

ALKANES : ORGANIC CHEMISTRY



- Alkanes are saturated hydrocarbons

 ↳ only single carbon-carbon bonds

- Can exist as a straight chain isomer, a branched isomer, or a cyclic isomer

PHYSICAL PROPERTIES :

- They are non-polar compounds / No overall polarity / No overall dipole

 ↳ No dipole moment

 - As C + H atoms have almost the same electronegativity

- Intermolecular forces are weak ID-ID / Van der Waal's forces

- States at RTP :

C₁ to C₄ : gases

C₅ to C₁₆ : liquids

C₁₆ and beyond : waxy solids

• Density increases (molar mass increases)

• MP / BP increases (Stronger ID-ID forces)

• No. of isomers increases (chain isomers)

• Viscosity increases

• Volatility decreases (as BP increases)

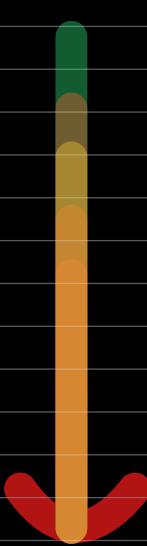
• Vapour pressure decreases (ID-ID forces get stronger)

SOURCE OF ALKANES : By fractional distillation of CRUDE OIL

Simplified Diagram of fractionating column.

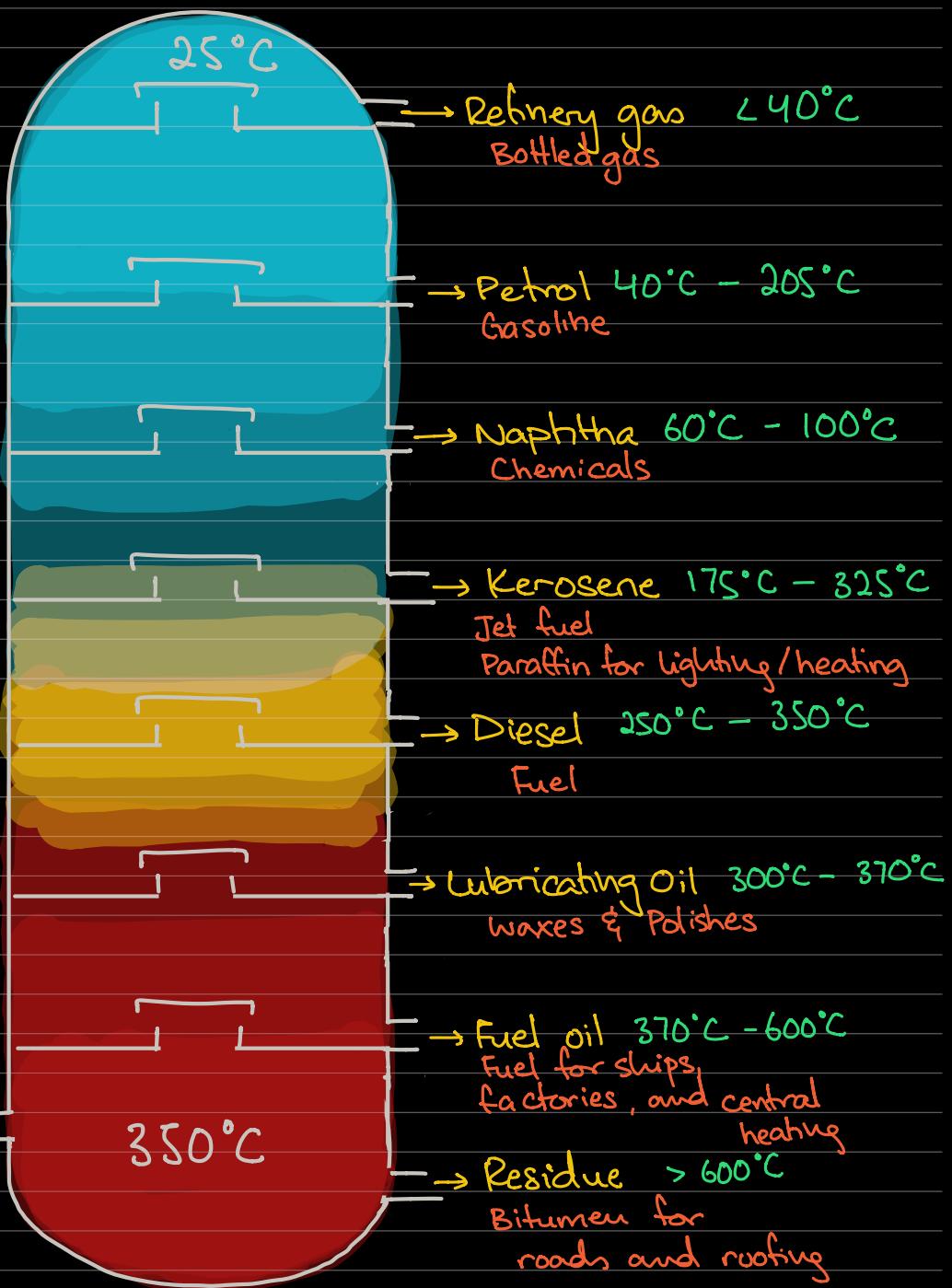
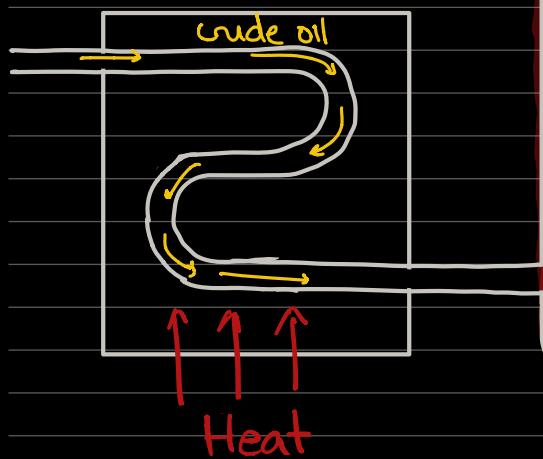
small Molecules

- Low Boiling Points
- Volatile



Large/Heavy Molecules

- High boiling points
- Harder to ignite



REACTIONS INVOLVING ALKANES:

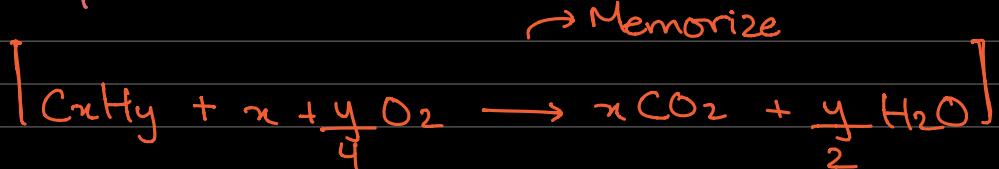
1. Combustion
2. Cracking
3. Free Radical Substitution

COMBUSTION OF ALKANES

- Lower alkanes (C_1 to C_4) are highly flammable and they undergo complete combustion to form CO_2 , H_2O (plus release of oxygen)
- As the number of carbons increase, the alkanes become more difficult to ignite (higher E_a) - and they burn with a more sooty flame.
- As the number of carbons increase, the reaction becomes more exothermic

$\Delta H^\circ_{\text{combustion}}$	
i.e.	CH_4
	- 890 kJ/mol
	C_2H_6
	- 1560 kJ/mol
	C_6H_{14}
	- 4163 kJ/mol
	C_8H_{18}
	- 5470 kJ/mol

Combustion Equation



order of balancing:
1. Carbon
2. Hydrogen
3. Oxygen

INCOMPLETE COMBUSTION:

- Incomplete combustion - when there is limited oxygen



→ Complete combustion required 5 mols



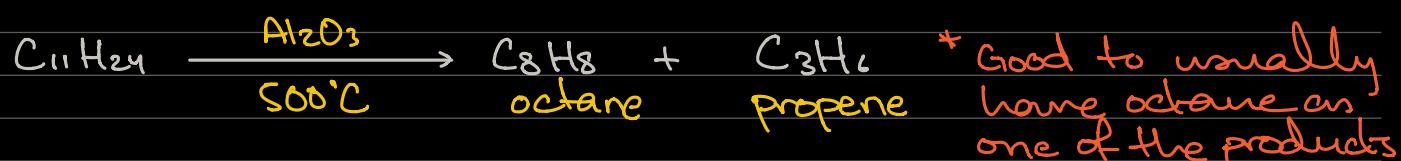
- As the moles of oxygen decrease, there is more and more incomplete combustion taking place.

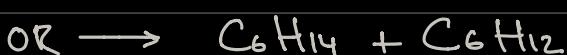
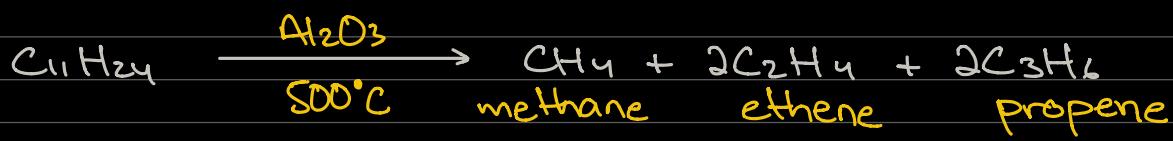
CRACKING OF ALKANES

- Is a process in which large hydrocarbon molecules are broken down using high temperature, high pressure, and catalysts, to obtain more useful molecules which have a greater demand
- The fractions obtained from fractional distillation of crude oil are mostly larger hydrocarbons
- To meet the demand for the smaller hydrocarbons (i.e. octane, ethene, butane, etc.) - cracking is carried out.
- Alkenes are used as chemical "feedstock" → i.e. they are the raw materials for other industries, e.g. polymers
- The smaller molecules are separated by fractional distillation

CATALYTIC CRACKING → uses high temperatures and catalysts

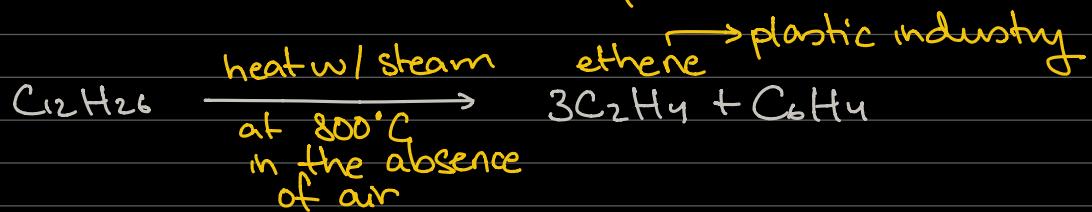
→ $\text{Al}_2\text{O}_3 / \text{SiO}_2$





THERMAL CRACKING - is optimised for ethene production

- Uses high temperatures ($\sim 800^\circ C$), moderate pressure, absence of air, but in the presence of steam



When is $H_2(g)$ a cracking product?



- H_2 is a product only when the other non-hydrogen products are alkenes only

Octane number: tells us the % of octane in petrol
(petrol is a mixture of octane and heptane)

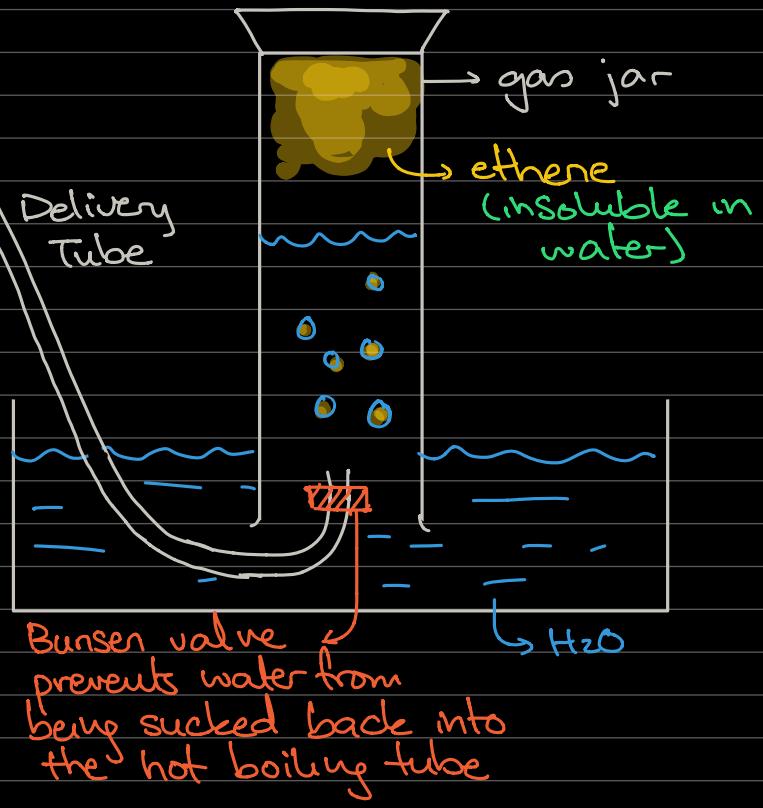
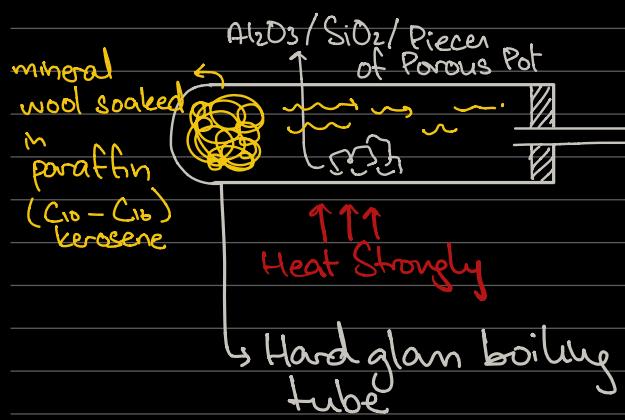
i.e. 95 octane = 95% octane + 5% heptane

- Octane used in petrol is a branched isomer:



CH_3
↳ burns more cleanly
and more efficiently

LAB SCALE CRACKING → to produce ethene in the lab

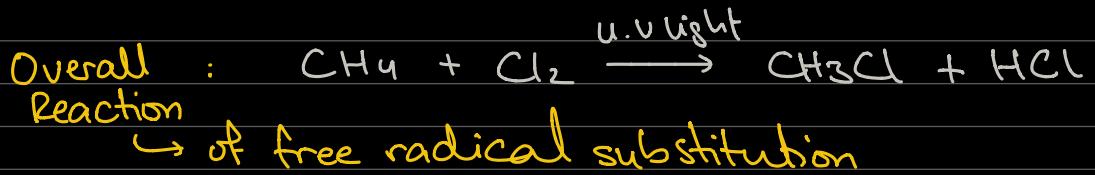


Note: Another way of preventing water from entering the boiling tube is to pull the delivery tube out of the water before it is cooled

FREE RADICAL SUBSTITUTION OF ALKANES

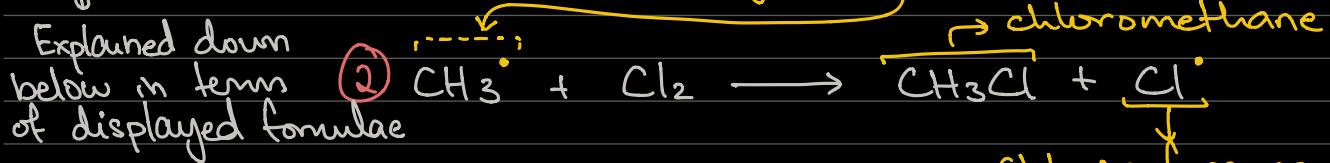
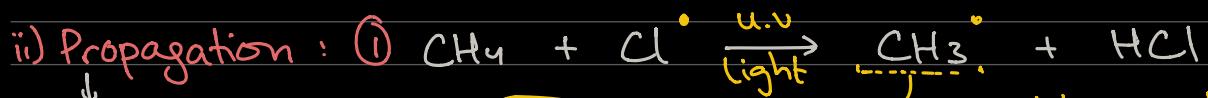
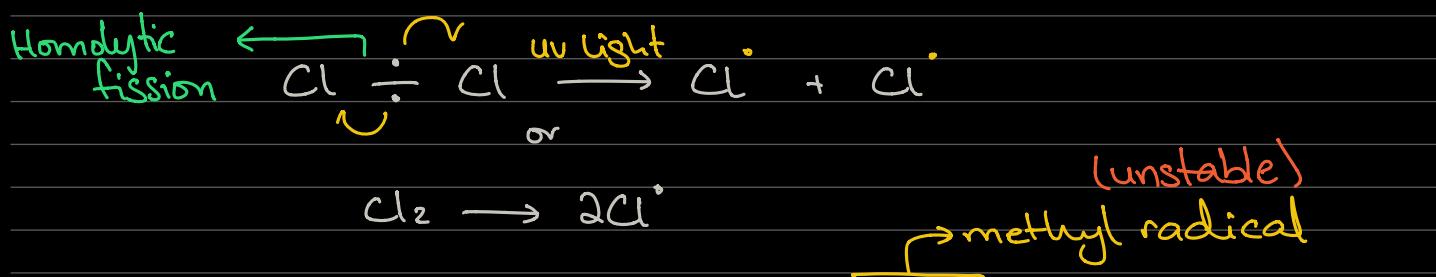
↳ Form alkyl halides

- Alkane: non-polar / hydrocarbon
 - C-C and C-H bond energies are very high
 - We need some E_a to break these covalent bonds and a very reactive species to react with these non-polar bonds.
- UV light provides the energy to break the Cl-Cl bond
 - ↳ Hence, these are photochemical reactions, where UV light initiates the reaction



MECHANISM: Describes how this ↑ reaction takes place, what bonds are broken, what new bonds are made, etc.

i) Initiation: A molecule is broken down into its free radicals

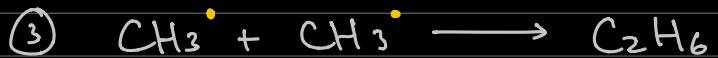


Chlorine free radical is re-generated, or "propagated"

Note: In a propagation step, there is a molecule and a radical on both sides of the equation (reactant and product side)

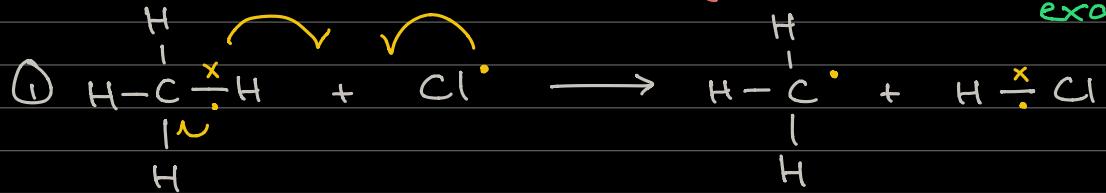
iii) Termination : Two radicals combine together to form a molecule

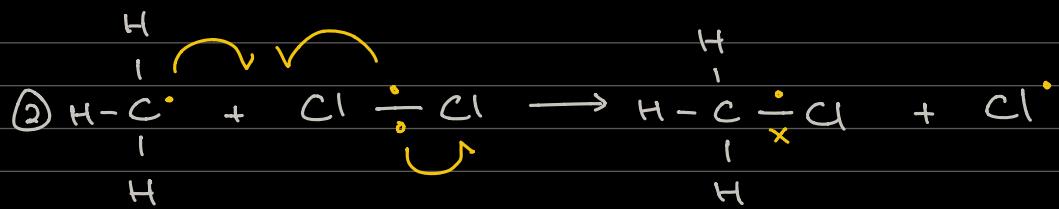
Three possible termination reactions in this case:



ethane → produced in trace amounts

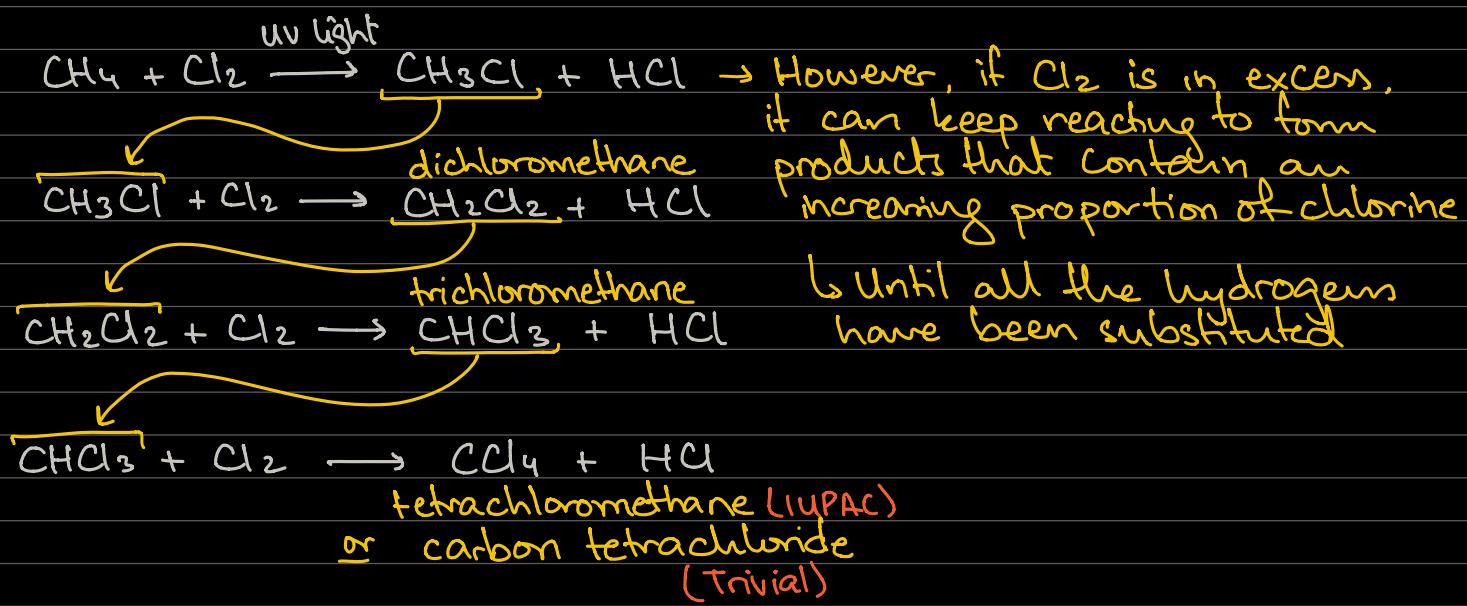
Propagation in term of displayed formulae: (for understanding only, don't show this in exam papers)





Note: When describing FRS (Free Radical Substitution), primarily use equations (No sentences or paragraphs)

FURTHER SUBSTITUTION (BY) PRODUCTS



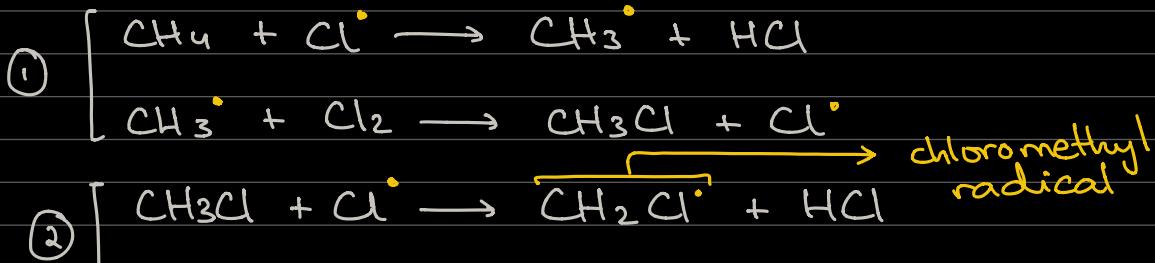
FRS MECHANISM for the formation of CH_2Cl_2



i) Initiation

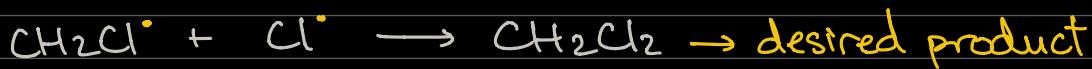


ii) Propagation





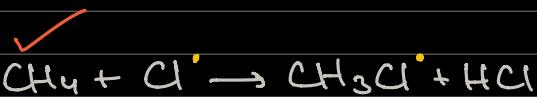
iii) Termination



Q. Why aren't H^\cdot (free radicals) formed?

Short answer: Because their formation is not energetically favourable

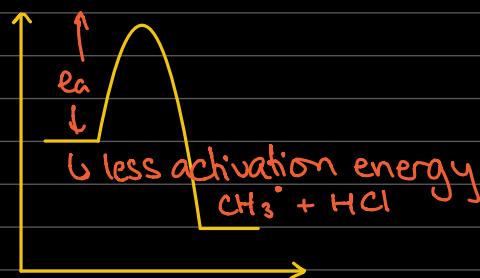
Long answer:



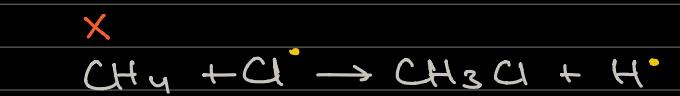
- CH_3^\cdot are favored energetically

- is exothermic

$$\Delta H = -18 \text{ kJ/mol}$$



- exothermic reactions are energetically favored as the products are at a lower energy level

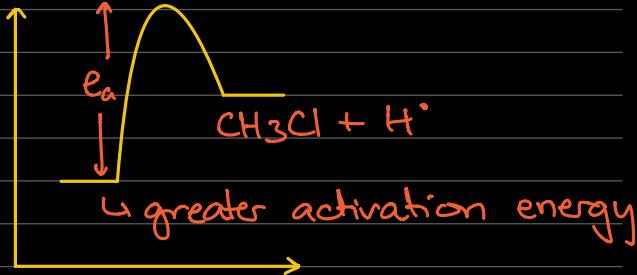


- H^\cdot radicals are never formed in FRS

- their formation is not energetically favourable

- It is endothermic

$$\Delta H = +75 \text{ kJ/mol}$$



- Products are at a higher energy level, so they are not favoured energetically

BYPRODUCTS OF FRS

(g) CH_3Cl → usually in the highest yield

(l) CH_2Cl_2

Boiling point increases

(l) CHCl_3

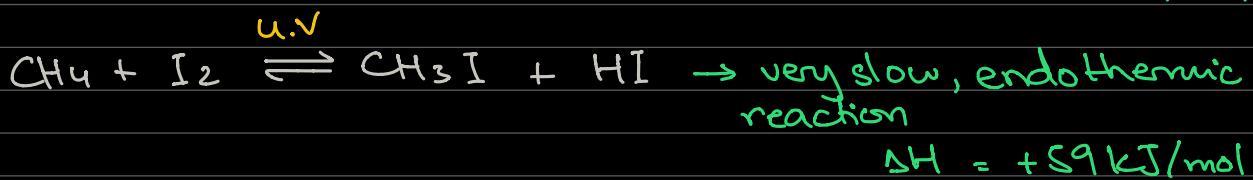
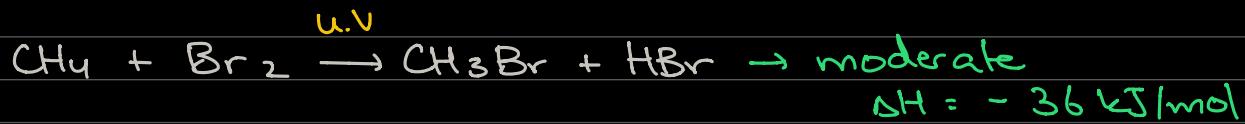
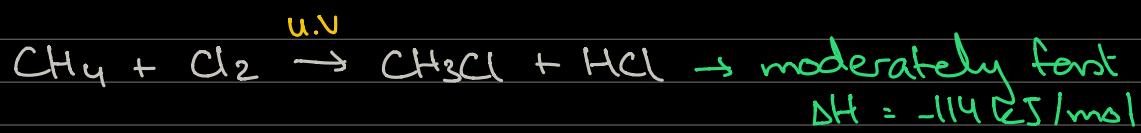
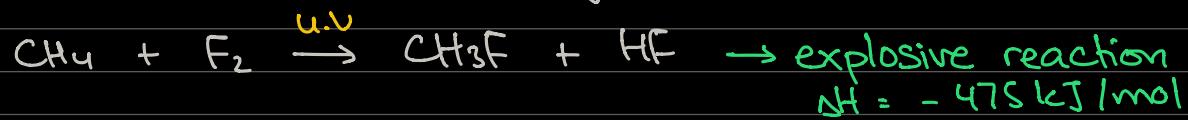
(l) CCl_4



↳ can be separated using fractional distillation

Note: Halogens other than chlorine can also be used in FRS, however, the rates of reactions vary greatly.

Substitution with other halogens:



These varying reaction speeds are because of different bond energies of the halogens.

FREE RADICAL SUBSTITUTION OF C_2H_6 (Ethane)



i) Initiation :



ii) Propagation :





iii) Termination :



PROPAGATION ALL THE WAY TO CCl_4

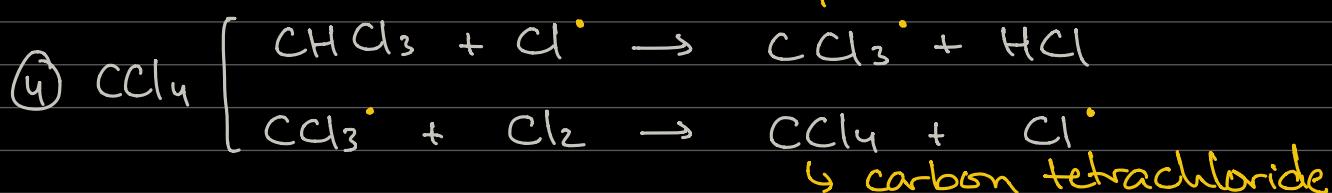
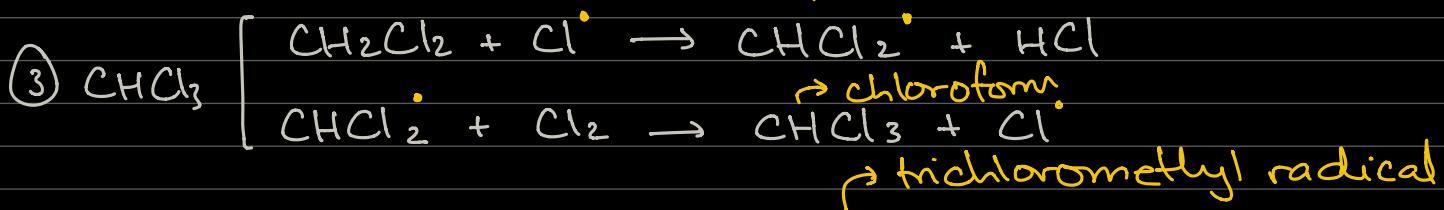
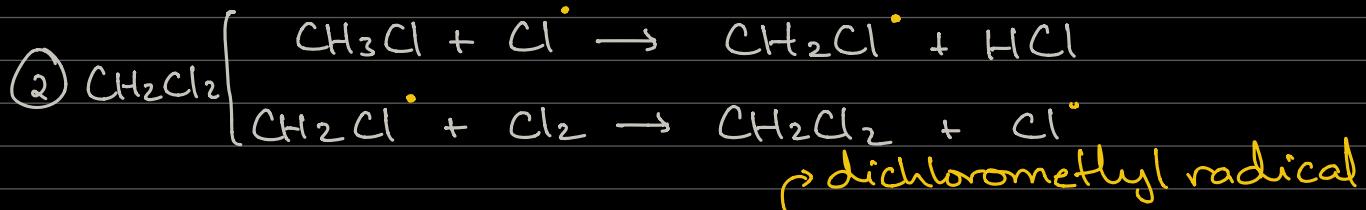
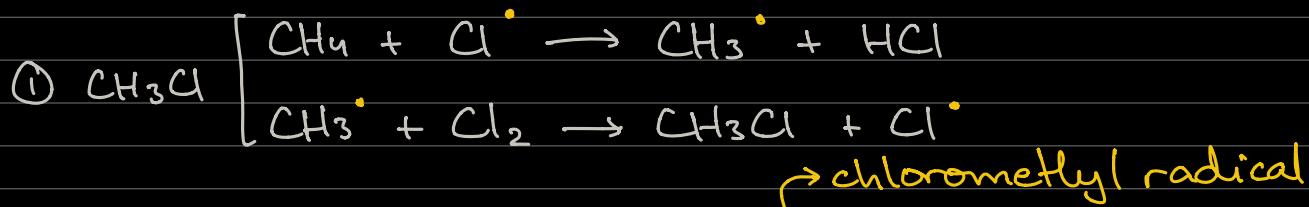


i) Initiation



ii) Propagation

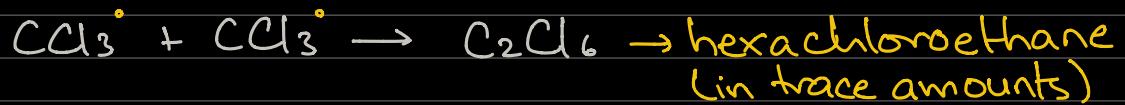
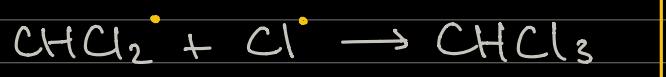
\rightarrow methyl radical



iii) Termination



$\left. \right] \rightarrow$ desired products



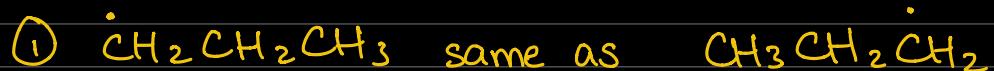
$x - \text{ } - \text{ } - \text{ } - x$

Example :



Q. How many different propyl radicals can be made from propane, if only one hydrogen is substituted?

Ans. Two :



RFS OF CYCLOHEXANE

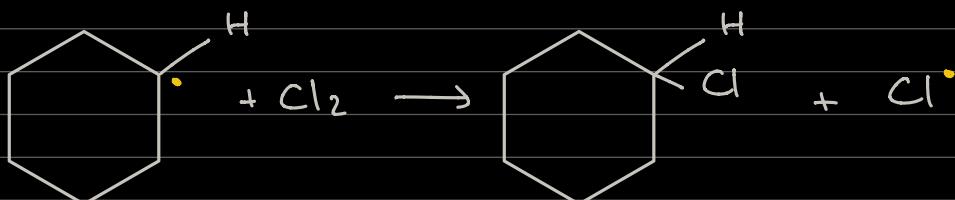
Mechanism :



i) Initiation



ii) Propagation



iii) Termination

