. Chain propagation



Solution:

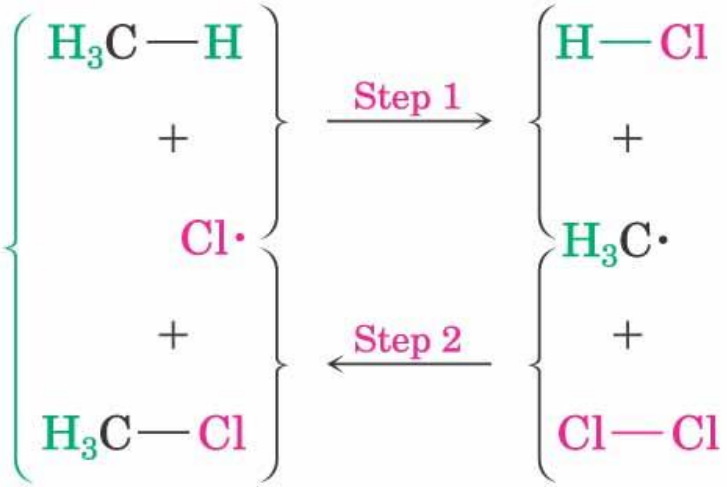
3. Chain termination



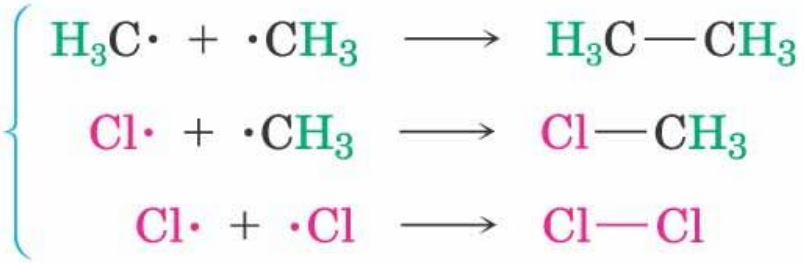
Mechanism For the Radical Halogenation of Methane

Initiation step

Propagation steps (a repeating cycle)



Termination steps



Overall reaction


Thank You For Listening