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Non-aqueous Solvents

- Introduction
- Classification
- Physical properties
- Chemical reactions
- Liquid ammonia as a solvent
- Solubilities of substances in liq. NH_3

Non Aqueous Solvents

What is solvent

- A substance which has the power of dissolving other substances.

Water

Water is an Example of Universal solvent/Most Useful Solvent due to: -

- Its high dielectric constant (80.10 at 20^0 C)
- Long liquid range ($0-100^0$ C)
- Liquid at ordinary temp.
- Availability
- Easily purified

Non Aqueous Solvents

- Non aqueous solvent is a solvent other than water.
- Non-aqueous solvents are water-free fluids that dissolve certain salts in the same way as water.

Non Aqueous Solvents

Common examples are:

- Liquid ammonia(NH_3)
- Liquid sulphur dioxide (SO_2)
- Hydrogen fluoride(HF)
- Dinitrogen tetroxide(N_2O_4)
- Phosphorus oxy-chloride($POCl_3$)

Classification

- Protic and aprotic solvents
- Ionizing and non-ionizing solvents
- Acidic Solvents, Basic Solvents and Amphiprotic Solvents

Classification

Protic solvents

- Protic or Protonic which have hydrogen as their constituent

  Example: Liq. NH_3, HF, HCN, H_2SO_4, CH_3COOH etc.

Aprotic solvents

- Aprotic solvents do not have hydrogen in the molecule

  Example: SO_2, N_2O_4, $POCl_3$

Classification

Ionizing solvents

- Polar
- Dissolve ionic compounds
- Ionic reactions occurs in these solvents
- Undergoes self-ionization
- Have high value of Dielectric constant

Example: NH_3, SO_2, N_2O_4, $POCl_3$, HF, H_2SO_4

Classification

Non-Ionizing solvents

- Non-polar
- Dissolves non-polar or neutral compounds
- No ionic reaction occurs in these solvents
- Do not undergo self-ionization
- Have low value of Dielectric constant

Example: Benzene, Carbon tetrachloride

Classification

Acidic Solvents

- Acidic solvents have strong tendency to give protons

e.g.- Liquid HF, H_2SO_4, CH_3COOH

Basic Solvents

- Solvents which have strong affinity for protons are called Basic Solvents

e.g.- Liq. NH_3, Pyridine, Hydrazine

Amphiprotic Solvents

- These have hydrogen in their formula and can act as both acid or base

e.g. : - Water, CH_3COOH

Auto-ionization (solvent system) theory of solvent

Based on the mode of self-ionization of the solvent

Solvent = acidic part + basic part

On auto-ionization it splits into these two parts

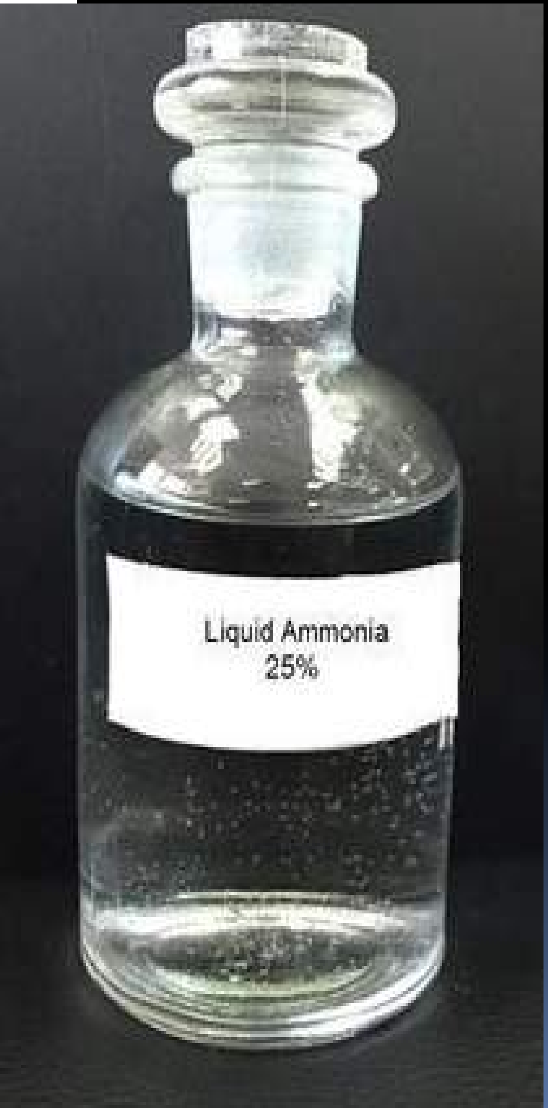
- Substance that increases the concentration of acidic part behaves as an acid.
- Substance that increases the concentration of basic part behaves as a base.

Physical properties of solvents

- Dielectric constant: $F = q^+q^- / Dr^2$
- Viscosity: High viscosity means precipitation, crystallization, filtration cannot take place, reduces the usefulness of a solvent.
- Melting point and boiling point
- Heat of fusion and vaporization gives an idea about intermolecular forces: high values means stronger intermolecular binding forces

Chemical reaction

- Acid base reaction
- Precipitation reaction
- Salt formation
- Redox reaction
- Solvation reaction



Liq. NH_3 as a solvent

Liquid Ammonia

- Liquid ammonia is one of the most extensively used non aqueous solvents.
- It is a protonic solvent and its water like properties have made it a highly useful solvent and a reaction medium for carrying out various types of organic and inorganic reactions.

Important characteristic of liq. NH_3 as a solvent

- Has lower dielectric value than water: liq. NH_3 is poor electrolytic solvent than water.
- Low viscosity: promotes greater ionic mobilities.
- M.P. and B.P. of ammonia are abnormal due to intermolecular association as a result of H-bonding. Its freezing and B.P. are lower than those of water, it requires precaution while working with it.

Important characteristic of liq. NH_3 as a solvent

- Nitrates, nitrites, thiocyanates and cyanides are soluble in liq. NH_3.
- Fluorides, oxides, hydroxides, sulphates, carbonates, phosphates, sulphites and sulphides are insoluble in liq. NH_3.
- It forms many solvates due to its ability of donation of lone pair of electrons and formation of coordinate bond and ion-dipole linkage.

Important characteristic of liq. NH_3 as a solvent

- Solubilities of covalent organic compounds in liq. ammonia are considerably higher than in water due to greater dispersion energy interactions.
- Specific heat of ammonia is higher than that of water.
- It posses unusual high thermal coefficient of expansion, i.e, its density decreases with rise in temperature.

Important characteristic of liq. NH_3 as a solvent

- It is an ionizing solvent.

$$NH_3 + NH_3 \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{NH_2^-}$$

$$K_{NH3} = [NH_4^+][NH_2^-] = 1 \times 10^{-33} \text{ at } 223K$$

$$K_{H2O} = [H^+][OH^-] = 1 \times 10^{-14} \text{ at } 291K$$

- Ionization of ammonia is very small, as can be seen from its low conductance and ionic product.

Reactions in liq. NH_3

Acid-Base reactions: Acids: Produces NH_4^+
Base: Produces NH_2^-

- Acid-Base neutralization occurs in liq. ammonia as in water. The reaction can be followed by conductometric titration or through indicators, eg. Phenolphthalein: colourless in liq. Ammonia & intense red in alkali amides.

$$HCl + NaOH \xrightleftharpoons{\text{water}} NaCl + H_2O$$

$$NH_4Cl + NaNH_2 \xrightarrow{\text{liq. } NH_3} NaCl + NH_3$$

Reactions in liq. NH_3

Redox reactions: Similar to the reactions in water

- Solutions of alkali and alkaline earth metals acts as electrons donors.

$$2Na + 2NH_4Br \xrightleftharpoons{\text{liq. } NH_3} 2NaBr + 2NH_3 + H_2$$

- Nitrous oxide oxidizes metallic potassium in liq. ammonia to K^+ and itself reduces to N_2.

$$N_2O + 2K + NH_3(l) \rightleftharpoons KHN_2 + KOH + N_2$$

Reactions in liq. NH_3

Precipitation or metathesis reactions

- Due to difference in solubilities of water and liq. ammonia, a number of reactions which do not occur in water has been carried out in liq. ammonia.
- Lithium chloride may be precipitated by the reaction of ammonium chloride and lithium nitrate in liq. ammonia.

$$NH_4Cl + LiNO_3 \xrightleftharpoons{\text{liq. } NH_3} NH_4NO_3 + LiCl \downarrow$$

Reactions in liq. NH_3

- Solutions of potassium iodide and ammonium chloride in liq. ammonia produces a white ppt. of KCl.

$$KI + NH_4Cl \xrightleftharpoons{\text{liq. } NH_3} KCl\downarrow + NH_4I$$

- Ammonium sulphides in liq. NH_3 is capable of precipitating many metal sulphides from the nitrate solutions of the metals.

$$Ba(NO_3)_2 + (NH_4)_2S \xrightarrow{\text{liq. } NH_3} BaS\downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + 2AgNO_3 \rightarrow Ag_2S\downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + Cu(NO_3)_2 \rightarrow CuS\downarrow + 2NH_4NO_3$$

Reactions in liq. NH_3

- Iodides and bromides get precipitated when solutions of various nitrates and ammonium halides are mixed together.

$$Sr(NO_3)_2 + 2NH_4Br \rightarrow SrBr_2 + 2NH_4NO_3$$

$$Zn(NO_3)_2 + 2NH_4I \rightarrow ZnI_2 + 2NH_4NO_3$$

Complex formation reaction

- Several complex formation reactions in liq. Ammonia are known which are similar to the reactions occurring in aqueous medium.

Reactions in liq. NH_3

Solvolysis/Ammonolysis reactions

- These reactions are analogous to hydrolysis reactions in water.
- Alkali and alkaline earth metal hydrides are ammonolysed to metal amide and hydrogen.

$$M^{+}H^{-} + NH_3(l) \rightarrow M^{+}NH_2^{-} + H_2$$

Reactions in liq. NH_3

- The solution contains solvated metal cation and solvated electron (imparts blue colour)

$$M \rightleftharpoons M^+ + e^-$$

$$M^+ + xNH_3 \rightarrow M(NH_3)_x^+ + e^-$$

$$e^- + yNH_3 \rightarrow e(NH_3)_y^-$$

- On evaporation of the solvent the electron returns to the parent ions

Solubilities of Substances in Liq NH_3

- Liq. NH_3 is very poor solvent for Ionic substances.
- Amongst the organic compounds, nitrates, thiocyanates, perchlorate and most of the Cyanides are soluble in it.
- Oxides, hydroxides, carbonates, phosphates, sulphates and most of the sulphides are insoluble in it.

Solubilities of Substances in Liq NH_3

- Halogen compounds, alcohols, ketones, esters, ethers, phenol and its derivatives are soluble
- Aromatic hydrocarbons are sparingly soluble
- Alkanes are insoluble
- Elements like Mg, Al, Zn, Ca, La, Ce, Mn have low solubility's in liq.NH_3

Advantages of liq. Ammonia as Solvent

- Ammonium salts dissolved in liq.NH_3 find valid application in Preparative chemistry
- The tendency for solvolysis is less in liq.NH_3 than in water

Disadvantages of liq. NH_3 as solvent

- Low temperature or high pressure is necessary while working with liq. Ammonia. This is because of its liquid range -33^0 C to -77^0 C
- It is hygroscopic in nature, hence all the reactions are to be carried out in sealed tubes
- The use of liq. NH_3 as a solvent and as a reaction medium requires special technique because it has an offensive odour

Liq. SO_2 as a solvent

- Introduction
- Physical Properties of liq. SO_2
- Solubilities of substances in liq. SO_2
- Chemical reactions of liq. SO_2

Liquid Sulphur dioxide (SO_2)

Characteristics of liq. SO_2

- Non protic solvent
- At R.T. SO_2 is a gas but it can be readily liquefied
- Has a wide liquid range (-10 ^{0}C to -75 ^{0}C)
- Low cost and easy to handle
- Low dielectric constant (17.4 at -10^o C)
- Therefore is a good solvent for covalent compounds but a poor solvent for ionic compounds

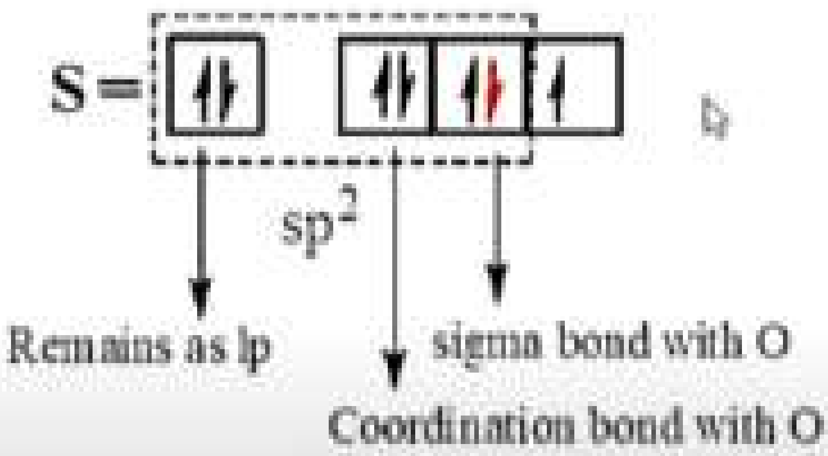
Physical properties of Liq. SO_2

S.N.	Properties	Values
1	Freezing Point	196.5 K
2	Boiling Point	2.63 K
3	Density	1.46 gml^{-1}(-10 ^{O}C)
4	Dielectric Constant	17.4 at -10 ° C
5	Dipole moment	1.61Debye (-10 °C)
6	Viscosity	0.428 Centipoise
7	Specific Conductance	4 X 10^{-8} $Ohm^{-1}Cm^{-1}$ (-10 °C)

Structure of SO_2

Bond angle = 119.5°

Bond length = 1.43 Å



Auto - ionization

$$SO_2 + SO_2 \rightarrow SO^{2+} + SO_3^{2-}$$

- By Analogy with water and liq. NH_3, self ionization of SO_2 takes place.

Solubility of Substances in Liq. SO_2

Amongst the Inorganic Compounds

- Iodides and thiocyanates are the most soluble
- Metal sulphates, sulphides, oxides, hydroxides are insoluble
- Many of the ammonium, thallium and mercury salts are soluble

Solubility of Substances in Liq. SO_2

Amongst the Organic Compounds

- Excellent solvent for covalent compounds
- Metals are insoluble in Liq. SO_2
- Aromatic hydrocarbon and alkenes are more soluble than aliphatic hydrocarbons.
- Pyridine, quinoline, ethers, halogen derivatives and acid chlorides are also soluble
- Alkanes are insoluble

Conductivity of salt solutions in SO_2

- Conductivity of electrolyte solutions in liq. SO_2 increases with the size of cation and has the following order:

$$Na^+ < NH_4^+ < K^+ < (CH_3)_3S^+ < (CH_3)_4N^+$$

- Conductivity of anions has the following order:

$$SCN^- < ClO_4^- < Cl^- < I^- \text{ etc.}$$

Chemical Reactions of Liq. SO_2

1. Acid – Base Reactions

Neutralization reactions

Acid + Base → Salt + Solvent

$SOCl_2$(Acid) + K_2SO_3(Base) → 2KCl (Salt) + $2SO_2$(Solvent)

$SOCl_2 + Cs_2SO_3 \rightarrow 2CsCl + 2SO_2$

$SOBr_2 + [N(CH_3)_4]_2SO_3 \rightarrow 2[N(CH_3)_4]Br + 2SO_2$

$SO(SCN)_2 + K_2SO_3 \rightarrow 2K(SCN) + 2SO_2$

Chemical Reactions of Liq. SO_2

- Compounds of Zn(II) and Al(III) shows amphoteric behavior in liq.SO_2

Acidic character

$$ZnCl_2 + K_2SO_3 \rightarrow 2KCl + ZnSO_3$$

$$2AlCl_3 + 3K_2SO_3 \rightarrow 6KCl + Al_2(SO_3)_2$$

Basic Character

$$ZnSO_3 + K_2SO_3 \rightarrow K_2[Zn(SO_3)_2]$$

$$Al_2(SO_3)_2 + 3K_2SO_3 \rightarrow 2K_3[Al(SO_3)_3]$$

Chemical Reactions of Liq. SO_2

2. Solvolytic Reactions/Solvolysis

- Only a limited number of salts undergoes solvolysis in liq. SO_2
- Ammonium acetate is solvolysed in liq. SO_2 as follows:

$$2CH_3COONH_4 + 2SO_2 \rightarrow (NH_4)_2SO_3 + (CH_3COO)_2SO$$

$$(CH_3COO)_2SO \rightarrow SO_2 + (CH_3CO)_2O$$

- Some covalent halides also undergoes solvolysis in liq. SO_2

$$PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$$

$$AsCl_5 + SO_2 \rightarrow AsOCl_3 + SOCl_2$$

$$UCl_6 + 2SO_2 \rightarrow UO_2Cl_2 + 2SOCl_2$$

$$WCl_6 + SO_2 \rightarrow WOCl_4 + SOCl_2$$

Chemical Reactions of Liq. SO_2

3. Solvation

- The formation of solvates (addition compounds with the solvent) takes place as follows

$$NaI + 4SO_2(l) \rightarrow NaI.4SO_2$$

$$KI + 4SO_2(l) \rightarrow KI.4SO_2$$

Chemical Reactions of Liq. SO_2

4. Precipitation Reactions

- Precipitation of a compound depends upon its solubility. A large number of precipitation reactions can be carried out in liq. SO_2 due to specific solubility relationship

$$BaI_2 + Zn(CNS)_2 \rightarrow Ba(CNS)_2 \downarrow + ZnI_2$$

$$PbF_2 + Li_2SO_4 \rightarrow PbSO_4 \downarrow + 2LiF$$

$$SbCl_3 + 3LiI \rightarrow SbI_3 \downarrow + 3LiCl$$

Chemical Reactions of Liq. SO_2

- Thionyl chloride in liq. SO_2 is used to prepare many compounds

$$2CH_3COOAg + SOCl_2 \rightarrow 2AgCl\downarrow + SO(CH_3COO)_2 \text{(Thionyl Acetate)}$$

$$2NH_4(SCN) + SOCl_2 \rightarrow 2NH_4Cl\downarrow + SO(SCN)_2$$

$$2KI + SOCl_2 \rightarrow 2KCl\downarrow + SOI_2$$

Chemical Reactions of Liq. SO_2

5. Complex Formation Reactions

- SO_2 does not itself takes part in complexation but it serves as a medium for complex formation.
- The solubility of iodine in liq. SO_2 is greatly increased by the addition of potassium and rubedium. This is due to the formation of the complex KI_3 or RbI_3

$$KI + I_2 \rightarrow KI_3$$

$$RbI + I_2 \rightarrow RbI_3$$

Chemical Reactions of Liq. SO_2

- When HgI_2 or CdI_2 is dissolved in liq.SO_2 in presence of KI, the solubility of these iodides is increased due to the formation of a soluble complex $K_2[MI_4]$
- When solutions of salt like $AlCl_3$, $ZnCl_2$ in liq. SO_2 react with the excess of a compound containing SO_3^{2-} ions, soluble sulphito complexes are formed

$$2\,AlCl_3 + 6K_2SO_3 \rightarrow 2K_3[Al(SO_3)_3] + 6KCl$$

$$ZnCl_2 + 2K_2SO_3 \rightarrow K_2[Zn(SO_3)_2] + 2KCl$$

- Hexahalo complexes in liq. SO_2 are formed by the action of covalent halides ($SbCl_3$, $SbCl_5$) on alkali metal halides (KCl, NOCl, $[N(CH_3)_4]Cl$)

$$SbCl_5 + NOCl \rightarrow NO[SbCl_6]$$

$$SbCl_3 + 3KCl \rightarrow K_3[SbCl_6]$$

$$SbCl_5 + KCl \rightarrow K[SbCl_6]$$

$$SbCl_5 + [N(CH_3)_4]Cl \rightarrow [N(CH_3)_4][SbCl_6]$$

$$SbCl_5 + CH_3COCl \rightarrow [CH_3CO]^+[SbCl_6]^-$$

Chemical Reactions of Liq. SO_2

6. Redox Reactions

- Gaseous SO_2 is known to behave as both oxidising and reducing agent.
- Liq. SO_2 does not have any strong oxidising or reducing properties. But it serves only as a medium for redox reactions.
- Liq. SO_2 can not reduce iodine, however, a sulphite in liq. SO_2 reduces iodine to iodide.

$$I_2 + 2R_2SO_3 \rightarrow R_2SO_4 + 2RI + SO_2$$

- KI is oxidised to free iodine by $FeCl_3$ or $SbCl_5$ in liq. SO_2

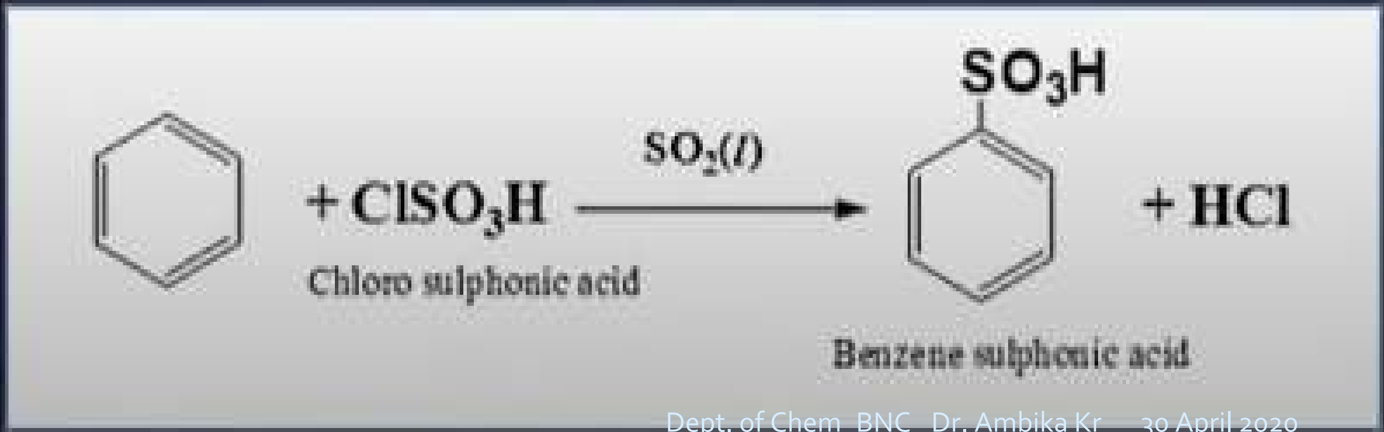
$$6KI + 3SbCl_5 \rightarrow 3I_2 + SbCl_3 + 2K_3[SbCl_6]$$

Chemical Reactions of Liq. SO_2

7 Organic reactions in liq. SO_2

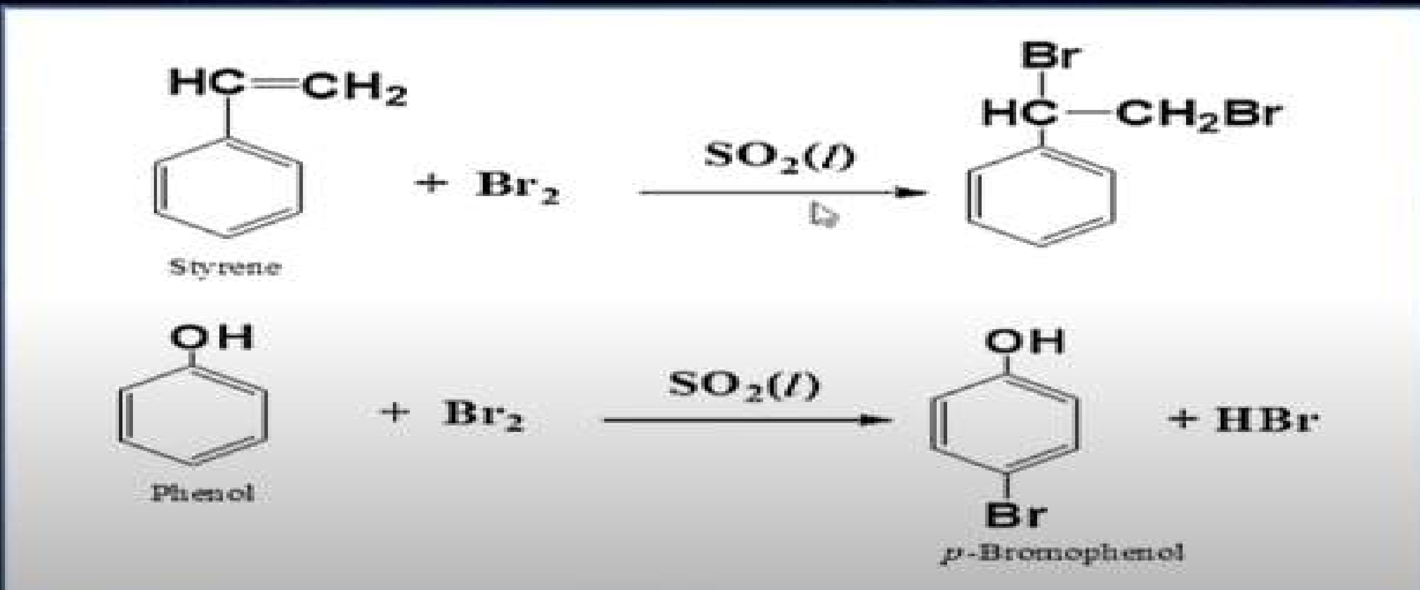
- SO_2 serves as one of the best medium for the reactions where inert and non-inflammable solvent is required.

✓ Sulphonation: In liq. SO_2 medium good yield is obtained

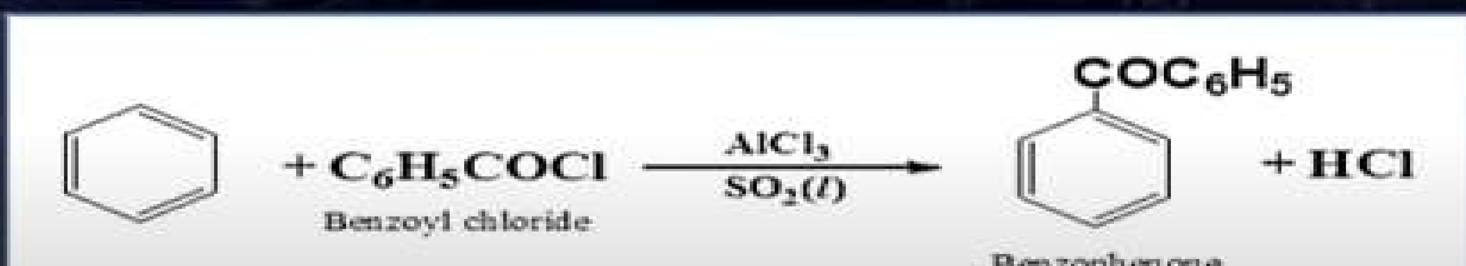


Chemical Reactions of Liq. SO_2

- ✓ Bromination: Liq. SO_2 is used for both addition and substitution reactions with Br



- ✓ Friedel-Crafts reaction: $AlCl_3$ is highly soluble in liq. SO_2 and therefore preferred over ether which is highly inflammable



Uses of liq. SO_2

- It is a solvent of intermediate dielectric constant: certain compound are soluble and some insoluble.

- Useful solvent for several types of synthetic reactions and in refining of certain types of petroleum products.

Suggestion: For more detail and explanation, visit following link provided by SWAYAM PRABHA e-learning platform

https://www.youtube.com/watch?v=9HTxnTCxc7c