Petrochemicals

By

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Hydrocarbon Intermediates

INTRODUCTION

- Natural gas and crude oils are the main sources for hydrocarbon intermediates or secondary raw materials for the production of petrochemicals.

- From natural gas, ethane and LPG are recovered for use as intermediates in the production of olefins and diolefins.

- Important chemicals such as methanol and ammonia are also based on methane via synthesis gas.

- On the other hand, refinery gases from different crude oil processing schemes are important sources for olefins and LPG.

- Crude oil distillates and residues are precursors for olefins and aromatics via cracking and reforming processes.

PARAFFINIC HYDROCARBONS

• Paraffinic hydrocarbons used for producing petrochemicals range from the simplest hydrocarbon, methane, to heavier hydrocarbon gases and liquid mixtures present in crude oil fractions and residues.

• These compounds are the precursors for olefins through cracking processes.

•The C_6–C_9 paraffins and cycloparaffins are especially important for the production of aromatics through reforming.

1) METHANE (CH_4)

• Methane is the first member of the alkane series and is the main component of natural gas.

• It is also a by-product in all gas streams from processing crude oils. It is a colorless, odorless gas that is lighter than air.

• It reacts with a limited number of reagents such as oxygen and chlorine under specific conditions.

• For example, it is partially oxidized with a limited amount of oxygen to a carbon monoxide-hydrogen mixture at high temperatures in presence of a catalyst.

• The mixture (synthesis gas) is an important building block for many chemicals.

2) ETHANE (CH_3-CH_3)

- Ethane is an important paraffinic hydrocarbon intermediate for the production of olefins, especially ethylene.

- It is the second member of the alkanes and is mainly recovered from natural gas liquids.

- Ethane, like methane, is a colorless gas that is insoluble in water. It does not react with acids and bases, and is not very reactive toward many reagents.

- It can also be partially oxidized to a carbon monoxide and hydrogen mixture or chlorinated under conditions similar to those used for methane.

- Ethane's relation with petrochemicals is mainly through its cracking to ethylene.

3) PROPANE ($CH_3CH_2CH_3$)

• Propane is a more reactive paraffin than ethane and methane. This is due to the presence of two secondary hydrogens that could be easily substituted

• Propane is obtained from natural gas liquids or from refinery gas streams.

•Liquefied petroleum gas (LPG) is a mixture of propane and butane and is mainly used as a fuel.

• LPG is currently an important feedstock for the production of olefins for petrochemical use.

4) BUTANES (C_4H_{10})

• Like propane, butanes are obtained from natural gas liquids and from refinery gas streams.

• Like ethane and propane, the main chemical use of butane is as feedstock for steam cracking units for olefin production.

• Dehydrogenation of n-butane to butenes and to butadiene is an important route for the production of synthetic rubber. n-Butane is also a starting material for acetic acid and maleic anhydride production.

•Dehydrogenation of isobutane produces isobutene, which is a reactant for the synthesis of methyl tertiary butyl ether (MTBE).

• This compound is currently in high demand for preparing unleaded gasoline due to its high octane rating and clean burning properties.

OLEFINIC HYDROCARBONS

- The most important olefins used for the production of petrochemicals are ethylene, propylene, the butylenes, and isoprene.

- These olefins are usually coproduced with ethylene by steam cracking ethane, LPG, liquid petroleum fractions, and residues.

- Olefins are characterized by their higher reactivities compared to paraffinic hydrocarbons.
- They can easily react with inexpensive reagents such as water, oxygen, hydrochloric acid, and chlorine to form valuable chemicals.
- Olefins can even add to themselves to produce important polymers such as polyethylene and polypropylene.

1) ETHYLENE ($CH_2=CH_2$)

• Ethylene (ethene), the first member of the alkenes, is a colorless gas with a sweet odor. It is slightly soluble in water and alcohol. It is a highly active compound that reacts easily by addition to many chemical reagents.

• Ethylene with water forms ethyl alcohol.

• Addition of chlorine to ethylene produces ethylene dichloride (1,2-dichloroethane), which is cracked to vinyl chloride. Vinyl chloride is an important plastic precursor.

• Ethylene is also an active alkylating agent. Alkylation of benzene with ethylene produces ethyl benzene, which is dehydrogenated to styrene. Styrene is a monomer used in the manufacture of many commercial polymers and copolymers.

• Ethylene can be polymerized to different grades of polyethylenes or copolymerized with other olefins.

• Catalytic oxidation of ethylene produces ethylene oxide, which is hydrolyzed to ethylene glycol. Ethylene glycol is a monomer for the production of synthetic fibers.

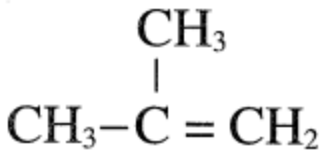
2) PROPYLENE ($CH_3CH=CH_2$)

• The main source of propylene is steam cracking of hydrocarbons, where it is coproduced with ethylene.
• There is no special process for propylene production except the dehydrogenation of propane.
• Propylene can be polymerized alone or copolymerized with other monomers such as ethylene.
• Many important chemicals are based on propylene such as isopropanol, allyl alcohol, glycerol, and acrylonitrile.

3) BUTYLENES (C_4H_8)

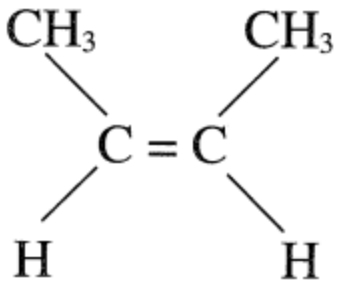
- Butylenes (butenes) are by-products of refinery cracking processes and steam cracking units for ethylene production.
- There are four butene isomers: three unbranched, “normal” butenes (n-butenes) and a branched isobutene (2-methylpropene).

- The three n-butenes are 1-butene and cis- and trans- 2-butene. The following shows the four butylene isomers:

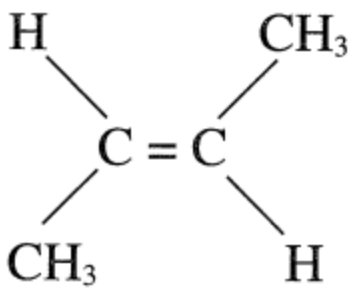


Isobutene

1- Butene



cis-2- Butene



trans-2-Butene

THE DIENES

• Dienes are aliphatic compounds having two double bonds. When the double bonds are separated by only one single bond, the compound is a conjugated diene (conjugated diolefin). Nonconjugated diolefins have the double bonds separated (isolated) by more than one single bond.

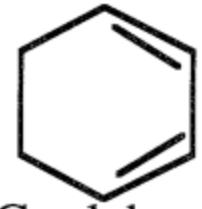
$CH_2=CH-CH_2-CH=CH_2$

1,4-Pentadiene

1,4-Cyclohexadiene

$CH_2=CH-CH=CH_2$

1,3-Butadiene



1,3-Cyclohexadiene

When polymerizing dienes for synthetic rubber production, coordination catalysts are used to direct the reaction to yield predominantly 1,4-addition polymers.

1) BUTADIENE (CH_2=CH-CH=CH_2)

• Butadiene is by far the most important monomer for synthetic rubber production.

• It can be polymerized to polybutadiene or copolymerized with styrene to styrene-butadiene rubber (SBR).

• Butadiene is an important intermediate for the synthesis of many chemicals such as hexamethylenediamine and adipic acid. Both are monomers for producing nylon.

• Chloroprene is another butadiene derivative for the synthesis of neoprene rubber.

• Butadiene is obtained mainly as a coproduct with other light olefins from steam cracking units for ethylene production.

2) Isoprene ($CH_2=C(CH_3)-CH=CH_2$)

- Isoprene (2-methyl-1,3-butadiene) is a colorless liquid, soluble in alcohol but not in water.
- Isoprene is the second important conjugated diene for synthetic rubber production.
- The main source for isoprene is the dehydrogenation of C_5 olefins (tertiary amylenes) obtained by the extraction of a C_5 fraction from catalytic cracking units.
- It can also be produced through several synthetic routes using reactive chemicals such as isobutene, formaldehyde, and propene.
- The main use of isoprene is the production of polyisoprene. It is also a comonomer with isobutene for butyl rubber production.

AROMATIC HYDROCARBONS

• Benzene, toluene, xylenes (BTX), and ethylbenzene are the aromatic hydrocarbons with a widespread use as petrochemicals.

• They are important precursors for many commercial chemicals and polymers such as phenol, trinitrotoluene (TNT), nylons, and plastics.

• Benzene, toluene, xylenes (BTX) and ethylbenzene are obtained mainly from the catalytic reforming of heavy naphtha.

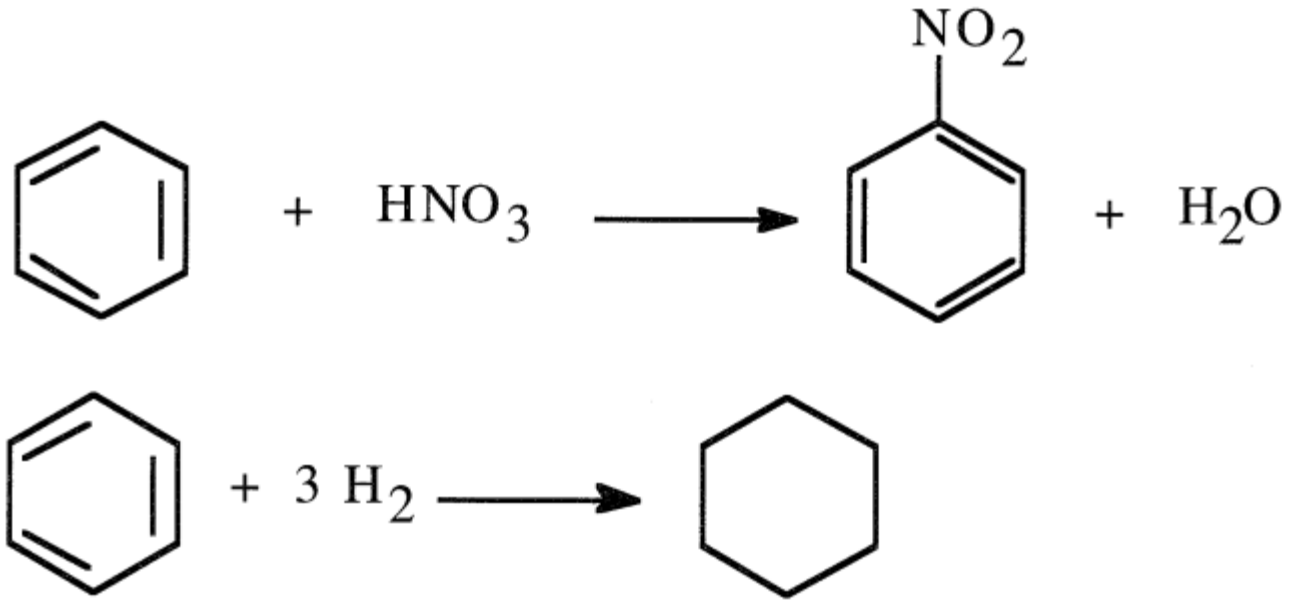
1) Benzene

• Benzene (C_6H_6) is the simplest aromatic hydrocarbon and by far the most widely used one.

• Before 1940, the main source of benzene and substituted benzene was coal tar. Currently, it is mainly obtained from catalytic reforming. Other sources are pyrolysis gasolines and coal liquids.

• Aromatic hydrocarbons, like paraffin hydrocarbons, react by substitution. They react by addition only under severe conditions.

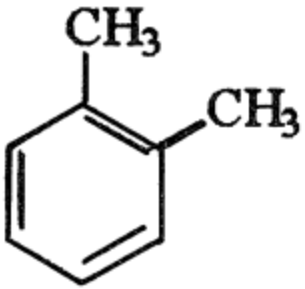
• For example, electrophilic substitution of benzene using nitric acid produces nitrobenzene under normal conditions, while the addition of hydrogen to benzene occurs in presence of catalyst only under high pressure to give cyclohexane:



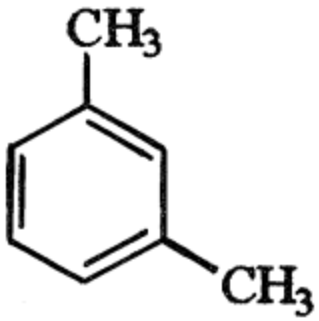
• Monosubstitution can occur at any one of the six equivalent carbons of the ring.

• Most of the monosubstituted benzenes have common names such as toluene (methylbenzene), phenol (hydroxybenzene), and aniline (aminobenzene).

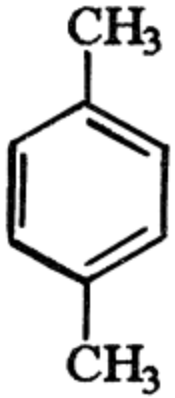
• When two hydrogens in the ring are substituted by the same reagent,three isomers are possible.
• The prefixes ortho, meta, and para are used to indicate the location of the substituents in 1,2- ; 1,3- ; or 1,4-positions. For example, there are three xylene isomers:



o-Xylene
(1,2-Dimethyl-
benzene)



m-Xylene
(1,3-Dimethyl-
benzene)



p-Xylene
(1,4-Dimethyl-
benzene)

2) Ethylbenzene

• Ethylbenzene ($C_6H_5CH_2CH_3$) is one of the C_8 aromatic constituents in reformates and pyrolysis gasolines.
• Most ethylbenzene is obtained by the alkylation of benzene with ethylene.

3) Methylbenzenes (Toluene and Xylenes)

• The primary sources of toluene and xylenes are reformates from catalytic reforming units, gasoline from catcracking, and pyrolysis gasoline from steam reforming of naphtha and gas oils.
• Currently, the largest single use of toluene is to convert it to benzene.
• para-Xylene is mainly used to produce terephthalic acid for polyesters.
• o-Xylene is mainly used to produce phthalic anhydride for plasticizers.

LIQUID PETROLEUM FRACTIONS AND RESIDUES

• Liquid Petroleum fractions are light naphtha, heavy naphtha, kerosine and gas oil.

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• The bottom product from distillation units is the residue.

• These mixtures are intermediates through which other reactive intermediates are obtained.

• Heavy naphtha is a source of aromatics via catalytic reforming and of olefins from steam cracking units.

• Gas oils and residues are sources of olefins through cracking and pyrolysis processes.