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Preparation and identification of 1-sulfo-profanol-2.

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PREPARATION AND IDENTIFICATION OF 1-SULFO-PROPANOL-2

by

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INTRODUCTION

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The lack of information available in the American and German[1] chemical literature on the aliphatic sulfonic acids was deemed sufficient cause for the carrying out of the following research work on the preparation and identification of 1-Sulfo-Propanol-2.

A very thorough search through the available literature on sulfonic acids disclosed the fact that three men are prominent in this line of research.

Farbenind[2] prepared the sodium salts of several aliphatic sulfonic acids by the interaction of a concentrated aqueous sodium sulfite solution and the alkyl halide. He suggests the possibility of obtaining the corresponding sulfonic acids from the sodium salts by repeated evaporation with concentrated hydrochloric acid.

Levene and Mikeska[3] have prepared the barium, ammonium, and mercury salts of some aliphatic and aromatic sulfonic acids, but give no information at all on the separation or identification of the acids themselves. They prepared an aqueous solution of butyl sulfonic acid by the oxidation of butyl mercaptan with concentrated nitric acid. The mercaptan was obtained by the interaction of a potassium acid sulfide solution and the desired alkyl halide. The barium salts were prepared by adding an excess of barium carbonate, filtering, and allowing it to crystallize out.

1. R. Stelzner, M.M. Richter, and L. Vanino.
2. Farbenind, Z. anorg. allgem. chem., 150:231, (1926)
3. Levene and Mikeska, J. Biol. Chem., 63:89, (1925)

A third possibility which presented itself was that of the addition of the sulfurous acid to an ethylenic linkage. As this method would be the simplest of the three above-mentioned processes, it was decided to start the investigation along this line.

The attempt to add sulfurous acid to n-amylene was not successful and it was next decided to use the above mentioned methods to obtain the sodium and barium salts of the sulfonic acids and then develop a technique for preparing, isolating, and identifying the acids themselves.

The first step in either process was the preparation of either propylene chlorohydrin or the similar bromohydrin. From this compound the sodium and barium sulfonates could be prepared and these converted to the sulfonic acid. Thus it would be possible to obtain the acid by two different methods; affording a good opportunity to check the results.

As only very limited amounts of the halogen-hydrins were available it was deemed advisable to first develop the technique for the preparation of the sulfonic acids by using butyl bromide as the parent substance and producing butyl sulfonic acid. The lack of information on the preparation and identification of this acid, governed the choice of the alkyl halide to be used in this development.

Many thanks are extended to John Philip Mason, Ph.D., Assistant Professor of Chemistry at Boston University, for his many helpful suggestions and criticisms.

DEVELOPMENT OF A TECHNIQUE FOR THE PREPARATION OF SULFONIC ACIDS

ADDITION OF SULFUROUS ACID TO AN ETHYLENIC LINKAGE

ADDITION OF SULFUROUS ACID TO AN ETHYLENIC LINKAGE

The sulfur dioxide used in these experiments was not generated by ordinary laboratory methods but was that which is now available in small cylinders. The unsaturated compound used was the practical n-amylene.

A steady stream of sulfur dioxide was passed through a water bottle to pick up moisture and form sulfurous acid, which was subsequently passed through fifty cubic centimeters of n-amylene for forty-five minutes. A slight cooling effect due to the evaporation of the n-amylene was all that was apparent. The introduction of mercuric oxide, mercuric chloride, and ferric chloride as possible catalysts for the reaction were of no avail.

In another run similar to the above, in addition to using mercury and copper salts to attempt to aid the reaction, it was also decided to pass the sulfur dioxide through hot water, thus raising the temperature of the sulfurous acid formed. This necessitated cooling of the n-amylene to prevent loss. This elevation of temperature seemed to have no effect on bringing about the reaction between the two.

No information was available in the literature regarding the heats of formation and combustion of the expected reaction products and therefore it was difficult to draw any conclusions as to how high a temperature would be required to bring about the reaction between the n-amylene and the sulfurous acid.

In a last attempt to bring about the reaction, it was decided to pass a mixture of n-amylene vapor, water va-

por, and sulfur dioxide over pumice stone in a pyrex tube which was heated to one hundred and eighty-five degrees centigrade. The vapors coming from the tube were condensed and it was noticed that these separated into two layers, which were later separated and identified as n-amylene and water. As there was no reaction even at this rather high temperature it was decided to prepare the sulfonic acids by some other method.

PREPARATION OF BUTYL SULFONIC ACID

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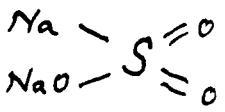
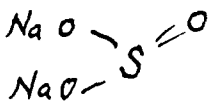
(Sodium butyl sulfonate method)

The preparation of butyl sulfonic acid by this method consists of first obtaining the sodium butyl sulfonate by the interaction of butyl bromide and a sodium sulfite solution, followed by the liberation of the sulfonic acid on acidifying with hydrogen chloride in an ether suspension of the salt.

In the alkylation of sodium sulfite H. Baggesgaard-Rasmussen and Sven Werner[4], suggest that sodium sulfite in solution exists in two forms as indicated by the formulas:-



(I)



(II)

They claim that the ratio in which the two exist is eighty-eight of (I) to twelve of (II). The sodium atom attached directly to the sulfur is the only one which is capable of being substituted by an alkyl group, and therefore form (I) is the only active form taking part in the reaction.

E. Evens, E. Mabbott, and E. Turner[5] found that on refluxing fifty grams of butyl bromide with a concentrated aqueous solution of sodium sulfite for twenty-four hours, the layers first formed, disappeared. They evaporated the

4. Baggesgaard-Rasmussen, Bull. Soc. Chim., 1073-87, (1921)
5. Evens, Mabbott, Turner, J.Chem.Soc., 130:1167, (1927)

solution in stages, the butyl sulfonate being obtained as the most soluble fraction. They thus obtained a fairly good yield of sodium butyl sulfonate.

After refluxing one hundred grams of butyl bromide with ninety grams of anhydrous sodium sulfite, in aqueous solution, for fifteen hours (the shortest length of time found to be efficacious), the sodium butyl sulfonate was obtained by fractional crystallization. The first and least soluble fractions were white flakes which when rubbed between the fingers felt like soft wax. In later fractions the material became more coarsely crystalline in appearance, harder, and also lost that wax-like feel; it more closely resembled an inorganic compound.

Thus on investigation it was found that contrary to what Evens, Mabbott, and Turner found, the sodium butyl sulfonate crystallizes out as the least soluble fraction.

The sodium bromide, the by-product of this reaction is the only source of bromide ions in this solution. If as Mr. J.F.Shillito, B.Sc., who did this part of the work for Evens,Mabbott, and Turner claims, the sodium butyl sulfonate comes out as the most soluble fraction, then after fractional crystallization a greater percentage of bromide ions should be found in the first few fractions rather than in later fractions. This was found to be contrary to the facts.

A rough semi-quantitative determination on each batch of crystals disclosed the fact that the first few

batches, the least soluble, contained the least bromide and were more nearly wholly organic material, proved so by its solubility in alcohol. All the following batches contained increasingly more bromide and were less soluble in alcohol.

The method of analysis consisted of taking up a weighed sample in alcohol, filtering of the residue, dissolving the residue in water, acidifying with HNO_3, precipitating as silver bromide and judging the sizes of the precipitates. The large difference between the first and eighth fractions showed that even this crude method of analysis sufficed to show the validity of the above statements.

Pure sodium butyl sulfonate can be prepared by dissolving, filtering, and recrystallizing from alcohol, as the sodium bromide is practically insoluble in absolute alcohol.

(Efflorescence of sodium butyl sulfonate)

On preparing a new batch of this salt, it was extracted in four fractions which were numbered 1, 2, 3, and 4; 4 being the most soluble fraction.

It was noticed that on remaining exposed to the atmosphere, a sample of the sodium salt changed from the flaky state to a fine white powder. This change resembled efflorescence. To determine the amount of moisture lost, a weighed sample of each fraction was left exposed to

the atmosphere for twenty-four hours and then the samples were reweighed. The following table summarizes the results:-

Sample No.	Wt. of sample	Loss on standing	Moles of water
1	1.4444 grams	0.2101 grams	1.38
2	3.6705 "	1.0132 "	1.51
3	2.1413 "	0.3901 "	1.63
4	3.2274 "	1.0808 "	2.97

It seems apparent from the above results that there is a loss in weight due to the loss of water(proved to be water by collecting the vapors evolved on heating). The moles of water as expressed above are probably inaccurate due to the fact that the samples were not properly dried of their excess moisture clinging to the faces of the crystals before the weighing of the samples.

Two methods were available to dry these crystals. The vapor pressure of the wet salt might be determined and a proper sulfuric acid and water misture obtained to absorb the excess moisture[6], or a drying agent could be made from the salt itself in the following manner. Ten grams of the salt were completely dehydrated over a low flame and mixed with ten grams of the same wet salt on which the determination was to be made.

Two weighed samples of the salt were placed in a dessicator containing the above mixture, and allowed to stand for forty-eight hours and were then reweighed. They were again placed in the dessicator for another twenty-

6. R. M. Bayer, Ind. and Eng. Chem., 14:913 (1922)

four hours and again reweighed; as there was no change in weight it was assumed that the samples were dry. The dried samples were then left exposed to the atmosphere until they came to a constant weight.

Wt. of Sample	Wt. after drying	Loss of Wt. on standing	Moles of water
4.0113 grams	3.8720 grams	0.7431 grams	2.14
5.2763 "	5.1423 "	1.2093 "	2.10

This work indicates that the sodium butyl sulfonate is efflorescent to the extent of liberating about two molecules of water. This work not directly influencing the main objective of the parent problem, it was deemed advisable not to further and more accurately determine the moles of water lost in this manner; although this could easily be done by vapor pressure determinations on the salt and by better and more accurate drying methods. Suffice it to say here that the salt is efflorescent.

(Purity of the sodium butyl sulfonate)

To determine the purity of the sodium butyl sulfonate a sample was first treated with concentrated hydrochloric acid to destroy any sulfite present, and then evaporated to dryness. It was next treated with concentrated nitric acid and again evaporated to dryness to remove any bromide present. During the first stages of the avaporation a brown gas was evolved and then the solution cleared until the final stages when the colored nitrogen dioxide appeared. The residue was then heated only strong enough to form sodium sulfate and not cause its decomposition. After cooling the residue was taken up in water and the sulfate precipitated with ba-

rium chloride solution and the determination carried out in the usual manner.

Wt. of sample	Theoretical $BaSO_4$	Actual $BaSO_4$
7.1431 g	10.4081 g	9.6427 g

Thus it seems as though the sodium salt were being obtained in a fairly pure condition. The slight impurity is the sodium bromide formed as a by-product of this reaction. It is unnecessary to purify the salt any further as this impurity is not undesirable in the following procedures.

(Butyl sulfonic acid from sodium butyl sulfonate)

The first attempt at this conversion was to suspend a sample of the sodium butyl sulfonate in about two hundred and fifty cubic centimeters of ether and pass a current of dry hydrogen chloride through the mixture until saturated. The solution was then filtered and the residue analyzed and found to be sodium chloride. The filtrate was concentrated by evaporating off the ether and an attempt was made to crystallize the residue by drying and cooling to below zero degrees; but to no avail.

In a second attempt it was found that better results could be obtained by pulverizing the salt previous to suspending it in the ether as the gas flow would keep the powder in suspension by agitation. The sulfonic acid appears to be rather stable at very low temperatures but at room temperature it becomes amber colored due to the formation of

colored sulfur compounds. On distillation this acid comes over water-white but on standing it takes on the amber hue. The butyl sulfonic acid is rather syrupy and extremely soluble in water, ether, and alcohol. Its specific gravity is 1.1387 at twenty-two degrees centigrade.

On distilling a twenty-eight cubic centimeter sample of the butyl sulfonic acid it was found that using a pressure of ninety-one millimeters of mercury a rapid rise in temperature to 73°C was perceptible at which temperature boiling began and then there was a gradual rise to 75°C during which time about 3-4 cc. of something distilled over. The residue then suddenly became black due to charring and an evolution of white sulfur dioxide fumes took place. The vacuum used in this distillation evidently was not enough to prevent the decomposition of the acid. The distillate which came over had a specific gravity of 1.0961, remarkably close to water and also gave a good test for the chloride ions.

The above facts would indicate that the distillate is a very weak solution of hydrogen chloride. The sodium butyl sulfonate as previously determined contained a couple of moles of water of hydration. On the introduction of the dry hydrogen chloride the butyl sulfonic acid was formed

$$CH_3CH_2CH_2CH_2SO_2ONa \xrightarrow{HCl} CH_3CH_2CH_2CH_2SO_2OH + NaCl$$

and the sodium chloride was left behind as a solid, and the excess hydrogen chloride merely dissolved in the water to

form a weak solution of hydrochloric acid. The reason that this weak acid solution did not separate out from the ether and form a separate layer was that maybe a ternary mixture was formed. That is to say, the sulfonic acid soluble in the water and also in the ether, was probably present in the proper ratio, or within the range which will form a ternary mixture with the ether and they all remain as one homogeneous solution.

If all this were true and if, assuspected, the sulfonic acid is more soluble in water than in ether, then the sulfonic acid should separate out as a separate layer on the addition of an excess of ether. All this was very well confirmed by experiment.

To overcome the above water impurity, the sodium butyl sulfonate was made anhydrous by heating in a warm closet at 70°C. for twenty-four hours. This material was then dissolved in alcohol, recrystallized from it and then again dehydrated. The salt (16.5 grams) was then suspended in two hundred and fifty cubic centimeters of absolute ether and dry hydrogen chloride passed through the mixture until saturated. The mixture was then maintained at a temperature of from 20-25°C. to obtain better results. This temperature was found to be best for this particular reaction. The mixture was then filtered and the ether removed by vacuum distillation. The material was dried for twenty-four hours over phosphorous pentoxide and a boiling-point determination run on

it, yielding a boiling-point of 68°C/60 mm. A micro-boiling point determined as described by O. Kamm[7] gave a value of 144°C/761 mm.

(PREPARATION OF BUTYL SULFONIC ACID)

(Barium butyl sulfonate method)

This method consists of first obtaining the butyl mercaptan through the reaction between butyl bromide and potassium bisulfide solution and then oxidizing the mercaptan to the sulfonic acid. The subsequent isolation of the butyl sulfonic acid is brought about by crystallizing out the barium salt and then treating this with a theoretical amount of concentrated sulfuric acid, filtering off the barium sulfate formed and evaporating off the ether to obtain the butyl sulfonic acid.

(Alcoholic potassium bisulfide)

The literature revealed several methods for the preparation of potassium bisulfide. E.E. Naef[8] explains a method in which he prepares this compound from sulfur, tar oil, and alkali metal sulfate. J.E.E. Ephraim[9] uses sodium sulfate, calcium oxide, and water with the addition of an excess of hydrogen sulfide, and then evaporates using vacuum.

In as much as an alcoholic solution of potassium bisulfide was desired, it was deemed advisable to prepare it

7. O. Kamm, "Qualitative Organic Analysis, Pg. 117-18, (1929)
8. E.E.Naef, U.S. 1,636,106 July 19, (1927)
9. J.E. Ephraim, Brit. 184,795 August 12, (1922)

by first dissolving one hundred grams of potassium hydroxide in three hundred cubic centimeters of alcohol and then passing through a very large excess of hydrogen sulfide. In using alcoholic potassium bisulfide made from a more concentrated solution of alcoholic potash than indicated above, difficulty was experienced in controlling the subsequent reaction with the butyl bromide; violent ebullition taking place. It was therefore decided to use the above strength of alcoholic potassium bisulfide.

(n.Butyl mercaptan)

Levene and Mikeska[10] prepared 2-mercapto-iso-hexane by refluxing for five hours a mixture of the iodo-compound and two equivalents of alcoholic potassium bisulfide solution. On pouring the whole into an excess of cold water, the mercaptan separated as an oil.

To one hundred cubic centimeters of alcoholic potassium bisulfide solution, twenty cubic centimeters of butyl bromide was added and the whole refluxed for one and a half hours and then the reaction products poured into cold water, in which the alcohol and potassium bromide were soluble, leaving as a separate layer the oily mercaptan, which was separated with the aid of a separatory funnel. This oil was subjected to distillation and the material distilling be-

10. Levene and Mikeska, J. Biol. Chem., 65:516-18, (1925)

tween 85-98°C. was saved as the butyl mercaptan. The yield was approximately fifty-two per cent.

(Barium butyl sulfonate)

Levene and Mikeska[11] suggest oxidizing the mercaptan tan with concentrated nitric acid. Therefore to ten grams of the mercaptan, twenty cubic centimeters of concentrated nitric acid and four cubic centimeters of water were added using a dropping funnel and a reflux condenser. The flask was cooled in an ice-water mixture during the addition of the acid. On refluxing, as soon as the contents of the flask became warm, spontaneous combustion took place with the rapid evolution of clouds of nitric acid and nitrogen dioxide fumes. The apparatus was completely demolished and the contents of the flask scattered about the laboratory. Evidently the normal oxidation of the mercaptan was hindered by the cooling and then on heating the reaction took place spontaneously.

It seems that the best method of oxidation is to cool the flask while adding the mercaptan and then allow the flask to remain overnight at room temperature. Mechanical agitation was provided for during the reaction. The contents of the flask can then be safely and gently refluxed.

$$CH_3CH_2CH_2CH_2Br + KSH \longrightarrow CH_3CH_2CH_2CH_2SH + KBr$$

$$CH_3CH_2CH_2CH_2SH + 6\ HONO_2 \rightarrow CH_3CH_2CH_2CH_2SO_2OH + 6\ NO_2 + 3\ H_2O$$

$$2\ CH_3CH_2CH_2CH_2SO_2OH + BaCO_3 \rightarrow (CH_3CH_2CH_2CH_2SO_2O)_2Ba + H_2O + CO_2$$

11. Levene and Mikeska, J. Biol. Chem., 63.89, (1925)

Increasing the length of time of the refluxing has very little effect on the efficiency of this step.

After refluxing the contents of the flask for a half hour, they were transferred to a casserole where the mixture was heated for another half hour. The nitric acid was then removed under reduced pressure and the residue taken up in water. An excess of barium carbonate was addes and the whole filtered. The filtrate was concentrated, and an excess of alcohol added. The solution was then put aside to crystallize. The crystals were removed, dried, and weighed. The efficiency of this step was 52%.

(Purity of the barium butyl sulfonate)

In order to determine the purity of the barium butyl sulfonate three samples of it were heated strongly in separate crucibles, and the weight of barium sulfate formed compared with that which theoretically ought to have been formed. The following table summarizes the results:-

Wt. of the sample	Theo. $BaSo_4$	Actual $BASO_4$
1.628 grams	0.923 grams	0.8653 grams
2.657 "	1.507 "	1.3783 "
4.762 "	2.699 "	2.4776 "

Treating with concentrated sulfuric acid before heating strongly seemed to make no difference as the following results show:-

Wt. of the sample	Theo. $BaSO_4$	Actual $BaSO_4$
3.1571 grams	1.7890 grams	1.6518 grams
1.3101 "	0.8892 "	0.6679 "

Another method used for this purpose was to suspend the barium butyl sulfonate in ether, and add the theoretical amount of concentrated sulfuric acid necessary to convert it to the sulfonic acid and precipitate the barium sulfate, which was filtered, washed, dried, and weighed in the usual manner. This method gave:-

Wt. of the sample	Theo. $BaSO_4$	Actual $BaSO_4$
7.1431 grams	10.408 grams	9.6427 grams.

These results indicated that the barium butyl sulfonate was being obtained in a fairly pure form.

(Butyl sulfonic acid from barium butyl sulfonate)

To bring about this conversion to the butyl sulfonic acid, the salt was treated with the predetermined amount of concentrated sulfuric acid and the barium sulfate formed was filtered off. The filtrate was allowed to remain in a crystallizing dish for several days, and as nothing crystallized from it, it was subjected to distillation. At about 100°C. about 1 cc. of some material, probably water, distilled over and then the temperature rose rapidly to 137°C. and the remaining residue turned black in color and sulfur dioxide fumes were evolved indicating that decomposition had taken place.

The best procedure fro this conversion was to suspend seventy-five grams of the dried and pulverized barium butyl sulfonate in five hundred cubic centimeters of absol-

ute ether in a flask fitted with a reflux condenser, a mechanical stirrer, and a dropping funnel through which the sulfuric acid was added.

$$(CH_3CH_2CH_2CH_2SO_2O)_2Ba + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH_2SO_2OH + BaSO_4$$

The theoretical amount of concentrated sulfuric acid to add was 10.0 cc. but only 9.6 cc. were added so as to avoid an excess. After filtering off the barium sulfate formed, the ether was allowed to evaporate off leaving the sulfonic acid behind. Using a pressure of 81 mm. of mercury, this butyl sulfonic acid distilled at 74-76°C. The micro boiling-point determined by Kamm's method gave a value of 140.5°C/761 mm. The distillate came over water white but was slightly amber-colored on reaching the receiving flask, probably due to slight decomposition.

The specific gravity of this acid is 1.1374.

(Comparison of Methods)

Both methods for the preparation of butyl sulfonic acid check very closely. The specific gravity of the acid from the first method is 1.1387 as compared to the 1.1374 of the second method. The boiling points under reduced pressure were 68°C/60 mm., and 75°C/81 mm. respectively. The micro boiling-points were 144°C/761 mm., and 140.5°C/759 mm. Both acids behaved the same on distillation, were of the same color, and formed the same products for identification purposes. They were both very deliquescent.

The method involving the alkylation of sodium sulfite with the subsequent liberation of the sulfonic acid was found to be the more desirable method of the two. There are fewer operations, the reactions proceed more smoothly, and the efficiency is much better. It was deemed advisable in working with the propylene halogen-hydrin to use this method for obtaining the sodium salt of the sulfonic acid, from which the sulfonic acid itself could later be obtained.

IDENTIFICATION OF BUTYL SULFONIC ACID

(IDENTIFICATION OF THE BUTYL SULFONIC ACID)

(Methods of Analysis)

The qualitative tests on all intermediate and final products were those described by Oliver Kamm[12] in his book "Qualitative Organic Analysis". The products were tested for sulfur, nitrogen, or halide, whenever they were present.

In running a qualitative test for sulfur in the presence of nitrogen such as in the sulfamides and sulfanilides, the following method was found very satisfactory and preferable to Kamm's method.

To one cubic centimeter of the alkaline filtrate obtained from the solution of the sodium fusion products, one cubic centimeter of concentrated hydrochloric acid was added. Then after the addition of one cubic centimeter of p-aminodimethylaniline-hydrochloride solution, one drop of a one per cent ferric chloride solution in dilute hydrochloric acid was added and the whole allowed to stand a short while. Within 5-15 minutes a very deep blue color, which was fairly permanent, was perceptible in the presence of sulfur.

The quantitative tests were those described by Gattermann[13] in his book on "Practical Methods of Organic Chemistry."

The sulfur, halogen, and nitrogen were checked in all compounds to determine in a qualtitative manner whether

12. O. Kamm, "Qal.Org.Anal.", Pgs. 121-25, (1929)
13. L.Gattermann, "Practical Methods of Organic Chemistry" Pgs. 101-113, (1914)

or not the desired reaction had taken place and whether the desired products were formed.

In preparing the samples for the carbon and hydrogen determinations they were first placed in a hot closet at 75°C. for twenty-four hours and then freshly distilled and kept over phosphorous pentoxide for a few hours. The following table summarizes the results:-

	Theoretical	Actual
Carbon	34.80%	34.26%
Hydrogen	7.25%	8.01%

This like other sulfonic acids of the aliphatic series is deliquescent as is indicated by the fact that after exposure to the atmosphere for a length of time it will not dissolve back into the ether with which it was extracted, and after drying over phosphorus pentoxide it dissolves very readily. The neutral equivalent of this acid is 162.5 and the index of refraction of the material is 1.435.

(Butyl sulfonyl chloride)

M. Duguet[14] in working on a study of the sulfamides and sulfanilides of the aliphatic series describes methods of making sulfonyl chorides of these members by treating the potassium salts of the sulfonic acids with phosphorus pentachloride. He says that the reaction proceeds normally.

14. M.Duguet, R. 21:77-81, (1902)

He does not say whether he mixed both together in the solid form, or whether he used a solvent for the salt.

If the potassium salt of the sulfonic acid will react with the phosphorus pentachoride so will the sulfonic acid itself; in fact, it would be preferable to use the acid and avoid the formation of the potassium chloride.[1] The gaseous hydrogen chloride thus formed could easily be removed.

Thirty grams of the butyl sulfonic acid was treated with the theoretical amount (48 g.) of the phosphorus pentachloride. This material was added slowly and cautiously as the reaction was very vigorous and highly exothermic. A large amount of hydrogen chloride was evolved and a rather syrupy, amber-colored liquid remained in the casserole. The reaction proceeds according to the following equation:-

$$CH_3CH_2CH_2CH_2SO_2OH + PCl_5 \longrightarrow CH_3CH_2CH_2CH_2SO_2Cl + POCl_3 + HCl$$

The hydrogen choride formed during the reaction was easily eliminated by applying vacuum and a little heat; but M. Duguet says nothing about the removal of the phosphorus oxychloride formed as a by-product in this reaction.

The butyl sulfonyl chloride formed decomposes at 180°C. and the phosphorus oxychloride formed boils at 107.1°C. and therefore it seems that the range is large enough so that by fractional distillation a separation might be brought about.

This step was attempted but the butyl sulfonyl chloride obtained was much inferior to that obtained by the following method. A much better method of obtaining a purer butyl sulfonyl chloride is to use thionyl chloride in place of the

phosphorus pentachloride. Thus the only by-products would be gases and they could easily be entirely removed. Therefore to twenty-five grams of the acid, twenty-five grams of the thionyl chloride was added, and very surprisingly it was found that the reaction was highly endothermic. The sulfur dioxide and hydrogen chloride formed were led away through a hood and the final traces dissolved in the butyl sulfonyl chloride formed were removed by the application of vacuum and heating. The butyl sulfonyl chloride thus formed was subjected to vacuum distillation using a pressure of twelve millimeters of mercury and found that it distilled over at 76-77°C., checking rather closely the figure of M. Duguet, which was 80°/15 mm.

This butyl sulfonyl chloride is a syrupy, amber-colored liquid which is a bit unstable; evidenced by a small sulfur deposit on standing a few hours.

(Butyl sulfamide)

The butyl sulfonyl chloride was mixed with about three hundred cubic centimeters of ether and a current of dry ammonia was passed through it until saturated. An immediate precipitation of ammonium chloride took place. There was no apparent heat change in the reaction.

$$CH_3CH_2CH_2CH_2SO_2Cl + NH_3 \longrightarrow CH_3CH_2CH_2CH_2SO_2NH_2 + NH_4Cl$$

The ammonium chloride was filtered off and the filtrate poured into ac crystallizing dish and allowed to stand. After one

hour crystals began to form and a good yield was obtained the next day. It was very hard to keep this material dry and it also had to be kept at very low temperatures to keep; it dry. The melting point on this white crystalline substance was 49.5°C.

An attempt was made to make the butyl sulfamide by the following reactions:-

$$CH_3CH_2CH_2CH_2SO_2OH + C_2H_5OH \longrightarrow CH_3CH_2CH_2CH_2SO_2OC_2H_5 + H_2O$$

$$CH_3CH_2CH_2CH_2SO_2OC_2H_5 + NH_3 \longrightarrow CH_3CH_2CH_2CH_2SO_2NH_2 + C_2H_5OH$$

Ten grams of the butyl sulfonic acid was refluxed with five grams of ethyl alcohol for two hours, and then a current of ammonia was introduced into the ester until saturated. No precipitation took place so the solution was put aside in a dish to crystallize. The next morning only a flaky white substance remained. I tested for sulfur and nitrogen and found both present. No positive test for an amide could be obtained however and this suggested that probably obly the ammonium salt had been formed instead of the amide.

To confirm the above assumption a stream of dry ammonia gas was led into a five gram sample of the butyl sulfonic acid in an ether solution, and the whole set aside for crystallization. The similarity between the substance obtained and the material formed in the former method indicates that the ammonium salt of the butyl sulfonic acid was formed in both cases. The water formed in the first reaction probably prevents the amide from being formed.

PREPARATION OF 1-SULFO-PROPANOL-2

PREPARATION OF 1-SULFO-PROPANOL-2

(Preparation of Propylene-bromohydrin)

The substances used in the attempt to prepare the propylene halogen-hydrin were propene and hypochlorous acid.

The propene was generated by the action of freshly prepared alcoholic-potash solution on n-propyl bromide. The n-propyl bromide was introduced by a dropping funnel into the alcoholic potash solution which was kept warm with a very low flame. The vapors of alcohol and the propene were led into an upright condenser which returned the alcohol to the flask and allowed only the propene to pass into the absorption tower filled with hypochlorous acid.

The hypochlorous acid was prepared by two different methods.[15,16] In the first, 150 cc. of solution containing 0.207 moles of sodium hypochlorite, 200 cc. of water were added and this mixture was introduced into 50 cc. of water through which a stream of chlorine gas was passing. On diluting the whole to 500 cc. approximately 0.407 moles of hypochlorous acid were presumable present.

Another batch of hypochlorous acid was prepared by dissolving one half pound of calcium hypochlorite in two and one half quarts of water and adding 0.37 pounds of soda ash.

After settling of the precipitate formed, the super-

15. Mathieson Alkali Works, Inc., Brit. 195,366 March 6, (1923)
16. Haworth and Irwine, U.S. 1,227,049 May, (1922)

natant liquor was decanted and placed in a tightly sealed flask.

On the introduction of the propene into the hypochlorous acid no reaction was apparent. Increasing the pressure within the reaction chamber and the use of mercury and copper salts as activators seemed of no avail.

G. R. Bancroft[17] in the American Chemical Society Journal, explains the preparation of propylene chlorohydrin from ally chloride which in turn is made from allyl alcohol.

He made allyl chloride from allyl alcohol by treating three moles of the alcohol with one mole of phoshporus trichloride. The allyl alcohol was placed in a distilling flask connected with a Liebig condenser, and the phosphorus trichloride added through a dropping funnel, the flask being cooled by ice water and shaken vigorously from time to time as the addition was carried on. The reaction is represented by the following equation:-

$$3\ CH_2{=}CH\text{-}CH_2OH + PCl_3 \longrightarrow 3\ CH_2{=}CH\text{-}CH_2Cl + H_3PO_4$$

When all the phosphorus trichloride had been added the temperature of the water-bath was maintained at 40°C. until all the hydrogen chloride was evolved, then raised sufficiently to distil off the fraction of allyl chloride boiling at 40-45°C. During the distillation the flask was shaken vigorously at intervals to assist in volatilzing the allyl chloride and separating it from the thick and heavy phosphoruus acid formed.

17. G.R.Bancroft, Am.Chem.Soc.J., 41:426, (1919)

In performing this fractionation it was found that if the temperature were permitted to rise to the vicinity of the boiling-point of the allyl alcohol, an explosion occurred wrecking the apparatus and setting free red phosphorus while at the same time a strong garlic odor of phosphene was formed. DeMole[18] and Bechamp[19] record the same difficulty in carrying on similar work.

Because of this difficulty the separation of the allyl chloride from the phosphorous acid was brought about by washing the mixture with water in which the acid is soluble leaving behind the insoluble allyl chloride. The allyl chloride thus separated was dried and redistilled, boiling at 46-47°C. The efficiency of this process is about 39% of the theoretical value.

The low yield of the above-mentioned method may be attributed to the difficulty of separating the ally chloride from the phoshporous acid formed. Therefore it was deemed advisable to form allyl bromide by the reaction of hydrobromic acid on allyl alcohol. O. Kamm and C. Marvel[20] worked out this method and obtained an efficiency of 92-96% although in this work the best efficiency obtained was 48.5%.

The hydrobromic acid was prepared by passing sulfur dioxide into a mixture of ice water and bromine in the ration of 580 grams to 410 grams respectively. This produced 1000 cc. of 48% HBr solution and 300 cc. of sulfuric acid. This mix-

18. DeMole, Rec.trav.chim., 9,48-49 (1876)
19. Bechamp, Compt. rend., 42,227-8 (1856)
20. Kamm and Marvel, "Organic Syntheses", Vol.I, Pg.3, (1921)

ture did not have to be distilled as the sulfuric acid present was not undesirable.

To this hydrobromic acid solution were added 385 cc. of practical allyl alcohol and then 300 grams of concentrated sulfuric acid and the distillate caught, which came over in two hours. Mechanical agitation was used. On purification of the allyl bromide, 286 grams was available.

To this 286 grams of allyl bromide was added 255 cc. of concentrated sulfuric acid and the mixture allowed to stand for twenty-four hours, when a thick, reddish-brown, oily substance was formed.

$$CH_2{=}CH\text{-}CH_2OH + HBr \longrightarrow CH_2{=}CH\text{-}CH_2Br + H_2O$$

$$\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2Br \end{matrix} + HOSO_2OH \longrightarrow \begin{matrix} CH_3 \\ CHOSO_2OH \\ CH_2Br \end{matrix}$$

Then the mixture was diluted with 3520 cc. of warm water and the whole refluxed for two hours.

$$\begin{matrix} CH_3 \\ CHOSO_2OH \\ CH_2Br \end{matrix} + H_2O \longrightarrow \begin{matrix} CH_3 \\ CHOH \\ CH_2Br \end{matrix} + HOSO_2OH$$

The hydrolysis products were distilled and the distillate collected until a temperature of 142°C. was reached, when sulfur dioxide was evolved and a good deal of charring took place.

The distillate was then neutralized with potassium carbonate and the oily liquid that separated was extracted with ether. The ether extract was then dried over fused potassium carbonate and the ether distilled off. The

residue passing over between 120@149°C. was saved. This distillate was redistilled and the material passing over between 138-145°C. was saved. The yield was seventeen grams.

Some doubt seemed to exist in regard to the way in which HOCl would add onto an unsymmetrically constructed hydrocarbon of the C_nH_{2n} series. B.T.Brooks[21] claims that propene and HOCl add and yield a mixture of the two isomers. J. Schmidt[22] and G. R. Bancroft[23] place the halogen on the first carbon and the hydroxyl group in the center carbon. It is safe to say that they are correct and the latter suggested arrangement is right.

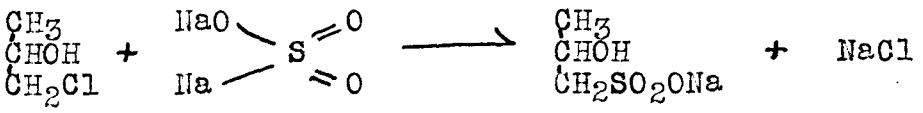
21. B.T.Brooks, "The Non-Benzenoid Hydrocarbons", Pg.124,(1922)
22. J.Schmidt, "Textbook of Organic Chemistry", Pg.48, (1926)
23. G.R.Bancroft, Am.Chem.Soc.J., 41:426, (1919)

(Preparation of 1-SULFO-PROPANOL-2)
(Sodium salt)

Twenty-one grams of the propylene chlorohydrin were refluxed with eighty cubic centimeters of sodium sulfite solution containing twenty-five grams of sodium sulfite. The layer formed by the insoluble chlorohydrin disappeared after twelve hours of refluxing. By concentrating and crystallizing the sodium salt of 1-sulfo-propanol-2 was obtained. The yield was about twenty grams. This salt is not waxy like the sodium salt of butyl sulfonic acid, but is more crystalline in form. This salt is only slightly efflorescent.

It seems that the mere disappearance of the two layers cannot be used as a criterion for the determination of the end-point of the reaction probably due to the solubility of the propylene chlorohydrin at elevated temperatures. I found this out by collecting some of the vapors evolved during the latter part of the refluxing period, and found that they separated out into two layers which were identified as water and propylene chlorohydrin. It was therefore decided to use a self-starting syphon at the bottom of the condenser to collect the condensing vapors and note when the layers ceased to form, indicating the end of the reaction.

The average efficiency of this step in three runs was 71.1%.



(Preparation of 1-Sulfo-Propanol-2)

In a first attempt to convert the sodium salt, into the corresponding 1-Sulfo-Propanol-2 it was suspended in 200 cc. of absolute ether, dry hydrogen chloride was passed into the suspension, and the sodium chloride formed was filtered off. On removing the ether under reduced pressure of twenty-eight millimeters of mercury, the acid distilled over at 47°C. Due to excessive bumping there is some doubt as to the accuracy of this value. A micro-boiling point on this batch gave a value of 79°C/761 mm. The specific gravity of this substance was 1.006. Sulfur was found present in this compound.

In the next batch of this acid that was prepared, the ether was removed by heating in an open vessel in a hot closet at 30°C. Any dissolved hydrogen chloride was removed by applying reduced pressure and gentle heating. Ten grams of the sodium salt yielded 6.5 grams of the acid. The specific gravity of this batch was 1.077 and its micro-boiling point was 81°C/761 mm. Sulfur was found present in this compound.

The residue filtered off after the treatment with dry hydrogen chloride was presumably sodium chloride, but on heating it up strongly it was noticed that a good deal of charring took place indicating the presence of a large amount of organic material. This fact indicated that the length of

time of this step was not long enough and should be increased.

In preparing the final batch of the 1-Sulfo-Propanol-2, an upright condenser, and a mechanical stirrer were used. After passing dry hydrogen chloride through the suspension until saturated, the flask was tightly sealed and allowed to stand twenty-four hours. Then it was filtered and the residue was treated with fresh batches of absolute ether and the mixtures again treated with hydrogen chloride, and again sealed and allowed to stand. The batches of ether were then combined and then concentrated under reduced pressure and the sulfonic acid thus obtained. From 33.1 grams of the sodium salt, 13.5 grams of the acid were obtained, an efficiency of ~~63.5%~~ 47.3%.

This acid is deliquescent. In preparing a sample of the acid for a carbon and hydrogen determination it was first heated in a hot closet a few hours and then freshly distilled under reduced pressure and then kept several hours in a dessicator over phosphorous pentoxide. The following table summarizes the results:-

	Theoretical	Actual
Carbon	25.71%	25.37% 25.89% 25.49%
Hydrogen	5.71%	5.62% 5.53% 5.59%

A sulfur test on this compound gave a value of 22.63% as compared to the theoretical value of 22.86%.

The boiling-point of this acid is 37.5°C/46mm.

IDENTIFICATION OF 1-SULFO-PROPANOL-2

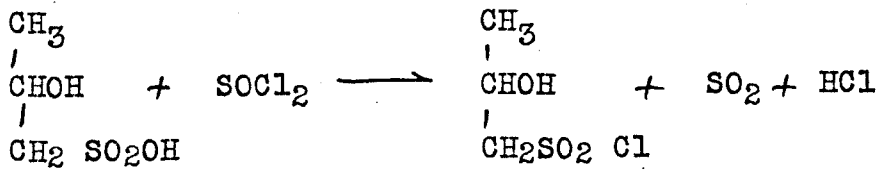
IDENTIFICATION OF 1-SULFO-PROPANOL-2

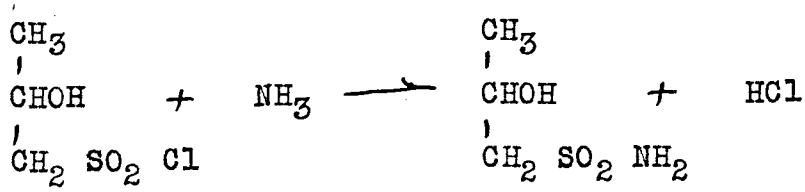
(Preparation of 1-Sulfamide-Propanol-2)

To a very well dried three gram sample of the 1-Sulfo-Propanol-2, two and a half cubic centimeters of thionyl chloride was added and the reaction products taken up with absolute ether. A stream of dry ammonia gas was then passed through and the white precipitated material was filtered off. The filtrate was allowed to evaporate and it was found that nothing remained. On treating the white residue, it was found that about one half of the material dissolved and after filtering it was recovered by evaporation of the alcohol. Sulfur and nitrogen were both found present, indiacting that the product was evidently the desired sulfamide. It was tested for an amide and a positive test was obtained. The melting-point was found to be well over 275°C. indicating that a good deal of inorganic material was present, probably ammonium chloride.

A pure sample of the 1-Sulfamide-Propanol-2 was obtained by shaking five grams off this material with 15 cc. of alcohol. long enough to dissolve only about three grams of the material. After filtration the amide was recovered by evaporation of the alcohol. This was again partially dissolved and after filtering was recovered by evaporation.

A one half gram sample was finally obtained, on which a melting-point was run. The value obtained was 41.5°C.





(Preparation of 1-Sulfanilide-Propanol-2)

To five grams of 1-Sulfo-Propanol-2 three and one half grams of thionyl chloride was added. To remove the dissolved gases of the reaction, particularly the hydrogen chloride, reduced pressure and gentle heating were applied. After cooling the sulfonyl chloride, three grams of freshly distilled aniline was added drop by drop to prevent overheating. The reaction products were then dissolved in as little alcohol as possible and the whole poured into 400 cc. of cold water, whereupon a white crystalline substance was precipitated. This sulfanilide melts rather sharply at 74°C. A qualitative test for sulfur and nitrogen gave a positive result in both cases. No halogen was found present; thus eliminating the possibility of this substance being aniline hydrochloride, or any of the compound being present at all. The melting-point is also much lower than that of the aniline hydrochloride.

Three carbon and hydrogen determinations on this sulfanilide gave the following results:-

	Theoretical	Actual
Carbon	46.75%	46.61% 46.44% 44.21%
Hydrogen	5.63%	5.58% 5.61% 4.87%

A sulfur determination by the bomb method gave a value of 13.54% as compared to the theoretical value of 13.87%.

On treating the sulfanilide with thionyl chloride I obtained a good reaction, indicating the presence of a hydroxyl group. This proves that the alcoholic hydroxy group is not reacted upon by the thionyl chloride when any other hydroxyl groups are present in either a sulfo- or a carboxyl group. A sample of butyl sulfanilide gave no reaction with thionyl chloride, proving that the reaction must have been due to the hydroxyl group and not to the sulfanilide grouping.

(Ammonium and barium salts of 1-Sulfo-Propanol-2)

The ammonium salt of 1-Sulfo-Propanol-2 was prepared by passing a dry stream of ammonia through an ethereal solution of the 1-Sulfo-Propanol-2. Both sulfur and nitrogen were found present.

The barium salt was prepared by adding an excess of barium carbonate, filtering and then adding an excess of alcohol, with subsequent crystallization.

On heating strongly a 0.807 gram sample of this barium salt, 0.494 grams of barium sulfate should be formed. The actual amount formed was 0.516 grams; a value within the experimental accuracy of the method.

These facts help to further establish the identity of 1-Sulfo-Propanol-2.

SUMMARY

SUMMARY

A technique for the production of aliphatic sulfonic acids has been developed which converts the sodium salts into the corresponding sulfonic acids by treating with dry hydrogen chloride in an ethereal solution. The results obtained were checked by preparing the same product through the conversion of the barium salt by the addition of concentrated sulfuric acid in an ethereal suspension. The barium sulfate was filtered off and the acid obtained by concentration.

By the above methods butyl sulfonic acid was prepared and identified. The specific gravity is 1.1387, the boiling-point is 68°C/60 mm., the micro boiling-point is 144°C/761 mm. It is very deliquescent and is water-white on distillation but soon takes on an amber hue. Carbon, hydrogen, and sulfur tests check well with the theoretical values.

The sodium salt is efflorescent, losing two moles of water on standing exposed to the atmosphere.

This acid was identified by preparing its sulfonyl chloride, and sulfamide, and checking the boiling-points and melting-points respectively; these values given by M. Duguet.

Having developed and perfected this technique, 1-Sulfo-Propanol-2 was prepared from propylene chlorohydrin and identified by preparing the sulfonyl chloride, the sulfamide, the

sulfanilide, the ammonium and barium salts.

The specific gravity is 1.077, is water-white on distillation turning amber, and is very deliquescent. The boiling-point is 37.5/46 mm. and the micro-boiling-point is 81°C/761 mm.

The carbon, hydrogen, and sulfur values obtained check the theoretical values within the limit of accuracy of the methods used.

The sodium salt of this acid is only slightly efflorescent.

The 1-Sulfo-Propanol-2 was further identified by establishing the proof of the hydroxy group in the compound.

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