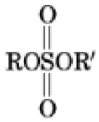
Kirk-Othmer Encyclopedia of Chemical Technology.

SULFURIC AND SULFUROUS ESTERS

Sulfuric and sulfurous acidsform a series of esters analogous to those from other acidic materials. The hydrogen of the acid is replaced by a carbon-containing group. Because two hydrogens are present in the sulfur-based acids, there are two series of esters. Replacement of one hydrogen results in an acid ester. If both hydrogens are replaced, whether with the same, with different, or with bifunctional substituents, symmetrical and unsymmetrical diesters form. The two series are represented by the following general formulas, where R is a carbon



$$\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{OR'}$$

$$\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{OR'}$$

group and R′ is a carbon group, hydrogen, or metal cation. In the acid ester series a chlorine or amine group may be present in place of the hydroxy group. These compounds can be used as intermediates in making diesters. The carbon groups most commonly present are those from short- and long-chain alcohols and from hydroxyaromatic and heterocyclic compounds. Table 1 illustrates the variety of known compounds and some of their properties.

Dimethyl sulfate, diethyl sulfate, and long-chain monoalkyl alkali metal sulfates are the compounds of practical interest. Dialkyl sulfates have been used to introduce a methyl or ethyl group into a wide variety of organic compounds. The alkylation chemistry of the lower alkyl hydrogen sulfates or their salts is of far lesser importance, but is closely related to that of dialkyl sulfates in that the monoalkyl esters are intermediate alkylating agents in those instances where both alkyl groups of the dialkyl sulfate are usable for alkylation. The long-chain monoalkyl hydrogen sulfates, in the form of their alkali metal or alkylammonium salts, are valuable as surface-active agents and are used commercially. The short-chain monoalkyl hydrogen sulfates are intermediates in commercial conversion routes from olefins to alcohols (see Ethanol; Propyl alcohols, isopropyl alcohol; Sulfonation and sulfation; Surfactants).

1. Physical Properties

The physical properties of sulfuric and sulfurous esters are best understood as resulting from the blending of the polar contribution of an acid or neutral sulfate group with the contribution of the usually nonpolar carbon group. The neutral sulfate group of esters is much less polar than the acid sulfate group, -OSO_3H. With lower

Table 1. Some Sulfuric and Sulfurous Acid Esters

Ester	CAS Registry Number	$\text{Bp}_{\text{kPa}}{}^{a}$, °C	Mp, °C
Sulfates, $(RO)_2SO_2$			
R			
open-chain			
methyl sulfate	[77-78-1, 75-93-4]	$188.8_{101.3}$, $69.70_{1.33}$	
ethyl sulfate	[64 – 67 – 5]	208, $89_{1.20}$	
n-propyl sulfate	[598 – 05 – 0]	$95_{0.670}$	
isopropyl sulfate	[2973 – 10 – 6]	$80_{0.530}$	
n-butyl sulfate	[625 – 22 – 9]	$103_{0.200}$	
ethyl *n*-butyl sulfate	[5867 – 95 – 8]	$117_{2.40}$	
chloromethyl sulfate	[73455 – 05 – 7]	$97_{1.87}$	
2-chloroethyl sulfate	[5411 – 48 – 3]	$150_{0.940}$	
n-decyl sulfate	[66186 – 16 – 1]		37.7
n-tetradecyl sulfate	[66186 – 19 – 4]		58.0
phenyl sulfate	[4074 – 56 – 0]	$194.6_{2.66}$	
cyclic			
ethylene sulfate	[1072 – 53 – 3]		99
1,3-propylene sulfate	[1073 – 05 – 8]		63
methylene (dimer) sulfate	[20757 – 83 – 9]		155
Sulfites, $(RO)_2SO$			
R			
open-chain			
methyl sulfite	[616 – 42 – 2]	$126–127_{101.3}$	
ethyl sulfite	[623 – 81 – 4]	$159–160_{101.3}$	
n-propyl sulfite	[623 – 98 – 3]	$82_{2.00}$	
isopropyl sulfite	[4773 – 13 – 1]	$78_{2.67}$	
n-butyl sulfite	[626 – 85 – 7]	$110_{1.73}$	
3-chloropropyl sulfite	[83929 – 99 – 1]	$162_{1.73}$	
phenyl sulfite	[4773 – 12 – 0]	$185_{2.00}$	13–16
cyclic			
ethylene sulfite	[3741 – 38 – 6]	$80_{3.72}$	
1,2-propylene sulfite	[1469 – 73 – 4]	$84_{3.92}$	
pentaerythritol,disulfite	[3670 – 93 – 7]		154
Organo hydrogen sulfates, $(RO)SO_3H$			
R			
methyl hydrogen sulfate	[75 – 93 – 4]	$130–140_{101.3}$ dec	
n-decyl hydrogen sulfate	[142 – 98 – 3]	liquid	
n-dodecyl hydrogen sulfate	[151 – 41 – 7]		25–27
n-tetradecyl hydrogen sulfate	[4754 – 44 – 3]		37–39
n-hexadecyl hydrogen sulfate	[143 – 02 – 2]		40–42
n-octadecyl hydrogen sulfate	[143 – 03 – 3]		51–52
phenyl hydrogen sulfate	[937 – 34 – 8]		
Organo halosulfates, $(RO)SO_2X$			
R, X			
methyl chlorosulfate	[812 – 01 – 1]	$134–135_{101.3}$, $42_{2.13}$	
methyl fluorosulfate	[421 – 20 – 5]	$92_{101.3}$, $45_{21.4}$	
ethyl chlorosulfate	[625 – 01 – 4]	$72_{15.6}$, $58_{2.66}$	
ethyl fluorosulfate	[371 – 69 – 7]	113_{100}, $21_{1.60}$	
n-propyl chlorosulfate	[819 – 52 – 3]	$53_{1.33}$	
isopropyl chlorosulfate	[36610 – 67 – 0]	$50_{0.67}$ dec	
Organo halosulfites, $(RO)SOX$			
R, X			
methyl chlorosulfite	[13165 – 72 – 5]	$35_{8.00}$	
ethyl chlorosulfite	[6378 – 11 – 6]	$50–53_{8.00}$	
n-propyl chlorosulfite	[22598 – 38 – 5]	$78_{10.0}$, $42_{1.69}$	
isopropyl chlorosulfite	[22598 – 56 – 7]	$71–73_{10.0}$, $55_{5.23}$	

[a] To convert kPa to mm Hg, multiply by 7.5; 101.3 kPa = 1 atm.

Table 2. Selected Physical Properties of Dimethyl and Diethyl Sulfate

Property	$(CH_3O)_2SO_2$	$(C_2H_5O)_2SO_2$
bp, at (101.3 kPa = 1 atm), °C	188.8	208 dec
13.3 kPa		143
1.33 kPa		88
mp, °C	−31.8	−24.4
sp $gr^{20}{}_{20}$	1.328	1.1803
$n^{20}{}_D$	1.3874	1.3396
solubility in water, wt %	2.8 at 18°C	0.7 at 20°C
flash point (open cup), °C	116	113
autoignition temp, °C	188	
heat of formation (liquid), kJ/mol[a, b]	687	757

[a] To convert J to cal, divide by 4.184.

[b] Ref. 3.

alkyl groups, the polar effects dominate, whereas with higher alkyl groups, the nonpolar interactions of the alkyl dominate.

The lower alkyl hydrogen sulfates are moderately viscous liquids. Higher alkyl hydrogen sulfates are hygroscopic, low melting solids; their hygroscopic nature results from the acid group, and their solid state results from the alkyl group orientation. They do not have boiling points, but decompose on heating.

Stability depends mostly on purity, with purer materials having longer shelf lives (1). For the higher alkyl groups, the anhydrous compounds are soluble and the monohydrates are insoluble in ether. Solutions in water are strongly ionized and acidic. The lower dialkyl sulfates are liquids with faint but pleasant odors; *n*-nonyl and higher normal aliphatic and cyclic sulfates are solids.

The diesters are moderately polar and therefore are miscible with most common organic solvents. Solubility in water is low-to-insoluble, with dimethyl sulfate having a water solubility of 2.8 g/100 mL at 18.0°C (2).

The sulfites have some laboratory use, but are not commercially important and are less known. Monoesters of sulfurous acid are quite unstable, although salts have been identified. The diesters of sulfurous acid are mostly liquids with boiling points somewhat less than those of the corresponding sulfates.

Many esters of halosulfurous acid and of halosulfuric acid are known, ie, halosulfites and halosulfates, respectively. With the smaller alkyl groups, the compounds are high boiling liquids with a penetrating odor and a lacrimatory action. Esters of halosulfuric acid are more stable to moisture when stored than those of halosulfurous acid.

Selected properties of dimethyl and diethyl esters of sulfuric acid are listed in Table 2.

2. Chemical Properties

2.1. Sulfates

The chemistry of alkyl sulfates is dominated by two fundamental process types: reaction with nucleophiles and reaction as acids. Reaction with nucleophiles results in alkylation.

2.2. Alkylation

In alkylation, the dialkyl sulfates react much faster than do the alkyl halides, because the monoalkyl sulfate anion ($ROSO^{-}{}_3$) is more effective as a leaving group than a halide ion. The high rate is most apparent with small primary alkyl groups, eg, methyl and ethyl. Some leaving groups, such as the fluorinated sulfonate anion, eg, the triflate anion, $CF_3SO^-{}_3$, react even faster in ester form (4). Against phenoxide anion, the reaction rate is methyl triflate [333-27-7] $\gg$ dimethyl sulfate $\gg$ methyl *p*-toluenesulfonate [23373-38-8] (5). Dialkyl sulfates, as compared to alkyl chlorides, lack chloride ions in their products; chloride corrodes and requires the use of a gas instead of a liquid. The lower sulfates are much less expensive than lower bromides or iodides, and they also alkylate quickly.

Although the first alkyl group is the most reactive, the second alkyl group on the intermediate anion can also alkylate. The temperature must be higher than needed for the first alkyl, and conditions favoring hydrolysis of sulfate ester, eg, the presence of water and alkali, should be minimized. As a general rule, alkylations by alkyl chloride are intermediate in rate between those of the corresponding dialkyl sulfates and alkyl hydrogen sulfates. In most reported reactions, only one alkyl group reacts. If the alkylated molecule acquires a positive charge, the monoalkyl sulfate anion becomes the negative counterion. This is illustrated in the common reaction of quaternization of a tertiary amine, eg, pyridine.

$$C_5H_5N + CH_3OSO_2OCH_3 \longrightarrow C_5H_5NCH^+{}_3 + CH_3OSO_3^-$$

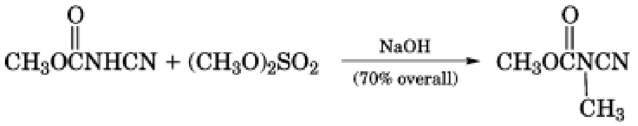
The reactions of these nucleophilic processes are usually S_N2 rather than S_N1. The reaction rate is methyl > ethyl > isopropyl, as with the alkyl halides. As the species to be alkylated becomes more nucleophilic, alkylation becomes faster, eg, a sulfur-containing anion alkylates more quickly than a phenolic anion.

Dimethyl sulfate and diethyl sulfate react with almost all types of compounds with unshared electron pairs, whether the reaction center is at oxygen, nitrogen, carbon, sulfur, phosphorus, some metals, or most other heteroatoms from Groups 15(VA) and 16(VIA). Alkylation at oxygen can occur with alcohols, phenols, or acids. Methylation of phenol to give the methyl ether or anisole is carried out commercially. With phenol alone, the reaction is slow with dimethyl sulfate at 100–120°C, giving anisole and some by-product dimethyl ether and sulfonation products (6). Reaction is much faster in basic medium, with phenolate ion as the reactant. The first methyl group reacts at 45–60°C upon addition of dimethyl sulfate to a mixture of molten phenol and sodium hydroxide containing very little water. Continuing the reaction by heating to 100°C results in the reaction of the second methyl group and a 95% yield of anisole (7–9). Ethylation of phenolate ion with diethyl sulfate requires higher temperatures, ie, ca 50–55°C, for the first ethyl group and 145°C for the second ethyl group. Numerous substituted phenols have been alkylated in either aqueous or alcoholic alkaline solutions, or dimethylformamide solution with K_2CO_3 (9–11). Thiophenols react faster than phenols in alkaline solution (12).

Alcohols react readily in alkaline solution. Conditions for pentaerythritol are typical (13). Use of alcoholic KOH in dimethyl sulfoxide gives fair to good ethyl ether yields with diethyl sulfate at 50–55°C (14).

Carboxylic acids react with the first alkyl group of dialkyl sulftes at 120°C to give esters in high yield, whereas the second alkyl group requires higher temperatures, ie, 200°C (15). The use of carboxylate salts of inorganic or organic bases gives fast esterification under neutral conditions (16). A highly branched acid, eg, trimethylacetic acid, converts readily to the methyl ester; dimethylformamide is a good medium (11, 17). Good conditions for diethyl sulfate with lower acids have been determined (18). Dimethyl or diethyl carbonate can be made by heating the corresponding sulfate and alkali–metal carbonate at 150–210°C, which illustrates the high activity of the sulfates (19). Sulfonic acids and their salts alkylate at 100°C (20, 21).

The nitrogen of aliphatic and aromatic amines is alkylated rapidly by alkyl sulfates yielding the usual mixtures. Most tertiary amines and nitrogen heterocycles are converted to quaternary ammonium salts, unless the nitrogen is of very low basicity, eg, in triphenylamine. The position of dimethyl sulfate-produced methylation of several heterocycles with more than one heteroatom has been examined (22). Acyl cyanamides can be methylated (23). Metal cyanates are converted to methyl isocyanate or ethyl isocyanate in high yields by heating the mixtures (24, 25).



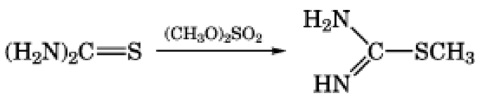
$$CH_3O\overset{O}{\overset{\|}{C}}NHCN + (CH_3O)_2SO_2 \xrightarrow[\text{(70\% overall)}]{\text{NaOH}} CH_3O\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{N}}CN$$

Carbon is alkylated in the form of enolates or as carbanions. The enolates are ambident in activity and can react at an oxygen or a carbon. For example, refluxing equimolar amounts of dimethyl sulfate and ethyl acetoacetate with potassium carbonate gives a 36% yield of the *O*-methylation product, ie, ethyl 3-methoxy-2-butenoate, and 30% of the *C*-methylation product, ie, ethyl 2-methyl-3-oxobutanoate (26). Generally, only one alkyl group of the sulfate reacts with beta-diketones, beta-ketoesters, or malonates (27). Factors affecting the O:C alkylation ratio have been extensively studied (28). Reaction in the presence of solid Al_2O_3 results mostly in *C*-alkylation of ethyl acetoacetate (29).

Carbanions in the form of phenyllithium, sodium naphthalene complex, sodium acetylide, or aromatic Grignard reagents react with alkyl sulfates to give a *C*-alkyl product (30–33). Grignard reagents require two moles of dimethyl sulfate for complete reaction.

Sulfur is reactive in many forms. Mercaptides are alkylated to thioethers, and thioethers react further to give sulfonium salts, $R_3S^+CH_3OSO^-{}_3$.

Suitable thiones also alkylate. Thioacridone (34) and thiourea (35) are examples: the first gives the alkylmetcaptoacridine and the second gives the isothiourea.



Several inorganic atoms have also been methylated by dimethyl sulfate. Sodium iodide gives methyl iodide, organoxytitanium dichloride gives several highly colored organoxytitanium methyl sulfates, titanium tetrachloride yields titanium chlorosulfates or methyl sulfates, and mossy tin gives dimethyltin sulfate (36–39).

These reactions involve mostly dimethyl and diethyl sulfate. Cyclic sulfates are also reactive, and several have been compared by determining reaction rates with a substituted pyridine or with water (40). In both cases, 1,2-ethylene sulfate is more reactive than 1,3-propylene sulfate or dimethyl or diethyl sulfates.

2.2.1. Hydrolysis

The hydrolysis of dialkyl and monoalkyl sulfates is a process of considerable interest commercially. Successful alkylation in water requires that the fast reaction of the first alkyl group with water and base be minimized. The very slow reaction of the second alkyl group results in poor utilization of the alkyl group and gives an increased organic load to a waste-disposal system. Data have accumulated since 1907 on hydrolysis in water under acid, neutral, and alkaline conditions, and best conditions and good values for rates have been reported and the subject reviewed (41–50).

Sulfates having alkyl groups from methyl to pentyl have been examined. With methyl as an example, the hydrolysis rate of dimethyl sulfate increases with the concentration of the sulfate. Typical rates in neutral water are first order and are $1.66 \times 10^{-4}\ s^{-1}$ at 25°C and $6.14 \times 10^{-4}\ s^{-1}$ at 35°C (46, 47). Rates with alkali or acid depend on conditions (42, 48). Rates for the monomethyl sulfate [512-42-5] are much slower, and are nearly second order in base. Values of the rate constant in dilute solution are 6.5×10^{-5} L/(mol·s) at 100°C and 4.64×10^{-4} L/(mol·s) at 138°C (44). At 138°C, first-order solvolysis is ca 2% of the total. Hydrolysis of the monoester is markedly promoted by increasing acid strength and it is first order. The rate at 80°C is $3.65 \times 10^{-4}\ s^{-1}$ (45). Alkaline solvolysis has been studied by a calorimetric method (49). Heat of hydrolysis of dimethyl sulfate to the monoester under alkaline conditions is 106 kJ/mol (25 kcal/mol) (51).

Cyclic esters show accelerated hydrolysis rates. Ethylene sulfate compared to dimethyl sulfate is twice as fast in weak acid (first order) and 20 times as fast in weak alkali (second order) (50). Catechol sulfate [4074-55-9] is 2×10^7 times faster than diphenyl sulfate in alkaline solution (52). Alcoholysis rates of several dialkyl sulfates at 35–85°C are also known (53).

Studies of reaction mechanisms in ^{18}O-enriched water show the following: cleavage of dialkyl sulfates is primarily at the C—O bond under alkaline and acid conditions, and monoalkyl sulfates cleave at the C—O bond under alkaline conditions and at the S—O bond under acid conditions (45, 54). An optically active half ester (*sec*-butyl sulfate [3004-76-0]) hydrolyzes at 100°C with inversion under alkaline conditions and with retention plus some racemization under acid conditions (55). Effects of solvent and substituted structure have been studied, with moist dioxane giving marked rate enhancement (44, 56, 57). Hydrolysis of monophenyl sulfate [4074-56-0] has been similarly examined (58).

Reactions other than those of the nucleophilic reactivity of alkyl sulfates involve reactions with hydrocarbons, thermal degradation, sulfonation, halogenation of the alkyl groups, and reduction of the sulfate groups. Aromatic hydrocarbons, eg, benzene and naphthalene, react with alkyl sulfates when catalyzed by aluminum chloride to give Friedel-Crafts-type alkylation product mixtures (59). Isobutane is readily alkylated by a dipropyl sulfate mixture from the reaction of propylene in propane with sulfuric acid (60).

2.2.2. Pyrolysis

Thermal stability of the dialkyl sulfate is of interest when using solutions in inert media, eg, hydrocarbons, or on storage of the neat compound. Heating dimethyl sulfate at ca 200°C produces dimethyl ether, SO_3, and other products (61). Higher alkyl sulfates, eg, the diethyl sulfates, decompose to give olefin and oxidation products rapidly at 220°C and slowly at 140°C (62). Heating higher monoalkyl hydrogen sulfates generally gives olefins also, but the monomethyl ester at 130–140°C gives dimethyl sulfate and sulfuric acid.

2.2.3. Sulfonation

Sulfonation is a common reaction with dialkyl sulfates, either by slow decomposition on heating with the release of SO_3 or by attack at the sulfur end of the O—S bond (63). Reaction products are usually the dimethyl ether, methanol, sulfonic acid, and methyl sulfonates, corresponding to both routes. Reactive aromatics are commonly those with higher reactivity to electrophilic substitution at temperatures $> 100°C$. Triphenylamine, diphenylmethylamine, anisole, and diphenyl ether exhibit ring sulfonation at 150–160°C, 140°C, 155–160°C, and 180–190°C, respectively, but diphenyl ketone and benzyl methyl ether do not react up to 190°C. Diphenylamine methylates and then sulfonates. Catalysis of sulfonation of anthraquinone by dimethyl sulfate occurs with thallium(III) oxide or mercury(II) oxide at 170°C. Alkyl interchange also gives sulfation.

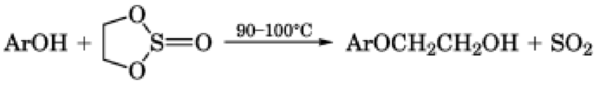
2.2.4. Miscellaneous

Halogenation of the methyl group of dimethyl sulfate by chlorine and by fluorine has been described (64, 65). Reduction of dimethyl sulfate by hydriodic acid occurs in a way that is comparable to that shown by sulfuric acid and results in reduction to sulfur (66).

2.3. Sulfites

The literature concerning dialkyl sulfites is extensive, although less than for sulfates. Reactions involving alkylation are similar to those of sulfates. Sulfites also undergo elimination, transesterification, and isomerization. The last two parallel reactions of phosphites.

In alkylation, phenols and amines are alkylated by sulfites in high yield and quaternary salts readily form (67). Ethylene sulfite reacts yielding hydroxyethyl derivatives and SO_2 elimination, corresponding to its activity as an ethylene oxide precursor (68).



Reaction of carboxylate ion with *p*-nitrophenyl sulfites gives the carboxylate *p*-nitrophenyl esters. If the *p*-nitrophenyl sulfite is unsymmetrical ($O_2NC_6H_4OS(O)OR$, where R is ethyl or phenyl), carboxylate attacks the *p*-nitrophenyl side (69). Some amino acids react with methyl and benzyl sulfites in the presence of *p*-toluenesulfonic acid to give methyl and benzyl esters of the amino acids as *p*-toluenesulfonate salts (70). With alcohols, the conversion of benzil to a monoacetal upon addition of sulfuric acid to the benzil in methanol and dimethyl sulfite proceeds in high yield (71).

Hydrolysis of dialkyl sulfites under acidic and alkaline conditions, which is followed by the use of $^{18}OH_2$, proceeds by attack at sulfur to give S–O cleavage (72). The rate of hydrolysis is generally faster for cyclic and aryl sulfites than for dialkyl sulfites (73). Activation parameters of hydrolysis are known for some sulfites, and the increased rate for ethylene sulfite results from a reduced entropy of activation which results from a rigid ring structure (74).

3. Manufacture

3.1. Monoester Hydrogen Sulfates

The hydrogen sulfates are prepared by the action of a sulfating agent on the corresponding alcohol or phenol. The following reagents are used for sulfation: sulfur trioxide, sulfuric acid, chlorosulfuric acid, sulfur trioxide–amine complexes, and sulfamic acid (see Sulfonation and sulfation). The latter two produce the amine salt of the sulfate ester directly. The reaction of sulfuric acid with olefins also gives hydrogen sulfates. These reactions are commercially important for the preparation of ethyl, 2-propyl, 2-butyl, and longer-chain sodium alkyl sulfates. The last are useful as detergents (see Alcohols, higher aliphatic–survey and natural alcohols manufacture). With the exception of ethylene, the olefins give esters of secondary alcohols.

Methyl hydrogen sulfate is obtained in yields of 98–99% upon treating sulfur trioxide with methanol below 0°C (75). Ethyl hydrogen sulfate [540-82-9] is obtained by the sulfation of ethylene with sulfuric acid to the mixed sulfate, followed by the addition of water to the reaction mixture and hydrolysis of any diethyl sulfate formed. It is usually carried out with 96–98 wt % sulfuric acid at 70 and 80°C and 500–1500 kPa (5–15 atm). The kinetics of this reaction have been thoroughly investigated (76). At 150°C and higher pressures with only 70 wt % acid followed by addition of just enough water for hydrolysis, the otherwise necessary reconcentration of the spent sulfuric acid is eliminated (77). Because of the severe corrosion under these conditions, tantalum equipment is necessary. Ethyl hydrogen sulfate can also be prepared in 87% yield by heating sodium hydrogen sulfate with ethanol; a 74–86% yield is obtained by the reaction of ethanol with sulfur trioxide in liquid sulfur dioxide solution or by treating diethyl sulfate with ethanol and distilling the ether *in vacuo* (78, 79).

$$(C_2H_5O)_2\,SO_2 + C_2H_5OH \longrightarrow (C_2H_5)_2\,O + C_2H_5OSO_3H$$

Propylene and butylene require much milder conditions for their sulfation with sulfuric acid. Butylene is sulfated at 30–50°C and 300–600 kPa (ca 3–6 atm) with 30–60 wt % sulfuric acid, and propylene is sulfated at 10–30°C and 500 kPa (ca 5 atm) with 65–85 wt % sulfuric acid. The rate of sulfation of propylene increases sharply with increasing pressure (80). It can also be increased by the addition of kerosene, which raises the concentration of olefin in the liquid phase (81).

Detergents have been manufactured from long-chain alkenes and sulfuric acid, especially those obtained from shale oil or cracking of petroleum wax. These are sulfated with 90–98 wt % acid at 10–15°C for a 5-min contact time and at an acid–alkene molar ratio of 2:1 (82). Dialkyl sulfate initially forms when 96 wt % acid is added to 1-dodecene at 0°C, but it is subsequently converted to the hydrogen sulfate in 80% yield upon the further addition of sulfuric acid. The yield can be increased to 90% by using 98 wt % sulfuric acid and pentane as the solvent at -15°C (83).

Long-chain alcohols, such as are obtained by the hydrogenation of coconut oil, polymerization of ethylene, or the oxo process (qv), are sulfated on a large scale with sulfur trioxide or chlorosulfuric acid to acid sulfates; the alkali salts are commercially important as surface-active agents (see Surfactants). Poly(vinyl alcohol) can be sulfated in pyridine with chlorosulfuric acid to the hydrogen sulfate (84).

Some substituted alkyl hydrogen sulfates are readily prepared. For example, 2-chloroethyl hydrogen sulfate [36168-93-1] is obtained by treating ethylene chlorohydrin with sulfuric acid or amidosulfuric acid. Heating hydroxy sulfates of amino alcohols produces the corresponding sulfuric monoester (85).

Because phenolic compounds are easily sulfonated, their sulfation must be accomplished with milder sulfating agents, eg, complexes of sulfur trioxide or chlorosulfonic acid with trimethylamine, dimethylformamide, pyridine, or dimethylaniline, in anhydrous or aqueous medium below 100°C (86–89).

Salts of alkyl hydrogen sulfates that are free of sulfuric acid can be prepared from crude hydrogen sulfates containing $ROSO_3H$ and sulfuric acid in a two-step reaction. First, the crude product reacts in aqueous solution with the hydroxide or carbonate of a metal whose sulfate is insoluble in water. After filtration of the insoluble metal sulfate, the necessary amount of a water-soluble metal sulfate is added to the filtrate, which precipitates the insoluble metal sulfate, leaving the desired salt of the alkyl hydrogen sulfate in solution.

3.2. Diorgano Sulfates

Dialkyl sulfates up to octadecyl can be made from the alcohols by a general method involving the following reactions (90):

$$\mathrm{ROH + SO_2CL_2 \longrightarrow ROSO_2Cl + HCl}$$

$$\mathrm{2\ ROH + SOCl_2 \longrightarrow (RO)_2\,SO + 2\ HCl}$$

$$\mathrm{ROSO_2Cl + (RO)_2\,SO \longrightarrow (RO)_2\,SO_2 + RCl + SO_2}$$

Another method involves the reaction of dialkyl sulfites with sulfuryl chloride (91):

$$\mathrm{2\ (RO)_2\,SO + SO_2Cl_2 \longrightarrow (RO)_2\,SO_2 + 2\ ROSOCl}$$

Mixed esters are synthesized by the reaction of one alkyl chlorosulfate with a different sodium alkoxide or a different dialkyl sulfite as follows (92):

$$\mathrm{ROSO_2Cl + NaOR' \longrightarrow ROSO_2OR' + NaCl}$$

$$\mathrm{ROSO_2Cl + \left(R'O\right)_2 SO \longrightarrow ROSO_2OR' + R'Cl + SO_2}$$

Table 3. Properties of a Commercial Dimethyl Sulfate

Property	Typical value
acidity as H_2SO_4, %[a]	0.11
bp, at 101.3 kPa ($= 1$ atm), °C	
at 95%	190.4
97%	192.0
1–97%	5.0 range
color[b]	passes 0.0001 *N* iodine
sp $gr^{15.6}{}_{15.6}$	1.334

[a] Determined by nonaqueous titration.

[b] This test is a visual comparison of the color of dimethyl sulfate with that of a 0.0001 *N* iodine solution. Commercial dimethyl sulfate should be lighter in color.

The only commercially important dialkyl sulfates are dimethyl sulfate and diethyl sulfate. Estimated worldwide production in 1996 for dimethyl sulfate was 90,000 metric tons per year. Dimethyl sulfate was initially made by vacuum pyrolysis of methyl hydrogen sulfate:

$$2\ CH_3OSO_2H \longrightarrow (CH_3O)_2\,SO_2 + H_2SO_4$$

Later it was synthesized in a batch process from dimethyl ether and sulfur trioxide (93) and this combination was adapted for continuous operation. Gaseous dimethyl ether was bubbled at 15.4 kg/h into the bottom of a tower 20 cm in diameter and 365 cm high and filled with the reaction product dimethyl sulfate. Liquid sulfur trioxide was introduced at 26.5 kg/h at the top of the tower. The mildly exothermic reaction was controlled at 45–47°C, and the reaction product (96–97 wt % dimethyl sulfate, sulfuric acid, and methyl hydrogen sulfate) was continuously withdrawn and purified by vacuum distillation over sodium sulfate. The yield was almost quantitative, and the product was a clear, colorless, mobile liquid. A modified process is described in Reference 94. Properties are listed in Table 3.

Diethyl sulfate can be prepared by a variety of methods. When ethyl hydrogen sulfate is heated with sodium chloride to 80°C, hydrogen chloride is liberated. The resulting reaction mixture is then distilled at 1.33–2.00 kPa (10–15 mm Hg) at a maximum kettle temperature of 190°C to give diethyl sulfate in 90% yield (95).

$$2\ C_2H_5OSO_3H + NaCl \longrightarrow C_2H_5OSO_3H + C_2H_5OSO_3Na + HCl$$

$$C_2H_5OSO_3H + C_2H_5OSO_3Na \longrightarrow (C_2H_5O)_2\,SO_2 + NaHSO_4$$

Passing a stream of nitrogen at 95–100°C through a reaction mixture of ethyl ether and 30 wt % oleum prepared at 15°C results in the entrainment of diethyl sulfate. Continuous operation provides a $>50\%$ yield (96). The most economical process for the manufacture of diethyl sulfate starts with ethylene and 96 wt % sulfuric acid heated at 60°C. The resulting mixture of 43 wt % diethyl sulfate, 45 wt % ethyl hydrogen sulfate, and 12 wt % sulfuric acid is heated with anhydrous sodium sulfate under vacuum, and diethyl sulfate is obtained in 86% yield; the commercial product is $>99\%$ pure (97).

Lower dialkyl sulfates were made from the alcohols in earlier work; the reaction mass at ca 100°C was stripped by a recirculated inert-gas stream, and the product was recovered by passage through a partial condenser. Yields of 90% for diethyl sulfate and 85% for dimethyl sulfate were reported (98).

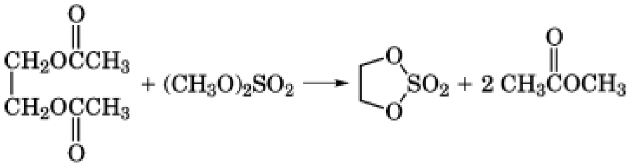
In the reaction of ethylene with sulfuric acid, several side reactions can lead to yield losses. These involve oxidation, hydrolysis–dehydration, and polymerization, especially at sulfuric acid concentrations >98 wt %; the sulfur trioxide can oxidize by cyclic addition processes (99).

Dimethyl and diethyl sulfate are available in a variety of containers from 0.5-kg glass bottles to tank cars. Diethyl sulfate is somewhat less toxic than dimethyl sulfate and is considered noncorrosive, but dimethyl sulfate is classified as a corrosive liquid and ICC regulations must be observed. Mild steel to 306 stainless steel is used for large-volume storage. Dimethyl sulfate is manufactured by E. I. du Pont de Nemours & Co., Inc., and diethyl sulfate by Union Carbide Corporation. Other producers are Rhône-Poulenc and Hoechst-Celanese.

Cyclic sulfates can be prepared by a variety of methods. Ethylene sulfate is obtained in low yield from ethylene oxide and sulfur trioxide (100). Methylene sulfate is produced from formaldehyde and sulfur trioxide (101).

Oxidation of cyclic sulfites with permanganate in acetic acid solution gives cyclic sulfates (102). Heating monohydroxyalkyl hydrogen sulfates with thionyl chloride causes ring closure (103).

Acidolysis of cyclic sulfites with sulfuric acid and ester interchange with dimethyl sulfate produce cyclic sulfates (104).



3.3. Diorgano Sulfites

Symmetrical or mixed dialkyl sulfites are prepared by the stepwise reaction of thionyl chloride either with two molecules of an alcohol or with stoichiometric quantities of two alcohols in pyridine (105).

$$\mathrm{ROH + SOCl_2 + C_5H_5N \longrightarrow ROSOCl + C_5H_5N{\cdot}HCl}$$

$$\mathrm{R'OH + ROSOCl + C_6H_5N \longrightarrow R'OSOOR + C_5H_5N{\cdot}HCl}$$

An alternative route is the reaction of iodine or bromine in pyridine with liquid sulfur dioxide at 20°C, which gives good to high yields of sulfites (106).

Heating the adduct of ethylene oxide and sulfur dioxide with primary alcohols in the presence of alkali hydrides or a transition-metal halide yields dialkyl sulfites (107). Another method for the preparation of methyl alkyl sulfites consists of the reaction of diazomethane with alcoholic solutions of sulfur dioxide (108).

$$\mathrm{ROH + CH_2N_2 + SO_2 \longrightarrow ROSOOCH_3 + N_2}$$

Cyclic sulfites can be prepared from the glycols and thionyl chloride in the presence of pyridine; this route is analogous to the preparation of dialkyl sulfites (109). Cyclic sulfites are also obtained when the polymerization product of alkylene oxides with sulfur dioxide is decomposed by heating (110). Ester exchange proceeds smoothly with dimethyl sulfite and glycerol or its chlorohydrins to yield the cyclic sulfites (111). Glycerol gives poor results with thionyl chloride.

Aromatic polysulfites can be produced if bisphenols, eg, bisphenol A, are heated with diphenyl sulfite in the presence of lithium hydride (112).

3.4. Halosulfates and Halosulfites

A general method for the preparation of alkyl halosulfates and halosulfites is the treatment of the alcohol with sulfuryl or thionyl chloride at low temperatures while passing an inert gas through the mixture to remove hydrogen chloride (113).

$$\mathrm{ROH + SO_2Cl_2 \longrightarrow ROSO_2Cl + HCl}$$

$$\mathrm{ROH + SOCl_2 \longrightarrow ROSOCl + HCl}$$

This method is also used with alcohols of the structure $\mathrm{Cl(CH_2)}_n\mathrm{OH}$ (114). Haloalkyl chlorosulfates are likewise obtained from the reaction of halogenated alkanes with sulfur trioxide or from the chlorination of cyclic sulfites (115, 116). Chlorosilanes form chlorosulfate esters when treated with sulfur trioxide or chlorosulfuric acid (117). Another approach to halosulfates is based on the addition of chlorosulfuric or fluorosulfuric acid to alkenes in nonpolar solvents (118).

4. Health and Safety Factors

The most commonly used dialkyl sulfate is dimethyl sulfate. This is also the most hazardous in liquid and vapor forms. The hazard arises from its toxicity, high reactivity, and to some extent, combustibility. Dimethyl sulfate is corrosive and poisonous, and its effects may be either acute or chronic. Because it has an analgesic effect on many body tissues, even severe exposures may not be immediately painful. Dimethyl sulfate is particularly dangerous to the eyes and respiratory system. It causes severe burns, but symptoms may be delayed. Exposed workers must be immediately and properly treated to avoid either permanent injury to eyes and lungs or even death. Skin burns can also be severe. Ingestion causes convulsions and paralysis, with later damage to the kidneys, liver, and heart (119–121). Genetic effects have been extensively reviewed, and its mutagenicity is correlated with carcinogenicity (122, 123).

According to the U.S. Department of Labor (OSHA), exposure to dimethyl sulfate shall not exceed an eight-hour time-weighted average of 1 ppm in air (119). Because both liquid and vapor can penetrate the skin and mucous membranes, control of vapor inhalation alone may not be sufficient to prevent absorption of an excessive dose. Dimethyl sulfate is listed as an industrial substance with suspected carcinogenic potential in humans (119). Thus, the ACGIH recommends a time-weighted average threshold limit value of 0.1 ppm, based on tests with laboratory animals.

Dimethyl sulfate lacks warning properties. It looks like water when spilled and has no distinctive odor; these characteristics mandate careful handling, but its high boiling point permits safe usage with careful attention to procedure. No work should be undertaken with dimethyl sulfate or diethyl sulfate until the worker has studied and understood the precautions, procedures, and exposure effects given in the material safety data sheets, in several government publications, and in the product bulletins for the materials (120, 121, 124–127). Protective equipment is essential. Clothing and gloves should be made of butyl rubber. All operations should take place in a hood or in an area with good ventilation. Concentrations in air of 10 ppm or higher are immediately dangerous to life and health, and self-contained breathing apparatus must be used (127). Exposure to 97 ppm for 10 min can be fatal. In the laboratory, only mechanical pipetting is safe. Protective sleeves, aprons, and face shields are used. If the liquid should contact the skin, the exposed areas should be flushed immediately with water and then soaped and rinsed thoroughly. The victim should receive medical attention. Treatment for other exposures is described in References 120 and 121.

Because dimethyl sulfate looks like water, operations are preferably not performed when water is present, eg, wet floors or rain. Any spills or leaks should not be left unattended; they should be contained, and runoff to sewers should be avoided. Minor spills should be flooded with water to dilute and hydrolyze the dimethyl sulfate. The area should then be covered with a dilute (2–5 wt %) caustic solution or a dilute (2–5 wt %) ammonia solution, or soda ash may be sprinkled over the neat liquid and the mix wetted with a gentle spray of water. The neutralizing agent should remain on the affected area for 24 h and then should be washed away. Only personnel wearing protective equipment should perform these operations. The product bulletins should be consulted for procedures to be followed for more severe spills. Concentrated ammonia should not be used with neat dimethyl sulfate because explosions have resulted after their contact (128).

In the laboratory, excess reagent in a product should be destroyed before workup. Addition of diluted aqueous ammonia is the most effective practice, if ammonia is otherwise acceptable. Combustibility is a minor problem. The open-cup flash point of 116°C for dimethyl sulfate is well above normal handling temperatures. Flammable, toxic vapors are given off at elevated temperatures.

The acute toxicities of various sulfates have been reported (126). Generally, dimethyl sulfate (LD_{50} 440 mg/kg in rats) is more toxic than diethyl sulfate (LD_{50} 880–1412 mg/kg in rats), which is more toxic than dibutyl sulfate (lowest observed toxic dose, 9500 mg/kg in rats). Ethylene sulfate is more toxic than dimethyl sulfate (40).

The monoalkyl derivatives in salt form appear to have low toxicity. The monomethyl sulfate sodium salt has an approximate oral lethal dose greater than 5000 mg/kg of body weight for rats (129). Monododecyl sulfate sodium salt is widely marketed as a detergent and shampoo ingredient (oral LD_{50} 1268 mg/kg for rats) (126). Both dimethyl sulfate and monomethyl sulfate occur in the environment in coal fly-ash and in airborne particulate matter (130).

5. Uses

The sulfuric acid esters as compared to the sulfurous esters are the most widely used. In nature they appear as solubilizing groups in detoxification–excretory mechanisms and as sulfated carbohydrate groups in modified proteins. The significant uses are alkylation, formation of long-chain alcohol monosulfates as surfactants, and formation of intermediates in preparation of some lower alcohols. Alkylation (qv) involves primarily dimethyl and diethyl sulfates in the preparation of a wide variety of intermediates and products, especially in the fields of dyes, agricultural chemicals, drugs, and other specialties. In particular, dimethyl sulfate is a powerful reagent yielding quaternary salts in the form of the methosulfates. The use of dimethyl sulfate instead of methyl iodide can be useful when alkylations are carried out in dimethylformide (131). Some quaternary ammonium salts are also surfactants and fabric softeners (132) (see Quaternary ammonium compounds).

Minor uses include those as dyes, intermediates, stabilizers, and some specialty polymers. It is not always clear which uses are commercial and which are only alleged. One type of fiber-reactive dye has a pendent alcohol sulfate group. This group reacts with cotton in an alkaline pad to produce both an ether–cellulose bond and thereby a washfast dye, eg, Remazol dyes (Hoechst). Methyl hydrogen sulfate was once used as a solvent in the bromination of indigo (133). Dimethyl sulfate is also used with boron compounds to stabilize liquid sulfur trioxide (134). Modified polymers, mostly in the form of polyquaternary salts, have some use as coagulants for slimes, suspensions, and emulsions and as antistatic agents (qv) (135) (see Flocculating agents).

Proposed uses of the esters are numerous, but their applications in the modification of cotton, in catalysis, and as solvents are most prominent. The introduction of the aminoethyl group into cotton by the reaction of aminoethyl sulfate on alkali-swollen cotton is well known (136). The basic group provides a dye site for acid dyes. Catalyst activity has been reported for ionic, organometallic, and free-radical routes. Acidic activity of monoalkyl sulfates is used to promote hydrolysis of poly(vinyl acetate) and to quench the base-catalyzed polymerization of epoxides (137, 138). Some pyrolysis reactions are catalyzed by the presence of dimethyl sulfate, eg, in the formation of ketene from the thermal cracking of acetic acid or alkyl acetate and in the formation of 1,3-dihydroxypropene ether and acrolein acetals from 1,1,3-trihydroxypropane ethers at 200–450°C (139, 140). The alkylation of phenol with isobutylenes is promoted by catalytic amounts of dimethyl sulfate (141). Some care is needed in interpreting the catalytic effect of dialkyl sulfates. Many reactions in which activity exists are probably susceptible to acid catalysis. The sulfate can cause the formation of acids either by hydrolysis or by pyrolysis. For example, dimethyl sulfate is a curing agent for furfuryl alcohol condensates, because the neutral ester is a source of sulfuric acid when heated to 180°C (142). Cationic activity in catalysis is shown in the promotion of tetrahydrofuran polymerization by ethyl chlorosulfate and in the initiation of polymerization of several heterocycles (143, 144) (see Polyethers, tetrahydrofuran and oxetane polymers).

Organometallic usage is shown in the preparation of titanium- or vanadium-containing catalysts for the polymerization of styrene or butadiene by the reaction of dimethyl sulfate with the metal chloride (145). Free-radical activity is proposed for the quaternary product from dimethylaniline and dimethyl sulfate and for the product from 1,1,4,4-tetramethyl-2-tetrazene and dimethyl sulfate (146, 147).

Several solvent uses have been proposed. Dimethyl sulfate has been used as a solvent for the study of Lewis acid–aromatic hydrocarbon complexes (148). It also is effective as an extraction solvent to separate phosphorus halide–hydrocarbon mixtures and aromatic hydrocarbons from aliphatics, and it acts as an electrolyte in electroplating iron (149–152). The toxicity of dimethyl sulfate precludes its use as a general-purpose solvent.

A mixture of dimethyl sulfate with SO_3 is probably dimethyl pyrosulfate [10506-59-9], $CH_3OSO_2OSO_2OCH_3$, and, with chlorobenzene, it yields the 4,4′-dichlorodiphenylsulfone (153). Trivalent rare earths can be separated by a slow release of acid into a solution of rare earth chelated with an ethylenediaminetetraacetic acid agent and iodate anion. As dimethyl sulfate slowly hydrolyzes and pH decreases, each metal is released from the chelate in turn and precipitates as the iodate, resulting in improved separations (154).

A number of mixed alkyl and aryl sulfites have been patented as insecticides and biocides (155) (see Insect control technology). Other proposed uses include a polysulfite as a sensitizer in photographic emulsion, diethyl sulfite for the removal of catalyst fragments in polypropylene, and ethylene sulfite as an accelerator for aminoplastic molding compositions (156–158) (see Amino resins and plastics; Photography). A mixed, cyclic sulfite–carbonate ester of pentaerythritol has been polymerized to high molecular weight solids, which can be used in preparing laminates (159). Use of dimethyl sulfate as an electrolyte in high energy-density batteries has also been described (160) (see Batteries).

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