Today. We're going to discuss about the

topic nitration, in that we are going to study about

introduction and nitrating agents. My name is Abhijeet Mainkar

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Science. And we'll start with

the topic. Today we are going to learn about introduction to

nitration. We're also going to study the various types of

nitrating agents, and we're going to look into the factors

affecting nitration.

Learning outcomes from this module it will help you to

define the nitration process.

It will also help you to compare the various nitrating agents and

you will be able to explain the various factors affecting the

Nitration process.

Introduction: Any commercial production of

chemicals is usually a combination of physical and

chemical changes for the systematic study of chemical

process industries, the physical and chemical changes which are

important for the manufacturing processes have been classified

as unit operations and unit processes respectively. So now

will look into unit operations. They may be defined as major

physical changes useful to the chemical industries. Important

unit operations are

Heat transfer, flow of fluids, material handling, filtration, distillation, extraction, drying, etc. Relatively few of the unit operations are required in any particular process. In majority of the cases, operations are to be done to set up the condition to carry out chemical changes. Now will look into the unit process. Unit processes may be defined as major chemical transformations which are important to the chemical industries. For example, reactions like nitration, halogenation, sulphonation, oxidation reduction, etc. The study of these processes include first the basic knowledge of a particular chemical reaction, second equipments required for the reaction. 3rd, running the reaction so as to get the purest product in minimum time and at minimum possible cost.

Nitration: The nitration reaction serves to introduce one or more Nitro groups that is NO_2 group into a reacting molecule. The Nitro group may become attached to the carbon to form a Nitro aromatic or a Nitroparaffilic compound. It may become attached to oxygen to form a nitrate Ester, whereas it may become attached to nitrogen to become a nitramine

In the nitration reaction, the entering

Nitro group, may replace a number of different monovalent atoms or groups of atoms. Certain alkyl halides can react with silver nitrate to form the corresponding nitrate esters, or with silver nitrate to form the corresponding Nitro compounds as shown on the next slide.

In the first reaction, you can see that alkyl halide is reacting with silver nitrate giving you nitrate Ester whereas in the second reaction you can see that alkyl halide is reacting with silver nitrate, giving you the Nitro compound.

Now uses and application of nitration reaction. Nitration is one of the most important reaction in the industrial synthetic organic chemistry. Not only do nitration products find wide application as solvents, dye stuffs, Pharmaceuticals, explosives, but they also serve as useful intermediates for the preparation of other compounds, particularly amides which are prepared by the reduction of corresponding Nitro groups.

Now, Nitrating agents of variety of reagents can be used to effect nitration. These include aqueous concentrated and fuming nitric acid. Sometimes we use mixtures of nitric acid with sulfuric acid, acetic anhydride, acetic acid, phosphoric acid or chloroform. Nitrogen pentoxide and nitrogen tetroxide are

also used to certain instances in order to make an intelligent

choice of nitrating system for a particular nitration

reaction, it is desirable to know what species are present in

the various systems and to understand the mechanism of the

reaction under consideration.

Function of sulfuric acid. It removes the water produced

during the nitration process and being a stronger acid than

nitric acid, it protonates the nitric acid to form the nitryl

or nitronium ion which is a strong nitrating agent. You can

see the following reaction takes place when nitric acid reacts

with sulfuric acid.

Now, evidence to support the formation of nitrile or

nitronium ion in the mixed acid

from the freezing point depression, the Vant Hoff I factor of nitric acid in

sulfuric acid is found to be 4, which indicates that the

ionization of nitric acid can be represented by the above equation.

Solution of nitric acid has three different UV spectra.

First one in dilute aqueous solution. Its spectrum is that

of nitrate ion. Second in an inert, weakly polar solvent, for

example chloroform. The spectrum is the same as that of ethyl

nitrate, indicating that HNO3 exists as an ionized

nitric acid and a third spectrum is a characteristic of sulfuric

acid solution of nitric acid and

its ester, indicating that nitric acid does not exist,

as nitrate ion or as unionized nitric acid.

The Raman spectrum of nitric acid in sulfuric acid is even

more informative. The solution of nitric acid in sulfuric

acid an in perchloric acid have only one Raman line,

moving to nitric acid, which occurs at 1400 centimeter

inverse and which is polarized.

Now, nitration in organic solvents

like nitromethane or acetic acid with nitric acid in large

excess. The kinetics of nitration process depends upon

the aromatic compound being nitrated. Compounds such as

Nitro benzene or ethyl benzoate with strongly deactivating group

are nitrated at a rate which is proportional to the

concentration of the substrate.

That is, the reaction is of 1^{st} order compounds which are more

reactive than benzene such as toluene, xylene, para chloroanisole

react at a rate which is independent of the concentration

of the substrate. That is, the reaction is of zero order. The

reaction rate of reaction with all substrate which shows zero

order kinetics is the same.

The result may be interpreted in the following manner. You can see the following two reactions.

The first step, which represents the transfer of proton from one nitric acid molecule to another, is very rapid rate at which the second step that is, the formation of nitrile and takes place, depends upon the medium in a strongly acidic and highly polar solvent like concentrated sulfuric acid. This takes place very quickly in less strong acid media, such as acetic acid or nitromethane. This step can be relatively slow.

The zero order kinetics shown by highly reactive substrate in these solvents indicates that the nitration step is fast as compared to the rate of formation of Nitrile ion. This is supported by the fact that all these highly reactive compounds are nitrated at the same rate, which is the rate of formation of nitryl ion. In the nitration of aromatic substrates of low reactivity, the formation of the nitryl ion is fast relative to the nitration step, which is rate determining step in the nitration of compounds of intermediate reactivity, both

steps occur at the compatible rate. Now, effect of nitrous acid on nitration. The inhibiting effect is observed in nitration of compounds having no activating groups where reactions are carried out either in strong nitric acid or in mixed acid that is the mixture of nitric acid with sulfuric acid. In this media, the nitrous acid forms the nitrosyl ion that is NO^+ and thus reduces the reaction rate. The catalytic effect is observed in the nitration of reactive substrates such as anisole or dimethyl aniline, which are nitrated in relatively weak nitric acid where the nitryl ion concentration is low because of nitrosyl iron, which is a much weaker electrophilic reagent then the nitryl ion.

It is able to react only with very reactive aromatic compounds such as anisole or dimethylaniline. Two conditions which are necessary for the catalysts by nitrous acid. First one the substrate must be sufficiently reactive so that it can be easily attacked by the Nitrosyl ion. Second, the reaction medium must be such that the concentration of nitryl ion is low, thus allowing the nitrosyl iron to complete favourably for the substrate.

These are the references. Thank you.