Unit 13. Alkylation. Exercises

1 **Read the description of alkylation mechanism stages Complete the alkylation mechanism with the name of each stage.**

Alkylation is one of the classic examples of a reaction or reactions proceeding via the **carbenium ion mechanism**. These reactions include an **initiation step** and a **propagation step** and may include an **isomerization step**. In addition, **polymerization**, **cracking steps** and **hydrogen transfer** may be involved. However, these side reactions are generally undesirable.

Isomerization
Isomerization is very important in producing good octane quality from a feed that is high in 1-butene. The isomerization of 1-butene is favored by thermodynamic equilibrium. Allowing 1-butene to isomerizes to 2-butene reduces the production of dimethylhexanes and increases the production of trimethylpentanes.

Hydrogen transfer
The hydrogen transfer reaction is most pronounced with propylene feed. The reaction also proceeds via the carbenium ion mechanism. In the first reaction, propylene reacts with isobutane to produce butylene and propane. The butylene is then alkylated with isobutane to form trimethylpentane.

Cracking disproportion
The larger polymer cations are susceptible to cracking or disproportionation reactions, which form fragments of various molecular weights. These fragments can then undergo further alkylation.

Initiation
The initiation step (generates the tertiary butyl cations that will subsequently carry on the alkylation reaction.

Overall reaction
From the viewpoint of octane, this reaction can be desirable because trimethylpentane has substantially higher octane than the dimethylpentane normally formed from propylene. However, two molecules of isobutane are required for each molecule of alkylate, and so this reaction may be undesirable from an economic viewpoint.

Propagation
Propagation reactions involve the tertiary butyl cation reacting with an olefin to form a larger carbenium ion, which then abstracts a hydride from an isobutane molecule. The hydride abstraction generates the isoparaffin plus a new tertiary butyl cation to carry on the reaction chain.

Polymerization
The polymerization reaction results in the production of heavier paraffins, which are undesirable because they reduce alkylate octane and increase alkylate endpoint. Minimization of this reaction is achieved by proper choice of reaction conditions.

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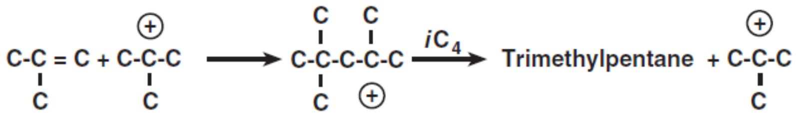
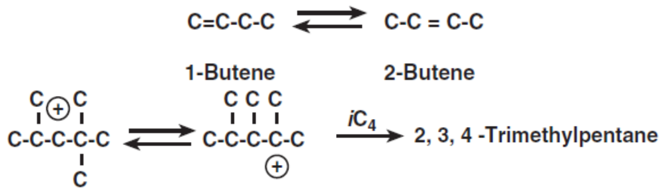
Alkylation mechanism.

1) ……………………………………………

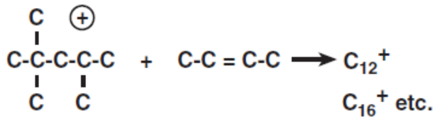
2) ……………………………………………



3) ……………………………………………



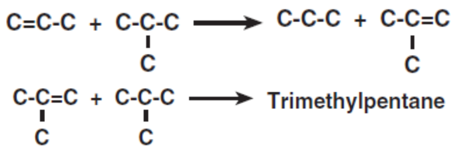
4) ……………………………………………



5) ……………………………………………

$$C_{12}^{+} \longrightarrow C_5^{+} + C_7^{+}$$

6) ……………………………………………



7) ……………………………………………

$$C_3H_6 + 2iC_4H_{10} \longrightarrow C_3H_8 + \text{Trimethylpentane}$$

2 **Match the type of alkylation process with its description.**

1) Alkylation without catalyst

2) Alkylation in presence of sulphuric acid

3) Alkylation in presence of hydrofluoric acid

4) Alkylation in presence of zeolite catalyst

A Process has no mechanical stirring. The catalyst of this process is a very hazardous material for humans because it can penetrate and damage tissue and bone. This type of process is less favourable because of the mitigation of acid catalyst vapour.

B In this process multiple reactors are used to allow for the catalyst regeneration cycle. This process is considered as less harmful for equipment, environment and people's health because of the fact that catalyst is not corrosive and does not vaporize.

C Alkylation between isobutane and olefin must be run under severe conditions such as T = 500 °C and P = 20–40 MPa.

D The contactor reactor is used in this type of alkylation technology as one of the technology configuration. Another configuration of this process represents a train of reactors with mixing devices.

1)………; **2)**………; **3)**………; **4)**……… .

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3 **Fill in the gaps with suitable words from the list.**

Alkylate

Alkylate is an excellent motor gasoline and aviation gasoline blend stock because of its high octane and low volatility. It is manufactured by the reaction of **1)** ____ in the presence of sulfuric acid (H_2SO_4) or hydrofluoric acid (HF) catalyst.

The alkylation unit feed originates from the **2)** _______________________. FCC gases are fractionated in a C_3/C_4 splitter to remove propane and lighter constituents. The bottom from the C_3/C_4 splitter is charged to the MTBE unit, which mainly depletes isobutylene from this feed. The raffinate from the MTBE unit containing ISO butylene and isobutane becomes **3)** ______________________________________. In case the MTBE unit is shut down, feed to the unit will not contain adequate isobutane to alkylate the olefin. So provision is made to supply isobutane separated from field butane.

The alkylation reaction is almost instantaneous and highly exothermic and is favored by **4)** ______________________________________. The process is carried out at 7 to 10 °C. The alkylate product is a mixture of **5)** _____________________________ in the gasoline boiling range. Alkylate has an RON of 93 to 98 and a MON of 90 to 95.

The reactors in which alkylation reactions occur are horizontal pressure vessels containing a mixing impeller, an inner circulation tube, and a **6)** _______________________ to remove heat generated by the alkylation reaction. The feed is injected into the suction side of the impeller inside the circulation tube. The impeller rapidly disperses hydrocarbon feed into the acid catalyst to form an emulsion. The emulsion is circulated by the impeller at high rates within the contractor. A portion of the **7)** _____________ is withdrawn from the contractor on the discharge side of the impeller. The emulsion flows to an acid settler where acid and hydrocarbon phase separate out. The acid, being heavier, settles to the bottom and is returned to the suction side of the impeller. Thus the impeller acts as an emulsion pump between the reactor and settler.

8) ______________________ acts as a catalyst for the alkylation reaction and theoretically remains unchanged. In reality, however, a certain amount of acid is consumed as a result of side reactions and feed contaminants. To maintain desired **9)** _______________________ (90 wt % H_2SO_4), a small amount of spent acid is withdrawn and an equivalent amount of 98.5 wt % fresh acid is charged to the reactor.

The impure alkylate stream contain some esters, which are removed by reacting with fresh sulfuric acid followed by washing with a dilute alkaline water stream. The treated contractor effluent is fed to an 10) _____________________________ to remove isobutene as overhead product, normal butane as side draw, and alkylate as bottom product.

emulsion	**sulfuric acid**	**isobutylene with isobutane**
acid strength	**FCC unit**	**feed for the alkylation unit**
isostripper tower	**tube bundle**	**low temperature conditions**
branched hydrocarbons	**isostripper tower**	