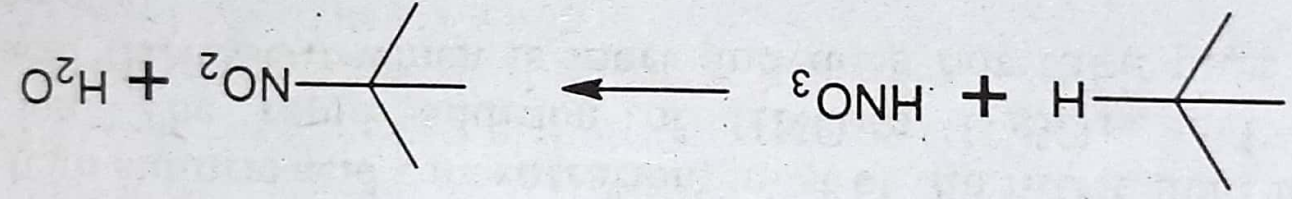


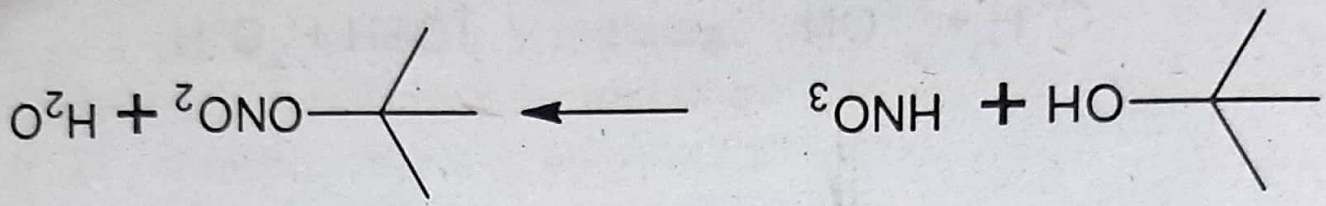
1.2.3. Nitration

The reaction between an organic compound and a nitrating agent such as nitric acid either to introduce a nitro group (-NO₂) into hydrocarbon or to produce a nitrate (an ester). The nitro group may be attached to the carbon atom of a hydrocarbon, oxygen atom and nitrogen atom. So nitration may be classified as;

C-nitration: If nitro group is attached to carbon atom to form nitro-aromatic or nitro-paraffinic compounds.



O-nitration: If nitro group is attached to the oxygen to form a nitrate ester. This is also an esterification reaction.



N-nitration: If nitro group is attached to a nitrogen atom it forms a nitramine.

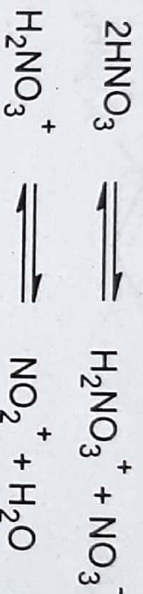


1.2.3.1 Nitrating agents

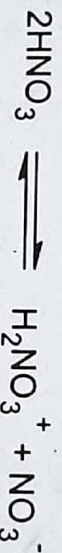
Some important nitrating agents are enlisted as under

i) Nitric acid

It is the simplest nitrating agent and can be used in varying degree of concentration. A few compounds can be nitrated by HNO_3 as the water liberated interferes with the reaction. It is used in vapor phase nitration in the manufacturing of nitro paraffin and pentaerythritol tetra nitrate in the manufacturing of cyclonite. It produces nitronium (nitryl) ion (NO_2^+). Pure nitric acid ionizes to a small extent to produce nitronium ion.



In dilute nitric acid solution, the nitratidumcation is thought to be the active nitrating agent.



ii) Mixed acid (HNO_3 - H_2SO_4 mixture)

It is the most common and economical nitrating agent. The sulfuric acid removes water formed in nitration. The strength of the nitrating acid and the amount of sulfuric acid required depend on the compound being nitrated and the desired degree of nitration.

Composition of mixed acid varies from

HNO_3	20% HNO_3	55%	H_2O	nil
H_2SO_4	60% H_2SO_4	48%		
H_2O	20%			

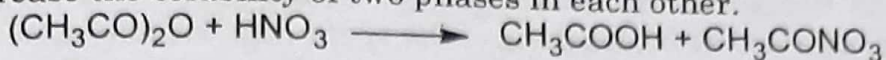
In mixed acid, the concentration of NO_2^+ increased significantly by the use of sulfuric acid. At high sulfuric acid concentration, most of the nitric acid ionizes to produce the nitronium ion. The rapid addition of HNO_3 to H_2SO_4 acid reacts to form nitrosylsulfuric acid (HNO_3SO_4) which is inert and does not take part in nitration and conductive to fume offs.



iii) Nitric acid and acetic anhydride

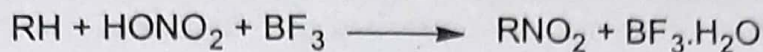
Compounds that are difficult to nitrate, a mixture of nitric acid and acetic anhydride is used. Acetic anhydride and nitric acid react to form acetic acid and acetyl

nitrate, which is also a nitrating agent. It is used for commercial N-nitration of hexamethylenetetramine $(\text{CH}_2)_6\text{N}_4$. Acetic acid or acetic anhydride also serves as solvent that tends to increase the solubility of two phases in each other.



iv) Nitric acid and Boron trifluoride

BF_3 is an effective promotor and dehydrating agent. Many organic compounds are nitrated quickly and almost completely with stoichiometric amounts of nitric acid in the presence of BF_3 .



v) Nitric acid and Nitrous acid

It is used for nitration at very mild reaction conditions involving compounds such as phenol or anisole. The nitrosium ion (NO^+) is thought to be the ion that initially attacks the aromatic ring.



vi) Nitrogen Dioxide (NO_2)

NO_2 is used for the vapor phase nitration of paraffin to nitroparaffins.

1.2.3.2 Nitration Process and Equipment

A technical process, nitration is both a batch and continuous process. In batch process, nitrator consists of a cylindrical vessel, temperature control system, agitation system, feed inlet and outlet and quick dumping line for emergency.

Cylindrical vessel: A nitration tank is usually a closed cast iron or mild carbon steel vessels.

Temperature control system: In nitrator, temperature control system consists of coils of tubes through which either cold water or brine for cooling and hot water or steam for heating may be circulated.

Agitation system: An agitation system consists of a vertical shaft with one or more propellers mounted on it in the cylindrical shaped center of one or more banks of cooling coils. A cylindrical sleeve is mounted in the center of cooling coils to ensure circulation of the nitrator contents as desired. If a feed is introduced at the top of the agitator sleeve, circulation by the propeller is down through the center and around and up through the cooling coils. If feed is introduced beneath the liquid level, circulation may be up through the sleeve and around and down through the banks of coils.

Emergency dump tank: If in the nitrator, the reaction gets out of hand or temperature rises because of failure of agitation, cooling or otherwise. The contents of the nitrator are quickly dumped into a large volume of water contained in the drowning tub.

Procedure: The sleeve and propeller nitrator, the spent acid that is cycle acid (some nitrobenzene and nitric acid in sulfuric acid) is charged so that it covers the cooling coils. Cold water is circulated through the heat exchange medium to keep the temperature at 50°C or lower. The benzene is pumped from the storage tank to the nitrator. The mixed acid is fed on undersurface with the help of a lead feed pipe just under the propeller. The temperature of nitration of benzene varies within the moderate limits that are kept $50-55^\circ\text{C}$.

Separation: After nitration, the nitrator contents are charged into a larger conical bottomed lead tank and are permitted to settle for 4-12 hours. The spent acid is drawn off from the bottom of the tank and sent to the spent acid tank for additional settling tank or by countercurrent washing of the spent acid with benzene.

Neutralization: The neutralization step of the nitrobenzene consists of three washes that is two washes with hot water and one with sodium carbonate solution. The nitrobenzene is charged to the neutralizer tank containing an air spider for agitation of the nitrobenzene or with sleeve and propeller agitator containing warm water. The charge is agitated thoroughly and warmed with live steam for 30 minutes or until it is neutral to Congo red and then allowed to settle. The supernatant acid water is run off through side outlets into a labyrinth to settle out the emmeshed nitrobenzene.

The charge is then washed with a warm sodium carbonate solution until it is alkaline to phenolphthalein at 40-50°C.

Finally the nitrobenzene is washed with a little warm water and is sent to storage tank where it is settled to remove the final traces of water.