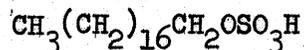


2431

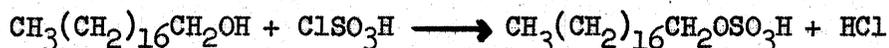
OCTADECYLSULFURIC ACID



Mol. wt. 350.5 ($\text{C}_{18}\text{H}_{38}\text{O}_4\text{S}$)

Submitted by E. W. Maurer, A. J. Stirton, and J. K. Weil,¹
Eastern Regional Research Laboratory, Philadelphia, Penna.

I. Principle



Octadecanol is sulfated with chlorosulfonic acid at ice bath temperature and the resulting octadecylsulfuric acid isolated at 0° under anhydrous conditions.

II. Starting Material

Good commercial grades of n-octadecanol, hexadecanol, tetradecanol and dodecanol were purified by fractional vacuum distillation and low temperature crystallization, and had the following constants: n-octadecanol, m.p. 58.1 - 58.6°, n 60/D 1.4380; n-hexadecanol, m.p. 49.3 - 49.6°, n 60/D 1.4359; n-tetradecanol, m.p. 37.2 - 38.0°, n 60/D 1.4318; n-dodecanol, f.p. 24.1°, n 25/D 1.4410.

III. Procedure

A 2-l. three-necked round-bottomed flask, with standard-taper ground-glass joints, is equipped for cooling with an ice bath, and fitted with a ball joint-sealed mechanical stirrer, a thermometer well, and a graduated side-arm type addition tube. The addition

¹ Eastern Utilization Research and Development Division,
Agricultural Research Service, U. S. Department of Agriculture.

tube, which should have a close-fitting stopcock well lubricated with heavy silicone grease, is placed so as to discharge chlorosulfonic acid well above the surface of the reaction mixture. Octadecanol (108 grams, 0.4 mole) and 540 ml. of chloroform² are added to the flask and sufficient heat applied in order to obtain complete solution of the alcohol at about 25°. This solution is then cooled to 4-5° by means of an ice bath, stirring continuously.³ Chlorosulfonic acid,⁴ 29 ml. (51.8 grams, 0.44 mole, 10% excess) is added dropwise from the addition tube to the stirred mixture over a period of 20 minutes. Shortly after the start of chlorosulfonic acid addition, HCl will be observed escaping from the side arm of the addition tube. The temperature rises to 7-8° when approximately two-thirds of the chlorosulfonic acid has been added, and drops gradually to 4-5° when the addition is complete.⁵ The ice bath is removed 5 minutes after completion of the chlorosulfonic acid addition. Stirring is continued for 1.5 hours permitting the mixture to rise to room temperature, 20-25°. Intermittent mild heat⁷ is then applied until an exothermic reaction is noted (rise of 1-2°); the temperature is permitted to rise to 30-32°.

After the mixture cools below 30° stirring is stopped and the very light yellow solution transferred to a 1-l. Erlenmeyer flask, stoppered and placed under refrigeration at 0° overnight.

² Chloroform was preferred over the other solvents such as carbon tetrachloride and tetrachloroethylene.

³ By first completely dissolving the alcohol and then cooling, a more uniform dispersion is obtained for sulfation.

⁴ Both E. K. Pract. and Matheson, Coleman and Bell (99%, Fe free) chlorosulfonic acids were used; the results were equally good with both acids.

⁵ Near the end of addition considerable foaming sometimes occurs because of the rapid release of HCl gas. By using a 2-l. flask for the suggested quantities of materials there is sufficient head-room to accommodate the foam. The addition of acid, of course, should be temporarily stopped when considerable foaming occurs.

⁶ The slurry becomes clear at about 15°.

⁷ Heat can be conveniently applied with a heat lamp or a heat gun (modified hair-dryer type).

Filtering⁸ is best accomplished under low humidity conditions in a cold room at 0°. A yield of 85-95 g. (61-68%) is obtained.

IV. Properties and Purity of Product

The octadecylsulfuric acid obtained has a neutral equivalent of 353-360 (calculated 350.5) depending on the degree of sulfation⁹ and the amount of moisture pick-up. The product is satisfactory for the preparation of a large variety of pure salts¹⁰ with a minimum of work.¹¹

⁸ Filtering at room temperature is possible provided the equipment and CHCl_3 are previously chilled to 0°. However, working at 0° decreases the possibility of moisture pick-up by the hygroscopic alkylsulfuric acids. In either case the following procedure is recommended:

- (a) A suitable synthetic filter medium such as polyethylene is used to ensure rapid filtration. Apparently the sulfating agent forms parchment with filter paper, hindering filtration.
- (b) A layer of inert vinyl sheeting, such as Dow Saran Wrap, is loosely placed on the Buchner funnel, separating the product from the rubber dam used to exclude moisture (See fig. 1). Direct contact with rubber stains the product and deteriorates the rubber.
- (c) Lower homologs are best filtered at 0° because of their lower melting points and greater solubility. Dodecyl- and tetradecylsulfuric acids were crystallized at -20° and filtered at 0°.
- (d) Solvent removal in a vacuum dessicator at 0° is speeded-up by changing the dessicant, CaSO_4 , every two hours; drying should be complete in 6-8 hours. Checking the product for weight constancy is done under anhydrous conditions.

⁹ Attempts to purify less pure octadecylsulfuric acid containing 4-6% unsulfated alcohol by recrystallization from chloroform, ether, carbon tetrachloride, Skelly B, or dichloromethane were unsuccessful.

¹⁰ E. W. Maurer, A. J. Stirton, and J. K. Weil, J. Am. Oil Chemists' Soc. 37, 34 (1960)

¹¹ Table I lists the analysis, melting point, yield and purity of alkylsulfuric acids prepared by the method outlined. Table II lists amine, amino acid, and metal salts prepared from octadecylsulfuric acid together with their melting points. Purity ranged from 90-100%; yields 50-93%. The metal salts are generally insoluble in water but soluble in butanol, aniline, plasticizers and lubricants.

Storage at 0° for over a year produced no discoloration of the acid; at room temperature darkening occurs gradually, particularly in sunlight.

V. Methods of Preparation

Dodecylsulfuric acid was prepared as a flaky hygroscopic mass by Ross and co-workers¹² by sulfation of dodecanol with chlorosulfonic acid, using liquid sulfur dioxide as the solvent. Dodecyl- and hexadecylsulfuric acids were prepared by Desnuelle and co-workers¹³ by acidification and extraction of aqueous solutions of sodium salts. However, these workers do not report melting points nor are the procedures they describe direct crystallizations from a reaction mixture.

Although the n-C₁₂-C₁₈ alkylsulfuric acids have been known for a long time in the form of one or more of their salts, their isolation in the form of free acids by crystallization from a reaction mixture has only recently been reported in the literature.¹⁰

The method we have described, which minimizes or excludes moisture, leads directly to the isolation of dodecyl-, tetradecyl-, hexadecyl-, and octadecylsulfuric acids in a pure state. The availability of the free acids enables one to prepare a large variety of pure salts with a minimum of purification steps. Amine and amino acid salts of long chain alkylsulfuric acids are of current interest in medicinals.¹⁴ The sulfation procedure and method of isolation as the alkylsulfuric acid is believed to be of general application to saturated higher primary alcohols.

12. J. Ross, J. H. Percy, R. L. Brandt, A. I. Gilbert, J. E. Mitchell, and S. Yolles, *Ind. Eng. Chem.*, 34, 924 (1942).

13. P. Desnuelle, R. Massoni, and O. Benoit-Micaelli, *Bull. Soc. Chim. France*, 1953, 595.

14. I. Utsumi and K. Harada, *Yakugaku Zasshi* 82, 96-101; *ibid.*, 102-107; *ibid.*, 114-119. (*Chemical Abstracts* 57, 6029-6031).

TABLE I

ALKYLSULFURIC ACIDS

<u>Alkyl</u>	<u>Melting Point</u>	<u>Yield %</u>	<u>Purity %</u> ^a
Dodecyl	25 - 7°	65	97
Tetradecyl	37 - 9°	75	98
Hexadecyl	40 - 2°	53	99 ⁺
Octadecyl	51 - 2°	65	99 ⁺

^a Purity by neutralization equivalent and also by conversion to the sodium alkyl sulfate and analysis for Na.

TABLE II

SALTS OF OCTADECYLSULFURIC ACID

<u>Amine and Amino Acid Salts</u>		<u>Metal Salts</u>	
	<u>M. P.</u>		<u>M. P.</u>
<u>dl</u> -Alanine	a	Aluminum	162° ^d
2-Amino-2(hydroxymethyl) 1,3 propanediol	124-127°	Barium	173° ^d
Ammonium	a	Cadmium	196° ^d
Aniline	124,8-125,8°	Calcium	> 200°
Aspartic Acid	a	Cobalt (pink)	180° ^d
2-Benzyl-2-thiopseudourea	95,8-97,2°	Copper (Blue-green)	140° ^d
Betaine	108-109°	Lithium	185,2° ^d
<u>l</u> -Glutamic acid	81-83°	Lead	152,2° ^d
Glycine	a	Magnesium	> 200°
Glycylglycine	a	Potassium	182-183,6°
Guanidine	145-146,4°	Silver	158° ^d
<u>dl</u> -Leucine	a	Strontium	166° ^d
Methionine	a	Zinc	indef.
Pyridine	103-106,5°		
Triethanolamine	86-86,8°		
Triethylamine	70-73°		
Urea	113-114°		

^a Amino acid salts in general do not have definite melting points.

