

The Alpha-Sulfonation of Alkyl Palmitates and Stearates¹

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Abstract

Methyl, ethyl, and isopropyl esters of palmitic or stearic acid were α -sulfonated directly by the dropwise addition of a 2.4 molar ratio of liquid sulfur trioxide to the ester, with or without solvent, at 0C.

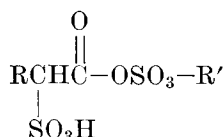
Scission of the ester apparently takes place during sulfonation. Yield of the ester $\text{RCH}(\text{SO}_3\text{Na})\text{CO}_2\text{R}'$ was increased, and yield of by-product disodium salt was decreased by re-esterification with methyl, ethyl, or isopropyl alcohol prior to neutralization. Direct sulfonation of the ester by sulfur trioxide, without solvent, gave 70–80% yields, increased 10% by the presence of a small amount of CCl_4 as the solvent (1 ml/g of ester). Mixtures of the α -sulfo ester and the disodium salt can be analyzed by infrared spectra.

Introduction

SODIUM SALTS of alkyl α -sulfopalmitates and stearates are readily prepared in a pure state by esterification of the α -sulfo acid or the monosodium salt (5,6). It might be an advantage to sulfonate the ester instead, particularly if the ester is readily available and liquid at room temperature, permitting sulfonation without the presence of solvent.

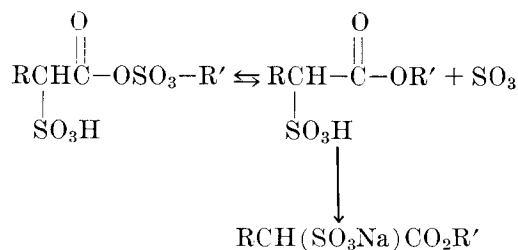
Methods for direct sulfonation have not been described except in the patent literature (1,2). In some cases the product may be the α -sulfo acid instead of primarily the α -sulfo ester (3).

The α -sulfonation of fatty acids apparently takes place with the initial formation of a mixed anhydride $\text{RCH}_2\text{CO}_2\text{SO}_3\text{H}$ (4). The sulfonation of esters may take place through the initial formation of a complex of SO_3 and ester, less definite in structure and composition. Formation of the complex or a rearrangement product therefrom could activate the α -H atom. Further reaction with a second mole of SO_3 would then accomplish α -sulfonation to give an intermediate



from which either the disodium salt $\text{RCH}(\text{SO}_3\text{Na})\text{CO}_2\text{Na}$ or the α -sulfo ester $\text{RCH}(\text{SO}_3\text{Na})\text{CO}_2\text{R}'$ could result.

Immediate neutralization of the reaction mixture gives only the disodium salt. If however the reaction mixture is allowed to stand at room temperature overnight or is heated one hour at 60C and carefully neutralized, the reaction mixture consists of about 60% ester. The mechanism leading to the re-formation of ester is not known, but the over-all process seems to involve a rearrangement to lose SO_3 prior to neutralization.



Experimental Section

The starting esters were prepared by heating commercial palmitic or stearic acid, purity 93%, with a 16:1 molar ratio of the alcohol for 8 hr at reflux temperature, with 3.8 mole % *p*-toluenesulfonic acid as the catalyst. The mixture was decanted into a large volume of water, washed free of acid, distilled through a one-foot Vigreux column, and crystallized from acetone at -25C . The esters are listed in Table I.

Preliminary experiments established the necessary ratio of SO_3 . Sulfonation with a 1:1 molar ratio at 60C gave sodium stearate and unreacted methyl stearate with only a trace of sulfonation. A 2.4 molar ratio of SO_3 was necessary to give a completely water-soluble sulfonation mixture, prior to neutralization, without the appearance of insoluble unreacted ester or fatty acid.

Low-temperature addition of liquid SO_3 to the ester was essential. The mixture could then be heated and kept at the required temperature. Sulfonation at 60C with SO_3 vapor was complete, with no unreacted ester or fatty acid, but the only product was the disodium salt.

Preliminary experiments also established that it was necessary to maintain the sulfonation mixture at an elevated temperature for some time. After sulfonation of methyl stearate with 2.4 moles of liquid SO_3 added at 0C, the mixture was then heated to 60C, cooled rapidly, and neutralized, giving only disodium α -sulfostearate, yield 93%.

It is important to use anhydrous conditions for sulfonation, including the use of freshly distilled sulfur trioxide. In the experiments of Table II a 2.4 molar ratio of SO_3 was added dropwise with stirring to 20 g of ester with or without CCl_4 solvent, at 0C to 5C. The mixture was then either stored at room temperature (A) or heated and stirred (B), and in some cases refluxed with methyl, ethyl, or isopropyl alcohol (C); then cooled to 0C, neutralized with

TABLE I
Alkyl Palmitates and Stearates

	Melting point °C	n_D^{40}	% Purity by GLC
Methyl palmitate	30.0–30.6	1.4331	99.2
Ethyl palmitate	20.6 ^a	1.4322	99.0
Isopropyl palmitate	12.8 ^a	1.4307	99.0
Methyl stearate	38.8–39.9	1.4363	99.2
Ethyl stearate	34.1–35.0	1.4354	99.0
Isopropyl stearate	24.1 ^a	1.4341	99.1

^a Freezing point.

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TABLE II
 α -Sulfonation of Esters

Expt.	Alkyl ester	Solvent ratio ml CCl ₄ per gram	Yield, %, of separated products		Total yield, %	Reaction condition after sulfonation prior to neutralization ^a
			α -Sulfo ester	Disodium salt		
1	Methyl palmitate	2.5	51	38	89	A
2	Ethyl palmitate	2.5	52	A
3	Methyl stearate	5.0	54	A
4	Methyl palmitate	1.0	58	26	84	B
5	Ethyl palmitate	no solvent	61	24	85	B
6	Isopropyl palmitate	no solvent	63	B
7	Methyl stearate	1.0	60	28	88	B
8	Isopropyl stearate	no solvent	60	12	72	B
9	Methyl palmitate	1.0	84	C
10	Methyl palmitate	no solvent	73	8	81	C
11	Ethyl palmitate	1.0	81	1	82	C
12	Ethyl palmitate	no solvent	72	9	81	C
13	Isopropyl palmitate	1.0	80	2	82	C
14	Methyl stearate	1.0	90	1	91	C
15	Ethyl stearate	1.0	88	2	90	C
16	Isopropyl stearate	no solvent	78	C

^a A—Stored 24 hours at room temperature. B—Stirred one hour at 60°C. C—Stirred one hour at 60°C, refluxed four hours with 40 ml CH₃OH, C₂H₅OH, or CH₃CHOHCH₃.

alcoholic NaOH and evaporated to dryness. The α -sulfo ester was separated by extraction with hot absolute ethanol, in which it is soluble. The disodium salt was recovered from the residue by crystallization from hot aqueous solution. Esters produced by direct sulfonation were identical with those from α -sulfo acids and equal in purity and color.

The data of Table II show the importance of solvent, equilibration temperature, and re-esterification in obtaining the maximum yield of α -sulfo ester (Experiment 14, 90%, sodium methyl α -sulfostearate). There is no significant difference in yield in a comparison of methyl, ethyl, and isopropyl esters, but stearates gave better yields, perhaps because of lesser

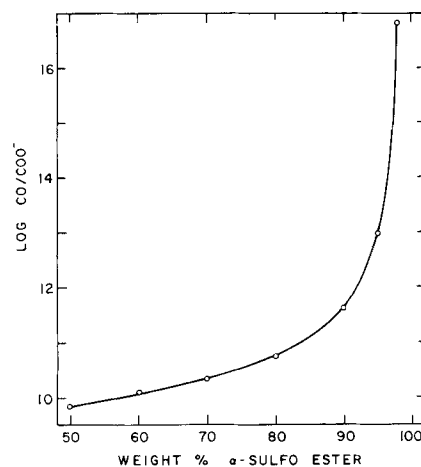


FIG. 1. Infrared absorption spectra of sodium methyl α -sulfopalmitate-disodium α -sulfopalmitate mixture.

solubility and more complete recovery on crystallization. Higher yields are obtained in the presence of solvent because of better mixing. Solvent ratio is not important. The lower melting esters of Table I are more easily sulfonated in the absence of solvent.

An analytical method was developed, based on the relative intensities of infrared absorption of carboxylate ion at 6.13 μ and ester carbonyl at 5.72. For this purpose Nujol mulls were made by thoroughly mixing different ratios of sodium methyl α -sulfopalmitate and disodium α -sulfopalmitate. Log CO/COO⁻ plotted against weight % α -sulfo ester gave a smooth curve (Figure 1), providing a method for determining the amount of ester in a crude reaction mixture or for checking the purity of an isolated α -sulfo ester.

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