

Title : AMINATION BY REDUCTION


PEC-II (3143616)

Date:

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Lecture No : (First)

Source of information : Wikipedia

The background of the slide features a light gray gradient with several large, realistic water droplets of varying sizes scattered across the surface. Faint, concentric circular lines are also visible, creating a ripple effect centered around the text.

AMINATION BY REDUCTION

WHAT IS AMINATION BY REDUCTION?

- Synthesis of amines by reductive methods.
- Amines can be produced by reduction of
 - NITRO
 - NITROSO
 - AZOXY
 - AZO,
- Amines can also be obtained by reacting compounds containing certain Labile groups (halogens) with ammonia.

USES OF AMINES.

- Amines are very important as intermediates in the chemical process industry.
- Production of dyes, rubber chemicals, nylon, pharmaceuticals, gasoline additives, sweetening agents, agriculture chemicals, printing ink, plastics etc.
- Now-a-days manufacture of diamines by reductive methods has increased.

E.g.:- 1. Hexamethylene diamine + adipic acid nylon

REDUCTION PROCESS OR METHODS

- There are various methods of reduction they are:-

1. Metal and acid
2. Metal and alkali method
3. Metal hydrides
4. Sulfide
5. Sulphite (piria method)
6. Sodium hyposulfite (hyposulfite)
7. Sodium & sodium alcoholate
8. Catalytic
9. Electrolytic
10. Strong caustic oxidation & reduction
11. Hydrogenated quinoline & naphthalene.

1. METAL & ACID-Iron & acid (bechamp method) is the major example in this category, but we can also use other metals like tin & zinc. Mainly HCL acid is preferred but sulphuric acid, acetic acid & formic acid can also be used.

2. METAL & ALKALI- This method is used Mainly for production of azoxy, azo, and hydrazo compound.

3. METAL HYDRIDES- like lithium aluminium hydride (LiAlH_4) is used in reduction process.

4. SULFIDE—used especially for partial reduction polynitro aromatic compound and for reduction of nitro amino anthraquinones.

5. SULPHITE— In this reaction sodium sulfite and sodium bisulfite + aromatic nitro compound mixture of amine and aminoaryl sulfonic acid.

6. SODIUM HYDROSULFITE—this method is inexpensive and safe reducing agent reduction of aromatic nitro and diazonium compound To aniline

7. CATALYTIC—hydrogen and catalyst such as Ni, copper, platinum palladium

8. ELECTROLYTIC- nitro group electrolytic sol. amines

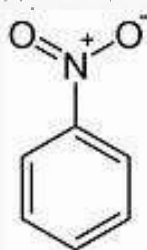
9. STRONG CAUSTIC OXIDATION AND REDUCTION- presence of oxidation and reduction in strong alkaline solution.

10. HYDROGENATED QUINOLINE & NAPHTHALENE- By hydrogenation we can obtain Amines.

- It is very important to select proper reducing agent to carry out reductive Amination.

• E.g.:-

hydrox

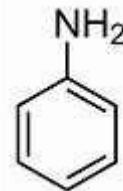


$\text{Zn} + \text{acid}$

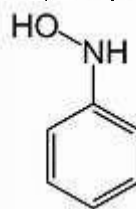
$\text{Zn} + \text{water}$

$\text{Zn} + \text{alkali}$

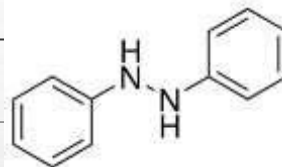
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Aniline



Phenyl




Hydrazobenzene

IRON AND ACID (BECHAMP) REDUCTION

- Bechamp in 1854 discovered that nitro compounds could be reduced in the presence of iron & acetic acid.
- Parkin commercially produced aniline by this reaction.
- In technical progress acetic acid is replaced by HCL.
- Due to ferrous salt action reduction can be carried out in less than theoretical amount of acid.
- $\text{C}_6\text{H}_5\text{NO}_2 + 2\text{Fe} + 6\text{HCL} \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O} + \text{FeCl}_3$
- There are many acid used successfully like aniline HCL, Aluminium chloride, Sodium hydrogen sulfate.
- Most important thing required is salt that act as an acid in water solution, liberating H₂O.
- Mechanism depends on reagents used & nature of electrophile.

CHEMICAL AND PHYSICAL FACTORS

1. AMOUNT OF IRON

- In plant practice, 2 moles Fe Per mole nitro compound is used to carry out the reduction process.
- Not all the iron ~~conve~~  ~~rt~~ ferrosoferric oxide. Reducto-active ferrous hydroxide is also present.
- If there is insufficient iron there is no effect of heat & acid in reduction & poorly filtering iron oxide sludge is obtained.
- To avoid this finely divided iron can be added this completes reduction of nitro compound.
- Range of iron used- 2.5-5.0 moles/mole of nitro compound.

There are various other factors-

- Physical condition of iron.
- Amount of water.
- Amount of acid.

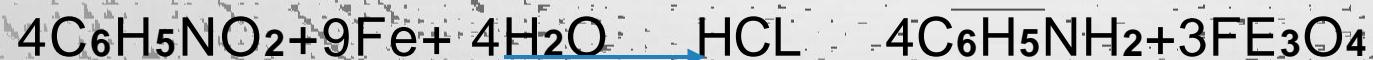
EQUIPMENT MATERIAL OF CONSTRUCTION

- Bechamp reduction is carried out in cast iron vessels & alkali reduction in carbon steel vessel of desired sizes.
 - Large one is preferred for economical operation.
 - To protect the vessel against the continuous erosive action of iron borings they are equipped with side & bottom cast iron-lining plates.
 - Wooden equipment are also used for reduction of solid nitro compounds like p-nitro aniline.
1. Agitation.
 2. Jacketing of reducers.

EXAMPLE OF APIs MANUFACTURING BY REDUCTIVE AMINATION

Name of chemicals	Quantity
Nitrobenzene	1390kg
Iron boring	1600kg
HCL	125kg

3. Reaction:-



Reactor –

- Crude nitrobenzene is placed into a reactor with reflux condenser.
- It is steam jacketed cast iron enclosed cylindrical having an agitator.
- Cast iron boring/ powder, water & catalyst are added in small quantities

- 10 to 20 % iron is added in beginning.
- mix. is heated by steam at 200°C.
- Remaining iron is added gradually maintaining pressure & temperature balance.
- Addition rate is fast to maintain reflux by the heat generated from the exothermic reaction but slow to prevent excessive hydrogen, pressure build up.
- Water is used in the form of aniline water which is obtained from separator or column in bulk at start & in small quantities with iron.
- Dil. HCL is added with H₂O as catalyst. Acid reacts with iron boring which forms catalytically active iron salts.
- After the last addition, reaction is heated with steam.
- At the end of the reaction, aniline is separated from reducer by several methods.
- Liquid water aniline mix. May be separated from the solid iron hydroxide sludge by steam distillation, etc.
- Finished reduction product is neutralized with small amount of sodium carbonate & allowed to settle.
- Most of the aniline, water & residual aniline is separated from sludge by steam distillation.

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- Assignment: 1. What is reduction. Explain amination by reduction with suitable reaction
2. Explain the bechamp reduction with chemical and physical factors associated with it
 - Hard copy submission date (31/3/2020).
 - Phone number of faculty: 9421183338