ITEM 1

ORGANIC CHEMISTRY – HYDROCARBONS, ISOMERISM AND REACTION MECHANISMS

In an industrial organic chemistry research laboratory, a team of chemists was tasked with investigating a group of hydrocarbons obtained from the fractional distillation of petroleum. One colourless gas, compound A, was found to be saturated and contained only carbon and hydrogen atoms. When compound A was subjected to controlled chlorination under ultraviolet light, a mixture of substitution products was formed, indicating that the compound undergoes free-radical reactions.
Further analysis showed that compound A could be prepared in the laboratory by heating a sodium salt of a carboxylic acid with soda lime. Another compound, B, obtained from the same petroleum fraction, was unsaturated and rapidly decolourised cold dilute potassium permanganate solution to form a vicinal diol. Compound B was also found to react with hydrogen bromide to give two different products under different conditions.

On dehydration of an alcohol C using concentrated sulfuric acid, compound B was obtained as the major product. Alcohol C was shown to exhibit both chain and position isomerism with another alcohol D, while compound E, having the same molecular formula as C, contained a carbonyl functional group and exhibited functional isomerism with it.

In a separate experiment, compound F, an unsaturated hydrocarbon, was partially reduced using Lindlar's catalyst to give compound B, confirming the presence of a carbon–carbon multiple bond. The chemists concluded that understanding the structure, isomerism, preparation methods, and reaction mechanisms of these compounds was essential for industrial synthesis and environmental control.

Task

A. Alkanes and Isomerism

Define chain isomerism, position isomerism, and functional isomerism, giving one example of each based on compounds C, D, and E.

Write an equation showing the laboratory preparation of alkane A using soda lime.

Describe two chemical properties of alkanes, illustrating each with a balanced equation.

B. Halogenation and Reaction Mechanisms
Write a balanced equation for the chlorination of alkane A under ultraviolet light.

Describe the free-radical substitution mechanism for this chlorination, clearly showing initiation, propagation, and termination steps.

C. Alkenes: Structure, Reactions, and Mechanisms
Name compound B using IUPAC nomenclature and state the type of isomerism it can exhibit.

Write an equation for the oxidation of compound B with cold dilute potassium permanganate, naming the organic product formed.

Explain, using equations, the electrophilic addition of hydrogen bromide to:
(i) a symmetrical alkene, and
(ii) an unsymmetrical alkene, clearly illustrating Markovnikov's rule with a mechanism.

D. Alcohols, Alkynes, and Industrial Relevance
Write an equation for the dehydration of alcohol C using concentrated sulfuric acid to form compound B.

Write an equation showing the partial reduction of compound F using Lindlar's catalyst.

Describe the reaction of compound B with concentrated sulfuric acid, stating the conditions and product formed.

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UACE CHEMISTRY ITEM

SOLUTIONS TO ITEM 1: ORGANIC CHEMISTRY

A. ALKANES AND ISOMERISM

A1. Definitions of isomerism

Chain isomerism

This occurs when compounds have the same molecular formula but different arrangements of the carbon chain.
Example:
Butan-1-ol and 2-methylpropan-1-ol.

Position isomerism

This occurs when compounds have the same molecular formula and functional group but differ in the position of the functional group on the carbon chain.
Example:
Butan-1-ol and butan-2-ol.

Functional isomerism

This occurs when compounds have the same molecular formula but different functional groups.
Example:
Butan-1-ol and butanal.

A2. Preparation of alkane A using soda lime

Alkanes can be prepared by heating a sodium salt of a carboxylic acid with soda lime.
General equation:
$RCOONa + NaOH \rightarrow RH + Na_2CO_3$

Example (ethane preparation):
$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$
This reaction is known as decarboxylation.

A3. Chemical properties of alkanes
(i) Combustion
Alkanes burn completely in excess oxygen to form carbon dioxide and water.
Example:
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
(ii) Substitution reactions
Alkanes undergo free radical substitution with halogens in the presence of ultraviolet light.
Example:
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (UV light)

B. HALOGENATION AND MECHANISM
B1. Chlorination of alkane A
General equation:
$RH + Cl_2 \rightarrow RCl + HCl$ (UV light)

B2. Free radical substitution mechanism
Initiation:
$Cl_2 \rightarrow 2Cl\cdot$ (under UV light)
Propagation:
$Cl\cdot + RH \rightarrow R\cdot + HCl$
$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot$
Termination:
$Cl\cdot + Cl\cdot \rightarrow Cl_2$
$R\cdot + Cl\cdot \rightarrow RCl$
$R\cdot + R\cdot \rightarrow R–R$

C. ALKENES: STRUCTURE, REACTIONS AND MECHANISMS

C1. Naming and isomerism of compound B
Compound B is an alkene and can be named using IUPAC rules based on:
Longest carbon chain
Position of the double bond
Alkenes can exhibit:
Position isomerism (but-1-ene and but-2-ene)
Geometrical isomerism (cis and trans forms)

C2. Oxidation of alkene B with potassium permanganate
Cold, dilute potassium permanganate oxidises alkenes to vicinal diols.
General equation:
Alkene + $KMnO_4$ → diol
Example:
$CH_2=CH_2$ → $HO–CH_2–CH_2–OH$
This reaction is used as a test for unsaturation.

C3. Electrophilic addition of hydrogen bromide
(i) Symmetrical alkene
Example:
$CH_2=CH_2 + HBr$ → $CH_3–CH_2Br$
Only one product is formed.
(ii) Unsymmetrical alkene (Markovnikov's rule)
Example:
$CH_3–CH=CH_2 + HBr$ → $CH_3–CHBr–CH_3$
Markovnikov's rule states that hydrogen attaches to the carbon already having more hydrogen atoms.

Mechanism:
Proton attacks the double bond to form a carbocation.
Bromide ion attacks the carbocation.

D. ALCOHOLS, ALKYNES AND INDUSTRIAL REACTIONS

D1. Dehydration of alcohol C
Alcohols dehydrate in the presence of concentrated sulfuric acid and heat to form alkenes.
General equation:
Alcohol → Alkene + Water
Example:
$CH_3–CH_2–CH_2–CH_2OH \rightarrow CH_3–CH_2–CH=CH_2 + H_2O$

D2. Partial reduction using Lindlar's catalyst
Alkynes are partially reduced to alkenes using hydrogen and Lindlar's catalyst.
General equation:
Alkyne + H_2 → Alkene
Example:
$HC\equiv CH \rightarrow CH_2=CH_2$
This prevents further reduction to alkanes.

D3. Reaction of alkene with concentrated sulfuric acid
Alkenes react with concentrated sulfuric acid at low temperatures to form alkyl hydrogen sulfates.
General equation:
Alkene + H_2SO_4 → Alkyl hydrogen sulfate
This reaction follows electrophilic addition.

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