Quadrant II – Notes

Programme: Bachelor of Science Second Year (S. Y. B. Sc.)

Subject: Industrial Chemistry

Paper Code: CHC153

Paper Title: General Industrial Chemistry

Unit: V – Nitration

Module Name: Benzene to Nitrobenzene and m-Dinitrobenzene.

Module No: 12

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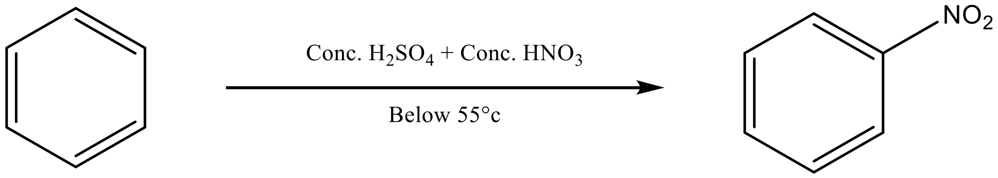
Mechanism for Preparation of Nitrobenzene from Benzene



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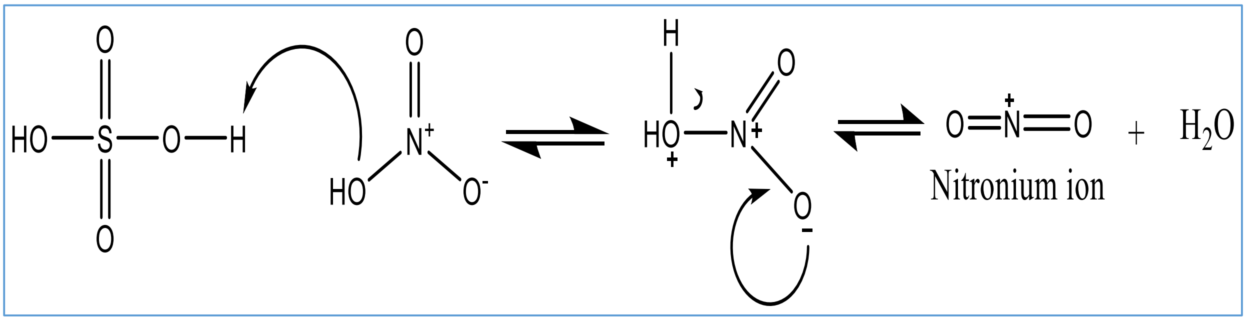

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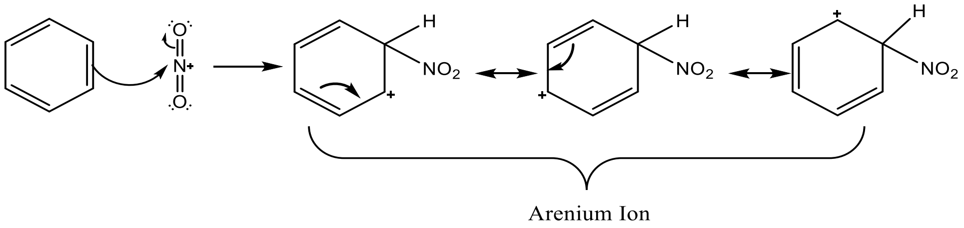

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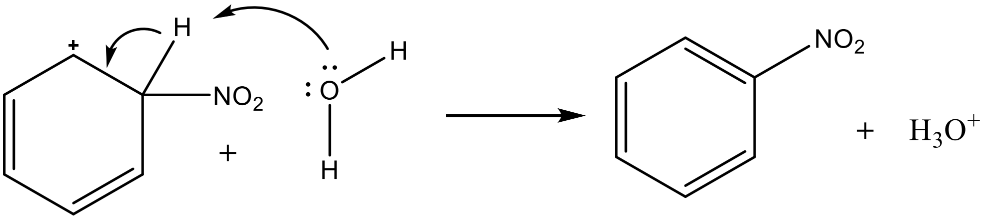


Preparation of Nitrobenzene

Nitrobenzene can be manufactured by

1. Batch Nitration with mixed acid.

- Use of cycle acid is not essential, particularly when the problem of heat transfer has been satisfactorily solved.
- The operation commence by delivering to the nitrator sufficient cycle acid, i.e. spent acid from a previous charge in which some nitrobenzene and nitric acid are still present, The amount of such acid required depends on the type of nitrator used.
- In the sleeve and propeller type, it should cover the cooling coils; in the Hough nitrator, it must cover and overflow through the parts of the machine.

- Cold water is then circulated through the heat-exchange medium, when the temperature is 50^0C or lower, the charge of benzene is pumped from the scale tank into the nitrator.
- The mixed acid for nitration can be fed on the top of the hydrocarbon or under surface.
- The temperature of nitration for benzene may very within moderate limits. When no cycle acids used, the temperature below 50^0C is kept, when fortified spent acid is employed the nitration temperature may be kept between 50^0C and 55^0C.

❖ Separation and Neutralization

- The separation of the nitrobenzene is done in large conical bottomed lead tanks, each capable of holding one or more charges.
- The nitrator charge is settled here for 4 to 12 hrs.
- When the spent acid is drawn off from the bottom of the lead tanks and delivered to the spent acid tanks for additional settling or for treatment with benzene next to be nitrated, in order to extract the residual nitrobenzene.
- The nitrobenzene is then delivered to the neutralizing house.
- The neutralizing tub may be either a large lead conical shaped tube containing an air spider, which is used for agitating the charge of nitrobenzene during the washing process, or a

standard cast iron kettle similar to the nitrator with sleeve and propeller agitation.

- The neutralizing vessel is prepared with **"heel"** of warm water, which is delivered from an adjacent vat, and the nitrobenzene is blown into it.
- The charge is thoroughly agitated and warmed with live steam for 30 min. or until neutral to Congo and then allowed to settle for a similar period.
- The supernatant acid water is then run off through side outlets into a labyrinth where practically all the immersed nitrobenzene will settle out.
- The charge is now given a neutralizing wash at 40-50^{0}C with a warm sodium carbonate solution, until alkaline to phenolphthalein.
- When the nitrobenzene is intended for aniline production, this may be followed by a wash with aniline water from the reducer house if any has to be worked up; otherwise, a final washing with a small quantity of warm water is made.
- The nitrobenzene is then delivered to its storage tanks, where it is again settled to remove final traces of water.
- The crude product can now be distilled for commerce or used directly for the preparation of aniline.

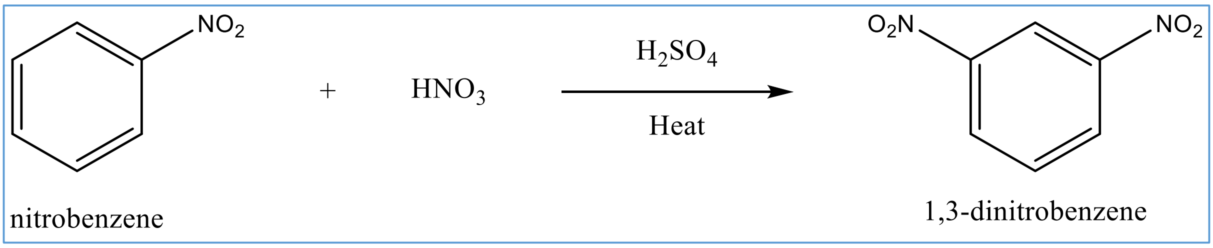
- In some plants where the nitrobenzene is used almost exclusively in the aniline plant, the neutralizing and subsequent washes are omitted.
- The nitrobenzene delivered to the reducer houses it.
- No harmful effects on the equipment are noticeable, if the acidity is kept below 0.5 percent.

Continuous nitration with fortified spent acid.

- Hot sulfuric acid at 90^0C is run from the heat insulated storage tank into one of a battery of nitrator.
- Under vigorous agitation, sufficient 63% nitric acid is added to the nitrator to produce a mixed acid containing 4% HNO_3.
- Sufficient benzene is then delivered from its storage tank to react with all the nitric acid in the nitrator.
- Upon completion of the reaction, that takes about 10 min.
- The agitation is stopped and the charge is permitted to settle.
- While the separation of nitrobenzene and spent acid proceeds, another nitration is started, thus providing a continuity of operations.
- The crude nitrobenzene is drawn off through side outlets on the nitrator and sent to the neutralizer.

- The spent acid which is free of nitric acid but contains small amounts of nitrobenzene is drawn off in operating sequence at the outlets located at the base of the nitrators.
- The spent acid is first directed to the acid heater which is heated by low pressure steam to maintain the sensible heat of the spent acid (72% H_2SO_4) and delivered to the vapor separator.
- The evaporator, operating under vacuum of 29 inch, effectively removes the water of nitration by virtue of the sensible heat of the spent acid and returns the sulfuric acid to the system at its original (75%) strength.
- The small quantity of nitrobenzene found with the water in the condenser is separated and added to the crude charge.

- Preparation of m-dinitrobenzene:



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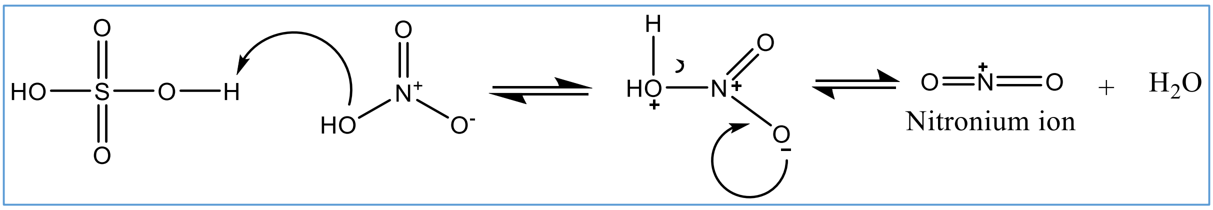

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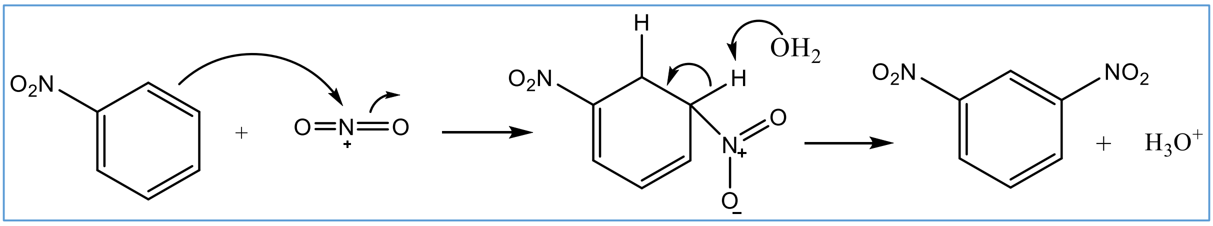

Preparation of m-dinitrobenzene:

- The preparation of m-dinitrobenzene from benzene is usually accomplished in two stages of nitration. Both may be made in the same vessel.
- The first stage is carried out under the conditions of nitration of benzene to form nitrobenzene.

- At the conclusion of the first nitration, the spent acid is run off from the base of the machine and is replaced by a storage nitrating acid for the second stage of nitration.
- The composition of the nitrating acids for the both stages of nitration is as shown above.
- It is readily seen from compositions that the second nitration required a more concentrated acid.
- Moreover, the reaction must be controlled at a higher temperature i.e. 90-100 °C.
- Although the heat of nitration for the second nitro group is not as great as for the introduction of the first.
- The operation is nevertheless much slower on account of the lower specific heat and greater integral heat of dilution of the more concentrated acids that are used.
- Since the rate of feed and time of reaction are determined by the efficiency of agitation and heat exchange, these are matters of special importance in this nitration.
- In the combined operations 2,200 Kg of spent acid from a dinitration (about 80% H_2SO_4) is retained in a jacketed cast-iron nitrator of 8 cu. ft. (2,112 gal) capacity that is provided with a lead cooling coil and sleeve in which a stirrer operates at 110 rpm.
- To this added 1900 Kg mixed acid analyzing 88% HNO_3, 11% H_2SO_4 and 1% H_2O.

- Then 2200 Kg benzene is introduced over a period of 4 hr. while controlling the temperature initially at 25^0C and finally at 40^0C.
- The temperature is then raised to 60^0C in 1 hr.
- The charge is permitted to stratify and the spent acid is discharged to a lead lined washer with stirrer where it is washed with either benzene or nitrobenzene.
- To the nitrobenzene retained in the nitrator, there is added over a 3 hr. period 5,000-6000 Kg. of mixed acid (Approx. 33 % HNO_3, 67% H_2SO_4) permitting a temperature rise from 25^0C to 40^0C.
- The temperature is then raised to 90^0C and maintained there for 1 hr. or until free of nitrobenzene by the steam distillation test.
- The charge is settled and the spent acid run into a large washer where several batches are washed with nitrobenzene.
- The dinitrobenzene is delivered to a tile lines or stainless steel washer, provided with a lead cover and stirrer
- it is washed first with 4,000 liters of hot water, then with caustic soda solution until neutral and finally with water
- About 4,500 kg of crude molten dinitrobenzene (85% m-, 13% o-, 2% p-) obtained from each nitrator charge is purified by mixing thoroughly with 3,000 liters water at 80^0C in a jacketed cast iron vessel.

- The contents are allowed to cool without heat exchange, until about 70^0C when pelleting begins and Then 650 kg sodium sulfite, which converts the para and ortho derivatives to nitramines, is added at a rate of 100 kg/15 minutes.