Quadrant II – Notes
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Unit: V – Nitration
Module Name: Kinetics and Mechanism of Nitration w.r.t. Paraffinic Hydrocarbons
Module No: 11
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<u>Kinetics of Nitration:</u>

The kinetics of the nitration can depends upon the reaction medium.

Let us consider 1st that the reaction is taking place in strong sulphuric acid, Compounds which are nitrated at a conveniently measurable rate in these systems are those which are having a strong – I and – M effects such as Nitrobenzene, anthraquinone and ethyl benzoate

The rate of all these nitration reactions will be proportional to the concentration of the added nitric acid and of organic substrate.

Rate =K (HNO3) (ArH)

1 1

Overall rate = 2

- The reaction rate rises sharply with increasing sulphuric acid concentration and reaches a maximum at about 90% H_2SO_4 and then falls off at higher acid concentrations.

- It was suggested that the rise in rate with increasing acid strength when acid is less than 90% is due to increase in the concentration of nitryl ion.
- Generally accepted mechanism which is compatible with the data is

$HNO_3 + 2\ H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2H_SO_4^-$ (Fast) Step - 1

$ArH + NO_2 \longrightarrow ArHNO_2^+$

(Slow: Rate determining step) Step – 2

$ArHNO_2^+ + HSO_4^- \longrightarrow ArNO_2 + H_2SO_4$ Step - 3

Thermodynamics of Nitration:

- Nitration reaction is highly exothermic.
- The heat released e.g. in nitration of 1lb of benzene is comparable to that released on condensation of 1lb of steam.
- The heat problem is much more important because of heat of dilution of nitrating acid and low heat capacity of medium.
- We must know how to develop and use thermodynamic data in designing nitrating equipment and providing safe and efficient operation.
- Since nitration is exothermic, its enthalpy change (ΔH) will be -ve.

Heat of nitration

- The nitration reaction must be controlled by systematic cooling design to withdraw the heat energy evolved.
- When all the energy set free by an exothermic reaction is forced to appear as heat, the quantity of it lost to the cooling mechanism equals the decrease in enthalpy

  i.e. $Q = -\Delta H$ where Q = heat of reaction,

  Represent the total amount of heat lost by the reacting system from the start of reaction till the products return to initial temperature and pressure of the system.

  Thermal properties of nitration acid

- Heat of solution: To determine the heat evolved during nitration of hydrocarbon by mixed acid, it is necessary to consider not only the heat of nitration but also various heats of solution.
- Heat of dilution: This is the quantity of heat evolved where dilution of mixed acid is carried out.
- Integrated heats of nitration :In nitration of hydrocarbon by means of a mixture of concentrated $HNO_3 + H_2SO_4$, total heat liberated is equal to heat of solution of initial mixed acid minus heat of solution of final spent acid minus heat of solution of the nitric acid entering into the reaction plus heat of nitration reaction
- Although heats of nitration are relatively large, the control of reaction is closely related to heats of dilution of nitrating acid.

- The simplest way to integrate heat effect involved is to sum up the enthalpies on the both sides of complete reaction equation by the use of heats of nitration and other experimental data.

<u>Thermal data relating to the preparation and use of nitro compounds</u>

It indicates that when nitration occurs, a considerable amount of heat is generated. It has been found that heats of nitration decreases with increase in the number of nitro groups.

<u>Nitration of Paraffinic Hydrocarbon:</u>

- They are inert to electrophilic reagent. It is not an electrophilic substitution reaction.
- It is a free radical reaction.
- Classification is done as

    i. Gas-phase nitration and

    ii. Liquid-phase nitration,

❖ <u>Gas-phase nitration</u>

- Paraffins are quite inert to electrophilic reagent such as the nitryl ion. The paraffins are attacked by certain atoms and free radicals.
- Nitration of these compounds is carried out in industries in vapor phase at 350– 450^{0}C. It is free radical reaction.
- Nitric acid of strength 70% or less is generally used. We can also use NO_2

Facts as a result of systematic study:

- There is optimum temperature at which highest yield is obtained.
- The addition of oxygen increases yield based on HNO_3 but also increases oxidation of alkane.
- NO_2 also reacts with paraffin to yield nitro-paraffin.
- Bromine has beneficial effect on both yield and conversion to nitro-paraffin using HNO_3.
- Highly branched hydrocarbons undergo less fission during nitration than to their less branched isomer. Correspondingly substitution is favored when highly branched structures are nitrated.
- Temperature coefficient for H substitution are in order 1° > 2 ° > 3°
- Rate of substitution is in reverse order at low temperature i.e. 3° > 2°> 1°.
- Mechanism of Gas Phase Nitration:

$$HONO_2 \longrightarrow {\circ}OH + {\circ}NO_2$$

$$R\text{-}H + {\circ}OH \longrightarrow R{\circ} + H_2O$$

$$R\text{-}H + {\circ}NO_2 \longrightarrow R{\circ} + HNO_2$$

$$R{\circ} + {\circ}NO_2 \longrightarrow R\text{-}NO_2$$

- The 2nd and 3rd step is about the alkyl radical formation
- And the final step is about the Nitroparaffin formation.

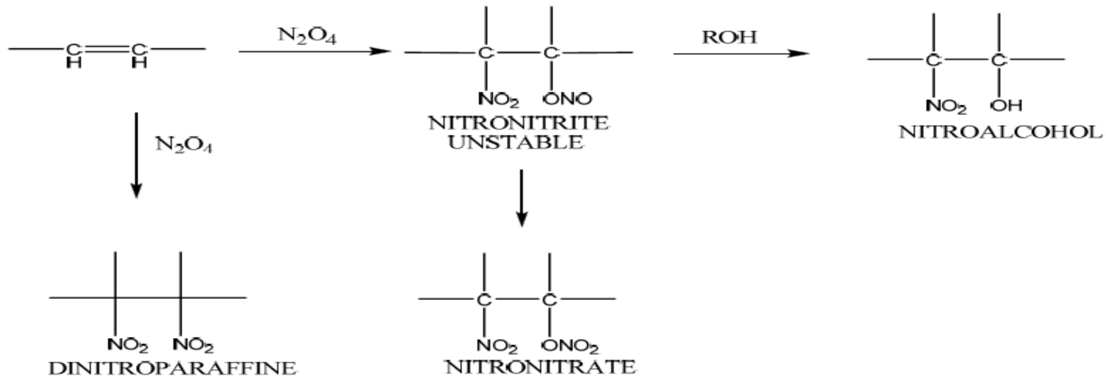
❖ Liquid phase nitration

The reaction is less important than the gas-phase nitration because

- Low yields
- Low conversions
- Unwanted side reaction occurs. (Oxidation and decomposition)

- In this reaction, hydrogen atom is replaced by nitro group. The alkyl groups are not replaced.
- The rate of formation of product is in following order $3^0 > 2^0 > 1^0$ nitro-paraffin.
- The reaction is slow because of low mutual solubility of paraffin and nitration medium.
- Because of higher boiling point, higher hydrocarbons can be nitrated at high temperature.
- The initially formed mononitroparaffin is more soluble in the HNO_3 than in hydrocarbon and undergoes further reaction to yield polynitroparaffins and decomposition and oxidative products including fatty acids, alcohols and oxides of carbon.
- The oxidation which occurs along with the nitration reduces HNO_3 to elementary nitrogen, which cannot be usefully utilized. This makes the process expensive.

- <u>Mechanism of Liquid Phase Nitration</u>



- The initial products are dinitroparaffin and nitro nitrite.
- The latter is unstable and is partially oxidized to stable nitro nitrate.
- The remaining nitronitrite is converted into nitro alcohol by treatment of reaction product with H_2O or ethanol before distillation.
- The reaction is carried out by slow addition of olefin to nitrogen dioxide at temperature -10 to 25^0C.
- The use of ether as solvent minimizes the oxidative side reactions.
- Ethylene reacts slowly but higher olefins react more rapidly and molar equivalent can be made to react completely in 1 to 2 Hr.
- Total yield of separated products are 65 - 85%.