

Alkanesulfonates and Hydroxyalkane-sulfonates from α -Sulfo Fatty Acids¹

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Continuation of research on long chain α -sulfo fatty acids has led to a decarboxylation (I)

and a reduction method (II) as shown by the equations:



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(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

TABLE I
SODIUM ALKANESULFONATES

Compound	Method ^a	Yield, %	Krafft point ^b	% Na		% C		% H		% S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₁₁ H ₂₃ SO ₂ Na	D	8	21.5°	8.90	8.94	51.13	50.98	8.97	9.07	12.41	12.50
C ₁₂ H ₂₅ SO ₂ Na	S	53	38°	8.44	8.37	52.91	52.51	9.25	9.35	11.77	11.28
C ₁₃ H ₂₇ SO ₂ Na	D	39	35.5°	8.03	7.86	54.51	54.17	9.50	9.63	11.20	11.14
C ₁₄ H ₂₉ SO ₂ Na	S	56	48°	7.65	7.55	55.97	55.89	9.73	10.08	10.67	10.79
C ₁₅ H ₃₁ SO ₂ Na	D	52	48°	7.31	7.35	57.29	57.33	9.94	10.15	10.20	9.90
C ₁₆ H ₃₃ SO ₂ Na	S	65	57°	7.00	6.78	58.50	58.25	10.13	10.24	9.76	9.76
C ₁₇ H ₃₅ SO ₂ Na	D	40	62°	6.71	6.51	59.61	59.68	10.30	10.37	9.36	9.07
C ₁₈ H ₃₇ SO ₂ Na	S	53	70°	6.45	6.20	60.63	60.65	10.46	10.56	8.99	9.05

^a D = decarboxylation, S = Strecker reaction. ^b Ref. 6.

Desulfonation rather than decarboxylation occurred on heating α -sulfopalmitic acid in *o*-dichlorobenzene at the reflux temperature. Palmitic acid was recovered in a yield of 77%. Attempts to use a recent method³ for the decarboxylation of sodium α -sulfostearic acid simply by heating the monosodium salt at 265° under a nitrogen atmosphere gave in our case similar desulfonation to stearic acid.

Alkaline fusion of the disodium salt of the α -sulfo acid gave 35–50% yield of sodium alkanesulfonate of one less carbon atom, according to equation I. The disodium salt was heated and stirred under nitrogen with excess sodium hydroxide to ensure a stirrable paste near the fusion temperature (300–320°). The product contained the sodium alkanesulfonate, unconverted disodium salt, and a by-product identified as the fatty acid of two less carbon atoms, apparently formed by conversion of the disodium salt to the soap of an α -olefinic acid, followed by chain degradation by the Varrentrapp reaction⁴: $\text{RCH}_2\text{CH}(\text{SO}_2\text{Na})\text{CO}_2\text{Na} + \text{NaOH} \rightarrow \text{RCH}=\text{CHCO}_2\text{Na} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{RCO}_2\text{Na} + \text{CH}_3\text{CO}_2\text{Na}$.

For comparison, sodium alkanesulfonates of an even number of carbon atoms were prepared by the Strecker reaction⁵ from the alkyl bromide and sodium sulfite. All sodium alkanesulfonates are recorded in Table I. The Krafft point, the temperature at which a 1% aqueous dispersion changes sharply to a clear solution, is related to melting point⁶ and serves to characterize these compounds. Alternations in Krafft point, shown in Figure 1, are similar to alternations in melting point in the fatty acid series.

Hydroxyalkanesulfonates, isolated as the sodium salt, were generally prepared by the lithium borohydride reduction of lithium methyl α -sulfolaurate, myristate, palmitate, or stearate. Sodium borohydride gave lower yields but higher than that previously indicated for use in ester reductions.⁷ In all cases the only products were the

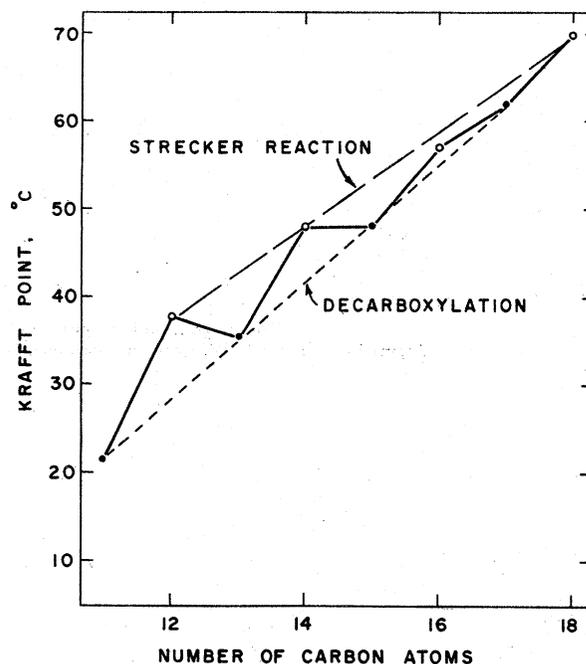


Fig. 1.—Krafft points for sodium alkanesulfonates as a function of chain length.

sodium 1-hydroxy-2-alkanesulfonate and the hydrolyzed unreduced ester isolated as the disodium salt. Use of the isopropyl ester, which is more resistant to hydrolysis than the methyl ester⁸ gave no improvement in yield of the reduction product. The high Krafft points and limited solubility are attributed to hydrogen bonding. Hydrogen bonding may also account for the limited solubility of the corresponding sodium α -sulfolauric, myristic, palmitic, and stearic acids, the Krafft points of which are 52°, 68°, 83°, and 94°, respectively.

The free acids, 1-hydroxy-2-hexadecanesulfonic acid and 1-hydroxy-2-octadecanesulfonic acid, were prepared from the sodium salts by ion exchange.

Experimental

Decarboxylation. Alkali Fusion of Disodium α -Sulfo-myristate.—Sodium hydroxide pellets (53 g.) were added to a resin flask containing a paste of 27 g. of disodium α -sulfo-

(3) H. S. Bloch (Universal Oil Products) U.S. Patent 2,822,387 (1958).

(4) R. G. Ackman, P. Linstead, B. J. Wakefield, and B. C. L. Weedon, *Tetrahedron*, **8**, 221 (1960).

(5) R. M. Reed and H. V. Tartar, *J. Am. Chem. Soc.*, **57**, 570 (1935).

(6) M. Démarecq and D. Dervichian, *Bull. soc. chim.*, **12**, 939 (1945).

(7) H. C. Brown, E. J. Mead, and C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(8) A. J. Stirton, J. K. Weil, and R. G. Bistine, Jr., *J. Am. Oil Chemists' Soc.*, **31**, 13 (1954).

TABLE II
SODIUM 1-HYDROXY-2-ALKANESULFONATES

Compound	Yield, ^a %	Krafft point ^b	% Na		% C		% H		% S	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₁₀ H ₂₁ CH(CH ₂ OH) SO ₃ Na	68	59°	7.97	8.01	49.98	50.09	8.74	8.77	11.12	11.13
C ₁₂ H ₂₅ CH(CH ₂ OH) SO ₃ Na	74	73°	7.27	7.25	53.14	53.13	9.24	9.09	10.13	10.21
C ₁₄ H ₂₉ CH(CH ₂ OH) SO ₃ Na	64	84°	6.68	6.72	55.78	56.13	9.66	9.65	9.31	9.27
C ₁₆ H ₃₃ CH(CH ₂ OH) SO ₃ Na	61 ^c	93°	6.17	6.12	58.03	58.08	10.01	10.02	8.61	8.99

^a Sum of the yield of the reduction product and the hydrolyzed ester, recovered as the disodium salt RCH(SO₃Na)CO₂Na = 100%. ^b Krafft points for corresponding monosodium salts RCH(SO₃Na)CO₂H are 52, 68, 83, and 94°, respectively, ^c Yield from C₁₆H₃₃CH(SO₃Na)CO₂CH₃ and NaBH₄ = 44%.

myristate⁹ with an equal weight of water. The reactants were stirred with a Hershberg stirrer and heated, leading a slow stream of nitrogen over the surface to remove water vapor and exclude oxygen. As the temperature increased and water was removed, the mixture became fusible at 300°. Heating was discontinued when the mixture began to darken above 320°.

The fusion mixture was cooled, taken up in water, and acidified with sulfuric acid. Solids were filtered, washed free of inorganic salts, and taken up in hot 95% ethanol. Insoluble unconverted sodium α -sulfomyristic acid, recovery 20%, was removed by filtration.

The alcoholic solution, treated with water and diethyl ether, formed two phases. Evaporation of the ether layer and crystallization of the residue from chloroform gave lauric acid (3.7 g., yield 23%) neut. equiv. 199.8 (theo. 200.3), m.p. 42.4–43.1°; confirmed by mixed melting point and infrared spectra. A gas-liquid chromatogram showed the purity of the isolated lauric acid by-product to be at least 90%.

Crystallization of the aqueous alcohol solution at 0° gave sodium tridecanesulfonate (6.0 g., yield 39%) with the analysis and Krafft point shown in Table I. Infrared spectra showed the presence of the SO₃⁻ group and absence of CO and COO⁻ groups. Sodium alkanesulfonates of 11, 15, and 17 carbon atoms prepared in the same way are recorded in Table I.

Reduction. Sodium 1-Hydroxy-2-octadecanesulfonate.—The general method was reduction of the lithium salt of the methyl ester of the α -sulfo fatty acid, dissolved in isopropyl alcohol, by addition of a 1.25-molar ratio (theo. 0.5) of lithium borohydride. Variations in the order of addition of reactants or by use of diglyme gave lower yields.

A solution of lithium isopropyl α -sulfostearate (22.6 g., 54.8 mmoles) in 270 ml. of isopropyl alcohol was heated and 50 ml. of the solvent distilled to remove traces of moisture. Lithium borohydride (Metal Hydrides, Inc.,¹⁰ 89.1%; 1.48

g., 68.5 mmoles) was added during 3 min., the solution was refluxed 24 hr., 300 ml. of water was added, and the mixture was refluxed an additional hour.

The aqueous isopropyl alcohol solution was poured through an ion exchange column containing 400 ml. of resin sulfonic acid (Dowex 50W-X8¹⁰), neutralized with sodium hydroxide to pH 10.0, and evaporated to dryness. The residue was taken up with 1200 ml. of water, heated to boiling, allowed to crystallize at room temperature, filtered, washed, dried at 60° in a vacuum oven, and extracted twice with 3 l. of boiling methanol. The residue insoluble in methanol was the hydrolyzed unreduced ester recovered as disodium α -sulfostearate (yield 39%). Crystallization of the methanol extract gave sodium 1-hydroxy-2-octadecanesulfonate (yield 61%).

Other sodium 1-hydroxy-2-alkanesulfonates recorded in Table II were obtained in a similar manner. Infrared examination of Nujol mulls showed strong OH absorption at 3400 cm.⁻¹ and SO₃⁻ absorption at 1250–1150 and 1060 cm.⁻¹.

1-Hydroxy-2-alkanesulfonic Acids.—Sodium 1-hydroxy-2-hexadecane-sulfonate (2.9 g.) was dissolved in 150 ml. of isopropyl alcohol by heating and stirring in the presence of 100 ml. of resin sulfonic acid, passed through a column containing 300 ml. of the exchange medium, and eluted with 900 ml. of isopropyl alcohol.

The isopropyl alcohol solution was evaporated in a rotary evaporator at 80° and 10 mm., the residue was redissolved in 100 ml. of chloroform, and water was removed azeotropically. Crystallization at -20° and drying at 75° for 1 hr. in a vacuum oven gave 1-hydroxy-2-hexadecanesulfonic acid, neut. equiv. 322.9 (theo. 322.5) as hygroscopic crystals which soften at 106°, pass through a glassy stage and melt sharply at 113°. 1-Hydroxy-2-octadecanesulfonic acid, neut. equiv. 350.8 (theo. 350.5), obtained in a similar manner, softens at 107.5°, becomes glassy and melts sharply at 114.8°.

Acknowledgment.—Microanalyses for C, H, and S were performed by Mr. Ronald Campbell and Miss Oksana Panasiuk and gas-liquid chromatography by Mr. Samuel F. Herb.

(9) A. J. Stirton, J. K. Weil, Anna A. Stawitzke, and S. James, *J. Am. Oil Chemists' Soc.*, **29**, 198 (1952).

(10) Reference to manufactured products does not constitute recommendation by the U.S. Department of Agriculture over similar products not mentioned.