

COMMERCIAL POTENTIAL OF SULTONES

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SUMMARY

Sultones are cyclic esters of sulphonic acids. They are reactive intermediates having commercial application in detergents, polymers, antistatics and other industrial applications. However, the establishment of carcinogenic activity in these sultones has led to a decline in their usage and most studies in this area have also declined.

The main objective of this work however was to assess the commercial potential of sultones in general.

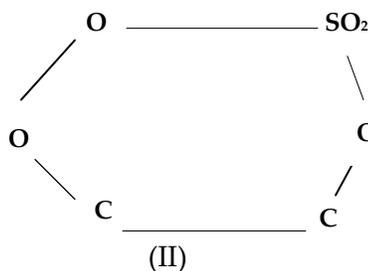
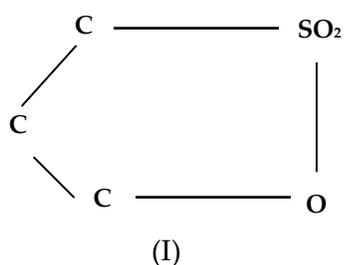
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INTRODUCTION

Sultones are internal esters of sulphonic acids and they contain the $-SO_2-O-$ group as part of a ring. They are sulphur analogues of lactones which are compounds considered to be derived by the intramolecular loss of water from hydroxyl and a carboxyl group of a hydroxyl acid. The resulting compounds are esters.

Sultones are classified as either aliphatic or aryl sultones. In the case of aliphatic sultones, one of the oxygen atoms of the sulphonic ester group forms a part of the ring while the aryl sultones term refers to those sultones which have one ring oxygen atom directly attached to the aromatic nucleus.

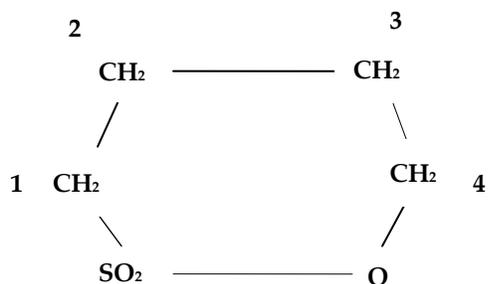
Most of the sultones prepared have five or six membered rings (I, II) and usually they have to be proven to be high-boiling liquids or low melting solids.



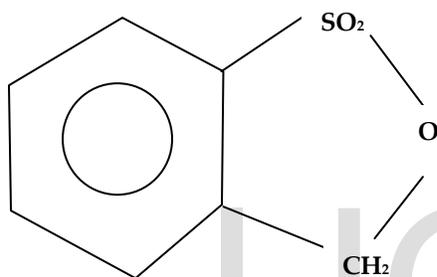
Sultones having other than five and six membered rings are very rare indeed. A number of four membered rings containing two hetero-atoms have been described in the literature. An example of this is the β -sultone and most β -sultones which have been prepared are obtained from the reaction, of sulphur trioxide with highly fluorinated olefins ^{1, 2, 3}. Non-halogenated sultones are unknown.

THE CHEMISTRY OF SULTONES

The nomenclature of sultones used in the Chemical Abstracts⁴ is to name the hydroxyl sulphonic acid which would have to be dehydrated to give the sultone and then to add the suffix "Sultone". This is illustrated by compounds (III) and (IV) below:



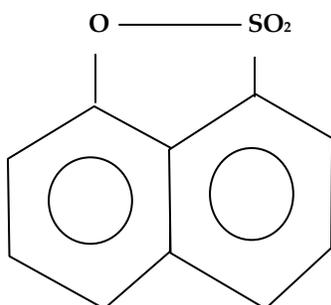
(III) 4 - Hydroxy-1-butane sulphonic acid



(IV) α -hydroxy-0-toluene sulphonic acid sultone.

Alternatively, sultones may be named as the heterocyclic compounds with the oxygen atoms attached to the sulphur being donated as "dioxide". Hence compound (IV) can be named as a derivative of benzothiole viz, 2, 1-benzothiole-1,1-dioxide.

The name "sultone" was coined by Erdman and the first sultone prepared was 1,8-naphtho sultone (V). Erdman⁶ also studied and confirmed the structure.



(V) 1,8-naphthosultone

Sultones are reactive intermediates and have found use⁵ as antistatics or hardeners in ammoplastics; in the manufacture of certain specialist detergent and in the preparation of modifiers for high polymers.

PREPARATION OF SULTONES

Sultones are prepared by various methods viz by dehydration of hydroxyl sulphuric acids^{5,7}, by intramolecular nucleophilic attack^{8,9}, by intramolecular electrophilic attack which is rare e.g. 2-hydroxy-2-sulpho biphenyl sultone⁽⁵⁾, by direct addition of SO_3 to an olefin and bicyclic sultones which are carbohydrate derived¹¹

Sultones having other than five and six membered rings are rare indeed. β -sultones, a four membered ring sultone has been prepared from reactions of SO_3 with highly fluorinated olefins^{12, 13, 14}

Non-halogenated four membered sultones are not known^{10,15}. Attempts at synthesising seven membered aliphatic sultones have not been very successful. Some other sultones derived from aliphatic and aromatic are discussed by Ahmed Mustapha^{6,21}.

Considerable literature has been devoted to sultones but the chemistry of the simplest member, propane sultone has not been made conveniently available because most references appear in the patent literature where reaction yield data are often only generally indicated and where analytical and other structural proofs are usually lacking.

Propane sultone as a versatile intermolecule which can react with a wide variety of compounds to introduce the propane sulphonic acid function. It is considered as a chemical intermediate, that is, as a modifying agent for other substrates. It has unique characteristics and often confers water solubility and anionic character under mildly alkaline conditions.

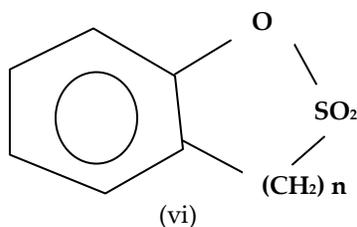
Properties of the products obtained depend on the preparative procedures and particularly on the number of propane sulphonic acid groups added. Propane sultone derivatives of amines, alcohols, phenols, mercaptans, sulphides and amides are useful in detergents as wetting agents, luthering agents and bacteriostats¹³⁻²⁹.

REACTIONS OF ALIPHATIC SULTONES

The reactions of aliphatic sultones have not been widely investigated and much of the work which has been done in this class of compounds involved ring opening nucleophilic reactions which occur readily with nucleophilic attack invariably resulting in the elimination of sulphate groups^{14,15,16}, pyrolysis reactions⁵, Friedel-Crafts reaction^{17,19}, and alkylation of organometallic and related compounds by sultones²⁰.

REACTIONS OF ARYL SULTONES

The term "aryl sultones" refers in this paper to structures of the type (vi) shown below and a typical member of this class of compounds is 1,8-naphtha-sultone(v) and it has proven most helpful to refer to it as much of the systematic work carried out has been with this compound.



Unlike the reactions of aliphatic sultones with nucleophiles, the aryl sultones do not undergo substitution reactions by loss of the sulphonate grouping because of the activation energy required for such a reaction would be very high. Instead nucleophiles tend to attack at the sulphonyl group of the aryl sultone. This form of attack is slow in the case of aliphatic sultones compared with the elimination of the sulphonate group.

With respect to electrophilic substitution the sulphonyl group is strongly deactivating hence electrophiles attack the naphthalene ring generally on the phenolic oxygen of the sulphonic ester group. A treatise on both electrophilic and nucleophilic attack on 1,8-naphtho sultone is described in the literature⁵.

Since aryl sultones react with nucleophilic reagents by cleavage to the oxygen carbon bond as aliphatic sultones, sulphonylation to give a sultone rather than alkylation would be a more likely reaction of aryl sultones under Friedel-Crafts conditions. No evidence of sulphonylation was however observed. This is consistent with report of Schetty⁽⁵⁾ that 1-naphthol-8-sulphonic acid sultone can be acylated in the 4-position by Friedel-Crafts reaction without cleavage of the sultone linkage.

Introduction of sultone in methanol gave esters as primary photoproducts and continued irradiation of the esters led to a completely new aromatic compound¹²

A comparative study of the alkaline hydrolysis of five and six membered aryl sultones showed that the five membered cyclic sultones undergoes alkaline hydrolysis 7×10^5 times faster than its open chain analogue. A more recent work has demonstrated that this rapid rate of solvolysis by hydroxide ion is a property of five membered sultones but that the rate of ring openings is very much reduced in six membered systems. The most favoured explanation for this rate of hydroxide ion at the sulphur atom varies enormously between sulphur atoms in cyclic and acyclic systems (23, 24, 25). The reason for this is presently not clear and might not be connected with the ring strain and geometry.

COMMERCIAL POTENTIAL OF SULTONES

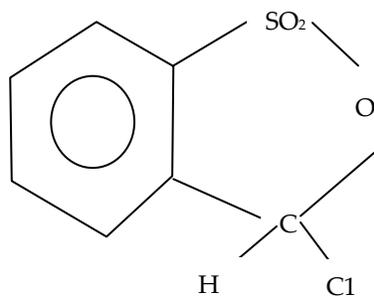
Sultones are cyclic esters of sulphonic acids and they are reactive intermediates having commercial application in polymers, antistatics, detergent and surfactant industry. Sultones have unique characteristics because they react with a wide variety of compounds to introduce the sulphonic acid function and they are also considered as modifying agents for other substrates.

This paper involves an assessment of the commercial potential of sultones in general and its implication in chemical industrialization.

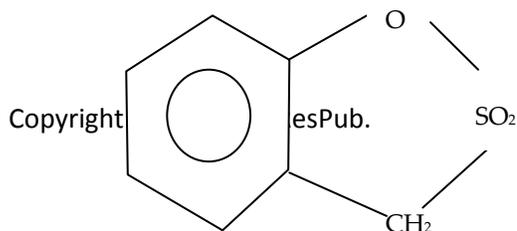
The simplest member of the sultone group is propane sultone and considerable literature has been devoted to it. The value of propane sultone as a chemical intermediate derives from its ability to act as a sulphopropylating agent in reactions with amines, alcohols and other similar compounds having an active hydrogen. Properties of the products depend on preparative procedures and particularly on the number of propane sulphonic acid groups added.

1. MANUFACTURE OF "SACCHARIN"

Oldershaw⁵ investigated the sulphonation and chlorosulphonation of aromatic hydrocarbons, with the ultimate aim of improving industrial preparation of benzene and toluene sulphonic acids and sulfonylchlorides which are highly important chemicals. The principal aim of the research was to improve the industrial process for the manufacture of the sweetening agent "saccharin". Sultones, (VII) and (VIII) were considered as possible intermediates in the preparation of sulphonamides in the absence of toluene sulfonylchlorides which could react with amines to give the corresponding sulphonamides. These compounds were prepared by various known methods⁵.



(VII) 3-Chloro-2,1-benzoxathiole-1,1-dioxide



(VIII) 1, 2 – benzothiole – 2, 2, - dioxide

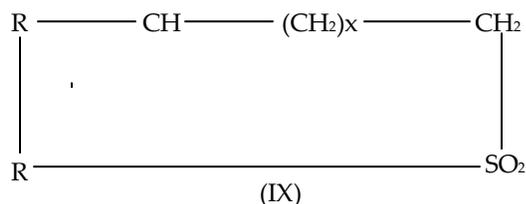
2. FATTY ACID DERIVATIVES OF PROPANE SULTONE AND THEIR PROPERTIES AS ANTISTATICS AGENTS

Various surface active agents such as alkyl phosphates have been used as antistatics agents for polyvinylchloride. Suya²⁸ and co-workers compared antistatic properties, and surface activities of 3-laurylamine propane sulphonic acid, which is a propane sultone derivative with established agent for polyvinylchloride, the alkyl phosphates. The antistatic properties of these propane sultone derivatives for polyvinylchloride sheet were examined and compared with those of other compounds. The results showed that apparently laurylaminopropane sulfonate was far more efficient than alkyl phosphate and other commercial samples.

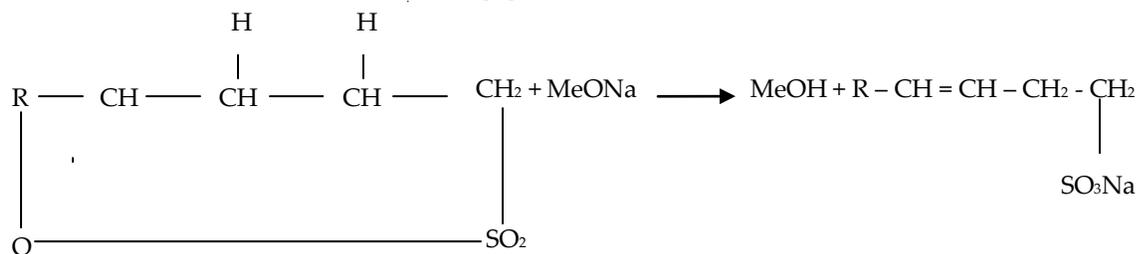
3. CONVERSION OF ALKYL SUBSTITUTED SULTONES TO ALKENE SULFONATES USING SUBSTANTIALLY ANHYDROUS CONDITIONS

Alkene sulfonates were known to be excellent detergents whose suds-forming properties differ from hydroxysulfonates in detergent systems.

Hydrolysis of sultones results in their conversion to alkene sulfonates and hydroxysulfonates; the formation of hydroxysulfonates appears to be favoured by the presence of hydroxyl ions during the cleavage step of the cyclic sultone. Reactions of the foregoing type have been describe in the patent literature²⁹⁻³⁶. As a result of the excellent properties of the alkene sulfonates in detergent systems, it is necessary to maximise the amount of sulfonates in the hydrolysis product and to minimise the hydroxylsulfonate species. A suitable sultone for conversion is of the general formular (IX)



Where R is substituted aliphatic group and x is an integer of at least 1. The process for this conversion has been described in the patent literature³⁷ and is exemplied by equation[1]



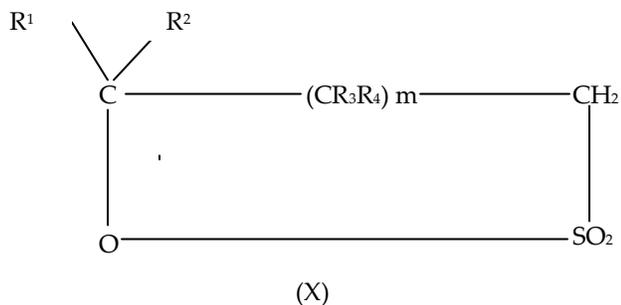
Me = alkyl group

Reaction Equation [1]

4. PREPARATION OF ALUMINIUM SULFONATES FROM SULTONES AND ITS APPLICATION

It is known that sultones, made from a long chain alpha olefin and sulphur trioxide may be hydrolysed to a product having a surfactant composition. However, the products of the hydrolysis reaction yield a mixture of hydroxyl sulfonates and alkene sulfonates. The former are undesirable because of their poor detergency characteristics. The presence of such impurities while of little importance in some applications is particularly detrimental to those surfactants used for more demanding applications such as tertiary recovery of oil from oil fields and separation of valuable hydrocarbons from tar sands and shales. Such detergent must not only have high detergent activity but and be of high purity but must also be thermally stable to hydrolysis.

These superior detergents are prepared by reacting a long chain aluminium alkyl compound of formula $Al(C_nH_{2n+1})_3$ with structure (X)



At a temperature of about 100-250°C

$n=10-22$

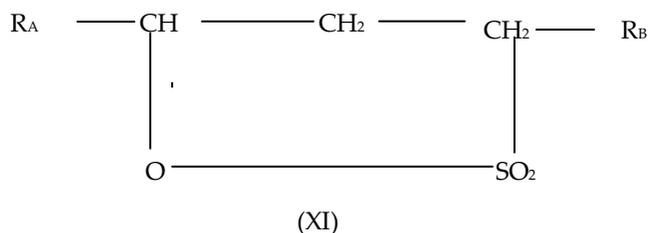
$m=1-2$

The process conditions involved are given in the patent literature³⁸. The reaction production is best handled simply by immediate reaction with water in the presence of an alkali to convert it directly to the corresponding surfactant.

Such compounds are also of particular value as detergents in secondary oil recovery from partially depleted wells because of their high detergency and hydrolytic stability at elevated temperatures. They are also useful in the gelation of hydrocarbons. Useful sultones are defined as five and six membered ring sultones, and will include 1,3 propane sultone and 1,4 butane sultone.

5. PRODUCTION OF SUPERIOR DETERGENT FROM GAMMA SULTONES

The structure of Gamma sultones (XI) is given below.



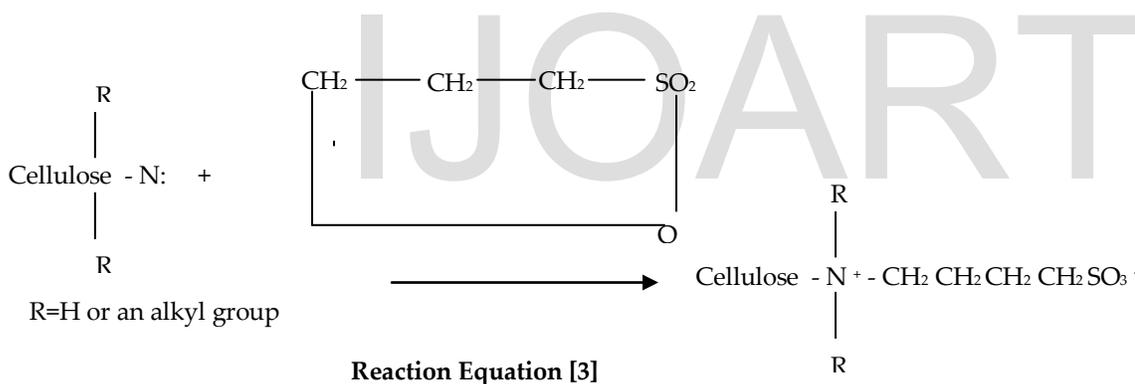
Where R_A is a monovalent hydrocarbon radical having 2-27 carbon atoms, are very important intermediates in the manufacture of surfactants.

The sulfonation product is a very complex "acid-mix" containing not only gamma sultones and delta sultones, but also unsaturated sulphonic acids when sultones are conveniently produced by sulfonating olefins with sulphur trioxide.

Ward⁴³ and co-workers also reacted propane sultone with cotton fabric modified to contain either a tertiary amine group (diethylamino ethyl –(DEAE)-cotton) or a primary amine group (aminized cotton). No reaction was obtained with cotton modified to contain a carboxyl group (carboxymethyl cotton). Freshly prepared DEAE-cotton that had been exposed to atmospheric conditions which could convert it to hydro-salt form. Products obtained from sodium celluloses have potential as cation exchangers and those formed from cottons containing amine groups as zwitterions of the sulfobetaine type.

8. THE PRODUCTION OF CELLULOSIC MATERIALS HAVING BOTH BASIC AND ACIDIC GROUPS

U.S. Patent 3,506,390⁴⁰ discloses the process wherein aqueous sodium hydroxide has been used to produce alkali cotton which was reacted in aqueous solutions of propane sultone to produce a material containing acid sites but no basic sites. It has now been discovered⁴⁴ that a cellulosic material with primary amine group attached (aminized cotton) can be reacted with propane sultone to produce material having both basic and acidic groups. The reaction proceeded readily without the need of a catalyst to yield a product with zwitterion properties. Likewise the said propane sultone has been reacted with cellulosic material with related tertiary amine grouping. Reaction equation [3] which would represent the pertinent reaction is given below:



The cellulose with the amine DEAE group attached is reacted with a hydrocarbon sultone in solution and in proper solvent. The preferred solvent for reacting DEAE-cellulose with the sultone is tertiary butanol while a primary alcohol such as methanol is required for aminized cellulose. The reaction is carried out whilst the cellulosic material is wet with propane sultone solution. Temperatures can be varied from 25 to 75°C, and the length of time can be varied from 1 to 24 hours. By varying the nitrogen content for the DEAE or aminized intermediate and by controlling the reaction of the sultone with the amine group by controlling the length of reaction or temperature, one can produce compounds with varying ratios of sulphur to nitrogen. Unreacted amine sites would increase the basic character of the product.

Although cotton fabric was employed in the investigation, it is obvious that any material containing cellulosic hydroxyls can be used. This includes, but is not limited to fibres, yarns, fabrics, or matrixes which contain cotton, rayon, wood or linen.

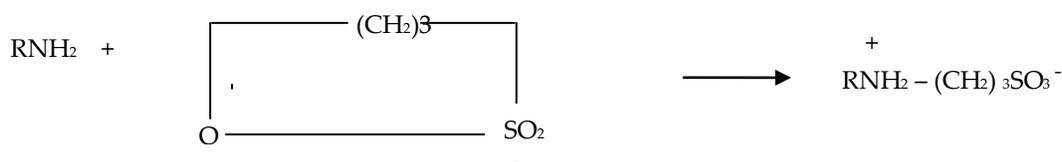
The products have excellent ion-exchange properties and other sultones like butane, pentane and higher sultones should react in similar manner.

9. ALKALINE EARTH METAL SALTS OF STARCH-SULTONE REACTION

Elizer⁴⁵ reported that the reaction of starch or starch fractions with alkyl or aryl sultones at 32-120°F and alkaline pH in the presence of 0.8-3.0 molecular equivalent of alkaline earth metal base per molecule of reacted sultone provides a rapid process for producing highly substituted starch ether sulphonic acid salts of the respective alkaline earth metals by the reaction of the sultone with hydroxyl groups of starch. These alkaline earth metal salts or said starch ether sulphonic acids have proven especially suitable as finishing agents for textiles. They function well with diverse types of natural rubber and synthetic fibre textiles such as cotton, nylons, polyesters, polyacrylonitrile, rayons and other synthetic fibres. The introduction of small proportions of sulphonyl or sulphoalkyl group into ungelatinized starch and the formation of alkaline earth metal salts notably calcium, barium or strontium salts provide improvements in aqueous starch dispersions or slurries of the dried starch in regard to viscosity, clarity and stability.

10. APPLICATION OF THE REACTION OF PROPANE SULTONE WITH MACROMOLECULES

Reaction equation [4] shows the reaction of sultones with amines to form the inner salt of amino sulphonic acids is well known⁶.

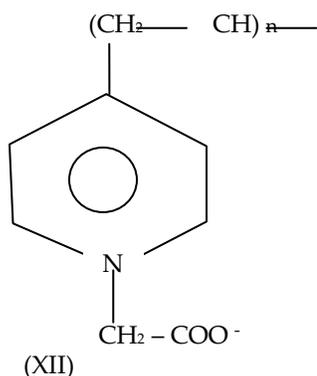


Reaction Equation [4]

This reaction has been applied to polymeric amine by Hart and Timmerman⁴⁶ who obtained a polyampholyte by reaction of butane and sultone with (2-vinyl pyridine). Natus and Geothals⁴⁷ have reported the reaction of propane sultone with poly(ethylenediamine). As this polyamine is commercially available it provided an easy way to obtain polyampholytes.

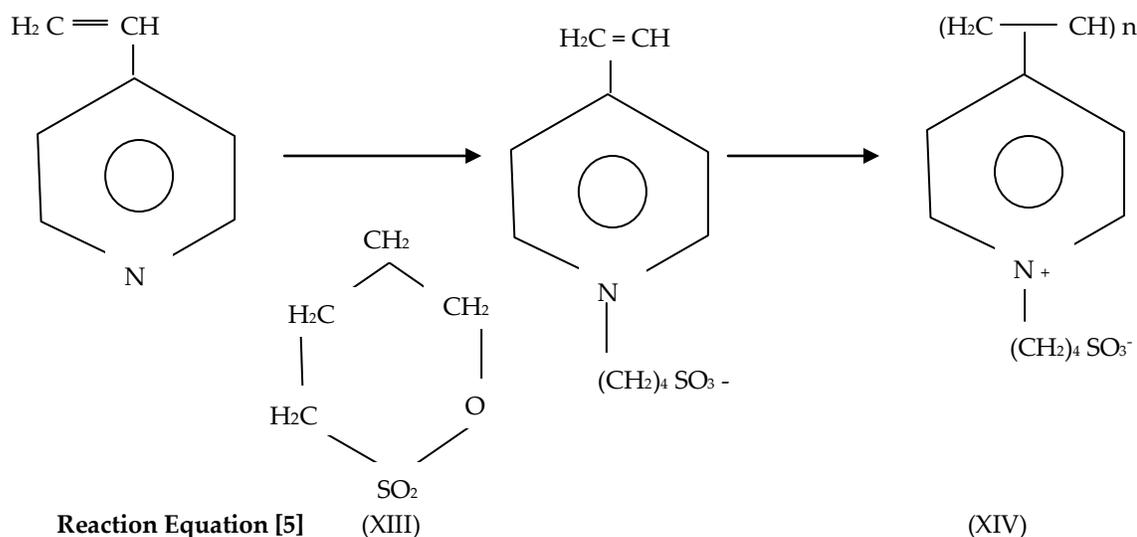
Many natural substances of biological importance are amphoteric polyelectrolytes and this has stimulated interest in the investigation of their synthetic analogues

Polyampholytes which have been described previously have random distributions of positive and negative charges^{48, 49, 50}. Ladenheim and Morawetz⁵¹ prepared a polymer with the structure in which a large number of zwitterionic are attached to the polymer backbone.(XII)

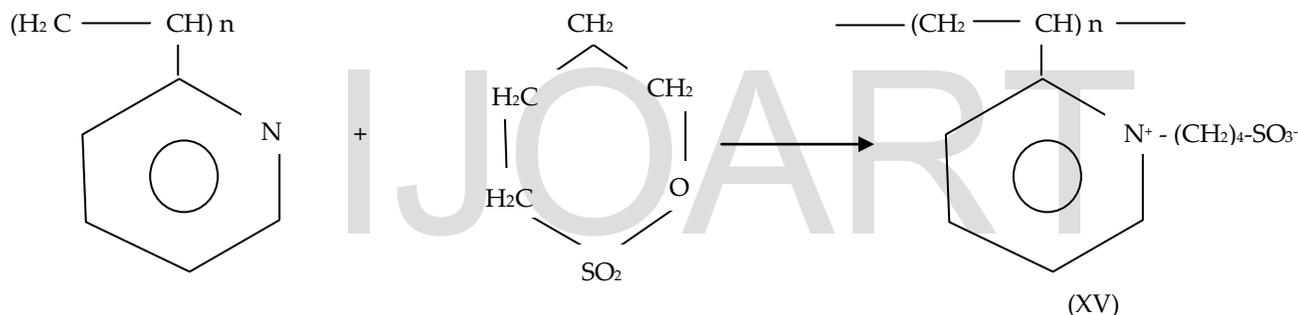


This prompted the investigation of sulfobetaines⁴⁶ of polymeric amines which are a new class of polyampholytes. These can be obtained by the reaction of monomeric tertiary bases such as 2 and 4-vinyl [pyridine with the sultones and the subsequent polymerisation of the monomeric sulfobetaines.

Reaction equation [5] illustrates the synthesis of poly-(4-vinyl pyridine N-butyl (XIV) using the sultone of 4-hydroxy-1-butane sulphonic acid (XIII).



Polysulfobetaines (XV) can also be synthesised by direct reaction of polymeric tertiary bases such as poly (2-vinyl pyridine) with sultone as shown by reaction equation [6].



Hart and Timmerman⁴⁶ reported some synthesis which are examples of the techniques according to which several polymers were prepared. The reaction of sultones with amines has even been used for derivating aliphatic amines in qualitative organic analysis⁵², sultone was found to be the most suitable after a preliminary study of possible reagents. More so, they are inexpensive and readily available. Propane 2,4-butane and 1,1,3-trimethyl propane sultones were examined in the investigation.

11.APPLICATIONS OF POLYELECTROLYTE AND POLY ELECTROLYTE COMPLEXES

A polyelectrolyte is defined as any polymeric substance in which the monomeric units of its constituent macromolecules possess ionisable group⁵³. In contrast to a simple electrolyte like sodium chloride, in which the sizes of the oppositely charged ions are similar in magnitude, a polyelectrolyte is always composed of a micro-ion in which the charged groups are interconnected by chemical bonds to an equivalent number of small oppositely charged counter-ions. Virtually all of the unique properties of the polyelectrolytes result from the intersection of interconnected ionic groups of the micro-ion with its compensating micro-ions. As a consequence of their electrostatic nature, polyelectrolytes are usually soluble in aqueous solution. Furthermore, since all naturally occurring polyelectrolytes are found in an aqueous environment, most of the chemical research in this field has been directed towards an understanding of polyelectrolyte behaviour in aqueous solution. Electrochemically, a polyelectrolyte can be classified as either a polyacid, a polybase or a polyampholyte depending upon the nature of its ionisation in water solution.

Polyelectrolyte complexes are the result of ionically cross-linking of two highly but oppositely charged polyelectrolytes. Whereas, the individual polyelectrolytes are water soluble, the complex undergoes limited swelling in water and electrolyte solutions. Polyelectrolyte complex hydrogels ranging from rigid solids to opaque spongy materials can be prepared by controlling the reaction conditions, the ionic stoichiometry and nature of the individual electrolytes.

These polyelectrolyte complexes are highly permeable to water and to small molecules; the permeability to solute molecules is selective. They have high electrical conductivity and controllable ion exchange capacity.

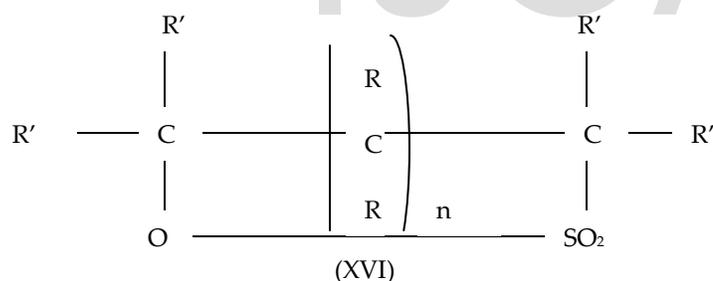
The major potential applications⁵³⁻⁵⁶ polyelectrolyte complexes are in membranes, battery separator and biomedical materials and they hinge upon the fact that these materials are (i) water soluble polymers capable of promoting major changes in the fluid properties of aqueous suspensions, solutions and slurries. (ii) substances which may be absorbed by neutral particles, thus imparting a surface charge to the particles, (iii) substances whose ionized groups interact very strongly with ions and colloidal aggregates of opposite charge, (iv) substances which frequently are fairly insensitive to chemical and biological degradation.

The major potential application of polyelectrolytes are in thickening, detergent, ion-exchange resins and textiles.

12. PRODUCTION OF SULTONE OR HYDROXYALKANE SULFONATE MODIFIED POLYAMIDES

The production and uses of polyamides such as nylon 66 are well known because such polyamides are widely used in the fibre form for the production of fabrics. Hence, it is important that they should be dyeable, for example, with basic dyes, but resistant to staining with acid dyes. While such materials generally possess a certain susceptibility to dyeing, there has now been discovered a method of enhancing the basic dyeability of such materials. According to this invention⁵⁷, there is provided a method of imparting basic dye reactivity to polyamides which comprises the incorporation of at least one of a hydroxyl sulphonic acid and an alkali metal hydroxide, in an amount sufficient to improve the basic dyeability of the polyamide. The alkane sultone is incorporated in the polymerisation recipe to produce a polyamide having an improved dyeability with basic dyes.

Suitable alkane sultones can be represented by the formula (XVI)



Where n is an integer of 0-10 and preferably 0-4. $R' = H$ or an alkyl radical having 1-4 carbon atoms, the total number of carbon atoms in each molecule of the alkane sultone being from about 2-20 and preferably about 2-6. A particularly suitable sultone is 1,3-propane sultone which is commercially available.

13. ADDUCTS OF A CYCLIC ETHER AND A SULTONE

It is known that the homopolymeric acrylonitrile and co-polymers of acrylonitrile into which no dye sites have been introduced chemically, that is, as an integral part of the molecule or by blending with a polymer containing dye sites are extremely difficult to dye satisfactorily with conventional acidic and basic dyes.

Various means have been suggested and are in use for overcoming or minimizing the problem of dyeing acrylonitrile polymers effectively and economically without adversely affecting the other useful commercial properties of shapes articles fabricated from the polymers. The production⁵⁸ of adducts from sultones and cyclic ethers is a different solution and has certain advantages over other processes. The sole aim of production of these adducts is to provide new compositions of matter, including a new cationic dye receptive adduct adapted for blending with a new dye resistant polymer, more particularly blends of a dye resistant polymer and a compatible dye receptive adduct, that can be spun cast or otherwise shaped to form filaments,

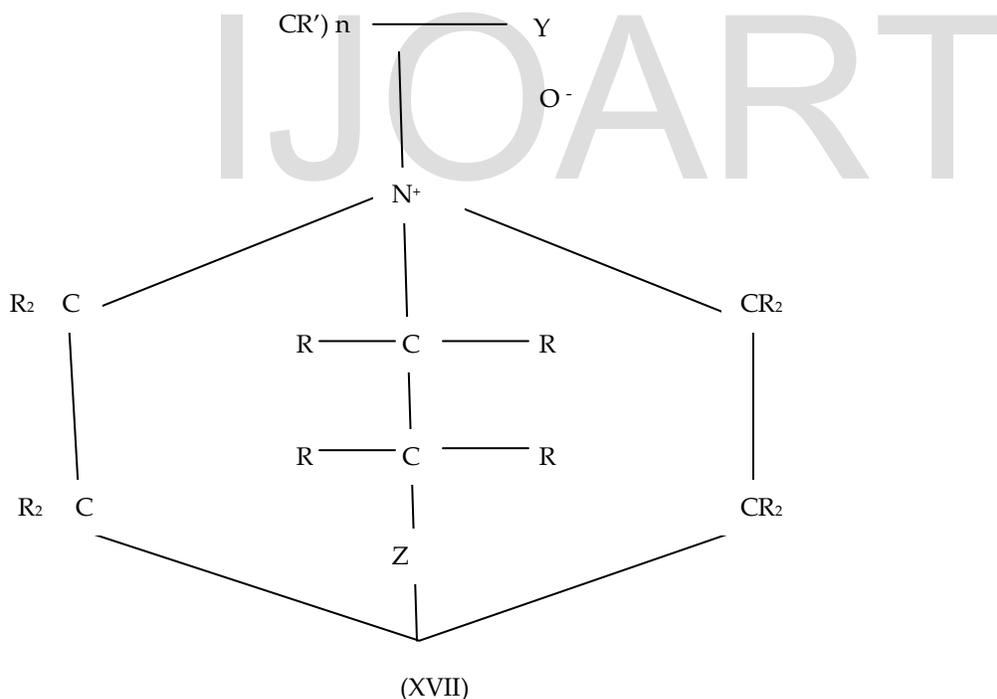
rods, tubes, bars, ribbons, tapes, sheets, yarns, and the like, and the shaped articles then dyed either before or after being oriented and made into fabrics in knitted, woven or other form. This aim is achieved by incorporation into a dye resistant polymer, (a) a particular polymerized cyclic ether with (b) a sultone of a particular class, and shaping the resulting composition to form useful articles of manufacture such as the ones already mentioned.

14. SULTONES ADDUCTS OF BICYCLIC TERTIARY AMINES

The sultone adduct contains 2 or 3 carbon atoms in the sultone ring with mono or diazo bicyclo(2.2.2) octane. These adducts are prepared by reacting the sultone with mono or diazo bicyclo(2.2.2) octane in an inert diluent under substantially anhydrous conditions. These adducts were prepared by Karl Brack⁷¹.

Any sultone containing 2 or 3 carbon atoms in the sultone ring can be used, as for example, propane sultone.

The adducts have the structure given below (XVII)



Where $Y=SO_2$, $n=2$ or 3 , R can be independently selected from the group hydrogen, methyl or ethyl, or one R can be hydroxy, alkoxy, aryloxy, acyloxy and the others hydrogen, methyl or ethyl; $2R$'s attached to the same carbon can be oxygen and the others hydrogen, methyl or ethyl. These adducts are useful as aids in cross-linking of unsaturated polymers present in adhesive and coating compositions. They are useful as stabilisers for polyvinylchloride sheets and as acid acceptors in rubber compounding.

15. APPLICATION OF SULTONE OF PERFLUOROALLYL FLUOROSULFONATE

This production⁵⁹ relates to the pure compounds perfluoroallyl fluorosulphate (CF₂=CF-CF₂OSO₂F) and its sultone (XVIII).



(XVIII)

And their preparation by reacting hexafluoroprene (CF₃-CF=CF₂) with SO₃ under anhydrous conditions in the presence of about 0.1-5% by weight based on SO₃ of trivalent boron compound selected from the group consisting of boric oxide, boron trichloride, boron trifluoride or tri(lower alkyl) borates where the alkyl groups contain 1-6 carbon atoms, for example tri-methyl borate at a temperature of about zero to about 150°C for a time sufficient to produce perfluoroallyl, BF₃, and boric oxide B₂O₃, because of their efficiency and availability.

The sultone of perfluoroallyl fluorosulphate can be rearranged to form β-fluorocarbonyl-β-fluoro sulfonyl trifluoroethyl fluorosulphate on standing.

The sultone can be also reacted with water to form tri fluorovinyl sulfonyl fluoride which is useful for preparing ion exchange resins and acid catalysts^{60,61}.

16. SOLVENT EXTRACTION WITH SULTONE SOLVENT

The solvent extraction of aromatic hydrocarbons is well known. Specifically, selective solvent extraction of aromatic hydrocarbons from a mixture of saturated and saturated and aromatic hydrocarbons utilizing glycol and sulfolane type compounds as solvents is well known, but the rise of sultone type compounds as solvents for selective extraction of aromatic hydrocarbons from a mixture of aromatic and saturated hydrocarbons has not been recognized.

The use of sultone in solvent extraction processes has been published in the patent literature⁶² and there is a promise of its development on a commercial scale. In terms of utility, the present process offers a device for the concentration of valuable aromatic hydrocarbons which can be utilized in a multitude of operations varying from gasoline production to the production of plastics. Aromatics most readily separable utilizing this process include benzene, toluene or the xylenes. The saturated hydrocarbons in a mixture with the aromatics generally comprise cyclo paraffins, the branched or straight chain paraffins boiling substantially at the same temperature range as the aromatic compounds.

Feedstocks which can be used in the process include those derived from various crude fractions including straight run gasoline, reformed hydrocarbons or some of the products of catalytic cracking or hydrocracking reactions.

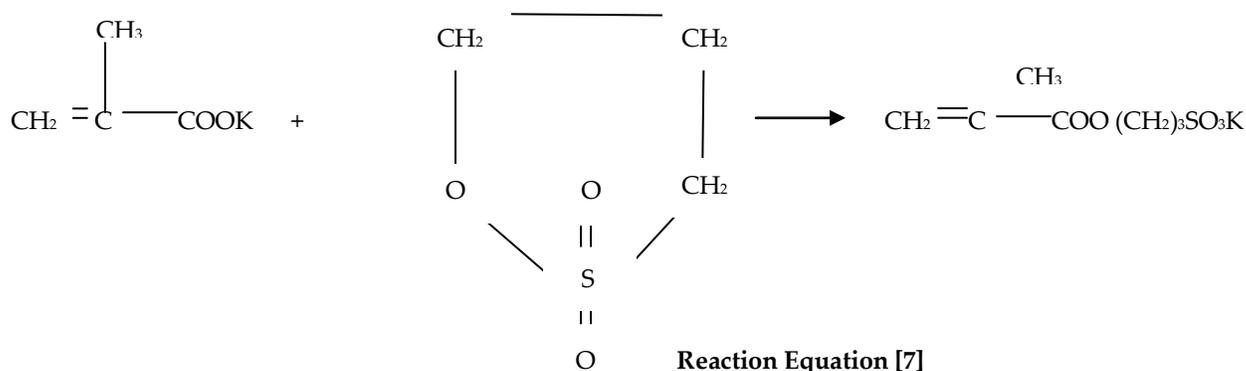
Sultones which have been used as solvents include 1,3-propane sultone, 1,3-butane sultone. The sultones may be utilized in relatively pure forms or mixtures with water and or other organic compounds including sulfonate type compounds or the ethylene glycols.

It has been found in extraction process that small quantities of the above substances can in many instances enhance the separation abilities of an extract for various feed components

Extraction conditions include liquid-liquid phase operations. Temperatures can include those from about ambient up to about 200°C. The higher temperature limitation may in some instances be required to be lower than that stated above where solvent easily decomposes at the temperature proposed.

17. PRODUCTION OF SULPHO-PROPYL METHACRYLATE⁶⁴

Mitsubishi Rayon Company Limited prepared sulpho-propyl methacrylate which has interesting polyelectrolytic properties as a co-monomer in an aqueous solution. The product was reported in high yield. The reaction scheme is given below in reaction equation [7].



TOXICITY AND CARCINOGENIC ACTIVITY OF SULTONES

Sultones are cyclic esters of sulphonic acids and the simplest member is propane sultone and it is a versatile intermediate. It has found much use commercially and therefore it is taken as a representative in discussing the toxicity and carcinogenic activity of sultones.

Propane sultone is a compound which has been produced industrially since 1964, It reacts with a wide variety of compounds to introduce the propane sulphonic (-CH₂CH₂CH₂SO₃H) function and also confers on the products other unique characteristic and, naturally that of solubility.

It is utilised as an intermediate in large scale manufacturing process:

- a. In the manufacture of detergent products, wetting, foaming and emulsifying agents
- b. In the activation of solubility of certain products in the pharmaceutical industry and in the manufacture of some insecticides and fungicides containing some sulphur and phosphorus
- c. In the dye and textile industry as antistatic agents for the treatment of some polyamide fibres; as a factor rendering the solubility of starch and as an auxiliary agent for dyeing.
- d. It is suited for the industrial preparation of plasticisers and in the manufacture of some synthetic resins in order to improve the characteristics of the products obtained.

PRIMARY ACUTE TOXICITY

Acute intoxication involving the animal caused a reaction followed by respiratory trouble and passing of blood contained diarrhoea. Simultaneously the victim suffers from trembling and convulsions.

- a. Oral
 - Rat : 350mg/kg
 - Mouse : 500mg/kg
- b. Dermal
 - Rabbit : 660mg/kg
- c. Subcutaneous
 - Rat : 135mg/kg
- d. Intravenous
 - Rat : 210mg/kg

SECONDARY IRRITATION

Propane sultone has a corrosive action on the skin of rabbit and a burning sensation was observed in the cutaneous layer of man

TERTIARY CHRONIC TOXICITY

Until now, no chronic intoxication has been reported in Man and the carcinogenic activity of propane sultone is well established from the experimental point of view.

The high reactivity of this molecule causes the development of a malignant phenomenon after a single application; and this does not occur via close contact of orally but via the transcutaneous layer after a single application.

Our knowledge of the carcinogenic activity of propane sultone dates back some years and it is due to the work of three groups of investigators, namely Druckrey, Ulland, Van Duuren⁶⁷⁻⁶⁹, and their co-workers

B-propiolactone and some reactive γ -lactones and are directly acting carcinogens. Therefore, amongst other alkylating substances, propane sultone has been tested for carcinogenic activity in rats 65, 68. By heterolysis, propane sultone readily reacts with a variety of nucleophilic substances and giving the corresponding alkyl sulphonic acids. It is rapidly hydrolysed in water with a pseudo-first order rate constant of 7.27×10^{-3} per minute at 40°C ⁶⁶. The reaction of propane sultone with a variety of nucleophiles has been studied and extensively used in the industry.

Subcutaneous injections of the redistilled propane sultone m.p. 31°C , dissolved in arachi's oil at a dosage of 30mg per body weight once a week for 21 weeks produced local sarcomas in 11 out of 11 rats. The experiments were repeated with a freshly prepared 3% aqueous solution. After weekly injections of 15mg per kg, all 18 treated rats developed large sarcomas at the sites of injection. \ the same result was obtained with a single dose of 100 mg per kg. The time elapsing till death occurred from tumour corresponded to a normal distribution and t_{50} was 280 ± 60 days in all groups. In experiments with oral or intravenous administration, the tumour yield was considerably less, probably due to reactions with the contents of the stomach or the blood, but malignant tumours of brain and nervous systems have been observed in 9 cases.

Propane sultone administered intragastrically at 2 dose levels gave rise chiefly to gliomas with similar incidence irrespective of dose and sex⁶⁷. In addition, there were several cases of leukemia, ear duct tumours and adenocarcinomas of the small intestine, and one case of colon adenocarcinoma.

There was a large number of mammary adenocarcinomas in females, related to the size of dose, some of which metabolised to lungs. 6 males and 6 females were killed at 61 weeks out of the group of negative control animals which also served as control for concurrent studies. A pituitary chromophobe adenoma was discovered in one female control but the remaining 11 were free from tumours. In addition, 1 female control died after 33 weeks of cerebral glioma.

A group of positive control animals treated with a known carcinogen responded in the anticipated manner. Druckrey and co-workers emphasized that subcutaneous injection of propane sultone leads to local sarcomas in all treated rats. The conclusion drawn was that although oral or intravenous administration was less effective but nonetheless, they also found tumours of the brain and nervous systems⁶⁹.

According to these results, propane sultone is to be considered as a potent carcinogen and adequate precautionary measures in handling propane sultone are necessary.

CORROSIVE PROPERTIES

Propane sultone is slightly corrosive to mild steel and this material might be used for storage and handling. Where trace contaminations with iron is significant to the product, alloy or lined equipment should be used.

Since the hydration product of 3-hydroxy-1-propane sulphonic acid is highly corrosive, gross quantities of water should not be permitted to contaminate the product.

Corrosion data⁷² for both wet and dry propane sultone are given below in Table 1.

Table 1

Alloy	Water added wt. (%)	Corrosion rate ml/year	Metal, ion contamination. ppm		
		Liquid	vapour	Iron	Aluminium
Control (glass)	0			3.5	0.6
Drum iron	0	0.04	0.04	15.0	
Aluminium	0	0.04	0.01		9.5
Control (glass)	1			2.8	1.3
Drum Iron	1	0.4	0.2	58.0	
Aluminium	1	0.3	0.1		110.0

CONCLUSION

Propane sultone is a compound which is very versatile and used in the industry as an intermediate. On the experimental plane it has shown evidence of serious carcinogenic activity. Its carcinogenic activity was established long before it was known that the same effect appears in man. As a result of this carcinogenic activity a host of producers of sultone compounds including Shell Chemical company which in 1961 pioneered and commercialised sultone stopped its production. The effect of this on man depends on the details of the circumstances in which he has been exposed. Thus it is necessary to take some strict precautions as the use of this product poses a certain causticity and can cause skin lesions.

In order to avoid the contact of propane sultone with the skin, eyes, and garments, all precautionary measures should be employed in the manufacture as well as during use. It is also necessary to wear gloves and protective clothing. In the case of accidental contact with eyes, a wash with water will be practical immediately and contaminated clothing should be washed before being worn again. In case of oral contamination, a mouth wash will be prescribed and water should be used to rinse the mouth while in the case of ingestion, it will be prudent to induce vomiting; and pregnant women should not be exposed to the risk.

Medicines should give special information and elaborate on the toxicity of the product and special attention should be given to those who have been exposed.

Finally, the attraction for the use of these versatile sultones as intermediates in the chemical industry still exists notwithstanding the carcinogenic nature. Improvement in precautionary measures as highlighted, well documented declaration in manufacturers safety codes regarding its usage and handling as well as advances in toxicological studies will lead to the revival of further research, production, evaluation and usage of sultones due to their versatility and great potential.

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