Hello students, I am Dr. B. L. Malik, Associate professor from P. E. S's. R. S. R. S. N. College of Arts and Science for Farmagudy, Ponda, Goa. Today in Industrial chemistry subject under course title General Industrial Chemistry, under Section B we are going to study types of oxidation and oxidizing agents. While studying this module you will come across certain terms like oxidation, oxidizing agents, uses of different oxidizing agents under different reaction conditions etc.

After going through this module you will understand different definitions of oxidations along with various examples, you will study oxidation of different organic compounds using different oxidizing agents under different reaction conditions. You will also be able to compare the utility of oxidizing agents based on the % yield of products obtained.

Oxidation can be defined in various ways. It is the most important reaction used in chemical industry for synthesis of variety of compounds. Oxidation can be carried out in various ways by using different reagents and also by using different methods. Some important reactions including important reagents are discussed below.

1. Dehydrogenation reaction in which primary alcohols are converted to aldehydes. Ethanol is converted to Acetaldehyde. The reaction is given here. Secondary alcohols can be converted to ketones. Reaction of 2-Propanol to Acetone is given here.

2. Introduction of Oxygen atom. By introducing Oxygen atom, aldehydes can be oxidized to carboxylic acids. Like Acetaldehyde is oxidized to Acetic acid. The hydrocarbons can be converted to an alcohols where we have diethyl methane converted to tertiary butyl alcohol.

3. Simultaneous dehydrogenation and oxygen introduction where we can convert hydrocarbons to aldehydes. The reaction of Methane to Formaldehyde is given here. We can also convert alcohols to acids, where Benzyl alcohol is converted to Benzoic acid. The reaction is included here.

4. Simultaneous dehydrogenation and molecular condensation, wherein removal of Hydrogen and the molecular condensation take place simultaneously. The examples are given here. Preparation of Biphenyl from Benzene and reaction of Toluene to form Stilbene.

5. Simultaneous a dehydrogenation, Oxygen introduction and Carbon Carbon bond breakage. All these three reactions are taking place simultaneously. The best example here is oxidation of Naphthalene to Phthalic anhydride.

6. Indirect oxidation through intermediates where Toluene is oxidized to Benzoic acid through Benzotrichloride.

7. Peroxidation with Sodium peroxide wherein oxidation of Benzyl chloride takes place to corresponding Benzoyl peroxide. We can also have oxidation of different amino compounds in which amino compounds can be oxidized to Azobenzene, p-Aminophenol or Nitrobenzene under moderate condition.

8. Oxidation of sulfur compounds in which permanganates can be used as oxidizing agent wherein sulfur compounds can be oxidized to Sulphonals, Trional and Tetranals, in which sulfide sulfur is oxidized to sulfonic group. We can take one examples here. Oxidation of Ethyl mercaptan to Ethane sulfonic acid. Mild oxidation of Ethyl mercaptan, gives Ddiethyl disulfide, the reaction of which is given here.

Now let us try to understand different oxidizing agents and their uses with different reaction conditions used for this reaction in acidic, alkaline and neutral medium to effect the desired change in the structure of the compound.

1. Permanganates. The most common and useful reagent used in organic oxidation is Potassium permanganate, which is available in the form of stable crystals. It functions as an oxidizing agent of different strength in alkaline, neutral and acidic medium.

A . Alkaline solution: Potassium permanganate alone used in aqueous solution becomes alkaline through the formation of Potassium hydroxide. The reaction is given here. 3 atoms of oxygen are released by two moles of permanganate. With this reaction conditions Toluene gives Benzoic acid. Ethyl benzene gives Acetophenone and Isopropylbenzene yields Propiophenone and Acetophenone respectively. These structures are given here. When the products are organic acids, potassium salts are formed. MnO_2 formed is removed by filtration and carboxylic acid is recovered by acidification with mineral acids. In presence of excess of alkali, Potassium permanganate can be used for oxidizing o-substituted derivatives of Toluene. Potassium Hypomanganet, K_3Mn0_4, reacts in presence of strong alkaline solution slowly, which oxidizes primary, secondary alcohols and ketones.

B. Neutral solution: KOH formed in the aqueous medium, can be neutralized by passing CO_2 or by adding Manganese sulfate. The neutralized solution increases the yield up to 80% as compared to 30% in alkaline solution.

C. Acidic solution. Acidic Potassium permanganate prepared by addition of Acetic acid or Sulfuric acid gives a powerful oxidizing agent to be used for very stable compounds. Oxidizing solution is added gradually to control the reaction. Two moles of permanganate yields 5 atoms of oxygen as per the reaction given below. Acid solutions are used for preparation of certain Naphthalene sulfonic acids incapable of formation by other methods. Both aliphatic and aromatic sulfides and hydrosulfides are oxidized to corresponding sulfonic acids.

2. **Dichromate**. Sodium or Potassium dichromate in Sulfuric acid is generally used as an oxidizing agent. The reaction is given below. Chromic anhydride in Acetic acid is sometimes used as an oxidizing agent. Two moles of Chromic anhydride give three atoms of Oxygen as per the following equation. Chromic acid in hot glacial Acetic acid oxidizes

Anthracene to Anthraquinone quantitatively, but the method is too expensive for commercial synthesis. Chromic acid and dichromates are extensively used as oxidizing agents in Organic chemical industry for preparation of Methylene blue, Safranin and other dyestuff.

3. **Hypochlorous acid and salts**, Hypochlorous acid, HClO decomposes slowly to liberate Oxygen. The rate of decomposition can be increased by using salts of Nickel, Cobalt, Lithium, Sodium and Calcium. Salts of Hypochlorous acid in wet forms decomposes easily. Chlorinated solutions of Zinc and Aluminium hydroxide are more active oxidizing agents compared to Hypochlorous acid.

4. **Sodium chlorite and Chlorine dioxide**: Sodium chlorite, $NaClO_2$ as a dry powder is used for bleaching. Sodium chlorite on reaction with Chlorine releases Chlorine dioxide ClO_2, which is a powerful oxidizing and bleaching agent, but due to its instability it can't be produced and stored. Chlorine dioxide has also been used in bleaching and maturing floors, treating water, checking blue mold in fruits and bleaching textiles.

5. **Chlorides**: 40% aqueous solution of Chloric acid $HClO_3$ is stable up to 40^0C is a powerful oxidizing agent. In controlled action it can oxidize Ethanol or Ethyl ether to Acetic acid, Ethylene to Ethylene glycol. Potassium chlorate $KCl0_3$ is a powerful oxidizing agent widely used in dry and finally divided form in the laboratory as a source of pure Oxygen. Sodium chlorate is more soluble compared to Potassium chlorate.

6. **Peroxides**: Important peroxides used as oxidizing agents are Lead peroxide, Manganese dioxide and Hydrogen peroxide. Lead peroxide PbO_2 is used in combination with Acetic acid, Sulfuric acid or Hydrochloric acid. One mole yields one atom of Oxygen, giving the salt of the acid. It must be used in finely divided form. The reaction of Lead peroxide with HCl is given here.

7. **Manganese dioxide**: MnO_2 in combination with Sulfuric acid, is widely used as oxidizing agent, where it gets reduced to Manganese sulfate,

releasing one atom of Oxygen per mole. It oxidizes methyl group to aldehyde hence used to convert Toluene to Benzaldehyde. Hydrogen Peroxide H_2O_2 is manufactured, marketed, and used as an aqueous solution, the strength of which is expressed in terms of the volume of free Oxygen equivalent. Most of the Hydrogen peroxide produced is used for textile pulp and paper bleaching. In alkaline solution, it is used in the preparation of organic peroxides, 3% solution of it oxidizes Pyridine to Glutaric acid. Phenols are converted to dihydric phenols or quinones in presence of small amount of ferrous salt. Hydroxy acids are converted to aldehydic or ketonic acid.

8. Sodium peroxide: Na_20_2 is used only to limited extent due to the hazards associated with its storage and uses.

9. Silver oxide: Ag_2O acts as a mild oxidizing agent can oxidize Glycerol to Glycolic acid & aldehydes to acids. It's an excellent oxidation catalyst for vapor phase oxidation reaction and specially used for oxidation of Ethylene to Ethylene oxide.

10**. Nitric acid and Nitrogen oxides** are assuming new significance as oxidizing agents. Nitric acid in presence of Sulfuric acid with catalytic amount of Mercury, Copper or Selenium is effective oxidising agent for Nitrogen containing aromatic compounds. Oxidation of Cyclohexanol with 67% Nitric acid at about 55 to $60^{O}C$ gives 90% Adipic acid. Nitric acid oxidation of Ethylene chlorohydrin gives glacial acetic acid as important chemical intermediate. Nitric acid oxidation of coal with or without oxygen, leads to mixture of benzenoid or aromatic organic compounds. Reaction of Cyclohexene with Nitrous oxide at high pressure and temperature between 200 to $350^{0}C$ results in Cyclohexanone.

11. Copper salts: Copper exists in two states of oxidation & passes readily from one to other. It acts as an oxidizing agent in its higher oxidation state. When used as an oxidizing agent in solution, it reduces itself from cupric to cuprous state. Fehling solution is essentially an alkaline, Cupric hydroxide

has weak oxidizing power, can oxidize aldehyde, hydroxyl ketones, di and tri phenols.

12. Alkali fusion: In this, fusion with Alkali in presence of air acts an oxidizing agent in the formation of certain Anthraquinone Vat dyes or mixture of caustic soda and Potassium nitrate, possesses oxidizing capacity.

13. Fuming sulfuric acid: Fuming Sulfuric acid (H_2S0_4 + SO_3) in presence of mercury salt acts as an oxidizing agent can oxidize Naphthalene to Phthalic anhydride at low temperature. It converts Alizarine and other hydroxyl derivatives of anthraquinones to tri hydroxy or hexa hydroxy derivatives, Ethyl mercaptan to diethyl disulfide, Piperidene to pyridine.

14. Ozone: As an oxidizing agent, is used in textile bleaching. Ozone in oxygen mixture, reacts slowly with low molecular weight paraffin. Hydrocarbons at room temperature, whereas vapor phase reaction is quite rapid.

Students at the end, some references are given so that you can go into the details about the reaction which is taking place along with different reaction conditions.

Thank you.