

BACHLEOR OF SCIENCE
SEMESTER-III
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(HEAVY AND FINE CHEMICALS)

Unit-6:

Speciality industrial solvents: Synthesis, properties and uses of Dimethyl-formamide (DMF), Dimethyl sulfoxide (DMSO), Tetrahydrofuran (THF), Dioxane, Diethyl ether and sulfolane.

Dimethylformamide

Introduction

Formamides are derivatives of the smallest of the aliphatic carboxylic acids, formic acid, and are thus structurally and chemically rather straight forward substances. Two of the simplest members of the family—formamide itself HCONH_2 , and *N, N*-dimethylformamide [$\text{HCON}(\text{CH}_3)_2$] have considerable industrial importance because of their chemical bifunctionality and high polarity. Formamide is especially valued for its chemical reactivity; *N, N*-dimethylformamide is used widely for its solvent properties.

Physical properties

Dimethylformamide is the organic compound with the formula $[(\text{CH}_3)_2\text{NC}(\text{O})\text{H}]$. Commonly abbreviated DMF, this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid.

Dimethylformamide is miscible in all proportions with water, alcohols, ethers, ketones, esters, and carbon disulfide, as well as with chlorinated and aromatic hydrocarbons. By contrast, it has only limited solubility or complete insolubility in aliphatic hydrocarbons. Many high molecular mass natural products and synthetics are quite soluble in DMF. Examples include poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl acetate), poly(vinyl ether), polyacrylate, polyacrylonitrile, polystyrene, polyester resins, alkyd resins, urea–formaldehyde resins, melamine – formaldehyde resins, phenol – formaldehyde resins, epoxy resins, and natural resins. It is also a good solvent for a number

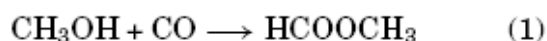
of drying oils, plasticizers, and cellulose derivatives, as well as for both natural and chlorinated rubber. Most halogenated hydrocarbons are also soluble in DMF. Various inorganic salts are highly soluble in DMF.

Chemical Properties

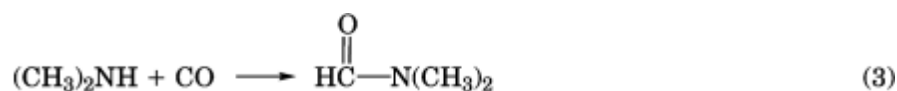
N, N-Dimethylformamide is stable to air and light and, unlike its parent compound formamide, can be distilled without decomposition at atmospheric pressure. Nevertheless, decomposition is observed at temperatures above the boiling point, the products being carbon monoxide and *N, N*-dimethylamine. The compound also shows fewer tendencies than formamide to hydrolyze. It is hygroscopic, however, and water absorbed from the air will produce traces of hydrolysis products; these produce the faint amine odor that frequently accompanies commercially DMF.

Manufacture method

There are two processes used commercially for DMF manufacture. A two-step process involves carbonylation of methanol to methyl formate, and reaction of the formate with dimethylamine.



The methanol carbonylation is performed in the presence of a basic catalyst such as sodium methoxide and the product isolated by distillation. In one continuous commercial process the methyl formate and dimethylamine react at 350 kPa (3.46 atm) and from 110 to 120°C to effect a conversion of about 90%. The reaction mixture is then fed to a reactor–stripper operating at about 275 kPa (2.7 atm), where the reaction is completed and DMF and methanol are separated from the lighter by-products. The crude material is then purified in a separate distillation column operating at atmospheric pressure.



A second process is the direct carbonylation of dimethylamine in the presence of a basic catalyst or a transition metal. This carbonylation is often run in the presence of methanol in order to help solubilize the catalyst, and presumably proceeds through methyl

formate as an intermediate. Again, the basic catalyst is typically sodium methoxide, although other bases such as phenoxides and basic anion-exchange resins have also been used. The reaction using sodium methoxide is performed at 4.9 MPa (48 atm) and 120°C.

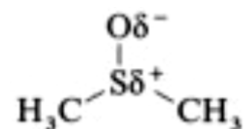
Storage and handling

Pure DMF is essentially non corrosive to metals; however, copper, tin, and their alloys should be avoided. Ideal materials for its handling and storage are non-alloy (carbon) steels, stainless steels, and aluminum. Seals and other soft materials should be made of polytetrafluoroethylene, polyethylene, or high molecular weight polypropylene. Oils and grease are not suitable as lubricants; however, graphite can be used to lubricate moving part in contact with DMF. Since DMF is hygroscopic, it should be kept under a blanket of dry nitrogen. High purity DMF required for acrylic fiber production is best stored in aluminum tanks.

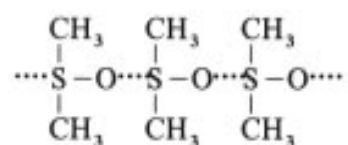
Uses

- The two largest uses for DMF in the United States had been in pharmaceutical processing and acrylic fiber production.
- The combined pharmaceutical applications account for an estimated 25% of DMF consumption. In the pharmaceutical industry, DMF is used in many processes as a reaction and crystallizing solvent because of its remarkable solvent properties.
- Another significant application for DMF is as a solvent for depositing polyurethane coatings on leather and artificial leather fabrics.
- Another use is in various extraction and absorption processes for the purification of acetylene or butadiene and for separation of aliphatic hydrocarbons, which have limited solubility in DMF, from aromatic hydrocarbons.
- DMF has also been used to recover CO₂ from flue gases. Because of the high solubility of SO₂ in DMF, this method can even be used for exhaust streams from processes using high sulfur fuels.
- DMF is used extensively as a solvent, reagent, and catalyst in synthetic organic chemistry.

Dimethyl Sulfoxide

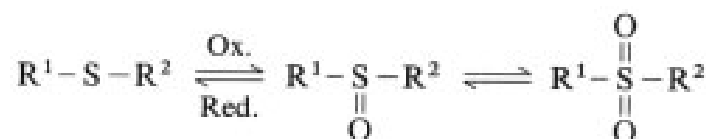


Dimethyl sulfoxide (DMSO) is a colorless, odorless, strongly hygroscopic liquid. It is readily miscible with water and other protic solvents such as alcohols. This property can be attributed to the formation of strong hydrogen bonds between the polarized S–O bond and water molecules. The strong polarity of the S–O bond, with a partial negative charge on oxygen is shown by the high dipole moment and basicity of dimethyl sulfoxide. Pure DMSO forms chain like polymeric association complexes at room temperature. This gives rise to considerably higher melting (18.5°C) and boiling points (189°C) compared to dimethyl sulfide.



Production

In principle, DMSO can be produced by oxidation of dimethyl sulfide.



These methods are, however, often suitable only for small quantities. In industry, DMSO is produced by catalytic oxidation of dimethyl sulfide with oxygen or by oxidation with nitrogen dioxide. The oxidation of dimethyl sulfide with oxygen at 7.2MPa and 105 °C gives good yields of DMSO.

The oldest and most frequently used method for the production of sulfoxides is by oxidation of sulfides. Since further oxidation to the corresponding sulfones can occur, a range of selective reagents and methods has been developed. Oxidation with hydrogen

peroxide, which has long been known, can be carried out in the presence of various catalysts. Acids, such as acetic, perchloric, and sulfuric acids, are suitable. A more recent industrial process uses 50% sulfuric acid and an organic acid, such as formic or acetic acid, in a 1:1 ratio as the catalyst.

Uses

Dimethyl sulfoxide is an excellent solvent that is widely used for reactions in modern chemistry. Because of its high polarity and good solvation of cations, DMSO dissolves not only a large number of organic compounds, but also many metal salts, particularly those of alkali and alkaline-earth metals. DMSO is also a good solvent for many polymers.

THF

Introduction



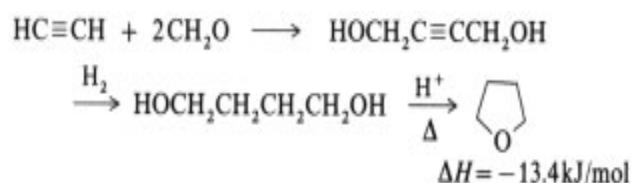
Tetrahydrofuran (THF) tetramethylene oxide, oxolane, is five-membered cyclic ether with wide application in the chemical industry.

Physical Properties

Tetrahydrofuran (THF) is a colorless, water-miscible organic liquid with low viscosity at standard temperature and pressure. This heterocyclic compound has the chemical formula $(\text{CH}_2)_4\text{O}$ having melting point (-108.5°C) and boiling point (66°C) . As one of the most polar ethers with a wide liquid range, it is a useful solvent. Its main use, however, is as a precursor to polymers. THF has an odor similar to its chemical cousin, diethyl ether, but is a much less potent anesthetic than diethyl ether.

Production

Acetylene/Formaldehyde

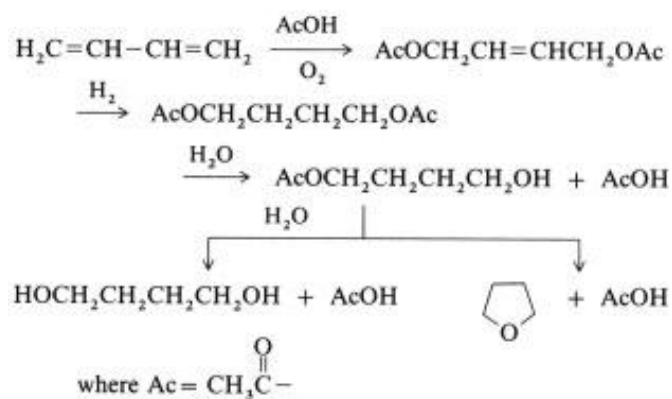


The process involves a reaction between acetylene and formaldehyde to give 2-butyne-1, 4-diol, with subsequent hydrogenation to 1,4-butanediol. The saturated diol is

very readily cyclized to THF with elimination of water by acid catalysis above 100°C. Suitable catalysts include inorganic acids, acidic aluminum silicates, and earth or rare-earth oxides

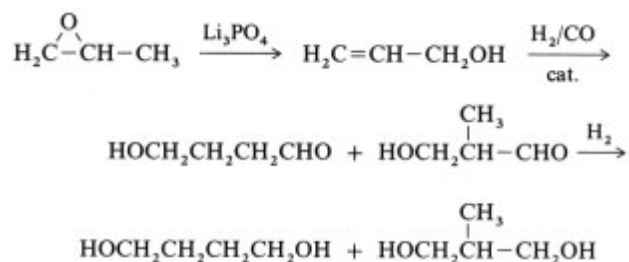
Butadiene Acetoxylation

Butadiene is oxidized at 3MPa/80 °C over a palladium – tellurium catalyst with acetic acid and a nitrogen – oxygen mixture to give 1,4- diacetoxy-2-butene. The olefin is hydrogenated to 1, 4-diacetoxybutane, which can be hydrolyzed to butanediol or THF.



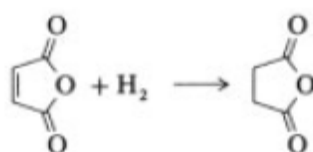
Propylene Oxide Process

Propylene oxide is isomerized to allyl alcohol by conventional means at 250 – 300°C/1MPa over a trilithium orthophosphate (Li₃PO₄) catalyst. The allyl alcohol is then hydroformylated to 4-hydroxybutyraldehyde and the byproduct 3-hydroxy-2-methylpropionaldehyde. Subsequent hydrogenation of the aldehydes gives 1, 4-butanediol as the main product together with 2-methyl-1, 3-propanediol.



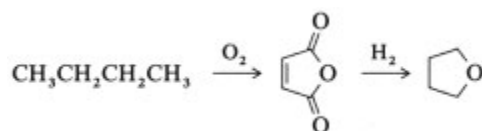
Maleic Anhydride Hydrogenation

Because of its structure, maleic anhydride is an attractive precursor for the preparation of THF.



***n*-Butane – Maleic Anhydride Process**

Du Pont has developed a new two-step process for producing THF from *n*-butane.



The process involves oxidation of *n*-Butane to maleic anhydride with subsequent hydrogenation of aqueous maleic acid solution over a special palladium catalyst.

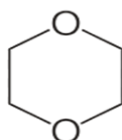
Pentosan/Furfural Processes

Because it takes advantage of a renewable raw material, THF production from furfural has attracted interest. Because of their widespread distribution in agricultural waste products, pentosans are especially promising as starting materials. The production of THF from furfural involves catalytic decarbonylation to furan and hydrogenation of the latter to THF.

Uses

- The most important area of application for THF from the standpoint of quantity and turnover is polymerization with simultaneous ring opening to give poly(tetramethylene oxide).
- Available in various molecular masses, this is a key component in the production of important elastic construction materials, thermoplastics and molded elastomers based on polyurethanes, polyesters and polyamides, elastic Spandex fibers, and polyurethane coatings.
- THF is also a versatile solvent for natural and synthetic resins as well as PVC.
- It is used extensively in the varnish and film industries and as a co-solvent for printing inks and adhesives.

Dioxane

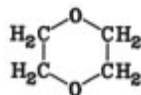


1, 4-Dioxane, often called dioxane because the other isomers of dioxane are rare, is a heterocyclic organic compound. It is a colorless liquid with a faint sweet odor similar to that of diethyl ether. It is classified as an ether. This colorless liquid is mainly used as a stabilizer

for the solvent trichloroethane. It is an occasionally used solvent for a variety of practical applications as well as in the laboratory.

Physical Properties

1, 4-Dioxane, $C_4H_8O_2$, is an extraordinary solvent, capable of solubilizing most organic compounds, water in all proportions, and many inorganic compounds. Dioxane is a cyclic diether forming a six membered ring with the following structure:



Synonyms for dioxane are *p*-dioxane, diethylene oxide, diethylene dioxide, diethylene ether, 1,4-dioxacyclohexane, dioxyethylene ether, and dioxan. At ambient temperature, dioxane is a clear liquid with an ether-like odor. Its relative stability is similar to other aliphatic ethers, and it forms peroxides on exposure to air as they do. In spite of its exceptional solvent properties, its largest use is in stabilizing 1, 1, 1-trichloroethane and keep it from reacting with aluminum.

Infinite *solubility* in dioxane can be expected from lower molecular mass aliphatic and aromatic liquid hydrocarbons, ethers, alcohols, ketones, and chlorinated hydrocarbons. Dioxane has solubility for animal and vegetable oils, paraffin oils, synthetic and natural resins, and some inorganic compounds and elements, such as iron chlorides, mercuric chloride, hydrochloric, sulfuric, and phosphoric acids, bromine, chlorine, and iodine.

Production

1, 4-Dioxane is manufactured commercially by *dehydration and ring closure of diethylene glycol*. Concentrated sulfuric acid (5 %) is used as a catalyst, although phosphoric acid, *p*-toluenesulfonic acid, and strongly acidic ion-exchange resins are recognized alternatives. Operating conditions vary; temperatures range from 130 to 200°C and pressures range from a slight pressure to a partial vacuum (25 – 110 kPa). A favorable temperature is reported to be 160°C. The process is continuous, with dioxane vaporized from the reaction vessel. The vapors are passed through an acid trap and two distillation columns to remove water and to purify the product. Yields of 90% are possible.

Uses

- The largest single use of 1,4-dioxane is the *stabilization of 1,1,1-trichloroethane* against chemical attack by aluminum. The aluminum oxide film prevents the metal from reacting with 1,1,1-trichloroethane until the film is disturbed. When the bare metal contacts 1,1,1-trichloroethane, chlorine is extracted from the solvent to form

AlCl_3 , which causes dehydrohalogenation of 1,1,1-trichloroethane to produce HCl and vinylidene chloride ($\text{CH}_2 = \text{CCl}_2$). Dioxane is the foremost inhibitor of these reactions. An insoluble dioxane–aluminum chloride complex is formed, which deactivates the catalyst and seals any openings in the Al_2O_3 film.

- Dioxane is used as a *solvent* in the formulation of inks, coatings, and adhesives, and as solvent for extracting animal and vegetable oils.
- As a *chemical intermediate*, dioxane reaction products are useful as insecticides, herbicides, plasticizers, and monomers.
- The oxonium complexes of dioxane with salts, mineral acids, halogens, and sulfur trioxide are used as *catalysts* and as *reagents* for anhydrous acid reactions, brominations, and sulfonations.
- In the laboratory, dioxane is useful as a *cryoscopic solvent* for molecular mass determinations and as a *stable reaction medium* for diverse reactions.
- Historically, dioxane is reported to be valuable in *polymer manufacture* and as a *solvent* for natural and synthetic resins, including cellulose derivatives, polyvinyl acetal resins, acrylonitrile – methyl vinyl pyridine copolymers, and others.

Diethyl Ether

Diethyl ether, also known as ethoxyethane or simply ether, $\text{CH}_3\text{CH}_2\text{--O--CH}_2\text{CH}_3$, is one of the most important ethers.

Physical Properties.

It is a clear, mobile liquid with a sweetish, slightly pungent, characteristic odor. Diethyl ether is completely miscible with common organic solvents, but only partially miscible with water.

Chemical Properties

- Unsubstituted ethers are chemically very stable. At room temperature, they are neither attacked by alkali metals nor undergo base hydrolysis. They are also resistant to acids, with the exception of hydroiodic acid which cleaves ethers with formation of alkyl iodide; this reaction is the basis of the Zeisel method for the determination of alkoxy groups.
- At higher temperature, ethers are also hydrolyzed by other acids, especially nitric and hydrobromic acids, acyl halides, and phosphorus pentachloride [10]. The rate of

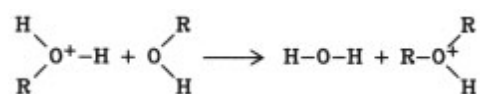
hydrolysis increases rapidly with the degree of branching of the alkyl group. Therefore, breakdown or removal of nonvolatile methoxy compounds or methyl-protecting groups by boiling with hydrobromic acid is advantageous.

- At higher temperature, ethers can be cleaved to produce olefins, water, and alcohol, especially in the presence of catalysts such as aluminum oxide.
- Ethers react more quickly with chlorine or bromine than do the corresponding alkanes, substitution taking place mainly in the α -position. Mono- as well as bis (1-haloalkyl) ethers can be obtained by appropriate control of the reaction.
- Ethers form peroxides in the presence of atmospheric oxygen, especially when exposed to light. This has long been known because violent explosions can occur toward the end of ether distillations due to the peroxides present in the distillation residue.

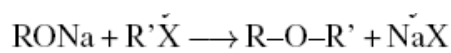
Synthesis

Ethers are generally prepared by catalytic dehydration of alcohols or by reaction of alkyl halides with alkoxides:

- *Catalytic dehydration of alcohols in the liquid phase.* Acids (particularly sulfuric acid) and electrophilic metal and nonmetal halides are effective catalysts for dehydrating alcohols in the liquid phase to produce ethers. Moderately strong acids and salts of weak bases and strong acids are most effective but favorable results are obtained only for the lower alcohols (1 – 3 carbon atoms). The reaction proceeds via intermediate formation of an oxonium compound:



- *Catalytic dehydration of alcohols in the gas phase* over, e.g., aluminum oxide, anhydrous alumina, or bauxite at a temperature of 180 – 250 °C gives ether yields of up to 75 %.
- *Reaction of alkyl halides with alkali-metal alkoxides* by the Williamson synthesis:

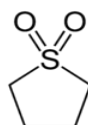


- Introduction of dimethyl sulfoxide as a solvent considerably improved yields in the Williamson ether synthesis [20]. A mixture of sodium hydroxide and alcohol can be used in place of the alkoxide.

Uses.

- Diethyl ether is a good solvent for many oils, fats, resins, alkaloids, odorants, and dyes and, therefore, is widely used as a solvent and as an extractant.
- When mixed with ethanol, diethyl ether is used to gel nitrocellulose and to dissolve collodion wool.
- Ether is used as a reaction medium in the laboratory and in industry due to its chemical stability, low boiling point, and solvent properties for organometallic compounds (Grignard reagents).
- It is also employed as an anesthetic in medicine.

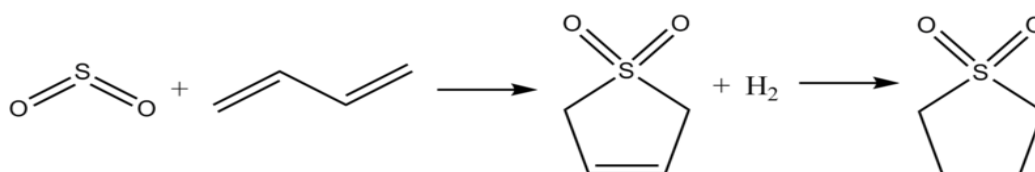
Sulfolane.



Sulfolane (also *tetramethylene sulfone*, systematic name: 2,3,4,5-tetrahydrothiophene-1,1-dioxide) is a clear, colorless liquid commonly used in the chemical industry as an extractive distillation solvent or reaction solvent. Sulfolane was originally developed by the Shell Oil Company in the 1960s as a solvent to purify butadiene. Sulfolane is an aprotic organosulfur compound, and it is readily soluble in water.

Synthesis

The original method developed by the Shell Oil Company was to first allow butadiene to react with sulfur dioxide. This yields sulfolene, which was then hydrogenated using Raney nickel as a catalyst to give sulfolane.



Shortly thereafter, it was discovered that both the product yield and the lifetime of the catalyst could be improved by adding hydrogen peroxide and then neutralizing to a pH of roughly 5-8 before hydrogenation. Recently, it was found that Ni-B/MgO showed superior catalytic activity to that of Raney nickel and other common catalysts that have been used in the hydrogenation of sulfolene.

Other syntheses have also been developed, such as oxidizing tetrahydrothiophene with hydrogen peroxide. This first produces tetramethylene sulfoxide, which can then be further oxidized to tetramethylene sulfone. Because the first oxidation takes place at low temperature and the second at higher temperature, the reaction can be controlled at each stage. This gives greater freedom for the manipulation of the reaction, which can potentially lead to higher yields and purity.

Uses

Sulfolane is widely used as an industrial solvent, especially in the extraction of aromatic hydrocarbons from hydrocarbon mixtures and to purify natural gas.