and outside of the swelling structure. Other evidence was also obtained to show that the sorbed water virtually attained the same salt concentration as the free water. (c) The shrinkage of all the sections was directly proportional to the moisture lost. The salt was shown to partly displace the sorbed water from the wood. Those salts which tended to displace the most sorbed water caused the greatest swelling.

MADISON, WISCONSIN RECEIVED FEBRUARY 7, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Preparation of Primary *n*-Alkyl Sulfates

BY CHAS. BARKENBUS AND JOHN J. OWEN

Many references can be found stating that alkyl sulfates are good alkylating agents; however, with the exception of methyl sulfate, ethyl sulfate, and possibly *s*-butyl sulfate, no easy methods for making them are available.

The action of alcohols on sulfuric acid is of no value, except in the case of methyl sulfate, because of the formation in large amounts of alkyl acid sulfates, ethers, and unsaturated compounds. The action of alcohols on sulfuryl chloride has been investigated by Bushong and others,[1] who have found that the chief products formed are alkyl chlorosulfonates, alkyl acid sulfates, alkyl chlorides and some alkyl sulfates. It is claimed[2] that both of the chlorine atoms in sulfuryl chloride are attached to the sulfur by co-valent bonds but we have observed that chemically they are widely different, which accounts for the poor yields when starting with this compound. Recently McKee[3] has patented the action of alcohols on sulfuryl chloride but in our experience with *n*-butyl alcohol the chief product formed was *n*-butyl chlorosulfonate. By using alkyl chlorosulfonates with sodium alcoholates Bushong[1] has made several alkyl sulfates though the yields were low and the method rather tedious. It was hoped that magnesium alkoxy bromide could be substituted for the sodium alcoholates since this type of reagent has been used successfully by Porter and Yabroff[4] in making *t*-isobutyl phenylacetate. In carrying out this reaction with *n*-butoxymagnesium bromide and *n*-butyl chlorosulfonate it was found that the chief product was *n*-butyl bromide, some *n*-butyl chloride, and that the sulfate group had combined with the magnesium as magnesium *n*-butyl sulfate. It is remarkable that the bromine leaves the magnesium for the butyl group.

The action of alkyl chlorosulfonates on alkyl nitrites, alkyl carbonates and alkyl orthoformates[5] has been used but low yields were obtained in all cases. The action of unsaturated hydrocarbons on either sulfuric acid or alkyl acid sulfate has been patented[6] though the alkyl sulfates beyond the ethyl cannot be primary. The patents also mention making mixed sulfates.

The oxidation of alkyl sulfites has been suggested[7] as a possible method of attack but outside of the use of potassium permanganate and chlorine, both of which gave poor yields, no further mention of this method could be found. The recent excellent synthesis of alkyl sulfites by Voss and Blanke[8] made the oxidation of sulfites a possible method of entering the alkyl sulfate series and led us to investigate this method rather extensively. Although no method of oxidation was found, it may be worth while to record a few of our observations.

It was found that an anhydrous medium is necessary, otherwise hydrolysis with formation of alkyl acid sulfates and sulfuric acid will result. This limits the number of oxidizing agents that can be used, and in addition the reagent must furnish oxygen. Dry nitrogen dioxide gas oxidizes the sulfites but apparently attacks only the carbon since sulfur dioxide was evolved and oxalic acid formed. Ozone has no effect, while hydrogen peroxide dissolved in quinoline was unsuccessful. The most promising reagent was benzoyl hydrogen peroxide dissolved in dry chloroform but yields of only 10% could be obtained with *n*-butyl sulfite since the carbon chains were attacked at the same time. Much time was spent

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(1) Bushong, *Am. Chem. J.*, **30**, 212 (1903); Levaillant and Simon, *Compt. rend.*, **169**, 854 (1919); Levaillant, *ibid.*, **188**, 261 (1929).

(2) Sugden, Reed and Wilkins, *J. Chem. Soc.*, **127**, 1525 (1925).

(3) McKee, U. S. Patent 1,641,005 (Aug. 30, 1927).

(4) Porter and Yabroff, THIS JOURNAL, **54**, 2453 (1932).

(5) Levaillant, *Compt. rend.*, **187**, 234 (1928); **190**, 54 (1930); **195**, 882 (1932).

(6) Hunt, U. S. Patents 1,744,164, 1,744,207, 1,744,227 (Jan. 21, 1930). Shell Development Co., U. S. Patent 1,854,581 (Apr. 19, 1932).

(7) Levaillant, *Compt. rend.*, **188**, 261 (1929); **189**, 465 (1929).

(8) Voss and Blanke, *Ann.*, **485** 258 (1931).

trying to control the conditions but nothing of a practical nature was obtained. In fact it seems impossible to obtain alkyl sulfates in good yields by this method.

The action of alkyl chlorosulfonates on alkyl sulfites has recently been described by Levaillant.[9] We had observed this reaction and had used it in making many alkyl sulfates before we were aware of his article. Since we had nearly finished the preparation of the normal alkyl sulfate series, it was thought advisable to finish the series and publish the results of our experiences. This synthesis is the most practical one so far discovered, and Levaillant merely mentions the use of it in two preparations without giving any details. This reaction has been used successfully in making the primary normal alkyl sulfates continuously through the decyl and the even numbered alkyl groups through the octadecyl.

Alkyl sulfites react with alkyl chlorosulfonates at a temperature of 100–130° with or without zinc chloride as a catalyst. Several reactions are possible, the two main ones being expressed by the equations

$$(RO)_2SO + ClSO_2OR = (RO)_2SO_2 + HCl + SO_2 + R'CH{=}CH_2$$

$$(RO)_2SO + ClSO_2OR = (RO)_2SO_2 + SO_2 + RCl$$

The reaction takes place with the formation of some tar but with all the lower members the sulfates can be distilled easily from a small amount of low boiling material as well as from the tar. The higher members can be crystallized directly from the reaction mixture by the use of ether. It is not necessary to isolate the alkyl sulfite and the chlorosulfonate since the crude reaction products give just as good yields as the pure materials. In the case of the higher members this is fortunate since both of the compounds would be very difficult or impossible to purify. The purity of the sulfates obtained from the crude reaction mixture is exceedingly high, most of the liquids distilling over a 2° range. Starting with compounds which are readily available this method gives yields of 50 to 75% of the theoretical in a very short time and with a minimum of effort.

The method apparently is not applicable to branched chain primary alcohols, or to secondary or tertiary alcohols, although further work along this line as well as with aryl compounds is being carried on.

In Table I are listed the primary *n*-alkyl sulfates with their physical properties, yields and analyses. The boiling points and melting points increase like other homologous series but it is interesting to note that the nonyl sulfate has a higher melting point than the even numbered *n*-decyl sulfate. This property has been observed for the higher alkyl bromides by Meyer and Reid.[10]

The melting points of the solids are very sharp although no attempt was made to detect polymorphism by determining their cooling curves.

TABLE I

YIELDS AND PHYSICAL PROPERTIES OF THE ALKYL SULFATES

Substance	Yield, %	B. p., °C. (corr.)	Press., mm.	M. p., °C. (corr.)	d^{25}_{25}	n^{25}_{D}	S analyses, %[b] Calcd.	Found
n-Butyl	71	97.4	3		1.0591	1.4210	15.25	15.09
n-Amyl	77	117.0	2.5		1.0265	1.4270	13.45	13.46
n-Hexyl	48	125.3	2		1.0039	1.4344	12.04	11.72
n-Heptyl	65	146.6	1.5	11.4	0.9819	1.4362	10.89	10.89
n-Octyl	76	166.1	2	20.3	.9661	1.4408	9.94	9.91
n-Nonyl	71			41.9–42.1			9.15	9.22
n-Decyl	54			37.6–37.8			8.49	8.47
n-Dodecyl	58			48.4–48.5			7.38	7.41
n-Tetradecyl	64			57.8–58.0			6.54	6.60
n-Hexadecyl	62			66.2–66.3			5.86	5.98
n-Octadecyl[a]	84			70.2–70.7			5.32	4.36

[a] Recrystallization did not alter the purity of the *n*-octadecyl sulfate.

[b] Because the percentage of sulfur is so nearly the same in the alkyl sulfites and sulfates, the products were tested qualitatively for the former with negative results.

We wish to express our thanks to Mr. Thomas Cross, of Johns Hopkins University, for supplying the higher alcohols used in this investigation, as they were of a high degree of purity and made possible the synthesis of the higher alkyl sulfates.

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(9) Levaillant, *Compt. rend.*, **197**, 648 (1933). Unfortunately Levaillant's article was not available when we started this investigation and was not noticed until it appeared in *Chemical Abstracts*, **28**, 97 (1934).

(10) Meyer and Reid, THIS JOURNAL, **55**, 1574 (1933).

Experimental

Preparation of *n*-Amyl Sulfate.—As an example of the general method of preparation of the alkyl sulfates the procedure for *n*-amyl sulfate is given in detail. *n*-Amyl alcohol, prepared by the Grignard synthesis[11] from *n*-butyl bromide and paraformaldehyde, and dried over anhydrous magnesium sulfate was used.

The chlorosulfonate was prepared by the action of the alcohol upon sulfuryl chloride:[12] 17.6 g. (0.2 mole) of *n*-amyl alcohol was added slowly and with shaking from a separatory funnel to 27.0 g. (0.2 mole) of sulfuryl chloride cooled in ice water. When all the alcohol had been added, a tube extending to the bottom of the flask was introduced, and a current of air, dried by bubbling through sulfuric acid, was passed through the reaction mixture until practically all the hydrogen chloride was removed. About ten minutes after the current of air was started the ice-bath was removed and the reaction mixture was allowed to come gradually to room temperature. Approximately one and one-half hours are required for the complete operation.

n-Amyl sulfite was prepared by a modification of the method of Voss and Blanke:[8] 26.2 g. (0.22 mole) of thionyl chloride was added slowly and with shaking to 38.8 g. (0.44 mole) of *n*-amyl alcohol starting at room temperature. There was an immediate rise in temperature, and the thionyl chloride was added at such a rate as to maintain the temperature at about 40–50°. When approximately two-thirds of the thionyl chloride had been added, it was necessary to warm the reaction mixture in a water-bath. A current of dry air was passed through the alcohol during the addition of the thionyl chloride and until practically all the hydrogen chloride had been removed. When all the thionyl chloride was added the water-bath was slowly heated almost to the boiling point of water, and this temperature was maintained until the hydrogen chloride was removed.

The crude chlorosulfonate was added slowly and with shaking to the crude sulfite previously heated on an oil-bath to 125–130°. In a short time there was an evolution of gases and a gradual darkening of the reaction mixture. A temperature sufficiently high to keep the reaction progressing slowly was maintained until no more gas was evolved. This varied from 115–140° with the different esters.

After cooling, ether and charcoal were added to the black, tarry reaction product. Ice water was then added, the mixture shaken vigorously and filtered. The water layer was separated, and the ether extract was washed successively with cold sodium carbonate solution and twice with ice water. Separation of the water layers was sometimes difficult because of the formation of emulsions which could be broken readily by the addition of sodium chloride. The ether layer was quickly dried with anhydrous magnesium sulfate and, after removing the ether, distilled under reduced pressure.

In the case of the higher esters, which are solids, the tarry reaction mixture was treated with ether and charcoal, refluxed for one hour and filtered. After removing a portion of the ether the ester was recovered by cooling the ether solution in an ice–salt mixture. The crude product was purified by recrystallization from ether. The solid esters crystallize in long, flat, white prisms or in plates.

Although one-tenth of a mole excess of alkyl sulfite was used in preparing *n*-amyl sulfate, equimolar quantities were used for all the higher alcohols.

Summary

1. A new method for making the neutral normal primary alkyl sulfates in good yields from the alcohols and sulfuryl and thionyl chlorides has been described.

2. Several normal alkyl sulfates having more than four carbon atoms in the alkyl radical have been prepared and their physical properties described for the first time.

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[11] "Organic Syntheses," John Wiley & Sons, Inc., New York, Vol. 6, 1926, p. 22.

[12] Bushong, *Am. Chem. J.*, **30**, 212 (1903); Behrend, *J. prakt. Chem.*, [2] **15**, 28 (1877).