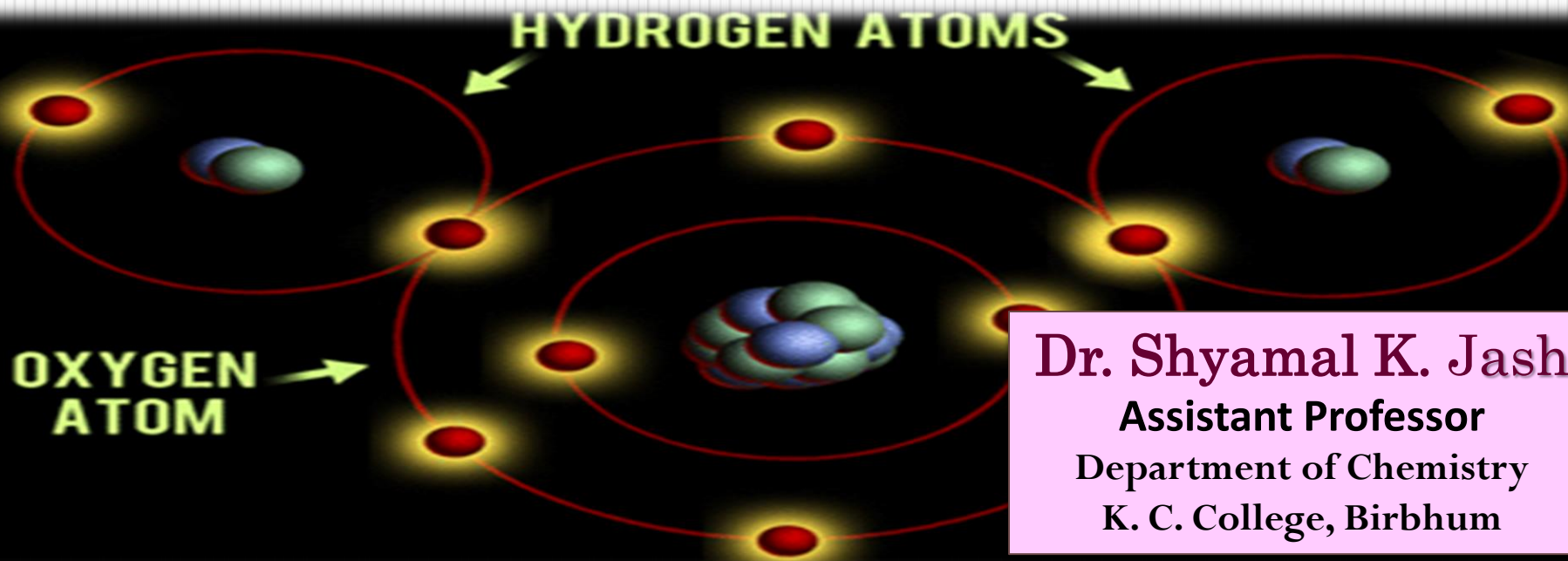


B.Sc SEM-II Chemistry (Honours)

PAPER-CC-4

Alkanes and Free Radical Substitution



The background of the slide features several faint, light-colored chemical structures. These include a complex heterocyclic ring system with multiple nitrogen atoms and carbonyl groups, a smaller five-membered ring with a nitrogen atom, and a linear chain of atoms with various functional groups. The structures are rendered in a light blue or grey tone, providing a scientific context for the title.

Preparation of Alkanes

Crude Oil as a Source of Alkanes

Petroleum Refining

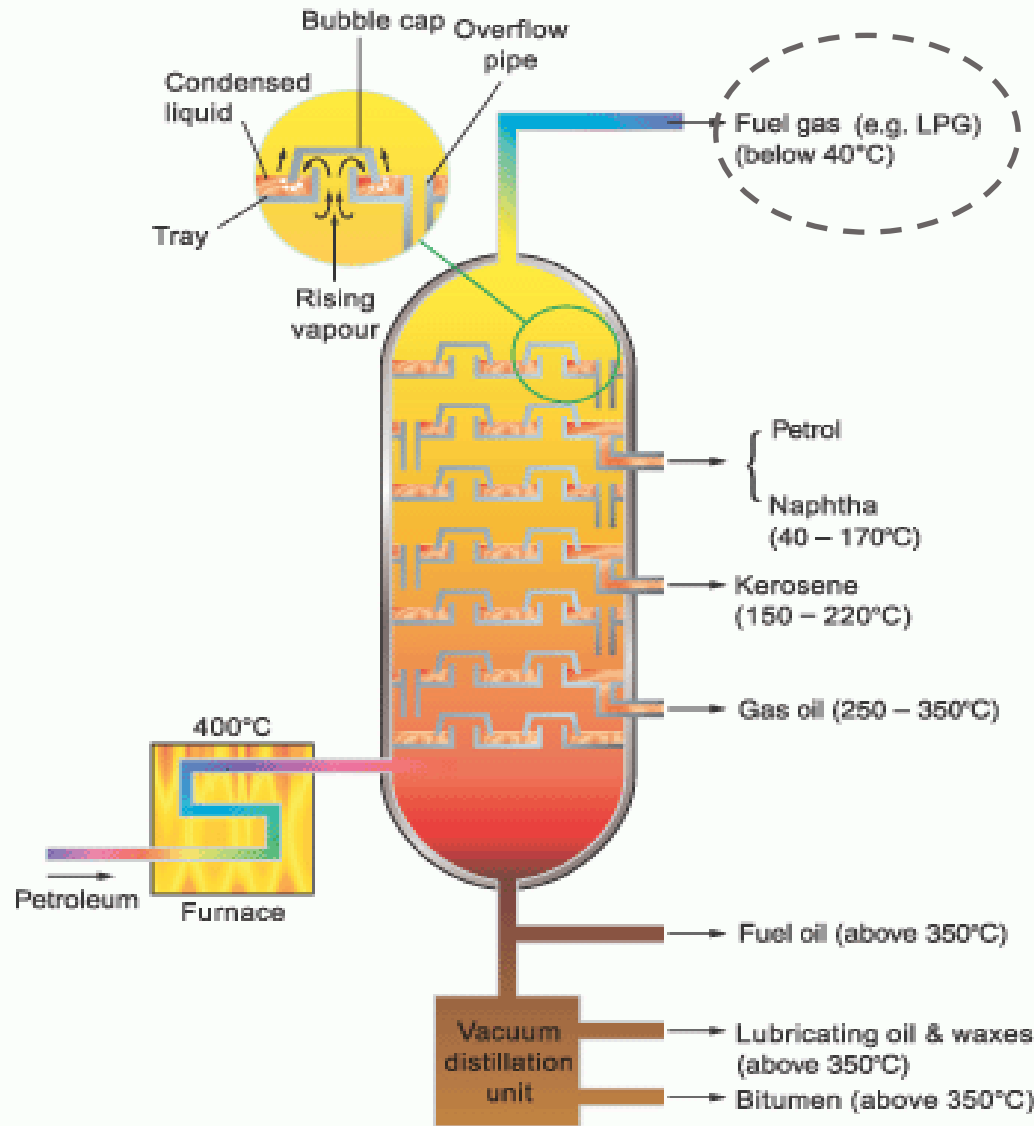
- The first step is fractional distillation
 - separate petroleum into fractions based on the volatility of its components
 - performed in a petroleum refinery
 - a fractionating tower is used

Petroleum Refining



A petroleum refinery

A simplified diagram of a fractionating tower



Contains H_2S
Removed by
treatment with
a weak base

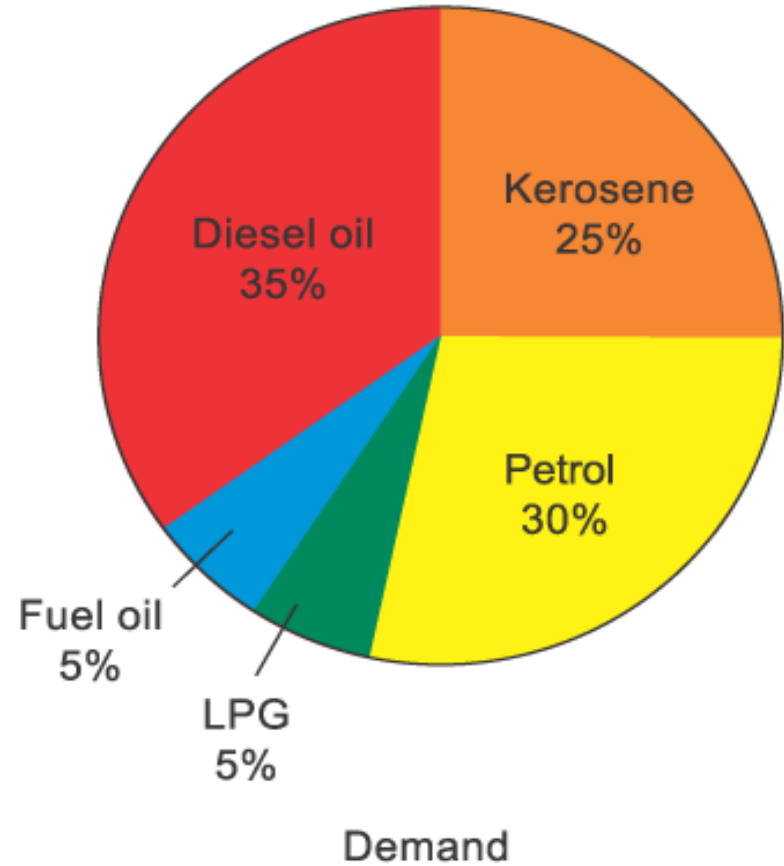
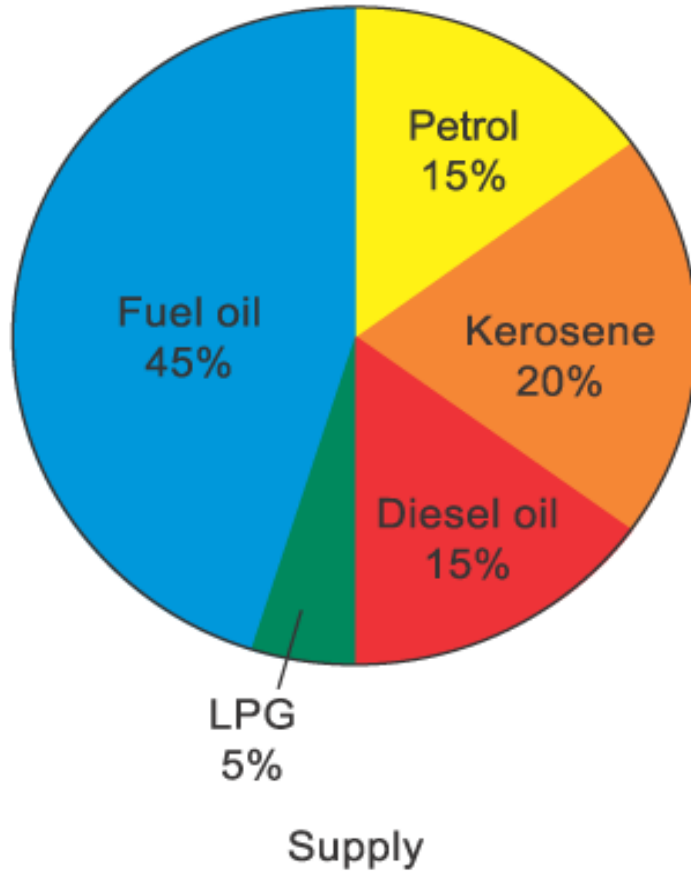
Typical fractions obtained by fractional distillation of petroleum

Fraction	Boiling point range (°C)	Number of carbon atoms that the molecules contain	Major uses
Fuel gas (e.g. LPG)	< 40	1 – 4	Gaseous fuel, raw materials for manufacture of chemicals
Petrol	40 – 150	5 – 10	Fuel for motor vehicles
Naphtha		10 – 14	For making town gas
Gas oil (Diesel oil)	220 – 350	14 – 25	Fuel for trucks, lorries and locomotives

Typical fractions obtained by fractional distillation of petroleum

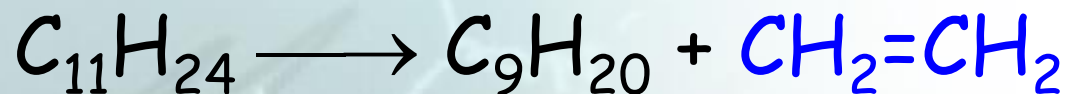
Fraction	Boiling point range (°C)	Number of carbon atoms that the molecules contain	Major uses
Fuel oil	> 350	> 25	Fuel for cargo ships and generating electricity in power stations
Lubricating oil	> 350	> 25	Lubricating oil for moving parts of machinery
Bitumen	> 350	> 25	For surfacing roads and roofs

Cracking of Petroleum



Cracking of Petroleum

- Convert hydrocarbons from heavier fractions into lighter fractions
- Performed in the absence of air
- Providing lighter fractions of petroleum, **alkenes** and sometimes **H₂** and **C**



Thermal Cracking

- The process is done at **high temperature** in the **absence of catalysts**

Hydrocracking

- The process is done at **very high pressure** of **H₂** in the **absence of catalysts**

Alkanes obtained are mainly unbranched

Catalytic Cracking

- When a mixture of alkanes from the heavier fractions is heated
 - at relatively low **T & P**
 - in the presence of **catalysts**
- The molecules break down and rearrange into smaller, highly branched hydrocarbons

Unbranched petrol is not a good motor fuel

It burns before it is ignited by the spark plug of the petrol engine (pre-ignition).

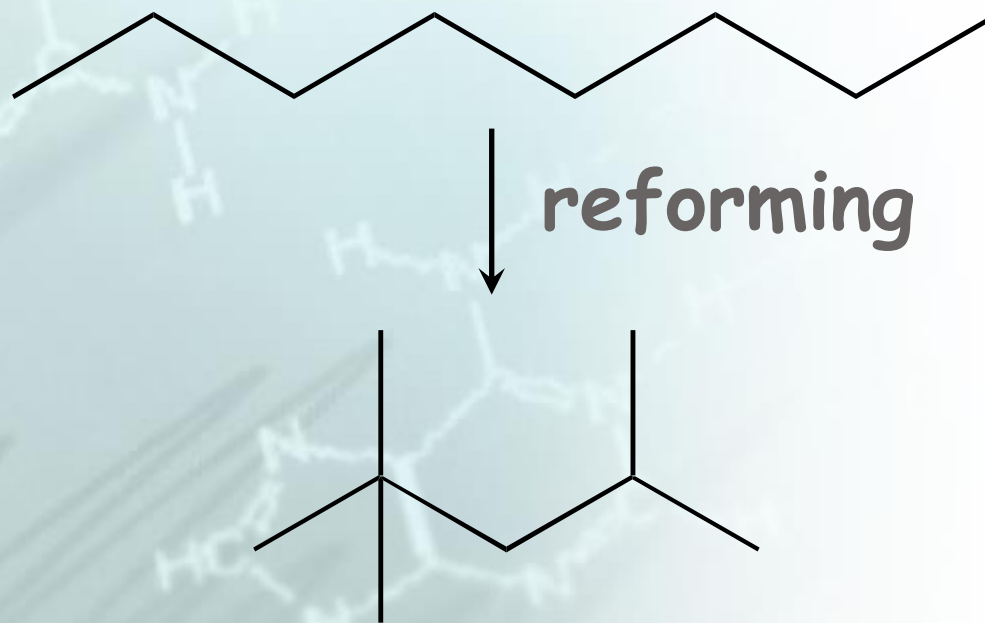
The shock wave creates the characteristic metallic pinging sound (engine knocking)

A waste of energy

Branched (anti-knocking) petrol can be produced by reforming.

Reforming

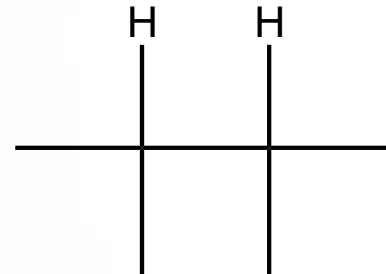
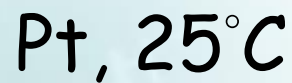
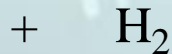
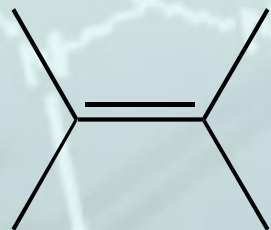
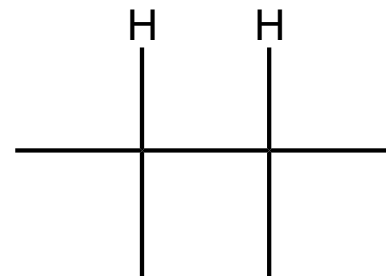
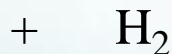
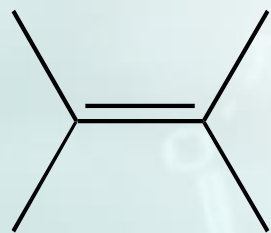
- Straight-chain alkanes are heated under pressure in the presence of a platinum catalyst



The background of the slide features a light blue gradient with several faint, semi-transparent chemical structures overlaid. These structures include various organic molecules, some with nitrogen and oxygen atoms, and some showing skeletal frameworks. The structures are scattered across the slide, with some appearing more prominent than others.

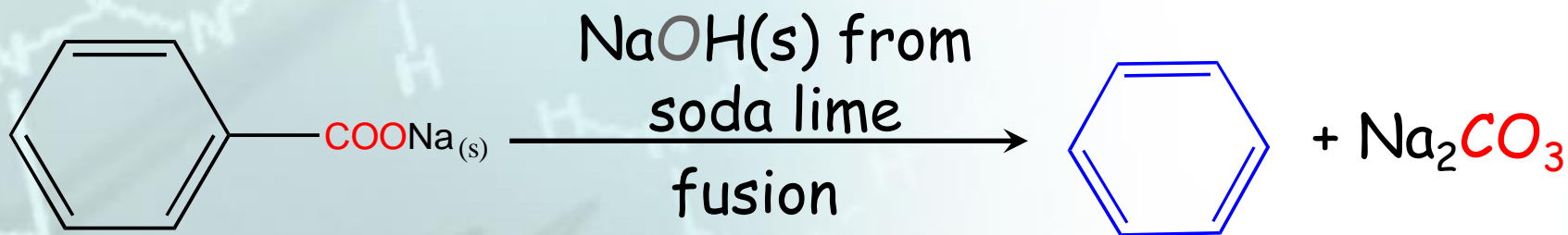
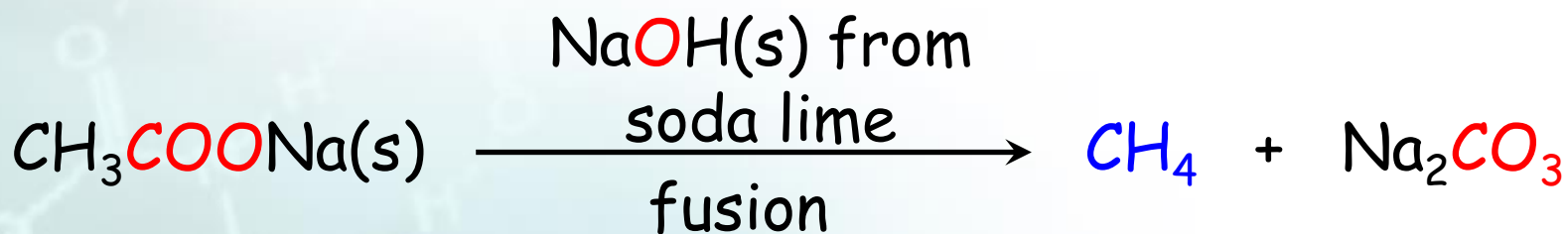
Laboratory Preparation of Alkanes

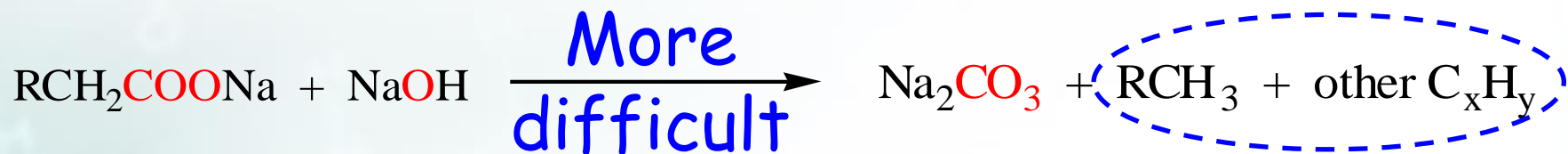
1. Hydrogenation of alkenes



Methods 2 and 3 below are specific to the preparation of methane and benzene.

2. Decarboxylation of sodium ethanoate or sodium benzoate by heating with soda lime (NaOH + CaO)





Not easy to separate mixture into individual alkanes.

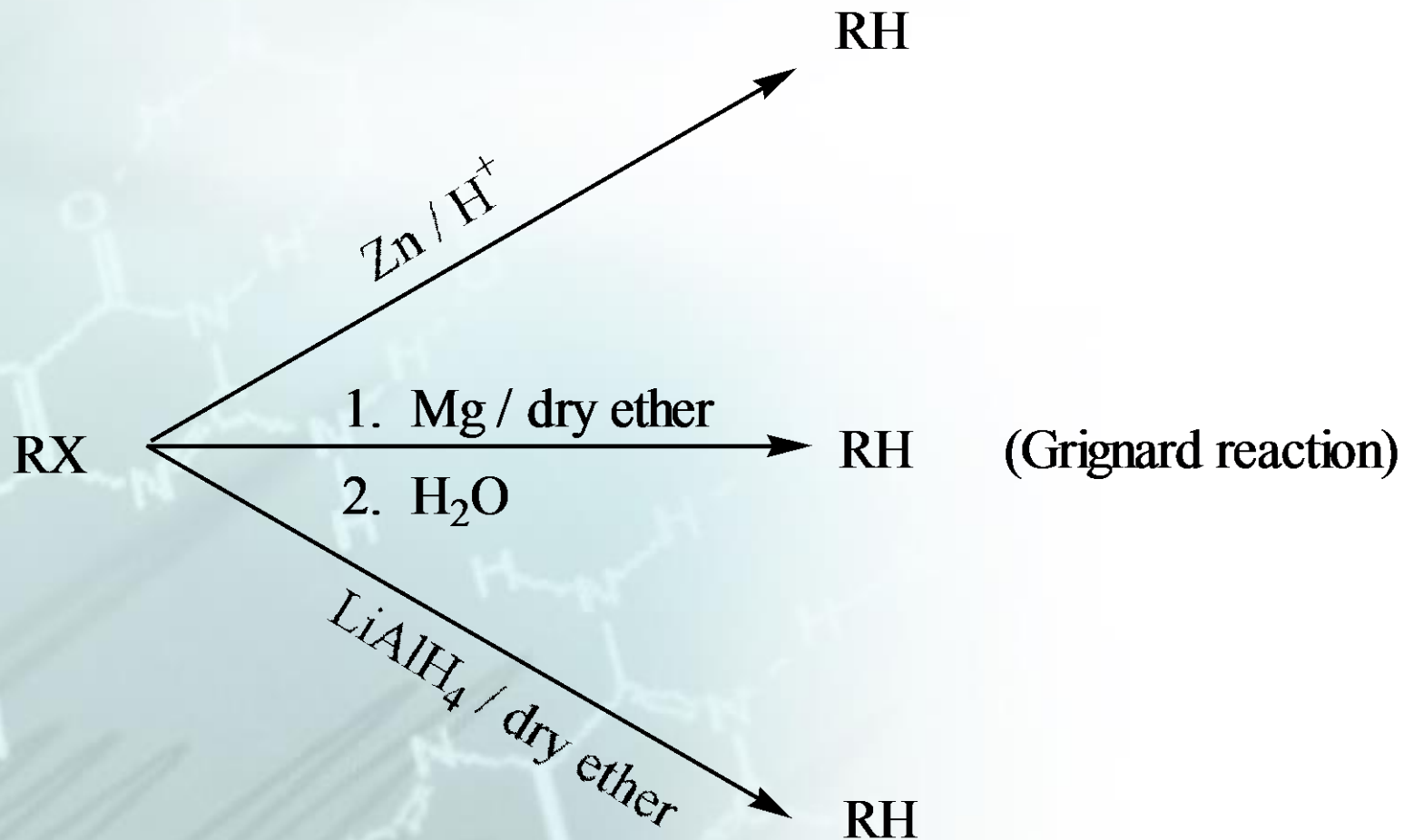
Not suitable for preparing alkanes other than methane.

3. Heating aluminium carbide with HCl

(Optional)



4. Reduction of halogenoalkanes (optional)



The background of the slide is a light blue gradient with a faint, semi-transparent pattern of various chemical structures, including alkanes, alkenes, and other organic molecules, scattered across the left and bottom portions of the page.

Reactions of Alkanes

Reactivity of Alkanes

- Inertness to chemical reactions
 - strong C—C and C—H bonds
- C and H have nearly the same electronegativity
 - C—H bonds are only slightly polarized
 - not easily attacked by charged particles

Alkanes ≡ paraffin ≡ little affinity

Two Ways of Breaking Covalent Bonds :

1. Homolytic fission
2. Heterolytic fission

Homolytic fission (homolysis)



Symmetrical breaking



Free radicals each containing an unpaired electron

Homolytic fission (homolysis)



The movement of single electron is represented by a half-curl arrow

Free radicals are very reactive (unstable). They tend to look for an additional electron to complete the octet.

Homolytic fission is favoured

1. when the bonding atoms have equal or similar electronegativities;
2. at high temperature;
3. when the reaction mixture is exposed to UV light;
4. in the presence of peroxides (- O - O -)

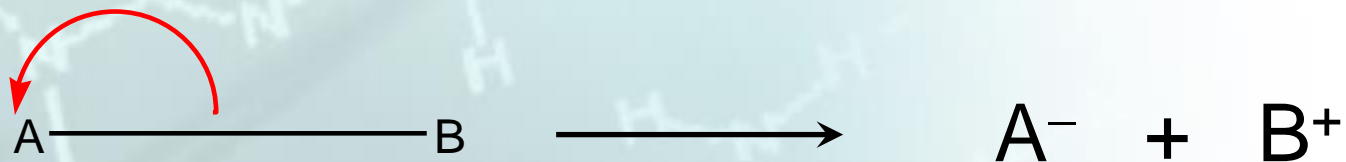
(All favour the formation of free radicals)

Heterolytic fission (heterolysis)



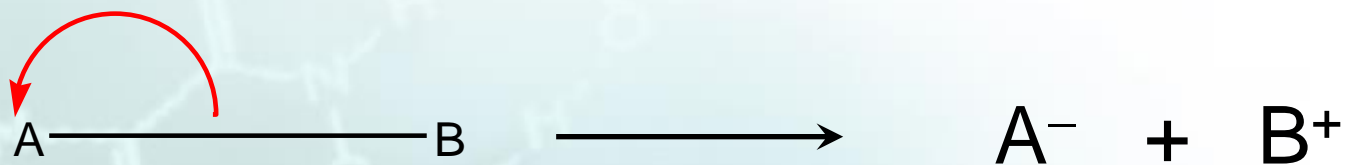
Unsymmetrical
breaking

when B is more
electronegative



when A is more
electronegative

Heterolytic fission (heterolysis)

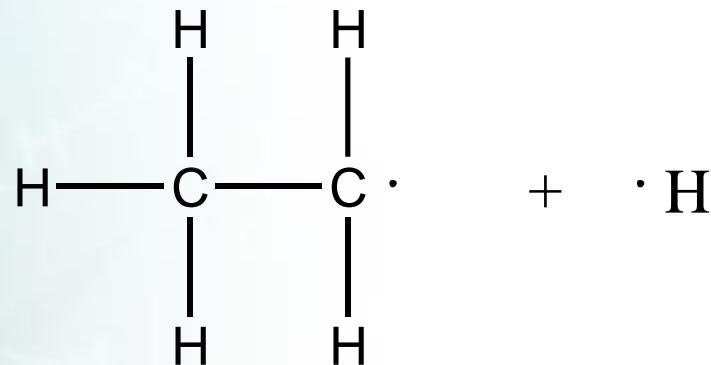
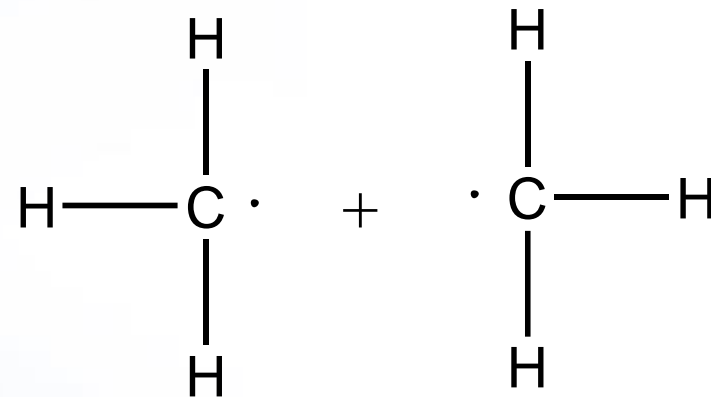
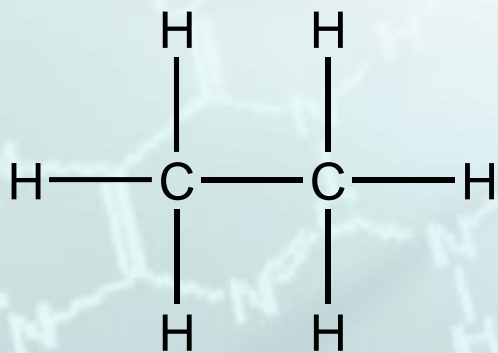


The movement of an electron pair is represented by a curly arrow.

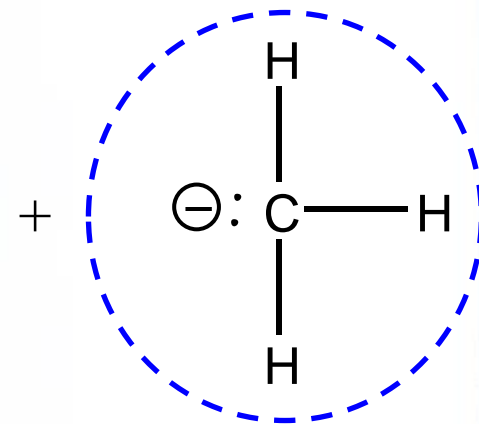
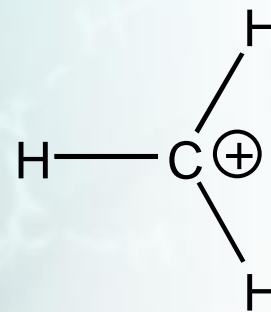
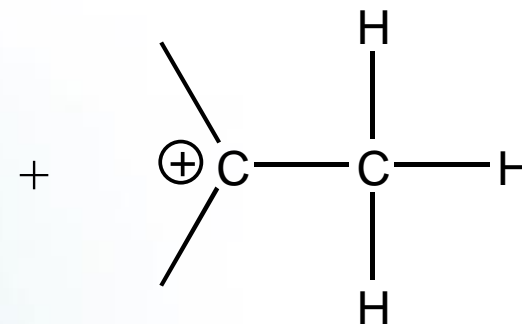
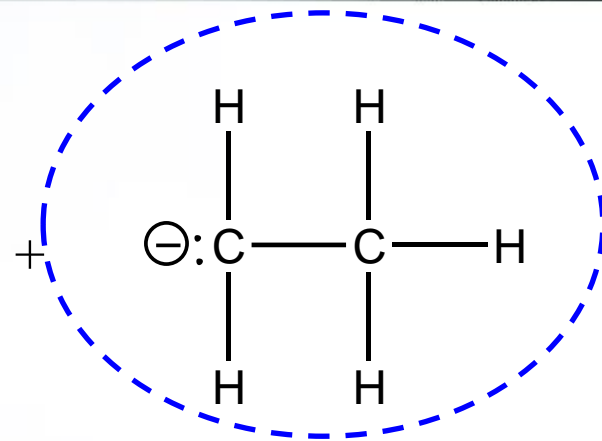
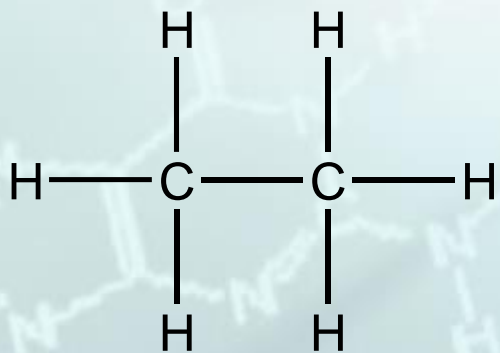
Heterolytic fission is favoured

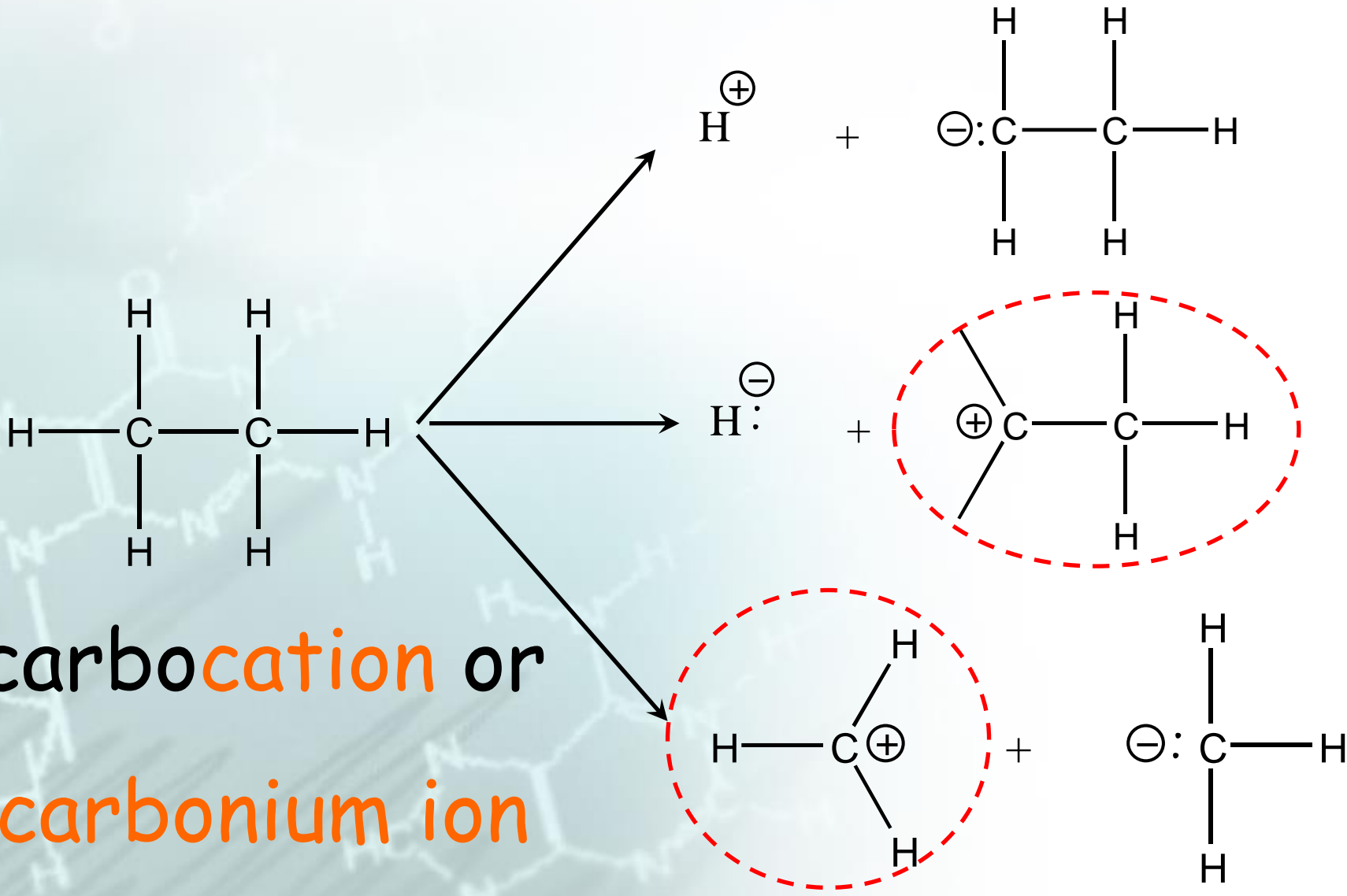
1. when the bonding atoms have significantly different electronegativities;
2. in the presence of a polar solvent which can stabilize the ions formed by **ion-dipole interaction**.

Homolytic fission



carbanion



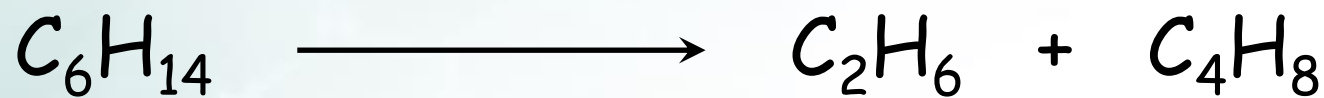


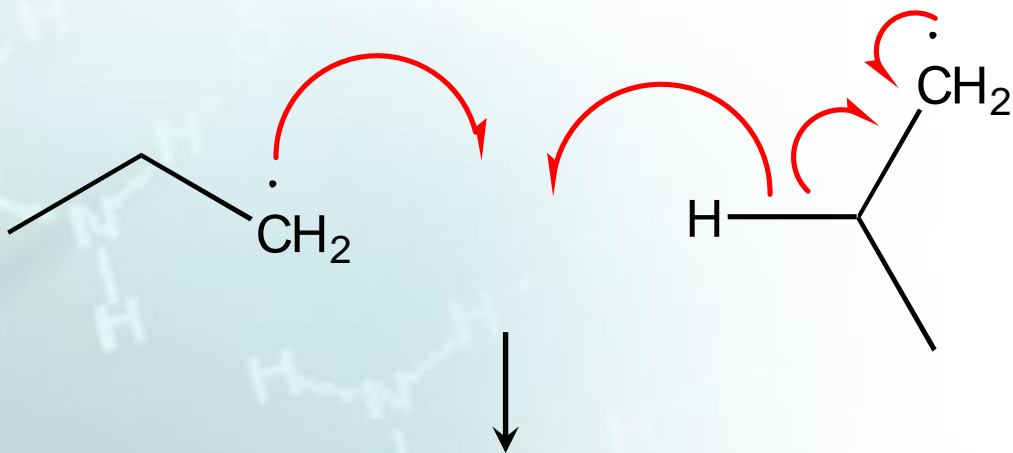
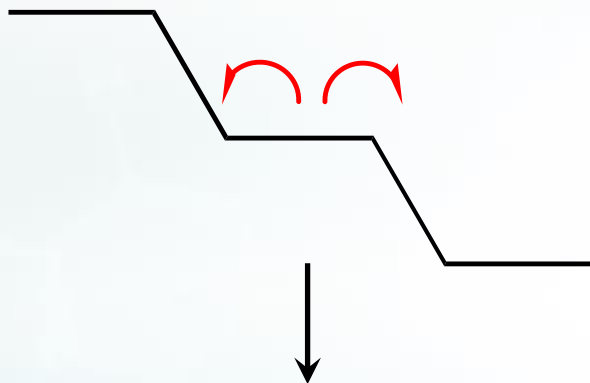
carbocation or
carbonium ion

1. Pyrolysis (Cracking)

Homolytic fission of C - C and/or C - H bonds





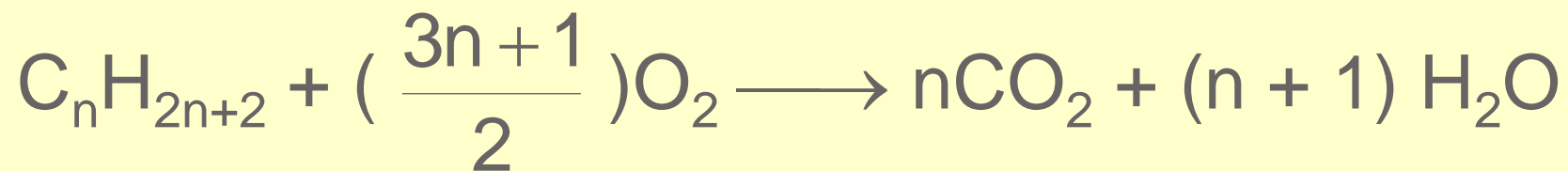


2. Combustion

- When alkanes react with sufficient oxygen
 - carbon dioxide and water are formed
 - release a large amount of heat
 - known as complete combustion

Combustion

- *General equation* for the complete combustion of an alkane:



Combustion

- Alkanes are a **common fuel**
- Methane is the **main component of natural gas**
- **Butane** is a component of **bottle gas**



Butane is used as the fuel for a portable gas burner

- In limited supply of oxygen,
- Large alkanes with high carbon contents



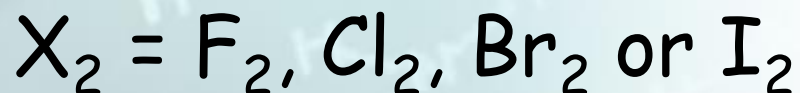
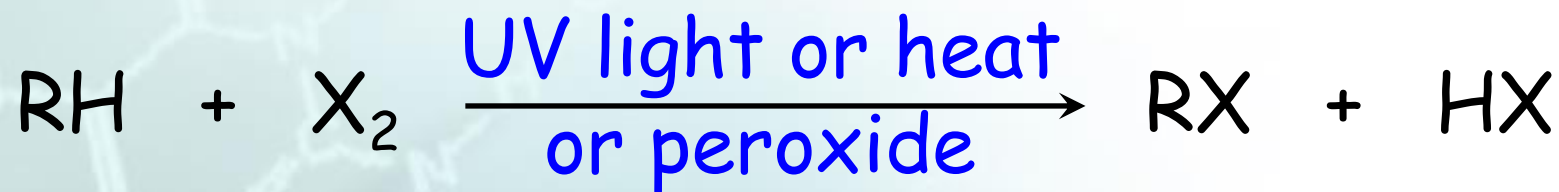
Free Radical Substitution Reaction



The background features a faint, light blue chemical structure diagram, possibly representing a polymer chain or a complex organic molecule, with various atoms and bonds visible.

3. Halogenation (free radical substitution)

Alkanes react with **halogens** to give **haloalkanes** and **hydrogen halide**



Halogenation

- One or more hydrogen atoms in methane are **substituted** by chlorine atoms
 - depend on the **relative amounts of methane and chlorine**

Halogenation



Halogenation

- When methane is in excess
 - chloromethane predominates in the products
- When chlorine is in excess
 - tetrachloromethane predominates in the products

Halogenation

- The reactivity of halogens **decreases** in the order:

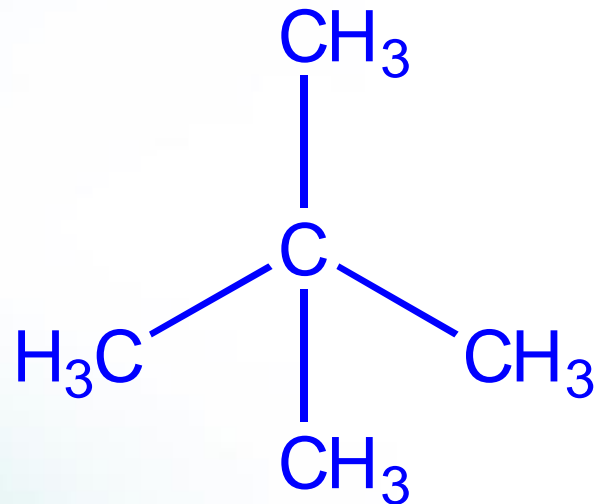


- Not a good method to prepare haloalkanes since it is difficult to separate the resulting mixture into individual haloalkanes.

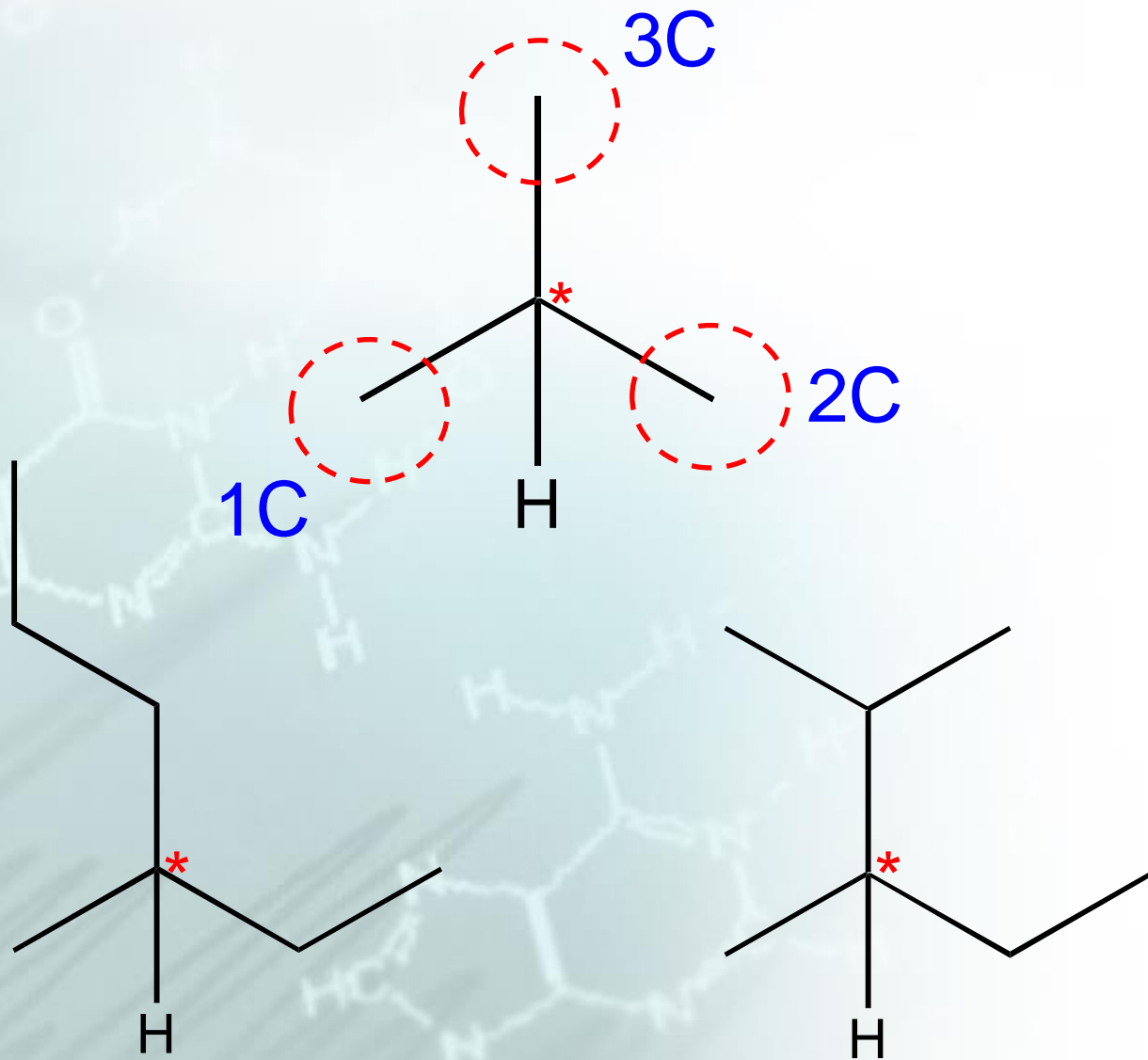
$$C_nH_{2n+2} = 72$$

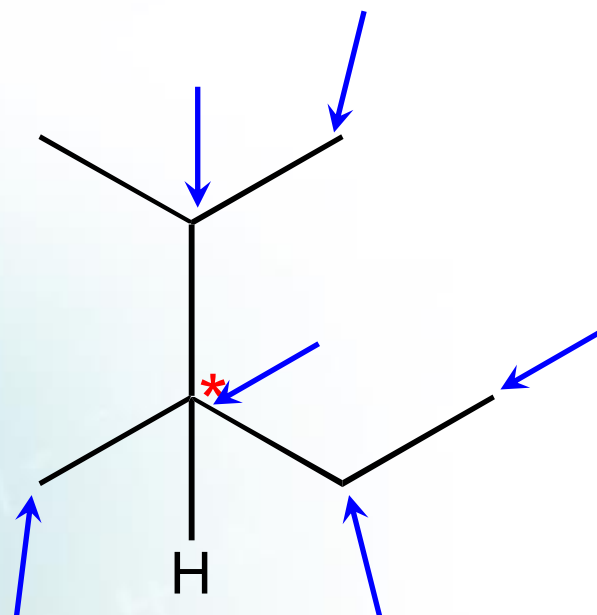
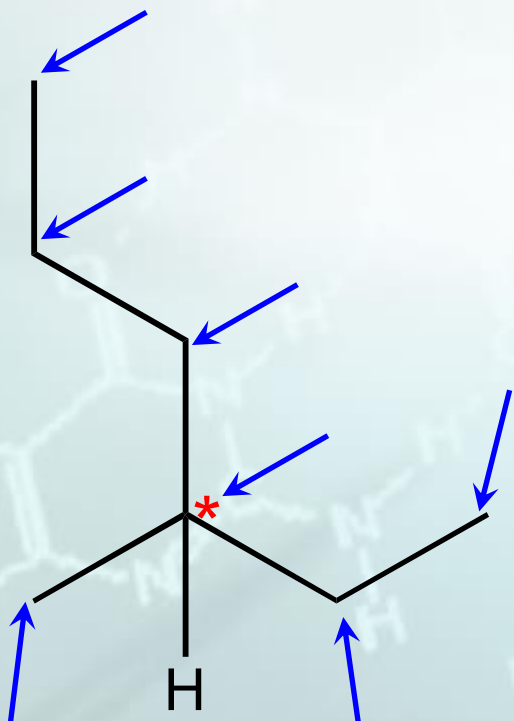
$$12n + 2n + 2 = 72$$

$$n = 5$$



All 12 H atoms are identical and only ONE kind of monochlorinated product can be obtained.



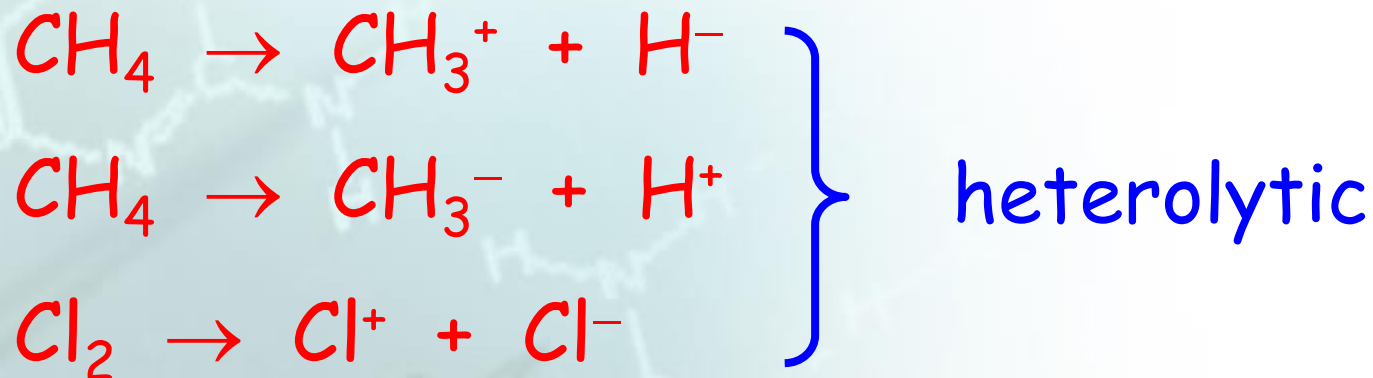
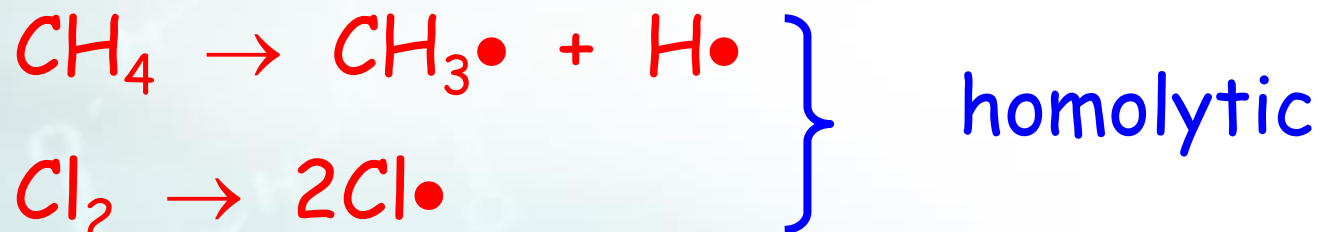


1. Which piece of evidence suggests that the reaction is a chain reaction ?

C

For each photon of light absorbed, many thousands of molecules of chloromethane are formed.

2. Which of the following is the first step of the mechanism?



For elementary steps, the structure of the transition state resembles that of the final products.

- ⇒ the stability of the transition state is determined by the stability of the final products.
- ⇒ the activation energy can be estimated by the enthalpy change of the elementary step

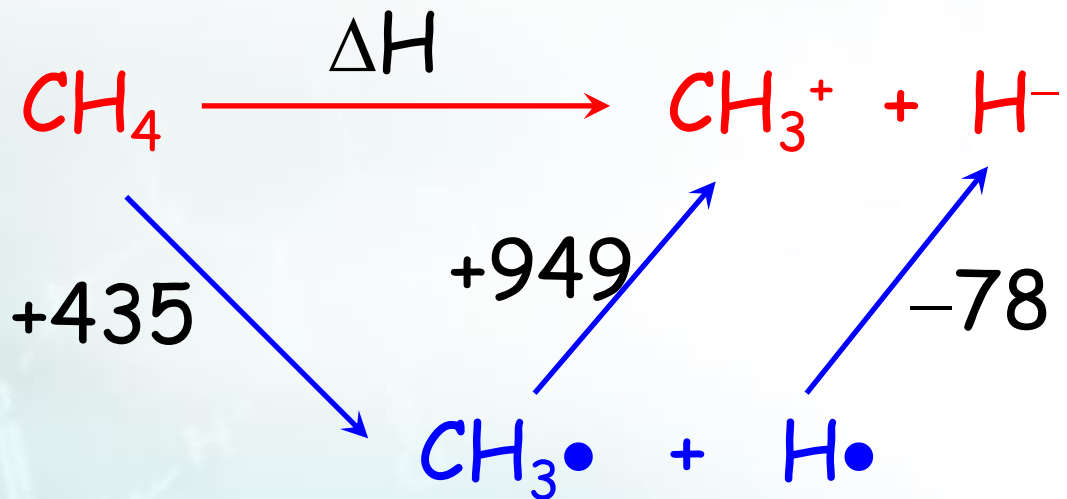
The more endothermic reaction proceeds more slowly.



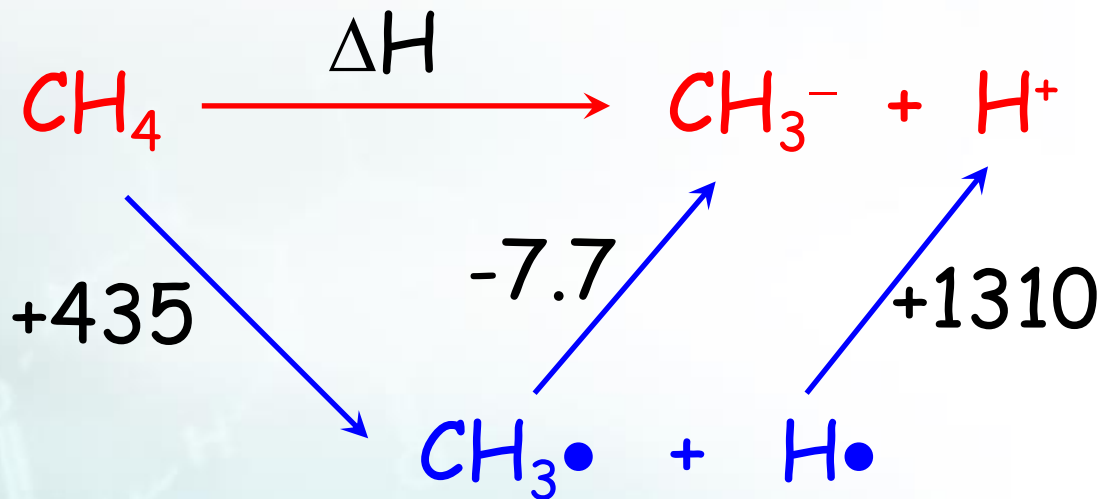
$$\Delta H = +435 \text{ kJ mol}^{-1}$$



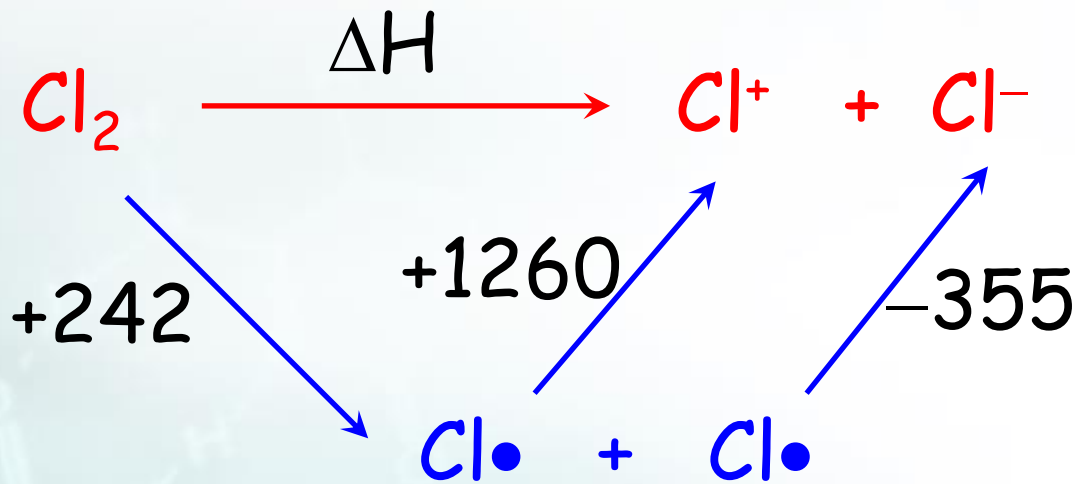
$$\Delta H = +242 \text{ kJ mol}^{-1}$$



$$\Delta H = +435 + 949 - 78 = +1306 \text{ kJ mol}^{-1}$$



$$\Delta H = +435 - 7.7 + 1310 = +1737.3 \text{ kJ mol}^{-1}$$



$$\Delta H = +242 + 1260 - 355 = +1147 \text{ kJ mol}^{-1}$$

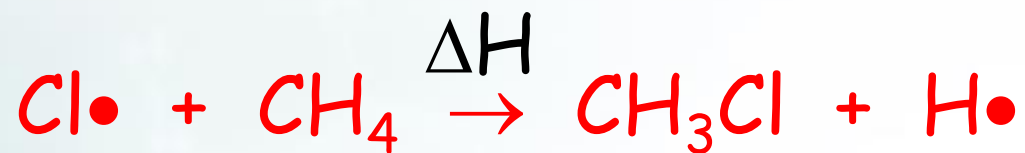


$$\Delta H = +242 \text{ kJ mol}^{-1}$$

First step of the mechanism

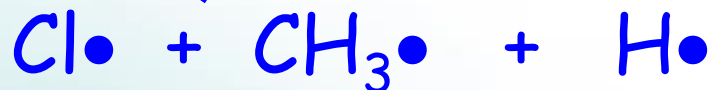
3. Second step of the mechanism



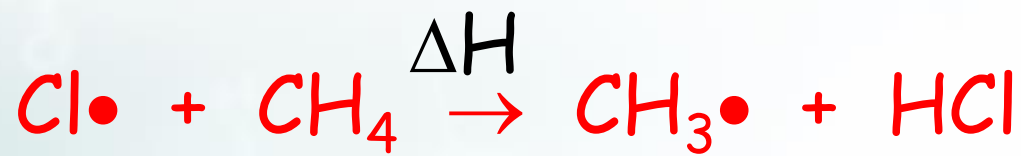


+435

-350



$$\Delta H = +435 - 350 = +85 \text{ kJ mol}^{-1}$$



+435

-431



$$\Delta H = +435 - 431 = +4 \text{ kJ mol}^{-1}$$

Less endothermic and
does not lead to formation of H_2 ✓

4. The 3rd step of the mechanism

It gives the other product $\rightarrow \text{CH}_3\text{Cl}$

It gives another $\text{Cl}\cdot$ to complete the chain cycle.



5. Termination steps



Reaction Mechanism: Free Radical Substitution Reaction

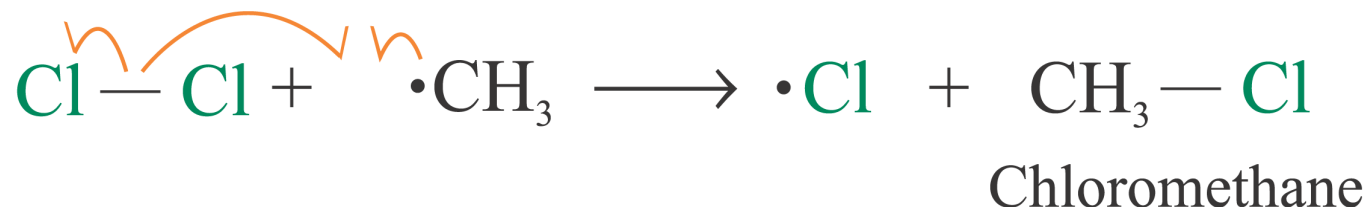
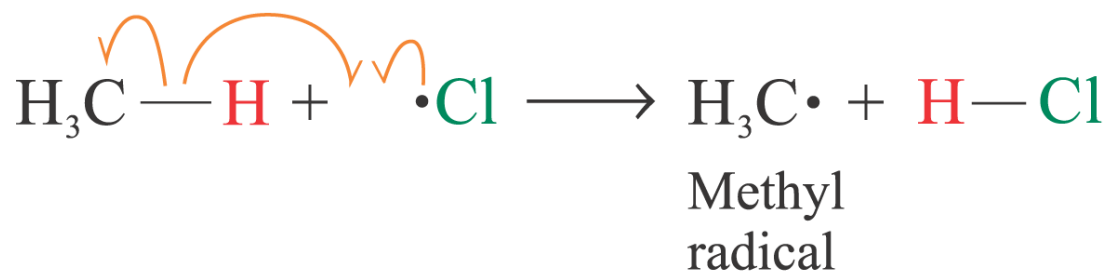
1. Chain initiation

- Homolytic fission of a chlorine molecule
- Two chlorine radicals are formed



Reaction Mechanism: Free Radical Substitution Reaction

2. Chain propagation



Reaction Mechanism: Free Radical Substitution Reaction

3. Chain termination



7. Which step is rate-determining ?

The propagation stage is the most time-consuming.



+242

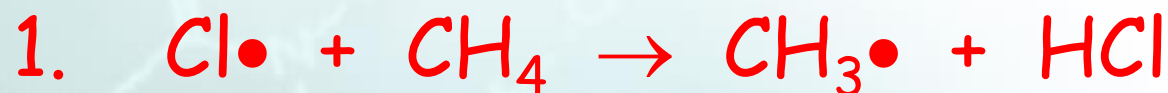
-350



$$\Delta H = +242 - 350 = -108 \text{ kJ mol}^{-1}$$

7. Which step is rate-determining ?

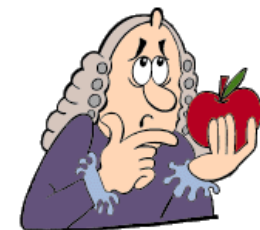
The propagation stage is the most time-consuming.



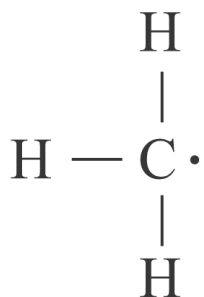
Step 1 has higher $E_a \Rightarrow$ rate-determining

Stability of Alkyl Radicals

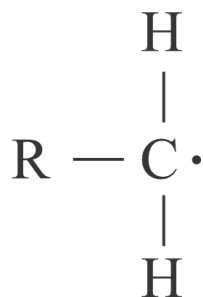
- According to the number of alkyl groups directly attached to the carbon that bears the unpaired electron
 - alkyl radicals are classified as primary, secondary or tertiary



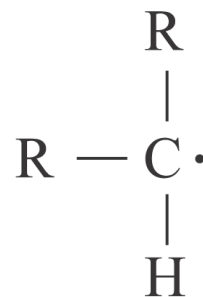
Stability of Alkyl Radicals



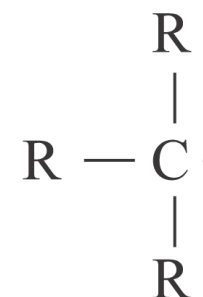
Methyl radical
(no alkyl group attached to the carbon that bears the unpaired electron)



Primary radical
(one alkyl group attached to the carbon that bears the unpaired electron)



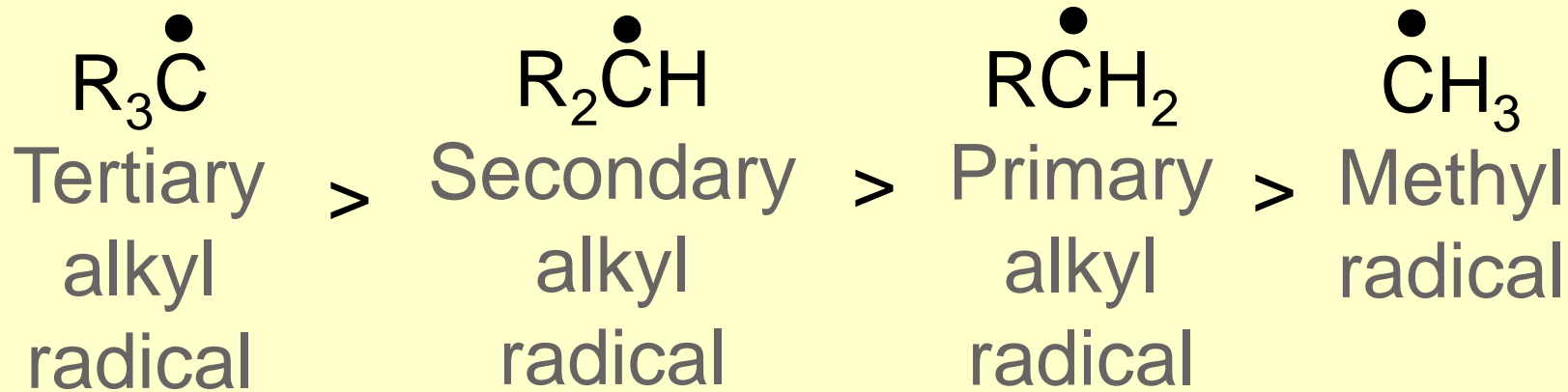
Secondary radical
(two alkyl groups attached to the carbon that bears the unpaired electron)



Tertiary radical
(three alkyl groups attached to the carbon that bears the unpaired electron)

Stability of Alkyl Radicals

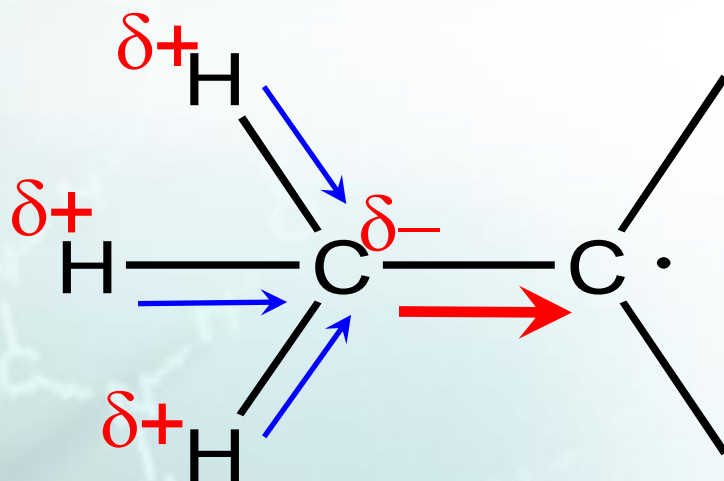
- The **stability** of the alkyl radicals **decreases** in the order:



Stability of Alkyl Radicals

- Alkyl radical has an unpaired electron
- Electron-deficient
- Stabilized by substituents (e.g. alkyl groups)
 - release electrons to the carbon atom bearing the unpaired electron

Electron-donating property of alkyl groups arises from the polarization of C - H σ bonds

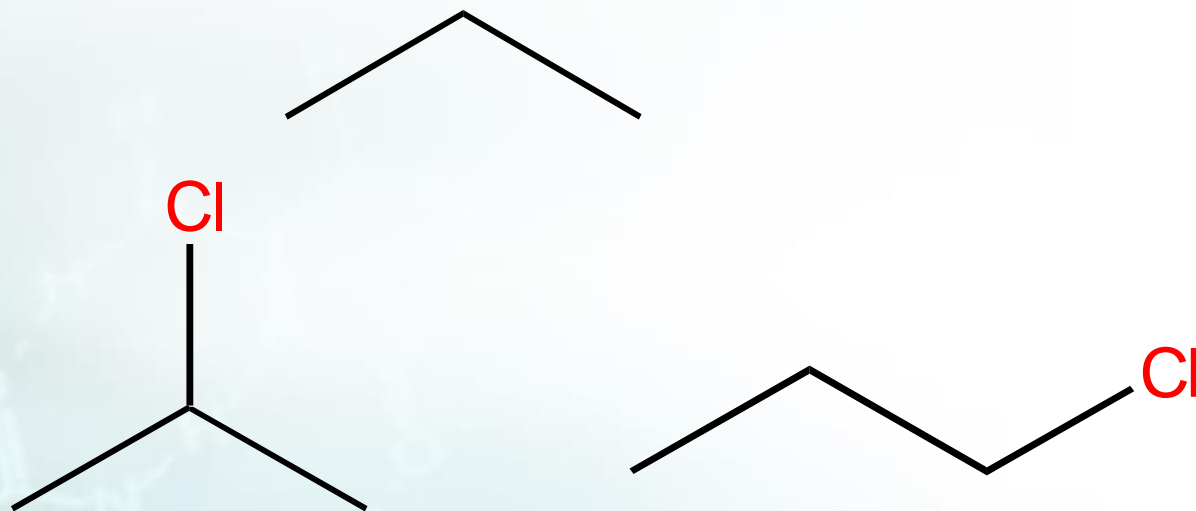


Electron-donating groups(e.g. alkyl groups) cause positive inductive effect on adjacent groups.

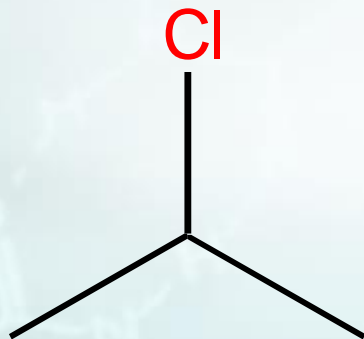
Electron-withdrawing groups(e.g. -F) cause negative inductive effect on adjacent groups.

Inductive effect arises from polarization of σ bonds.

Q.1(a)



No. of reaction sites



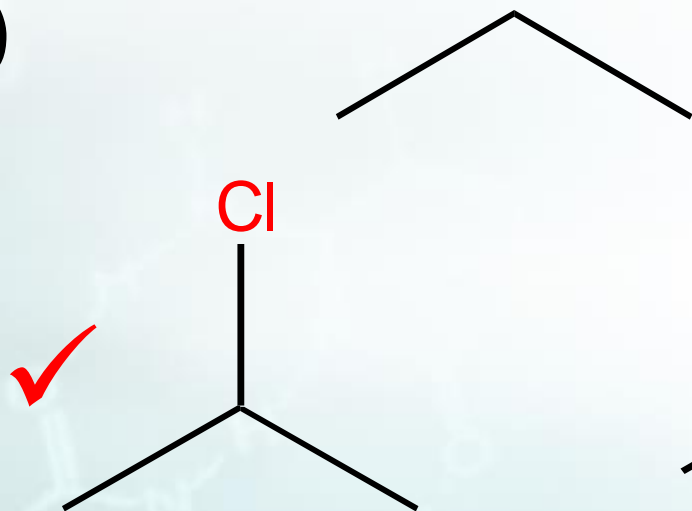
2
reaction
sites



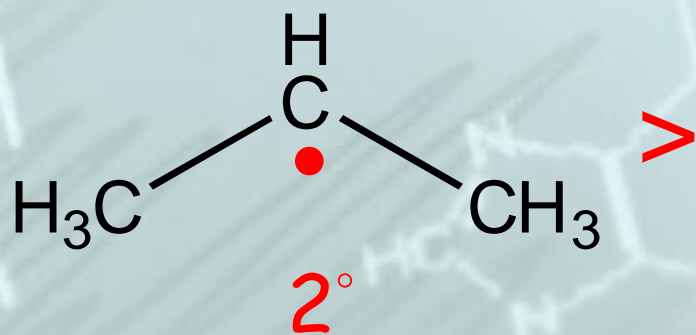
3
reaction
sites

Stability of free radical intermediates is more important than the no. of reaction sites available

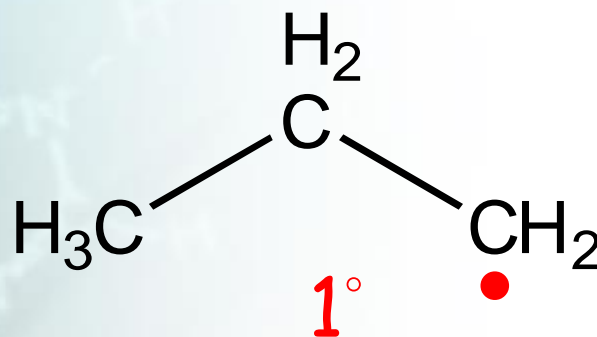
Q.1(a)



Stability :-

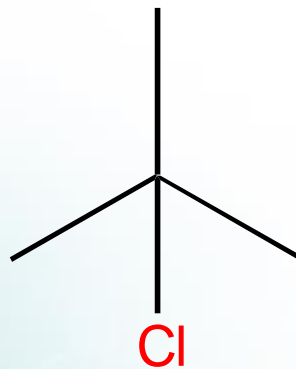
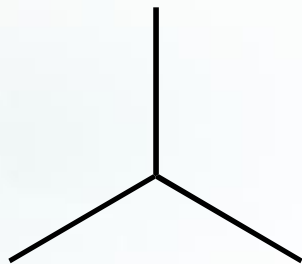
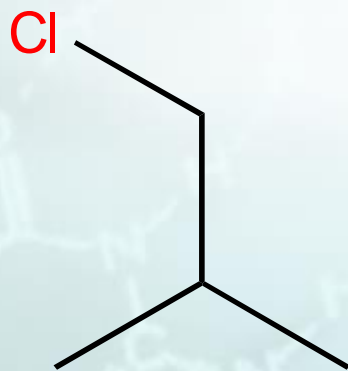


2°

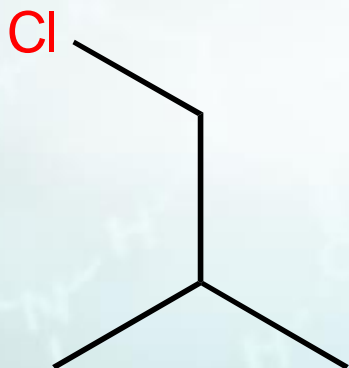


1°

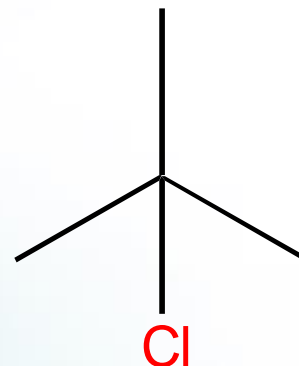
Q.2(b)



No. of reaction sites



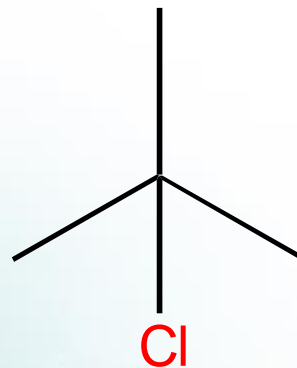
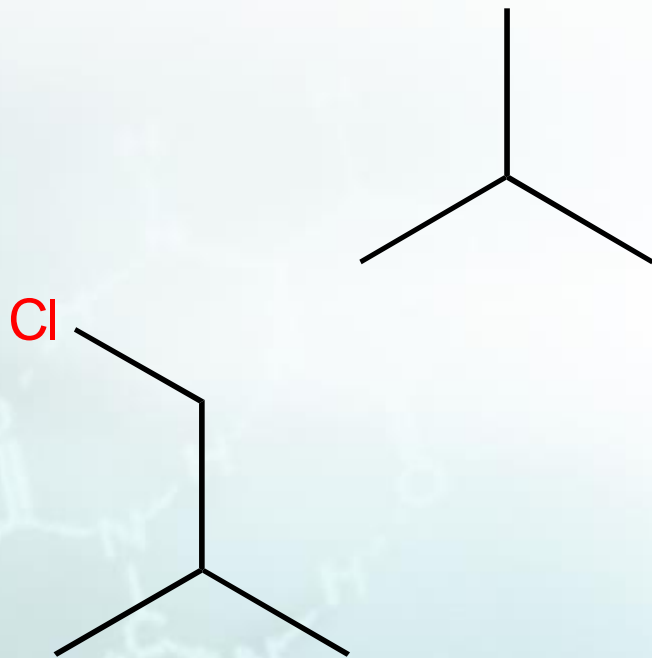
3
reaction
sites



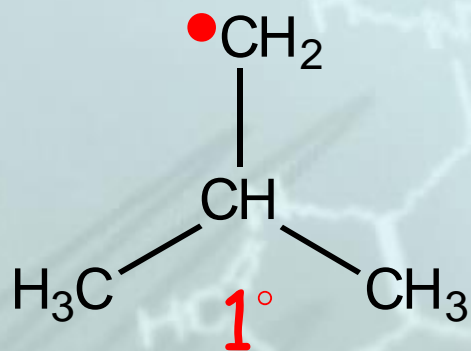
2
reaction
site

Stability of free radical intermediates is more important than the no. of reaction sites available

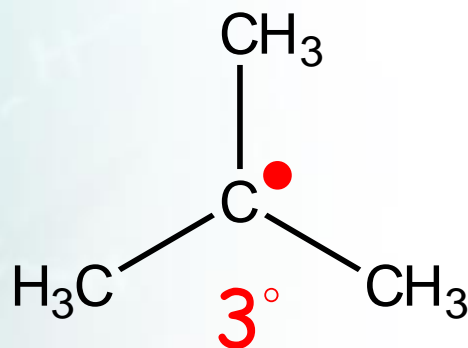
Q.2(b)



Stability :-



<



Hammond's Postulate

“If two states, for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures”

George S. Hammond, J. Am. Chem. Soc. 1955, 77, 334-338.

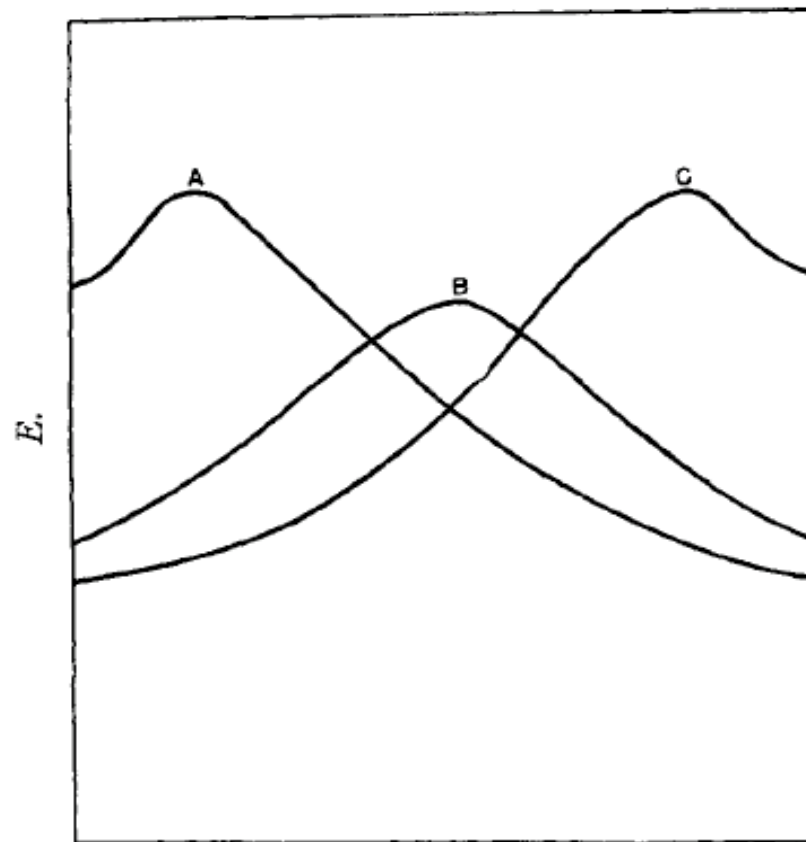
Hammond's Postulate

“The structure of the transition state for an exothermic reaction is reached early in the reaction, so it resembles reactants more than products. Conversely, the structure of the transition state for an endothermic reaction step is reached relatively late, so it resembles products more than reactants.”

— From your Textbook

Hammond's Postulate

- In reactions where the starting material is higher in energy (A), the transition state more closely resembles the starting material
- In reactions where the product is higher in energy (C), the transition state more closely resembles the product



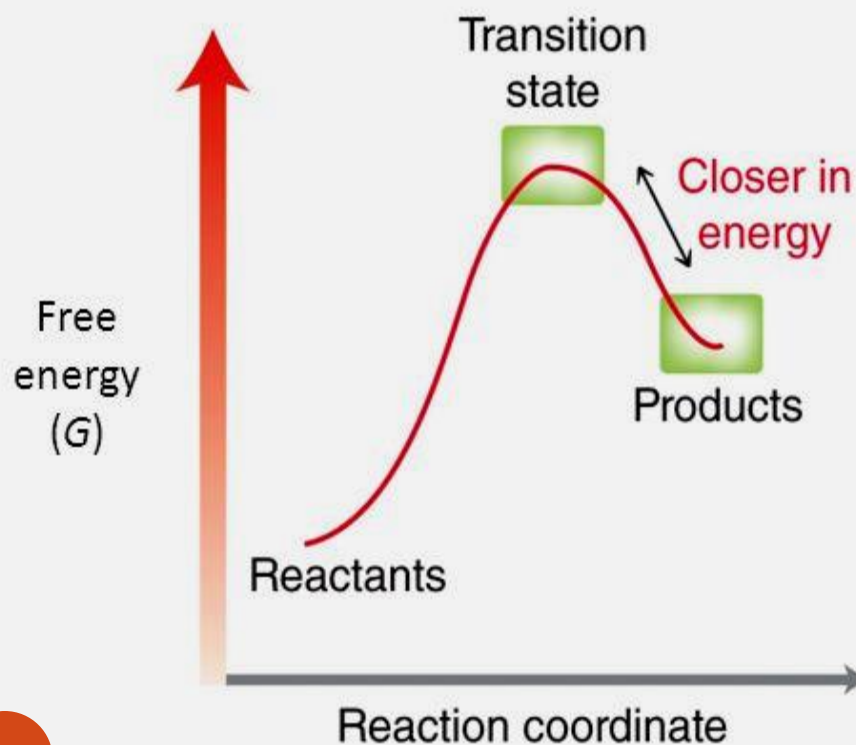
Reaction coördinate.

Fig. 1.

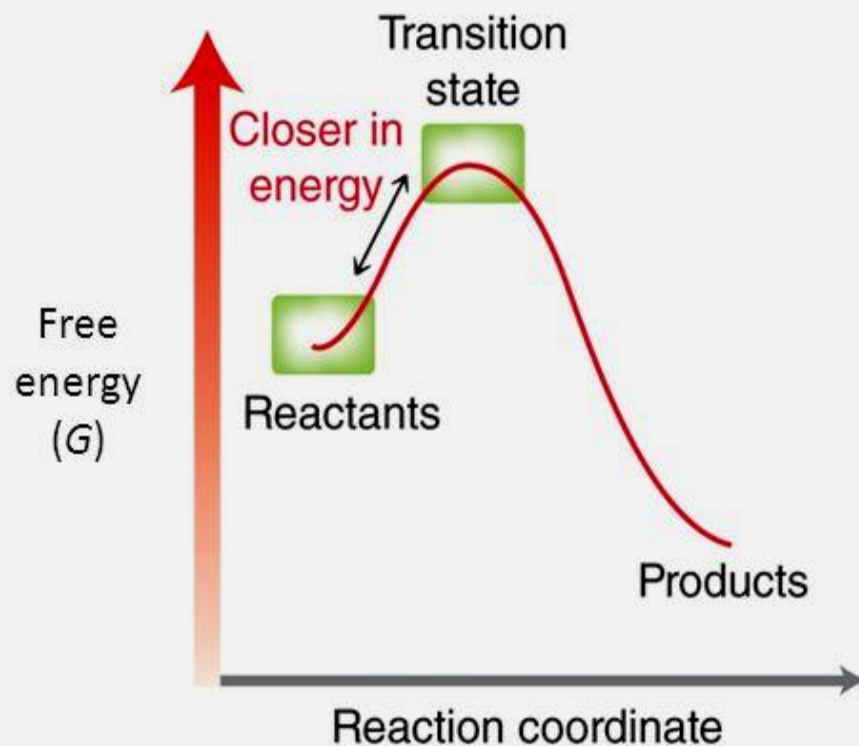
The Hammond Postulate

- For each of the diagrams below, will the transition state structure look more like the reactants or the products?

Endothermic process



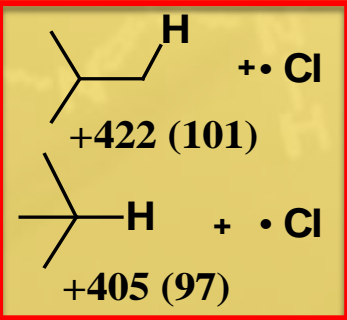
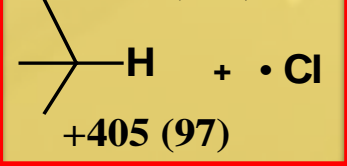
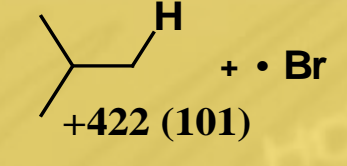
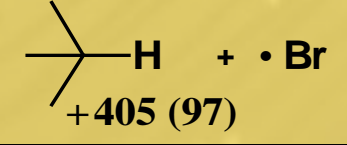
Exothermic process



Implications of Hammond's Postulate

- Because hydrogen abstraction for chlorination is **exothermic**,
 - the transition state resembles the alkane and a chlorine atom.
 - there is little radical character on carbon in the transition state.
 - regioselectivity is only slightly influenced by radical stability.

Higher in Energy

Reaction step	ΔH^0 [kJ (kcal)/mol]
 <chem>CCCC[CH2] + Cl2 -> CCCC[CH2] + HCl</chem> +422 (101)	-9 (-2)
 <chem>CC(C)(C)C + Cl2 -> CC(C)(C)C + HCl</chem> +405 (97)	-26 (-6)
	-431 (-103)
	-431 (-103)
	17 (4)
 <chem>CCCC[CH2] + Br2 -> CCCC[CH2] + HBr</chem> +422 (101)	+54 (+13)
 <chem>CC(C)(C)C + Br2 -> CC(C)(C)C + HBr</chem> +405 (97)	+37 (+9)
	-368 (-88)
	-368 (-88)
	17 (4)

Implications of Hammond's Postulate

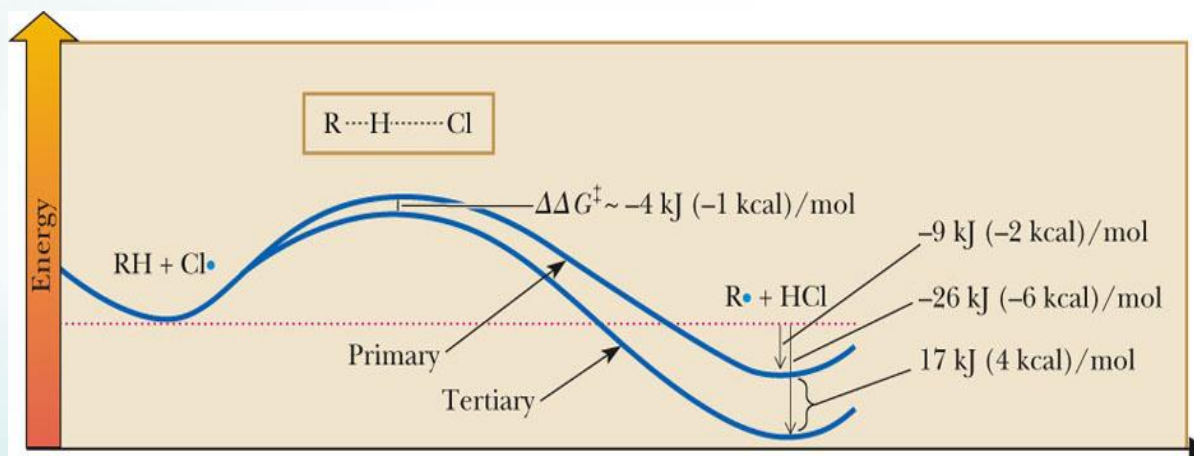
- Because hydrogen abstraction for bromination is **endothermic**,
 - the transition state resembles an alkyl radical and HBr
 - there is significant radical character on carbon in the transition state.
 - regioselectivity is greatly influenced by radical stability.
 - radical stability is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$, and regioselectivity is in the same order.

Reaction step	ΔH° [kJ (kcal)/mol]
<chem>CC(C)CC + \cdot Cl \rightarrow CC(C)C\cdot + H-Cl</chem> +422 (101)	-9 (-2)
<chem>CC(C)C + \cdot Cl \rightarrow CC(C)\cdot + H-Cl</chem> +405 (97)	-26 (-6)
] 17 (4)	
<chem>CC(C)CC + \cdot Br \rightarrow CC(C)C\cdot + H-Br</chem> +422 (101)	+54 (+13)
<chem>CC(C)C + \cdot Br \rightarrow CC(C)\cdot + H-Br</chem> +405 (97)	+37 (+9)
] 17 (4)	

Higher in Energy

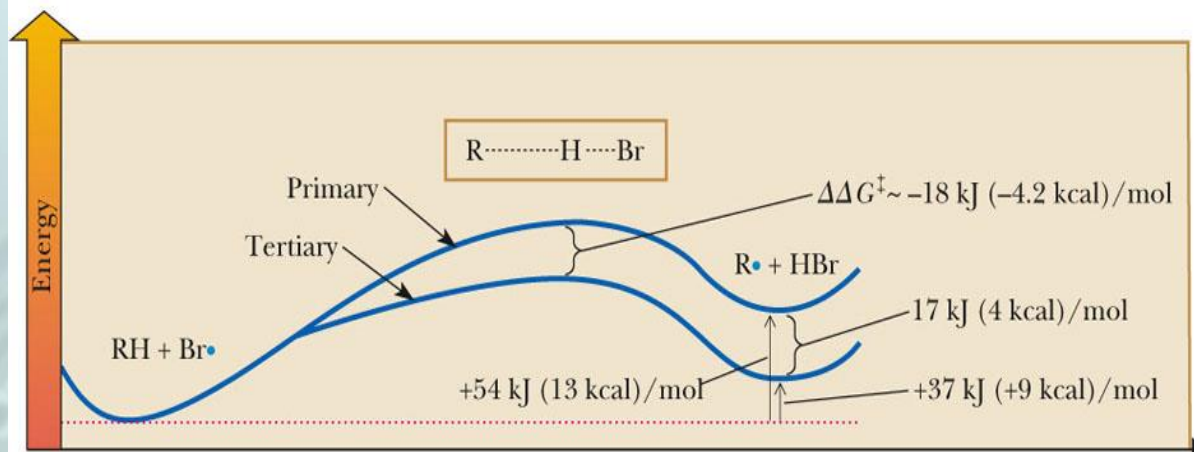
Selectivity of Halogenation Reactions

- Very small energy difference in transition state between primary and tertiary chlorination transition states. **Non-Selective**



(a) Chlorination

- Larger energy difference in transition state between primary and tertiary bromination transition states. **Selective**

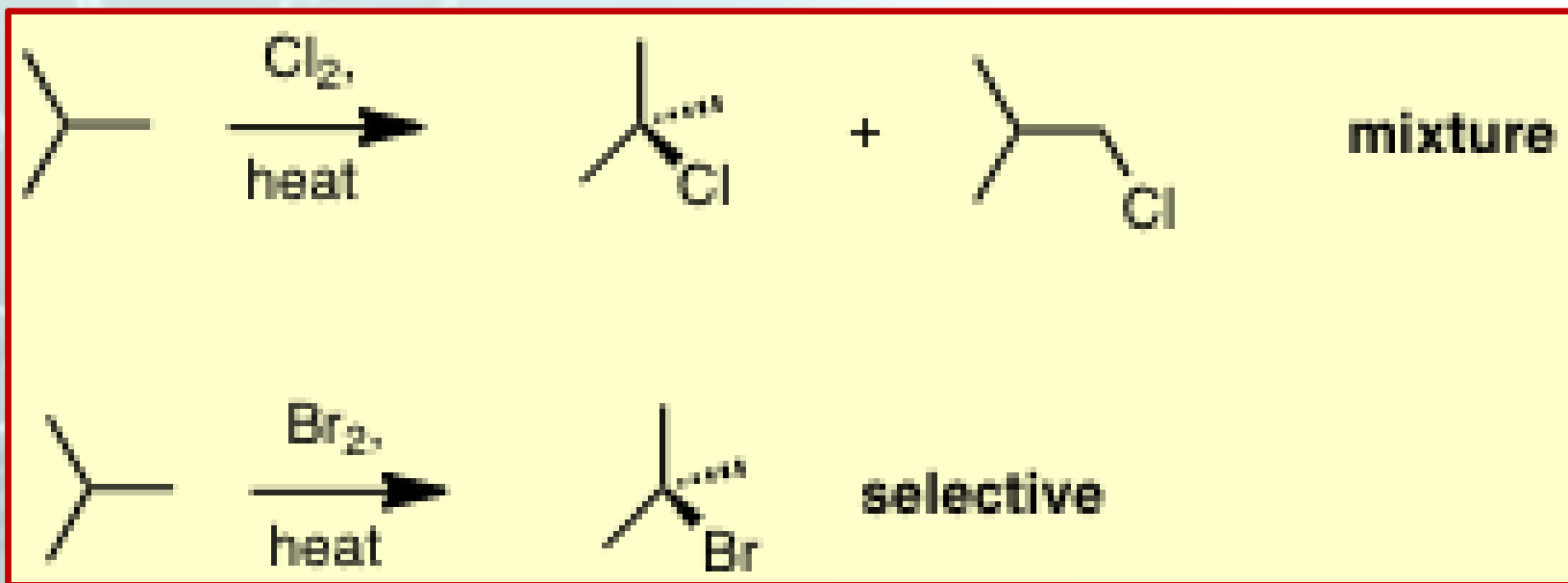


(b) Bromination

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Hammond's Postulate Summary

- Transition state resembles higher energy component of reaction
- Bromination of alkanes is selective, while chlorination is not





The END

**Thank You for
Your Attention**