Theoretical Aspects of Sulfonation and Sulfation

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Sulfonation of Aromatics

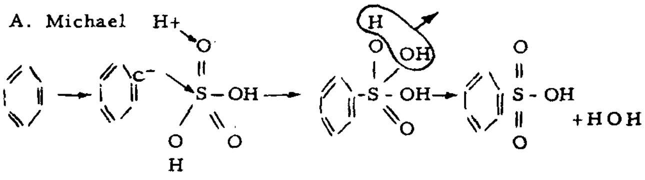
A. Introduction

During the past 10 years much fundamental research has been done on the composition of sulfuric acid solutions. Workers at Penn State (1), the University of London (2), and the University of Glasgow (3, 4), using precise techniques and modern optical methods, have measured the true acidity of sulfuric acid-water mixtures and have determined rates of reactions of these mixtures with different aromatic compounds. All this work has resulted in some rather complicated equations, which appear to indicate what is happening during sulfonation reactions. Rather than attempt to discuss these equations, I plan to summarize some of their findings, then to tie together a number of aspects of sulfonation.

B. Dilute Sulfuric Acid

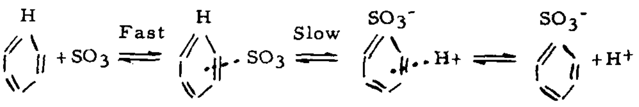
First, let's consider the reaction of dilute sulfuric acid (77–87%) with benzene. Not too long ago it was proposed (5) that the benzene reacted by ionizing and adding across one of the S = O bonds:

A. Michael



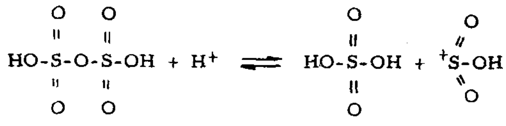
Many other theories have also been proposed. The most recent is by some English workers (2), who studied this reaction and came to the conclusion that free sulfur trioxide present in trace amounts is the actual sulfonating agent. This mechanism is based on a study of desulfonation reaction and an analysis of their kinetic data. These steps are much more plausible as far as modern theories of reaction are concerned and have experimental data to back them.

B. Gold $H_2SO_4 \rightleftharpoons H_2O + SO_3$



On going to fuming H_2SO_4, there appears to be a different type of reaction. Between 98 and 101% H_2SO_4 there is an abrupt rise in the acidity (3). In this region pyrosulfuric acid, a stronger acid than sulfuric acid, is appearing (Figure 1). Under strong acid conditions this pyrosulfuric acid can break down into two ionic species:

$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7$ (Pyrosulfuric Acid)



$$\mathrm{HO\text{-}\overset{O}{\underset{O}{S}}\text{-}O\text{-}\overset{O}{\underset{O}{S}}\text{-}OH} + H^+ \rightleftharpoons \mathrm{HO\text{-}\overset{O}{\underset{O}{S}}\text{-}OH} + {}^+\mathrm{\overset{O}{\underset{O}{S}}\text{-}OH}$$

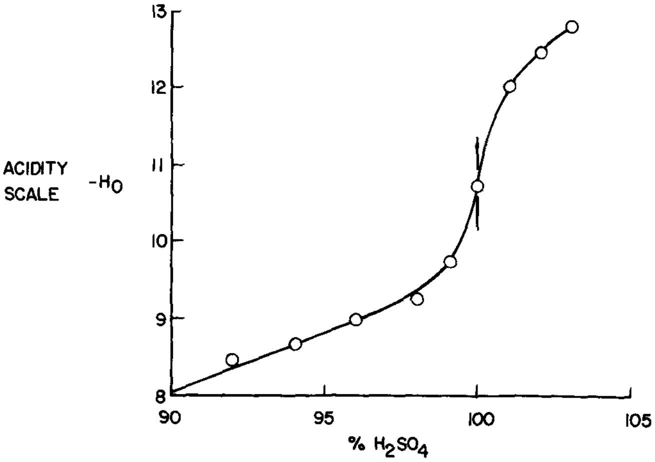
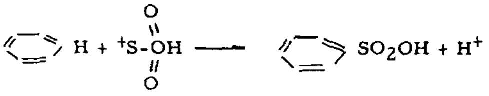
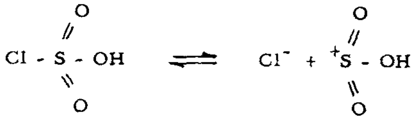


FIG. 1. Plot of data from brand: aromatic sulfonation J. Chem. Soc., p. 1002 (1950).

During sulfonation this cation is believed to be the reacting species

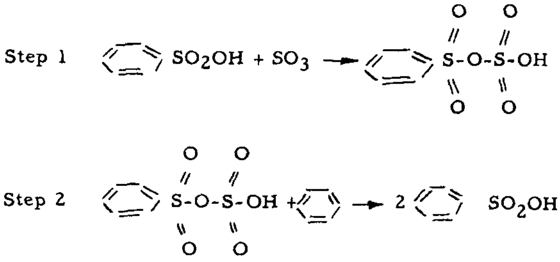


Chlorosulfonic acid, another sulfonating agent, also involves this cation

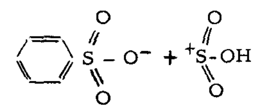


$$\mathrm{Cl\text{-}\overset{O}{\underset{O}{S}}\text{-}OH} \rightleftharpoons \mathrm{Cl^-} + {}^+\mathrm{\overset{O}{\underset{O}{S}}\text{-}OH}$$

However chlorosulfonic acid is not generally used for aromatic sulfonations as it tends to form sulfonyl chlorides by a side reaction. In connection with this cation a recent patent (6) claims to avoid sulfone formation by a 2-step reaction.



The mixed anhydride formed in Step 1 must break to give the following ions:



The same cation then is again the actual sulfonating agent.

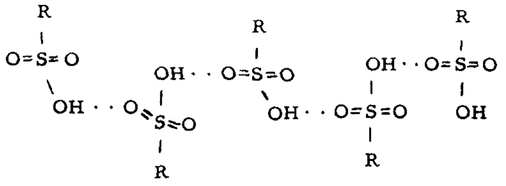
Sulfur Trioxide. As one goes to the higher fuming acid concentrations towards sulfur trioxide, one finds side reactions becoming more and more important. Sulfuric acid will not react with low molecular weight normal hydrocarbons, even at elevated temperatures, whereas sulfur trioxide will at almost any temperature. To prevent undesirable reactions it is usually complexed with other hydrocarbons such as dioxane, pyridine, or even polyethylene oxide. These complexes tie it up and then release it to permit an orderly reaction. To minimize color degradation, sulfur trioxide is usually directly reacted with dodecyl benzene by one of three methods:

a) an "acid heel" technique [here a small amount (about 10 vol. %) of 96% sulfuric acid in the alkylate reacts with an air stream containing about 6% sulfuric trioxide to generate $H_2S_2O_7$];

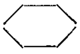
b) use of a dilute air stream containing SO_3 (this gives a low salt product, but heat transfer, mixing, and color problems become quite important; higher temperatures may be used with this and the above method); and

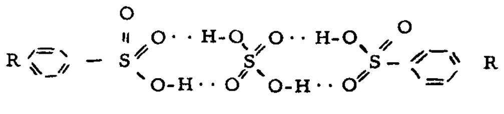
c) sulfonation with a liquid mixture of SO_3 plus an inert low boiling liquid as SO_2 (here the low temperature evaporation of the SO_2 removes the heat of reaction and fluxes the mix).

One of the major problems met with in the b) method is the large increase in viscosity found near the point at which all the dodecyl benzene has reacted. This may well be caused by association of the acid groups to give some such polymeric structure as:

A.


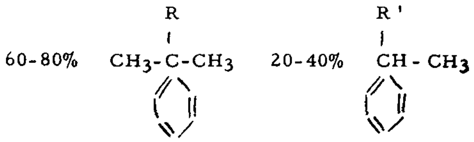
Addition of free sulfuric acid appears to break up such structures as the viscosity drops abruptly.

It is possible to extract what appears to be an $H_2SO_4 - R$  SO_2OH complex from an anhydrous sulfonation mix made from dodecyl benzene by the use of light paraffins, such as 2-methyl pentane. Analysis of the extract shows approximately two moles of sulfonic acid to one of sulfuric acid in the complex. Moreover infrared shows that −OH bonds of the free sulfuric acid are missing. This complex may then be some structure such as:

B.


C. Steric Factors in Sulfonation

If toluene is sulfonated with concentrated sulfuric acid, there will be formed a ratio of about 4 to 1 of paratoluene sulfonic acid to ortho toluene sulfonic acid. On going to more complicated mono-alkyl benzenes (ethyl benzene, isopropyl benzene, and t-butyl benzene) the amount of ortho sulfonation greatly decreases. T-butyl benzene has very little, if any, ortho sulfonation. Commercial dodecyl benzene is a mixture of about 60–80% of the t-butyl-type structure adjacent to the benzene ring and 20 to 40% of the isopropyl-type structure:

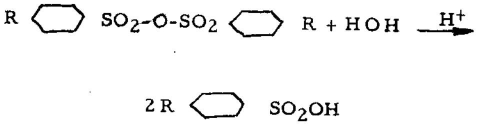


There is thus a strong influence, presumably because of the above mentioned steric factors, toward para substitution. Infrared analyses show 95+% para substitution. This selective sulfonation is a result of both the large size of the alkyl group and the bulk of the entering acid ion.

D. Side Reactions

Sulfone Formation. In sulfonating dodecyl benzene, one rarely finds large amounts of sulfones (>1%). This is somewhat surprising as the literature contains numerous references to sulfonates of toluene or xylene which contain 10 to 20% sulfones. It appears that most of these workers used higher temperatures and other conditions unsuitable for detergent manufacture. For instance, some time ago we investigated the sulfonation of toluene with a 60% concentrated fuming sulfuric acid. The initial experiments were rather erratic as to mixing and temperature control and products having 8 to 12% sulfone were obtained. The equipment and technique were then improved, reaction temperatures were carefully controlled and now products having about 1% sulfone were obtained, even though the same ratios of reactants were used.

Sulfonic Anhydride. This unusual compound was identified only recently in a neutralized sulfonation mix, in which the sulfonation had been made by an air stream containing SO_3 (7). It is found in neutralized slurry, in which some excess sulfur trioxide had been added prior to neutralization. It is separable by means of hydrocarbon solvents from the neutralized sulfonate. If it is not destroyed by addition of a small percentage of water to the mix prior to neutralization, it will give an acid pH drift to the sulfonate. Ordinary "watering out" procedures used in detergent manufacture will destroy this compound, if present.



Oxidation of the Aromatic Nucleus. If one attempts to sulfonate benzene with a 60% fuming acid mix, a light-colored product usually results; with toluene a darker product results; and with xylene, under the same conditions, a very dark-colored product is always found.

Here the aromatic nucleus is being oxidized to give dark-colored quinoid-type compounds. The effect is enhanced by the presence of alkyl side-chains. One is tempted to conclude that dodecyl benzenes which contain any dialkyl benzene would give dark-colored products. This could also explain why dodecyl toluene sulfonates give a darker product than dodecyl benzene.

Oxidation of Side Chain. Most of the oxidation reactions appear to be taking place on the branched side-chain. Although the exact mechanism is uncertain, the sulfuric acid is reduced in the process, accompanied by hydrogen removal and oxidation to water. The initial attack appears to be taking place at the tertiary hydrogen atoms where the chain branches. A number of possible reactions then may occur such as hydrogen transfer, chain scission, proton ejection, and cyclization (Figure 2). The olefins produced by the second and third reactions may be sulfated or sulfonated. Some of the products are dark in color and extremely difficult to bleach.

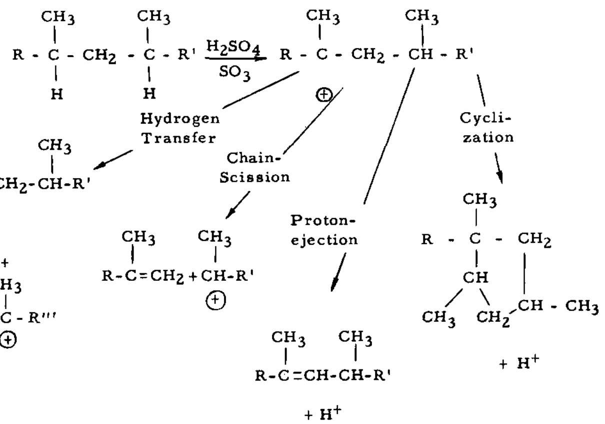


FIG. 2. Reactions of the alkyl side chain.

Three aspects of this oxidation should be noted. The sulfur dioxide that is formed is a measure of the oxidative degradation. As water is also formed during this degradation, it will combine with the sulfur trioxide and eventually end up as inorganic salt in the detergent. Dark-colored sulfonates will tend to have high salt contents when SO_3 is used as a sulfonating agent to make low salt products.

Dealkylation. In any strong acid medium, *e.g.*, the sulfonation mix, it might be expected that a reverse alkylation could take place giving back the original olefin and benzene. Under the sulfonation conditions the benzene would certainly sulfonate, but we have so far failed to find any evidence of benzene sulfonic acid in the spent acid.

Alcohol Sulfates or Pyrosulfonates in Alkyl Aryl Sulfonates. If one sulfonates the bottoms from dodecyl benzene manufacture under rather drastic sulfonating conditions, these sulfonic acids will be formed. They are similar in many respects to the previously mentioned anhydrides except that they liberate sulfuric acid under hydrolysis conditions. This can affect the salt content of oil-soluble sulfonates where low salt products are desired. The hydrolysis reaction is as follows:

Either

$$R\text{'}O\cdot SO_2ONa + HOH \rightarrow ROH + NaHSO_4$$

Or

$$RSO_2OSO_3Na + HOH \rightarrow RSO_2ONa + H_2SO_4$$

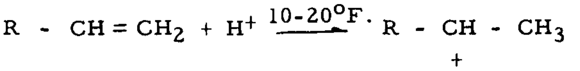
Products in the Alkylate that Can React to Give Sulfonate Color. There are two products often found in the alkylate that can cause dark colored sulfonate. In any alkylation a certain amount of the polymer winds up with the spent alkylation catalyst. Here it undergoes considerable chemical changes. On hydrolysis of the catalyst it is recovered as a yellow- or red-colored oil. Some of it boils in the dodecyl benzene range. This oil gives a very intense color instantaneously with 96% H_2SO_4.

A second by-product is found when too much catalyst or too long a contact with the catalyst occurs. Here the dodecyl benzene is actually degraded to give cyclo alkyl-type benzene compounds. These may be identified by their slower darkening during sulfonation or in contact with 96% H_2SO_4 at room temperature.

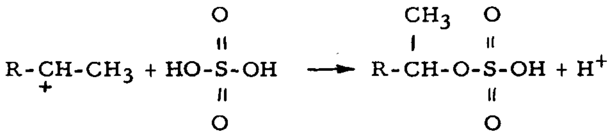
Sulfation of Olefins

For our purposes olefins can be divided into three types: a) primary olefins—propylene; b) secondary olefins—butene-2; and c) tertiary olefins—isoamylene or isobutylene. Because of certain rules of substitution discovered by Markownikoff many years ago, the a) and b) types always give a secondary alkyl sulfate derivative. The c) type is undesirable as it gives an unstable tertiary sulfonate and subsequent side reactions.

At low temperatures the carbonium ion will react with the 96% sulfuric acid.



$$R-CH=CH_2 + H^+ \xrightarrow{10\text{-}20°F.} R-CH-\underset{+}{CH_3}$$



$$R-\underset{+}{CH}-CH_3 + HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH \rightarrow R-\overset{CH_3}{CH}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH + H^+$$

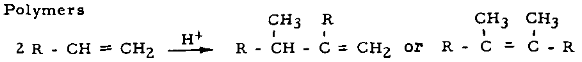
On passing into excess caustic, the sodium salt of the alcohol sulfate is obtained.

The reaction is shown, using the primary or α olefin as they are often called, as the nearer the sulfonate is to the end of the hydrocarbon chain, the better the foaming ability of the resulting surfactant.

There is some rather tricky chemistry here to lead one astray. The following are important to reduce side reactions:

a) *a low temperature*—if the temperature is raised to 30–40°F., side reactions take over completely and only dimers are found. These can further polymerize

Polymers



$$2R-CH=CH_2 \xrightarrow{H^+} R-\overset{CH_3}{CH}-\overset{R}{C}=CH_2 \text{ or } R-\overset{CH_3}{C}=\overset{CH_3}{C}-R$$

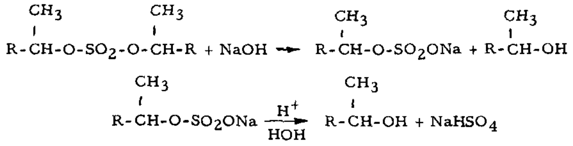
and are quite unsuitable, being tertiary-type olefins. It appears that "Teepol" is sulfonated with refrigeration, *e.g.*, liquid propane.

b) *concentrated sulfuric acid*—96% is satisfactory, more dilute will initiate reactions, but it takes a relatively strong acid to stabilize the desired sulfonic acid so that it does not undergo side reactions.

c) *a high ratio of acid to olefin*—not only is sufficient acid needed to react with olefin, but it appears that excess is desirable to complex with the sulfonic acids once they have been formed.

d) *an apparatus which gives a short contact time with very rapid mixing*—the olefin must be dispersed rapidly so that it can react with the acid and not polymerize with itself. Once reacted, it should be neutralized quickly as reverse reactions can take place. One other reaction should be mentioned here. During the sulfonation considerable amounts of dialkyl sulfates are formed. These are decomposed in a hydrolysis step which uses up part of the excess alkalinity. There is thus formed an additional molecule of detergent and one of the free alcohol.

I have mentioned the "careful control" of the excess caustic. If this system goes strongly acid and is heated another side reaction occurs.



$$\text{R-}\overset{\text{CH}_3}{\text{CH}}\text{-O-SO}_2\text{-O-}\overset{\text{CH}_3}{\text{CH}}\text{-R} + \text{NaOH} \longrightarrow \text{R-}\overset{\text{CH}_3}{\text{CH}}\text{-O-SO}_2\text{ONa} + \text{R-}\overset{\text{CH}_3}{\text{CH}}\text{-OH}$$

$$\text{R-}\overset{\text{CH}_3}{\text{CH}}\text{-O-SO}_2\text{ONa} \xrightarrow[\text{HOH}]{\text{H}^+} \text{R-}\overset{\text{CH}_3}{\text{CH}}\text{-OH} + \text{NaHSO}_4$$

One might find a pot full of high molecular weight alcohol instead of the expected detergent.

Sulfation of Alcohols from Reduced Fats or the Oxo Process

Many of the same considerations involved in sulfating olefins are found in sulfating primary alcohols with H_2SO_4. There are a few differences however. First the primary alcohol might be considered as an intermediate in the sulfation of the olefins; thereby the tendency to form polymers is reduced. Also primary alcohols are somewhat more stable than secondary alcohols; this also helps decrease side reactions. One can thus use "slightly" higher temperatures. One disadvantage is that water is now produced in the reaction:

$$\text{R-CH}_2\text{OH} + \text{H}_2\text{SO}_4 \longrightarrow \text{R-CH}_2\text{OSO}_2\text{OH} + \underline{\text{H}_2\text{O}}$$

This means that an access of H_2SO_4 must be present to maintain the acidity. With the primary alcohols another type of reaction—ether formation—is also found. Other oxidation reactions are also possible.

In order to avoid some of these problems. chlorosulfonic acid is commonly used. Although large amounts of corrosive HCl gas are formed, only a mole of chlorosulfonic acid is required, no water is formed, and a high active product is obtained directly.

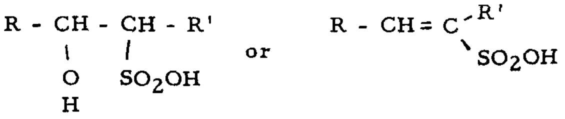
$$\text{R-CH}_2\text{OH} + \text{ClSO}_2\text{OH} \longrightarrow \text{RCH}_2\text{OSO}_2\text{OH} + \text{HCl}\uparrow$$

One cannot react chlorosulfonic acid with olefins; only side reactions occur, giving undesirable products.

One method of avoiding some of these problems would be to use SO_3 complexed with, say, pyridine, dioxane, polyethylene oxide, SO_2, etc. All these have been used successfully. However one has the additional problem of recovering the complexing agent from one's product.

Sulfonation of Olefins

It is possible under certain conditions to form a carbon to sulfur bond with olefins:



$$\text{R - }\underset{\text{OH}}{\text{CH}}\text{ - }\underset{\text{SO}_2\text{OH}}{\text{CH}}\text{ - R}' \quad \text{or} \quad \text{R - CH}=\text{C}\begin{smallmatrix}\text{R}'\\ \text{SO}_2\text{OH}\end{smallmatrix}$$

One of the Tergitol detergents has this structure.

These can be formed by two methods: reaction of S_2O_6 with olefins (1) and by reacting a mixture of acetic aicd and fuming sulfuric acid with olefins. The latter reaction, involving acetyl sulfuric acid, is an anti-Markownikoff reaction and permits sulfonation of branched-chain olefins. The presence of the acetic acid gives yields of three to four times that of the straight SO_3 reaction.

Sulfoxidation or Paraffins

All the previous reactions that have been discussed so far are intimately tied up with strong acid-type reactions. There is a second class of reactions involving what are called "free radicals." Free radical-type reactions are found in emulsion polymerization, chlorinations, and oxidations. They are usually susceptible to inhibitors, require catalysts to start the reaction, and, once started, proceed in a cyclic fashion known as chains. The reaction of sulfur dioxide and oxygen with paraffins is a reaction of this type (9, 10). It requires a catalyst, such as light or a diazo compound, which "kicks" off the reaction probably by pulling off a hydrogen atom from the paraffin:

$$\boxed{\begin{array}{lll} \text{R}\cdot + \text{SO}_2 & \longrightarrow & \text{RSO}_2\cdot \\ \text{RSO}_2\cdot + \text{O}_2 & \longrightarrow & \text{RSO}_2\text{OO}\cdot \\ \text{RSO}_2\text{OO}\cdot + \text{RH} & \longrightarrow & \text{R}\cdot\text{SO}_2\text{OOH} + \text{R}\cdot \end{array}}$$

In the German process acetic anhydride was added. It has a dual purpose. It appears to stabilize the peroxidic compound against undesirable side reactions and ties up impurities that could stop the chain.

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