

Similarly, methyl 9(10) mercaptostearate has been converted to the corresponding disulfide (10).

Sulfur-containing polymers have been prepared from some of these dicarboxylic acids, i.e., heating at 90°C of 11-(acetylthio)-undecanoic acid with hexamethylene diamine results in the formation of polyamides (18). These polyamides (Mol Wt 11,000-20,000) have been converted into fibers.

*Uses of Sulfur Derivatives of Long-Chain Acids.* Patent literature contains references describing the commercial value of sulfur derivatives of long-chain acids. Some of these products are useful as lubricant additives, coatings, and rubber substitutes; however, from the point of view of an organic chemist, a great

deal of work remains to be done. Studies of relationships of structures to properties must be continued before we can expect much greater benefits of these materials to the fat and oil industry.

#### REFERENCES

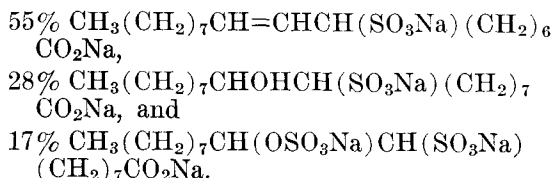
- Dearborn, F. E., U. S. 2,169,793 (1939).
- Ralston, A. W., E. W. Segebrecht, and S. T. Bauer, J. Org. Chem. 4, 502 (1939).
- Pratt, L. S., and E. E. Reid, J. Am. Chem. Soc. 37, 1934 (1915).
- Sasin, G. S., Richard Sasin, and N. Capron, J. Org. Chem. 21, 852 (1956).
- Sasin, Richard, W. F. Ashley, J. W. Manning, Jr., A. Paolinini, Jr., and G. S. Sasin, JAOCS 35, 192 (1958).
- Sasin, Richard, G. S. Weiss, A. E. Wilfond, and G. S. Sasin, J. Org. Chem. 21, 1304 (1956).
- Sasin, G. S., F. R. Longo, O. T. Chortyk, P. A. Gwinner, and Richard Sasin, J. Org. Chem. 24, 2022 (1959).
- Markley, K. S., Fatty Acids, Interscience Publishers, Inc., N.Y., 1947, page 521.
- Kabayashi, F., and H. Susuki, U. S. 2,273,379 (1961).
- Koenig, N. H., G. S. Sasin, and Daniel Swern, J. Org. Chem. 23, 1525 (1958).
- Sasin, G. S., P. R. Schaeffer, and Richard Sasin, J. Org. Chem. 22, 1138 (1957).
- Sasin, Richard, G. S. Binns, R. M. Haff, and G. S. Sasin, J. Org. Chem. 24, 1143 (1959).
- Koenig, N. H., and Daniel Swern, J. Am. Chem. Soc. 79, 4235 (1957).
- Henkel & Cie, G.m.b.H., Brit. Pat. 470,717 (1937).
- Sasin, G. S., Sally Dym, L. Cerankowski, and Richard Sasin, unpublished results.
- Koenig, N. H., and Daniel Swern, J. Am. Chem. Soc., 79, 362 (1957).
- Sasin, G. S., F. R. Longo, Richard Berger, Wm. DeSantis, and Richard Sasin, J. Org. Chem. 26, 3538 (1961).
- Champetier, G., and J. Khaladj, Bull. Soc. Chim., 823 (1958).

## $\alpha$ -Sulfo Fatty Acids and Derivatives. Synthesis, Properties and Use

A. J. STIRTON, Eastern Regional Research Laboratory,<sup>1</sup> Philadelphia, Pennsylvania

**S**ATURATED long chain fatty acids react with sulfur trioxide, chlorosulfonic acid or dioxane sulfur trioxide to give monosulfonation in the  $\alpha$ -position. The reaction is simple, inexpensive and specific. The  $\alpha$ -sulfo acid is a versatile intermediate for salts, esters, amides, and other derivatives. Use of  $\alpha$ -sulfo compounds has been proposed in ore flotation, as surface active and detergent compositions, detergent bars, wetting agents, lime soap dispersing agents, as paint additives, and in lubricant greases.

The higher fatty acids can be sulfonated directly in the  $\alpha$ -position by reaction with sulfur trioxide, chlorosulfonic acid, or dioxane sulfur trioxide.  $\alpha$ -Sulfonation can be accomplished less directly by the Strecker reaction of an  $\alpha$ -bromo fatty acid with sodium sulfite (23,27). Direct sulfonation of the higher saturated acids is specific and leads only to monosulfonation in the  $\alpha$ -position. Reaction of sulfonating agents with unsaturated higher fatty acids is complex (29): the reaction of sulfur trioxide in liquid sulfur dioxide with oleic acid at -10C gives a product estimated to be about



Studies on the lower aliphatic sulfocarboxylic acids carried out by Backer and collaborators over a period of several years have been summarized by de Boer (8).

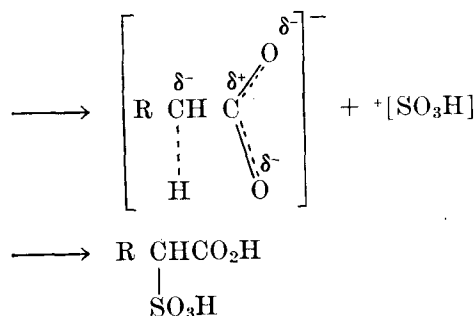
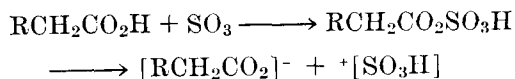
The sulfonation of dicarboxylic acids such as glu-

taric, adipic, azelaic, or sebacic acids by means of liquid sulfur trioxide, with trichloroacetic acid as the solvent, results in monosulfonation at the  $\alpha$ -position (16). Methods also exist for the direct sulfonation of amides, anhydrides, esters (24), soaps (11), and nitriles (6).

#### Mechanism of $\alpha$ -Sulfonation

The direct sulfonation of saturated long chain fatty acids by means of the vapor of sulfur trioxide or with the stabilized liquid of sulfur trioxide, in the presence of a relatively inert solvent, appears to take place with the initial formation of a mixed anhydride. Further heating is necessary to convert this to the  $\alpha$ -sulfo acid. Some evidence for the existence of the mixed anhydride can be found in the early literature on the lower sulfocarboxylic acids (15), also in the fact that perfluorobutyric acid reacts with  $\text{SO}_3$  to form a mixed anhydride sufficiently stable to be purified by distillation (13).

$\alpha$ -Sulfonation apparently occurs as follows:

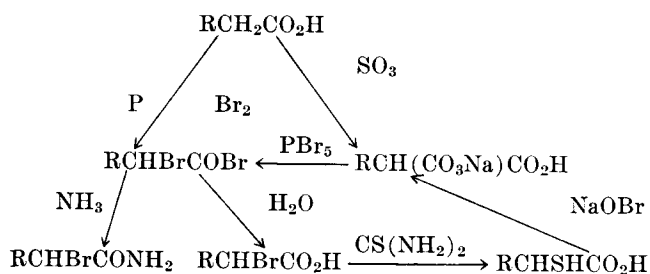


<sup>1</sup> Eastern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

This mechanism is similar to that for the  $\alpha$ -bromination of fatty acids by the Hell-Volhard-Zelinski reaction, catalyzed by phosphorus to form the acid bromide as an intermediate (39). There are other similarities in the two reactions. Both reactions are simple, direct, and specific. Only mono-substitution occurs and only in the  $\alpha$ -position; and no reaction takes place in the absence of an  $\alpha$ -hydrogen atom.

### Proof of Structure

Proof that sulfonation occurs in the  $\alpha$ -position is furnished by the following reaction cycle (52):



$\alpha$ -Bromopalmitamides identical in melting point and X-ray pattern were obtained from palmitic acid, in each of three routes: (I) sulfonation, reaction with phosphorus pentabromide, reaction with aqueous ammonia; (II) bromination to the  $\alpha$ -bromo acid bromide, hydrolysis to  $\alpha$ -bromopalmitic acid, conversion to  $\alpha$ -mercaptopalmitic acid, oxidation to sodium  $\alpha$ -sulfopalmitic acid, reaction with phosphorus pentabromide, and reaction with aqueous ammonia; (III) bromination to  $\alpha$ -bromopalmitic acid bromide and reaction with aqueous ammonia.

### Comparison of Sulfonation Methods

**Sulfur Trioxide.** Sulfur trioxide may be used as the liquid or as the vapor mixed with air or nitrogen. A convenient laboratory method, applicable to solid saturated fatty acids from lauric to behenic, and to commercial hydrogenated tallow acids is illustrated (43). Stabilized liquid sulfur trioxide, 1.25 moles, was added dropwise in 30 min to a stirred slurry of 0.78 moles of palmitic acid in 500 ml of carbon tetrachloride. The mixture was stirred and heated 1 hr at 60–65°C, cooled to 0°C, and filtered. The filter cake was washed with cold carbon tetrachloride and dried in a vacuum desiccator to constant wt to give an 85% yield of  $\alpha$ -sulfopalmitic acid as a gray product, estimated purity 98%. Lighter colored products can be obtained by the use of sulfur trioxide vapor, distilled from the stabilized liquid and mixed with nitrogen. Chloroform or tetrachloroethylene can be used in place of carbon tetrachloride.

Methods in the patent literature include sulfonation with sulfur trioxide dissolved in liquid sulfur dioxide, added to the fatty acid in liquid sulfur dioxide (24); and sulfonation with the mixed vapor of sulfur trioxide and butane, with butane as the solvent (7).

**Sulfonation Without Solvent.** Direct sulfonation without use of solvent is possible, particularly with fatty acids liquid or semi-liquid near room temp. The dark viscous reaction mixture and difficulties in filtration may require isolation of the sulfonation product as the sodium salt or as an easily purified derivative, rather than as the  $\alpha$ -sulfo fatty acid (17, 49).

Direct sulfonation without use of solvent is illustrated in the  $\alpha$ -sulfonation of a commercial coconut oil fatty acid forerun composed of about 42% caprylic, 28% capric, 24% lauric and 6% myristic acid, with an average composition corresponding to capric acid. The sulfonation product was not isolated but esterification at the carboxyl group was accomplished in the same vessel, catalyzed by the presence of the sulfonic acid group in the same molecule (32).

A mixture of sulfur trioxide vapor 1.12 moles, and nitrogen was passed into 0.95 mole of the semi-liquid forerun at 14°C with agitation. The temp of the dark viscous reaction mixture reached a maximum of 64°C. Toluene and 10% excess of 2-ethylhexanol were added and the sulfonated acids were esterified; water was removed azeotropically. The reaction mixture was neutralized with sodium hydroxide and the product was isolated after recovery of solvent as the sodium salt of the 2-ethylhexyl ester of  $\alpha$ -sulfo coconut oil fatty acid forerun—an excellent wetting agent quite stable to acid or alkaline hydrolysis.

**Chlorosulfonic Acid.** Chlorosulfonic acid is a convenient sulfonating agent and may be used in about the same way as liquid sulfur trioxide (3,17). It is somewhat more expensive and the hydrogen chloride evolved may cause corrosion difficulties.

Very little reaction with the higher fatty acids takes place below 50°C and a final temp of 70°C is required to complete the reaction. In contrast liquid sulfur trioxide accomplishes 30% sulfonation in 30 min at 25°C and reaction is complete at 60°C. Because of the higher reaction temp there is no improvement in color of the product.

**Dioxane Sulfur Trioxide.** Dioxane sulfur trioxide is useful in the  $\alpha$ -sulfonation of substituted long chain fatty acids such as 9,10-dichlorostearic acid, 9,10-dihydroxystearic acid and phenylstearic acid, to avoid reactions which involve the chlorine atoms, hydroxyl groups, or the benzene ring (38,49).

Phenylstearic acid from the Friedel and Crafts reaction is a mixture of several isomers with the benzene ring substituted at various positions in the fatty acid chain, apparently mainly at the penultimate C atom with little or no substitution at the  $\alpha$  or  $\omega$  position (26).

Sulfonation with dioxane sulfur trioxide in carbon tetrachloride gave disodium  $\alpha$ -sulfophenylstearate in a yield of 57%.

$\alpha$ -Sulfonation rather than ring sulfonation was established by ultra-violet absorption spectra and oxidative degradation. Sulfonation of palmitic or stearic acid with dioxane sulfur trioxide results in color improvement and the isolation of a white or cream colored  $\alpha$ -sulfo fatty acid (49).

### $\alpha$ -Sulfo Fatty Acids and Their Salts

Most of our research has concerned the reaction of sulfur trioxide with the saturated acids of tallow, isolation of the  $\alpha$ -sulfo acid, further reaction to form salts, esters, amides and other derivatives, and characterization of the  $\alpha$ -sulfo acids and their derivatives to demonstrate the relation between structure and useful properties (4,5,20,31-36,40-52).

$\alpha$ -Sulfonation of the higher saturated fatty acids with sulfur trioxide has many economic advantages. The reactants are cheap, reaction is simple and specific, and there is a large increase in molecular weight. The isolated  $\alpha$ -sulfo fatty acid has several

TABLE I  
 $\alpha$ -Sulfo Fatty Acids and Mono- and Disodium Salts

|   | Solubility<br>in water,<br>25°C, % | Surface<br>tension,<br>25°C, 0.1%<br>dynes/cm. | Critical<br>micelle<br>concentra-<br>tion <sup>a</sup><br>25°C, % |
|---|------------------------------------|--|---|
| $\alpha$ -Sulfolauric acid.....                 | .... <sup>b</sup>                  | 40.9   | 0.36  |
| $\alpha$ -Sulfomyristic acid.....               | .... <sup>b</sup>                  | 37.1   | 0.07  |
| $\alpha$ -Sulfopalmitic acid.....               | 25                                 | 41.5   | 0.02  |
| $\alpha$ -Sulfostearic acid.....                | 13                                 | 43.5   | 0.005   |
| Na $\alpha$ -Sulfopelargonic acid.....          | 18                                 | 49.6   | 1.00 <sup>c</sup>   |
| Na $\alpha$ -Sulfolauric acid.....              | 0.42                               | 32.7   | .... <sup>d</sup>   |
| Na $\alpha$ -Sulfomyristic acid.....            | 0.11                               | 30.2   | .... <sup>d</sup>   |
| Na $\alpha$ -Sulfopalmitic acid.....            | 0.02                               | .... <sup>c</sup>                              | .... <sup>d</sup>   |
| Na $\alpha$ -Sulfostearic acid.....             | 0.01                               | .... <sup>c</sup>                              | .... <sup>d</sup>   |
| Na <sub>2</sub> $\alpha$ -Sulfopelargonate..... | .... <sup>b</sup>                  | 60.2   | .... <sup>e</sup>   |
| Na <sub>2</sub> $\alpha$ -Sulfolaurate.....     | 4.30                               | 69.3   | .... <sup>e</sup>   |
| Na <sub>2</sub> $\alpha$ -Sulfomyristate.....   | 1.50                               | 62.8   | .... <sup>e</sup>   |
| Na <sub>2</sub> $\alpha$ -Sulfopalmitate.....   | 0.25                               | 44.3   | .... <sup>d</sup>   |
| Na <sub>2</sub> $\alpha$ -Sulfostearate.....    | 0.10                               | .... <sup>c</sup>                              | .... <sup>d</sup>   |

<sup>a</sup> Pinacyanole Chloride method (10).

<sup>b</sup> Solubility greater than 25%.

<sup>c</sup> Not measured; solubility less than 0.1% at 25°C.

<sup>d</sup> Solubility of the sodium salts is an approximate value for the cmc.

<sup>e</sup> Do not form micelles except at high concentrations.

indicated uses and is a versatile intermediate for the formation of surfactants and other types of useful products. Because of this  $\alpha$ -sulfo tallow acids are potentially the cheapest derivatives that can be made from animal fats.  $\alpha$ -Sulfopalmitic acid and  $\alpha$ -sulfostearic acid are now commercially available (1,2).

The  $\alpha$ -sulfo higher fatty acids are easily soluble in water and organic solvents. They exist as colloidal electrolytes in aqueous solution, lower the surface tension of water and have the detergent, wetting, foaming, emulsification and other characteristics of surface active agents. The cmc (critical micelle concentration, the concentration at which micelles begin to form from simple ions and molecules) has been measured by surface tension, dye titration and conductance methods (46). The  $\alpha$ -sulfo acids are both strong and weak acids with pH values of 4.5 and 8.8 at the equivalence points (40). Comparisons of the  $\alpha$ -sulfo acids and the mono and disodium salts are shown in Table I.

On neutralization of the sulfonic acid group to form the monosodium salt there is a sharp decrease in solubility. Disodium salts formed by complete neutralization are somewhat more soluble. Because of the limited solubility of the monosodium salt the sulfonation product can be easily isolated in a pure state by precipitation as the crystalline monosodium salt, by adding aqueous sodium chloride or sodium sulfate, or by partial neutralization. Disodium salts are easily converted to monosodium salts by heating with dilute sulfuric acid. Solubility of the sodium salts increases rapidly with temp.

Sodium  $\alpha$ -sulfopelargonic acid and disodium  $\alpha$ -sulfopelargonate, laurate and myristate are easily soluble but at ordinary use concentrations (0.1–0.4%) they are primarily simple electrolytes, do not markedly lower surface tension, and do not have significant wetting, foaming or detergent properties (34).

A comparison of alkali, alkaline earth and triethanolammonium salts of  $\alpha$ -sulfopalmitic and  $\alpha$ -sulfostearic acids showed that the acid lithium, acid triethanolammonium and neutral magnesium salts readily form concentrated micellar solutions at room temp. In general salts forming micellar solutions at lower temp have better foaming and detergent properties (44).

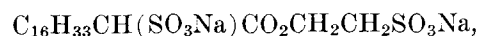
#### Monoesters and Diesters

The carboxyl group of an  $\alpha$ -sulfo fatty acid or the monosodium salt is readily esterified with a primary or secondary alcohol to give a wide range of

esters of the general formula  $RCH(SO_3Na)CO_2R'$  (4,5,31,32,34,40-42,46). Three examples illustrate convenient laboratory methods to obtain esters of analytical purity.

**Sodium Isopropyl  $\alpha$ -Sulfostearate.** A mixture of 3.3 moles of isopropanol and 0.3 mole of  $\alpha$ -sulfostearic acid heated and stirred 6 hr at reflux temp, cooled, neutralized with solid sodium carbonate, decolorized with carbon and crystallized at  $-10^\circ C$  gave sodium isopropyl  $\alpha$ -sulfostearate, yield 79%.

**Disodium 2-Sulfoethyl  $\alpha$ -Sulfostearate.** A mixture of 0.207 mole of sodium isethionate, 0.20 mole of  $\alpha$ -sulfostearic acid and 250 ml of toluene was heated and stirred 6 hr at reflux temp with azeotropic removal of water of esterification. The esterification mixture was neutralized with alcoholic sodium hydroxide and evaporated with recovery of solvent. The residue was dissolved in water, unreacted  $\alpha$ -sulfo acid was removed as the monosodium salt, ethanol was added and disodium 2-sulfoethyl  $\alpha$ -sulfostearate,



was crystallized from aqueous alcohol at  $-15^\circ C$  in a yield of 66%.

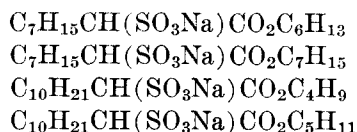
**Sodium Nonyl  $\alpha$ -Sulfopelargonate.** A mixture of 0.11 mole of n-nonanol, 0.10 mole of sodium  $\alpha$ -sulfopelargonic acid, 200 ml of toluene and 2 ml of concentrated sulfuric acid was heated and stirred at reflux temp with azeotropic removal of water. The esterification mixture was neutralized with aqueous sodium carbonate and evaporated with recovery of solvent. Crystallization from 50% ethanol at  $-20^\circ C$  gave sodium nonyl  $\alpha$ -sulfopelargonate, yield 70%.

The examples show that use of the  $\alpha$ -sulfo fatty acid does not require an esterification catalyst. Toluene to remove water of esterification facilitates the reaction and makes it possible to use low molar ratios of the reactants. Sulfonation and esterification in situ was described under sulfonation methods.

**Properties of Monoesters.** Blocking the carboxyl group by esterification results in a much more soluble surface active agent, more resistant to precipitation by metal ions than the corresponding sodium  $\alpha$ -sulfomyristic, palmitic, or stearic acid. The esters as a class are characterized by an unexpected resistance to hydrolysis, which increases their general field of application. Esters of primary alcohols are more resistant to acid than to alkaline hydrolysis; esters of secondary alcohols are very stable to either acid or alkaline hydrolysis. Resistance to hydrolysis may be generally attributed to protection of the carboxylate linkage by the adjacent sulfonate group through steric hindrance. Relative rates of hydrolysis of these and related esters are shown in Table II (5,31,34,41).

Examination of a series of esters of general formula  $RCH(SO_3Na)CO_2R'$  of 14–19 C atoms derived from propionic, butyric, pelargonic, lauric, myristic, palmitic, and stearic acids showed the esters were primarily either wetting agents or lime soap dispersing agents, depending on structure and chain length. Properties examined were surface and interfacial tension, cmc,  $Ca^{++}$  stability, wetting, foaming, detergency, and lime soap dispersion power (31,32).

Esters which are primarily wetting agents are those of 15–17 C atoms with the hydrophilic portion at or near the middle of the molecule, a symmetrical or nearly symmetrical structure. These are characterized by relatively high cmc and low surface tension values. Examples are:



Esters which are primarily lime soap dispersing agents have an unsymmetrical structure with the hydrophilic portion at or near the end of the molecule; characterized by lower cmc and higher surface tension values and greater  $Ca^{++}$  stability. Examples of the best detergents and lime soap dispersing agents are:

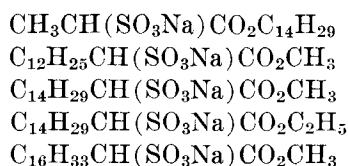


Table III lists representative esters to illustrate relations between structure, chain length, and properties. The sodium methyl, ethyl, propyl, butyl, and amyl  $\alpha$ -sulfolaurates, myristates, palmitates, and stearates have sharp melting points; others do not melt below 200C or pass through a glassy state prior to melting. Branching by the use of a secondary alcohol or a branched chain primary alcohol improves wetting properties.

Sodium dodecyl  $\alpha$ -sulfofbutyrate  $C_2H_5CH(SO_3Na)CO_2C_{12}H_{25}$  and sodium ethyl  $\alpha$ -sulfofmyristate  $C_{12}H_{25}CH(SO_3Na)CO_2C_2H_5$  are counterparts, with R and R' interchanged, and have remarkably similar properties.

The isethionate esters, with two hydrophilic centers, are very soluble, have high cmc values, excellent  $Ca^{++}$  stability and are excellent lime soap dispersing agents (41,42,46).

**Dieters.** Reaction of the mono- or disilver salt of  $\alpha$ -sulfofpalmitic or stearic acid, or of the silver salt of an alkyl ester, with alkyl iodides, gave corresponding esters as shown (48):



The silver salt method is a convenient and traditional laboratory method. A practical method is the reaction of an  $\alpha$ -sulfo fatty acid with ethylene, catalyzed by boron trifluoride (21):

TABLE II  
Rate Constants, Acid and Alkaline Hydrolysis

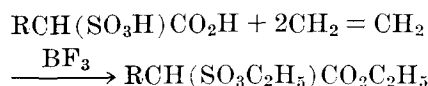
| Ester   | N/3 H <sub>2</sub> SO <sub>4</sub> , 100C |               | N/10 NaOH, 100C             |               |
|---|---|---------------|-----------------------------|---------------|
|   | k <sub>1</sub> <sup>a</sup>               | Relative rate | k <sub>2</sub> <sup>b</sup> | Relative rate |
| Na di(2-ethylhexyl) $\alpha$ -sulfofsuccinate.....          | $\alpha$ 0.0033                           | 21            | ....                        | ....          |
| Na hexyl $\alpha$ -sulfof-pelargonate.....                  | $\beta$ 0.0156                            | 100           | 0.9 approx                  | 100           |
| Na capryl $\alpha$ -sulfof-pelargonate <sup>d</sup> .....   | 0.0020                                    | 13            | 0.16                        | 18            |
| Na methyl $\alpha$ -sulfof-palmitate.....                   | 0.0010                                    | 6             | 0.0092                      | 1             |
| Na sec. butyl $\alpha$ -sulfof-palmitate.....               | 0.0047                                    | 30            | 0.14                        | 16            |
| Na <sub>2</sub> 2-sulfoethyl $\alpha$ -sulfofpalmitate..... | ....                                      | ....          | 0.0021                      | 0.2           |
| Na 2-sulfoethyl oleate.....                                 | 0.0051                                    | 33            | 1.0                         | 110           |
|   | too rapid to measure                      | ....          | 4.3                         | 480           |

<sup>a</sup> k<sub>1</sub> (First order) = 1/t ln a/a-x, min<sup>-1</sup>.

<sup>b</sup> k<sub>2</sub> (Second order) = 1/t x/a(a-x), l./moles  $\times$  min.

<sup>c</sup> Acid hydrolysis occurs in stages, first at the unprotected ester linkage ( $\beta$ ), then at the linkage adjacent to the sulfonate group ( $\alpha$ ). The value for alkaline hydrolysis is an approximation at the mid point; hydrolysis is too rapid to measure rates stepwise.

<sup>d</sup> Ester of C<sub>6</sub>H<sub>13</sub>(CHOHCH<sub>3</sub>).



The dialkyl esters are low melting solids soluble in organic solvents; they are insoluble in water and are not surface active. From infrared spectra (48) and analogy with dialkyl malonates, dialkyl sulfoacetates (15,22), and trialkyl phosphonoacetates (19), they may possess an active  $\alpha$ -H atom and have malonic ester characteristics. They are quite susceptible to hydrolysis at the sulfonic acid ester linkage (48).

### Monoamides and Diamides

Monoamides of  $\alpha$ -sulfo lower fatty acids have been prepared by dehydration of the amine salt (8), the Strecker reaction (8,23), and reaction of the  $\alpha$ -sulfo-carboxylic acid chloride with ammonia or an amine. The latter method was applied to palmitic and stearic acids (47).

Reaction of  $\alpha$ -sulfofpalmitic or stearic acid with excess of thionyl chloride and further reaction with an amine in a chlorinated solvent gave the amide, isolated as the sodium salt, with properties shown in Table IV. Diamides are by-products as will be shown later.

The monoamides have properties similar to corresponding monoesters but lower values for the critical micelle concentration. The alkanolamides and the N-methyl tauride are easily soluble, very resistant to

TABLE III  
Structure and Properties of Monoesters

| Ester  | Total number of C atoms | m.p.        | cmc <sup>a</sup> % | Wetting time, 0.1%, seconds <sup>b</sup> | Lime soap dispersion power % <sup>c</sup> | Ca <sup>++</sup> stability p.p.m. CaCO <sub>3</sub> <sup>d</sup> |
|--|-------------------------|-------------|--------------------|--|---|--|
| Na dodecyl $\alpha$ -sulfofbutyrate <sup>e</sup> .....                       | 16                      | .....       | 0.068              | 5.5                                      | 14  | ..... <sup>f</sup>   |
| Na amyl $\alpha$ -sulfof-pelargonate.....                                    | 14                      | .....       | 0.515              | 12.1                                     | >100                                      | 630  |
| Na octyl $\alpha$ -sulfof-pelargonate.....                                   | 17                      | .....       | 0.080              | 1.3                                      | 14  | 500  |
| Na capryl $\alpha$ -sulfof-pelargonate <sup>e</sup> .....                    | 17                      | .....       | 0.134              | 1.3                                      | 18  | 520  |
| Na 2-ethylhexyl $\alpha$ -sulfof-pelargonate.....                            | 17                      | .....       | 0.070              | instan-<br>taneous                       | 24  | 530  |
| Na 2-ethylhexyl ester of $\alpha$ -sulfo coconut oil fatty acid forerun..... | 18                      | .....       | .....              | 3.5                                      | 15  | 500  |
| Na methyl $\alpha$ -sulfofmyristate.....                                     | 15                      | 125-6C      | 0.096              | 12.5                                     | 9   | ..... <sup>f</sup>   |
| Na ethyl $\alpha$ -sulfofmyristate <sup>e</sup> .....                        | 16                      | 118-19.2C   | 0.068              | 6.7                                      | 8   | ..... <sup>f</sup>   |
| Na methyl $\alpha$ -sulfof-palmitate.....                                    | 17                      | 180.9-2.8C  | 0.015              | 25.0                                     | 9   | ..... <sup>f</sup>   |
| Na methyl $\alpha$ -sulfof-stearate.....                                     | 19                      | 179.8-180C  | 0.003              | 47.0                                     | 9   | 800  |
| Na propyl $\alpha$ -sulfof-stearate.....                                     | 21                      | 72.3-3.6C   | 0.005              | 113.0                                    | 12  | 460  |
| Na isopropyl $\alpha$ -sulfof-stearate.....                                  | 21                      | 75.8-7.2C   | 0.004              | 94.0                                     | 12  | ..... <sup>f</sup>   |
| Na allyl $\alpha$ -sulfof-stearate.....                                      | 21                      | 99.2-100.5C | 0.004              | 90.0                                     | 12  | 740  |
| Na <sub>2</sub> 2-sulfoethyl $\alpha$ -sulfof-stearate.....                  | 20                      | .....       | 0.100              | 500.0                                    | 5   | ..... <sup>f</sup>   |

<sup>a</sup> Critical micelle concentration, Pinacyanole Chloride method (10).

<sup>b</sup> Draves test, time in seconds required to sink a 5g cotton skein (14).

<sup>c</sup> The number of grams of ester required to disperse the Ca soap formed from 0.025g of Na oleate, expressed as %. Lower values indicate greater compatibility with soap in hard water (9).

<sup>d</sup> Titration to a turbidimetric end point with Ca acetate, expressed in terms of stability of the indicated value of water hardness (53).

<sup>e</sup> Counterparts, R and R' of RCH(SO<sub>3</sub>Na)CO<sub>2</sub>R' interchanged.

<sup>f</sup> Excellent Ca<sup>++</sup> stability, >1800 p.p.m.

<sup>g</sup> Ester of C<sub>6</sub>H<sub>13</sub>(CHOHCH<sub>3</sub>).

TABLE IV  
 Sodium  $\alpha$ -Sulfopalmitamides and  $\alpha$ -Sulfostearamides

| RCH(SO <sub>3</sub> Na)CONR'R''   | m.p. <sup>a</sup>          | Krafft point <sup>b</sup> | cmc % <sup>c</sup> | Ca <sup>++</sup> stability p.p.m. CaCO <sub>3</sub> (53) | Lime soap dispersion power % (8) |
|---|----------------------------|---------------------------|--------------------|--|----------------------------------|
| <b><math>\alpha</math>-Sulfopalmitamides</b>                              |                            |                           |                    |  |                                  |
| -NH <sub>2</sub> .....  | (105C)                     | 61C                       | 0.029              | 430  | 5                                |
| -NHC <sub>2</sub> H <sub>5</sub> .....                                    | 188.5-9C                   | 29C                       | 0.024              | 840  | 6                                |
| -NHC <sub>2</sub> H <sub>4</sub> OH.....                                  | .....                      | 34C                       | 0.025              | >1800  | 7                                |
| <b><math>\alpha</math>-Sulfostearamides</b>                               |                            |                           |                    |  |                                  |
| -NH <sub>2</sub> .....  | (143-54C)                  | 78C                       | .....              | .....  | .....                            |
| -NHC <sub>2</sub> H <sub>5</sub> .....                                    | 184-5C                     | 38C                       | 0.007              | .....  | .....                            |
| -NHC <sub>2</sub> H <sub>4</sub> OH.....                                  | .....                      | 42C                       | 0.010              | 1540   | 5                                |
| -NHCH <sub>2</sub> CHOHCH <sub>2</sub> .....                              | (78-9C)<br>164-5C<br>(85C) | 5C                        | 0.005              | 1350   | 7                                |
| -N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub> .....                   | 198C dec.                  | 5C                        | .....              | 1500   | 18                               |
| -N(CH <sub>3</sub> )C <sub>2</sub> H <sub>4</sub> SO <sub>2</sub> Na..... | .....                      | 5C                        | .....              | >1800  | 7                                |

<sup>a</sup> Five amides did not melt nor decompose below 200C; others passed through a glassy stage at the point indicated in parentheses, prior to melting.

<sup>b</sup> The Krafft point is a convenient way of expressing relative solubility. It is the temperature at which a 1% dispersion becomes a clear solution on gradual heating (12).

<sup>c</sup> Critical micelle concentration, Pinacyanole Chloride method (10).

hydrolysis and have excellent calcium stability and lime soap dispersion power.

**Diamides.** Diacid chlorides would be useful intermediates for the formation of diesters or diamides but attempts to form the diacid chloride indicate the actual product is a carboxylic acid chloride sulfonic acid anhydride, [RCH(COCl)SO<sub>2</sub>]<sub>2</sub>O, which on reaction with ammonia or an amine gives a mixture of mono and diamides (48).

Reaction of disodium  $\alpha$ -sulfostearamide and phosphorus pentachloride in phosphorus oxychloride, and amidation with dry ammonia gave 72% yield of product found to be 58% monoamide, 42% diamide. Melting points of the simple diamides of  $\alpha$ -sulfopalmitic and stearic acids and the diamides of  $\alpha$ -sulfostearic acid from ethanolamine and isopropanolamine are as follows, respectively: 166.8-167.5C, 166.4-166.9C, 160-165C, 84-85.6C.

Like the diesters the diamides are not very water soluble and are not surface active agents in the usual sense. Because of the acidic sulfonamide group they are soluble or dispersible in alkali.

### Reduction and Decarboxylation

Besides esterification and amidation other methods for the transformation or elimination of the carboxyl group are the metal borohydride reduction of the carboxylic ester to a primary alcohol; and alkaline decarboxylation to an alkanesulfonate of one less C atom (45).

**Reduction.** 1-Hydroxy-2-alkanesulfonates, isolated as the sodium salt were prepared by sodium or lith-

 TABLE V  
 Sodium  $\alpha$ -Sulfo Fatty Acids, Hydroxyalkanesulfonates and Alkanesulfonates

|   | Total number of C atoms | Krafft point (12) |
|---|-------------------------|-------------------|
| RCH(SO <sub>3</sub> Na)CO <sub>2</sub> H                                      |                         |                   |
| C <sub>12</sub> H <sub>25</sub> CH(SO <sub>3</sub> Na)CO <sub>2</sub> H.....  | 14                      | 68C               |
| C <sub>14</sub> H <sub>29</sub> CH(SO <sub>3</sub> Na)CO <sub>2</sub> H.....  | 16                      | 83C               |
| C <sub>16</sub> H <sub>33</sub> CH(SO <sub>3</sub> Na)CO <sub>2</sub> H.....  | 18                      | 94C               |
| RCH(SO <sub>3</sub> Na)CH <sub>2</sub> OH                                     |                         |                   |
| C <sub>12</sub> H <sub>25</sub> CH(SO <sub>3</sub> Na)CH <sub>2</sub> OH..... | 14                      | 73C               |
| C <sub>14</sub> H <sub>29</sub> CH(SO <sub>3</sub> Na)CH <sub>2</sub> OH..... | 16                      | 84C               |
| C <sub>16</sub> H <sub>33</sub> CH(SO <sub>3</sub> Na)CH <sub>2</sub> OH..... | 18                      | 93C               |
| RSO <sub>3</sub> Na   |                         |                   |
| C <sub>13</sub> H <sub>27</sub> SO <sub>3</sub> Na.....                       | 13                      | 35.5C             |
| C <sub>14</sub> H <sub>29</sub> SO <sub>3</sub> Na.....                       | 14                      | 48C               |
| C <sub>15</sub> H <sub>31</sub> SO <sub>3</sub> Na.....                       | 15                      | 48C               |
| C <sub>16</sub> H <sub>33</sub> SO <sub>3</sub> Na.....                       | 16                      | 57C               |
| C <sub>17</sub> H <sub>35</sub> SO <sub>3</sub> Na.....                       | 17                      | 62C               |
| C <sub>18</sub> H <sub>37</sub> SO <sub>3</sub> Na.....                       | 18                      | 70C               |

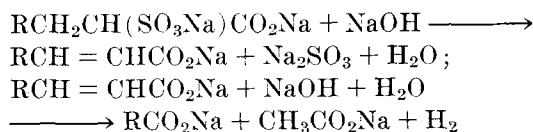
ium borohydride reduction of sodium or lithium alkyl  $\alpha$ -sulfolaurates, myristates, palmitates or stearates.

In all cases the only products were the sodium 1-hydroxy-2-alkanesulfonate and the hydrolyzed un-reduced ester recovered as the disodium salt. The yield of the sulfo alcohol, corrected for recovered starting material was 100%.

**Decarboxylation.** Desulfonation rather than decarboxylation occurred on heating  $\alpha$ -sulfopalmitic acid in boiling *o*-dichlorobenzene in the presence of phosphoric acid, and palmitic acid was recovered in a yield of 77%. Attempts to use a recent decarboxylation method (7) by simply heating sodium  $\alpha$ -sulfostearic acid at 265C under nitrogen gave in our case similar desulfonation to stearic acid.

Alkaline fusion by heating and stirring disodium  $\alpha$ -sulfomyristate, palmitate, or stearate with excess sodium hydroxide under nitrogen to 300-320C gave 30-50% yield of the sodium alkanesulfonate of one less C atom.

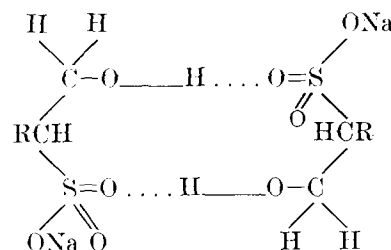
A by-product was identified as the soap of two less C atoms apparently formed by desulfonation to the soap of an  $\alpha$ -olefinic acid followed by the Varrentrapp reaction:



Alkaline fusion of disodium  $\alpha$ -sulfomyristate and separation of the products gave 20% recovered as sodium  $\alpha$ -sulfomyristic acid, 39% sodium tridecanesulfonate and 23% sodium laurate, verified by mixed melting point, infrared spectra and gas liquid chromatography of the fatty acid.

The Krafft points of the monosodium salts of  $\alpha$ -sulfo acids, sodium 1-hydroxy-2-alkanesulfonates, and sodium alkanesulfonates are shown in Table V. Sodium alkanesulfonates of an even number of C atoms were prepared from alkyl bromides by the Strecker reaction.

The sodium alkanesulfonates have the lowest Krafft points and are the most soluble. Hydrogen bonding, such as indicated by the diagram, may explain the limited solubility of the salts of the sulfo alcohols and sulfocarboxylic acids:



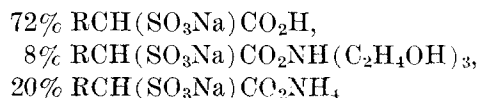
### Uses

Many potential uses, some of which may be close to realization have been suggested and described for the long chain  $\alpha$ -sulfo acids, their salts, esters, and amides.  $\alpha$ -Sulfopalmitic acid and  $\alpha$ -sulfostearic acid have been suggested for use in ore flotation, the non-metallic beneficiation of sand, in emulsion polymerization, and as a versatile inexpensive chemical intermediate (1,2). Recent patent and technical literature shows the use of the monosodium or monoammonium salt of  $\alpha$ -sulfo-palmitic or  $\alpha$ -sulfostearic acid as a dye intermediate (28,30), the use of lithium and calcium salts in high

dropping point grease compositions (25), and barium sulfostearate as a paint additive to improve hardness, flexibility, adhesion, and corrosion resistance (37). Figure 1 outlines the reactions of the  $\alpha$ -sulfo acids and the types of useful products.

Our laboratory evaluation methods include the measurement of several properties to disclose or suggest appropriate application as surface active agents. Properties of particular interest are solubility, surface and interfacial tension, the critical micelle concentration, stability to hard water and various metal ions, stability to acid and alkaline hydrolysis, wetting, foaming, detergent, emulsifying, and lime soap dispersion properties. Based on this type of laboratory evaluation the various  $\alpha$ -sulfo compounds have many useful properties.

Disodium salts of  $\alpha$ -sulfonated hydrogenated tallow acids may be used to advantage as a component in detergent compositions along with tallow alcohol sulfates, sodium dodecylbenzenesulfonate, and inorganic builders (33,35). Experimental detergent bars, 100% active, based on the monosodium salt of  $\alpha$ -sulfonated hydrogenated tallow acids with the carboxyl group partially neutralized with ammonia and amines, were made in small scale conventional soap bar forming equipment. Detergent bars with a representative composition



have attractive hardness, solubility, lather, and dish life characteristics (50,51).

Soap-syndet bars containing 10–20% sodium methyl  $\alpha$ -sulfostearate have been made by melting the soap, adding the ester, and permitting the mass to cool in cake form (18).

Esters of the general formula  $\text{RCH(SO}_3\text{Na)CO}_2\text{R}'$  because of stability to acid, alkali, hard water, and various metal ions appear to have excellent characteristics as industrial surface active agents in appli-

cations such as acid dyeing, pickling, and electroplating (34). Symmetrical esters with the hydrophilic portion in about the middle of the molecule, with  $\text{R} = \text{R}'$ , such as sodium capryl  $\alpha$ -sulfopelargonate, were found to equal or surpass the most efficient commercial wetting agents and to have much greater stability to acid and alkaline hydrolysis (31,32). Polymerized sodium allyl  $\alpha$ -sulfopalmitate and stearate are excellent emulsifying agents (4,5).

Several of the  $\alpha$ -sulfo compounds are sufficiently soluble to enter into liquid syndet formulations. Examples are triethanolammonium  $\alpha$ -sulfopalmitic acid, sodium isopropyl  $\alpha$ -sulfostearate, disodium 2-sulfoethyl  $\alpha$ -sulfopalmitate and the isopropanolamide of sodium  $\alpha$ -sulfostearic acid. The unsymmetrical esters of  $\alpha$ -sulfomyristic, palmitic, and stearic acids, such as the methyl, ethyl, and isopropyl esters, are good lime soap dispersing agents compatible with soap in hard water. Disodium 2-sulfoethyl  $\alpha$ -sulfostearate and sodium  $\alpha$ -sulfopalmitamide are also good or excellent lime soap dispersing agents (32, 41, 42, 47).

## REFERENCES

1. Anonymous, Chemical Processing 24, No. 5, 43–45 (1961).
2. Armour Industrial Chemical Co., Technical Bulletin G-7 (1956), G-7R1 (1957), G-14 (1957); Chem. Eng. News 39, No. 38, 18 (1961).
3. Bert, L., M. Procoff, and V. Blinoff (Sinnova ou Sadic), U. S. Patent 2,460,968 (1949).
4. Bistline, R. G., Jr., W. S. Port, A. J. Stirton, and J. K. Weil (to the Secretary of Agriculture), U. S. Patent 2,844,606 (1958).
5. Bistline, R. G., Jr., A. J. Stirton, J. K. Weil, and W. S. Port, JAOCS 33, 44–45 (1956).
6. Blaser, B. (Henkel & Cie), U. S. Patent 2,785,193 (1957).
7. Bloch, H. S. (Universal Oil Products Co.), U. S. Patent 2,822,387 (1958).
8. Boer, J. H. de, Rec. trav. chim. 71, 814–821 (1952).
9. Borghetty, H. C., and C. A. Bergman, JAOCS 27, 88–90 (1950).
10. Corrin, M. L., H. B. Klevens, and W. D. Harkins, J. Chem. Phys. 14, 480–486 (1946).
11. Crittenden, E. D. (Solvay Process Co.), U. S. Patent 2,195,145 (1940).
12. D mareq, M., and D. Dervichian, Bull. soc. chim. 12, 939–945 (1945).
13. Dowdall, J. F. (Minnesota Mining and Manufacturing Co.), U. S. Patent 2,628,253 (1953).
14. Draves, C. Z., Am. Dyestuff Repr. 28, 425–428 (1939).
15. Franchimont, A. P. N., Rec. trav. chim. 7, 25–33 (1888).
16. Gilbert, E. E., and S. L. Giolito (Allied Chemical and Dye Corp), U. S. Patent 2,647,925 (1953).
17. G nther, F., PB30081 (1932). Office of Technical Services, U. S. Dept. of Commerce; F. G nther, J. Conrad, and K. Saftien (I. G. Farbenindustrie A. G.), U. S. Patent 2,043,476 (1936); F. G nther and J. Hetzer, U. S. Patent 1,926,442 (1933).
18. Kise, M. A., and J. F. Vitcha (Solvay Process Co.), U. S. Patent 2,303,212 (1942).
19. Kosolapoff, G. M., and J. S. Powell, J. Am. Chem. Soc. 72, 4198–4200 (1950).
20. Lutz, D. A., J. K. Weil, A. J. Stirton, and L. P. Witnauer, JAOCS 38, 493–494 (1961).
21. McBride, J. J., Jr., and E. J. Miller, JAOCS 39, 105–107 (1962).
22. Manzlius, R., Ber. 21, 1550–1552 (1888).
23. Mehta, T. N., and D. M. Trivedi, Mellind Textilber. 21, 117–119, 288–293 (1940).
24. Moyer, W. W. (Solvay Process Co.), U. S. Patents 2,195,186–8 (1940).
25. Nelson, J. W. (Sinclair Refining Co.), U. S. Patent 2,951,809 (1960).
26. Nenitzescu, C. D., and A. M. Glatz, Bull. soc. chim. France 1961, 218–222.
27. Pasquali, R. (Soc. anon. de mat. color et prod. chim. Francolor), Fr. Patent 983,965 (1951).
28. Popeck, S. P., and H. Schulze (General Aniline & Film Corp.), U. S. Patent 2,829,975 (1958).
29. Sauls, T. W., and W. H. C. Rueggeberg, JAOCS 33, 383–389 (1956).
30. Schulze, H., and S. P. Popeck (General Aniline & Film Corp.), U. S. Patent 2,974,152 (1961).
31. Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, and W. C. Ault, JAOCS 39, 55–58 (1962).
32. Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, W. C. Ault, and E. W. Maurer, JAOCS 39, 128–131 (1962).
33. Stirton, A. J., E. W. Maurer, and J. K. Weil, JAOCS 33, 290–291 (1956).
34. Stirton, A. J., J. K. Weil, and R. G. Bistline, Jr., JAOCS 31, 13–16 (1954).
35. Stirton, A. J., J. K. Weil, and E. W. Maurer (to the Secretary of Agriculture), U. S. Patent 2,915,473 (1959).
36. Stirton, A. J., J. K. Weil, Anna A. Stawitzke, and S. James, JAOCS 29, 198–201 (1952).
37. Tidridge, W. A., and R. A. Creed, Am. Paint J. 46, No. 5, 88, 90–91, 94, 98 (1961).
38. Truce, W. E., and C. E. Olson, J. Am. Chem. Soc. 75, 1651–1653 (1953).
39. Watson, H. B., Chem. Rev. 7, 173–201 (1930).
40. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton, J. Am. Chem. Soc. 75, 4859–4860 (1953).
41. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton, JAOCS 32, 370–372 (1955).
42. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton (to the Secretary of Agriculture), U. S. Patent 2,806,044 (1957).
43. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton, "Organic Syntheses," 36, 83–86 (1956).

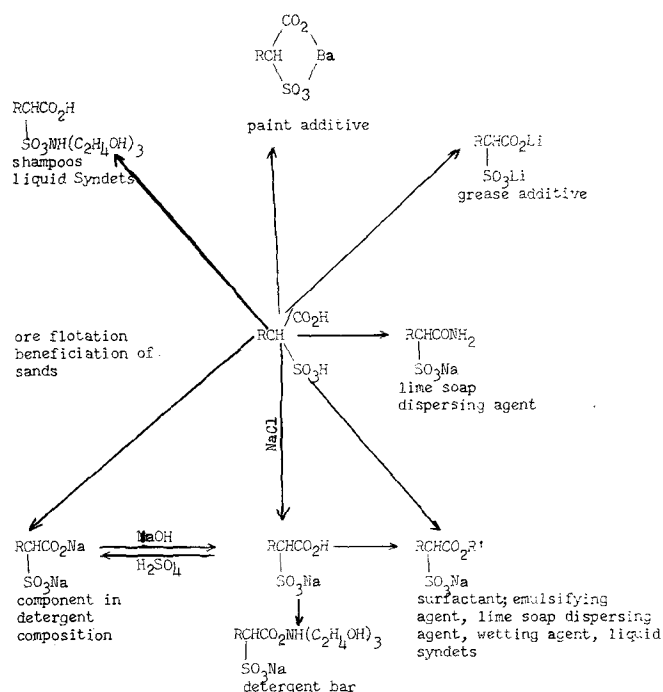


FIG. 1. Reactions of  $\alpha$ -sulfo fatty acids and types of useful products.

44. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton, *JAACS* 34, 100-103 (1957).  
 45. Weil, J. K., F. D. Smith, and A. J. Stirton, *J. Org. Chem.* 27, 2950-2952 (1962).  
 46. Weil, J. K., and A. J. Stirton, *J. Phys. Chem.* 60, 899-901 (1956).  
 47. Weil, J. K., A. J. Stirton, and R. G. Bistline, Jr., *JAACS* 37, 295-297 (1960).  
 48. Weil, J. K., A. J. Stirton, and R. G. Bistline, Jr., *JAACS* 39, 168-170 (1962).

49. Weil, J. K., A. J. Stirton, R. G. Bistline, Jr., and W. C. Ault, *JAACS* 37, 679-682 (1960).  
 50. Weil, J. K., A. J. Stirton, and E. W. Maurer (to the Secretary of Agriculture), U. S. Patent 2,867,586 (1959).  
 51. Weil, J. K., A. J. Stirton, E. W. Maurer, W. C. Ault, and W. E. Palm, *JAACS* 35, 461-465 (1958).  
 52. Weil, J. K., L. P. Witnauer, and A. J. Stirton, *J. Am. Chem. Soc.* 75, 2526-2527 (1953).  
 53. Wilkes, B. G., and J. N. Wickert, *Ind. Eng. Chem.* 29, 1234-1239 (1937).

## Aldehydic Materials by the Ozonization of Vegetable Oils<sup>1</sup>

E. H. PRYDE and J. C. COWAN, Northern Regional Research Laboratory,<sup>2</sup> Peoria, Illinois

OZONIZATION of oleic acid to produce azelaic and pelargonic acids is a well-known commercial process (3). These acids, which are used for preparing various synthetic lubricants and plasticizers, result from oxidative decomposition of the ozonolysis products. Alternatively, reductive decomposition either with zinc and acetic acid or with hydrogen over a palladium-charcoal catalyst produces aldehydic materials. This paper discusses the preparation of various aldehydic compounds by the ozonization of unsaturated vegetable oil products followed by reductive decomposition of the ozonolysis products and summarizes the research carried out for the past several years at the Northern Laboratory.

The ozonization of monounsaturated compounds will be described first, followed by a discussion of polyunsaturated compounds and the more complex unsaturated vegetable oil systems. Reactions and potential uses for these aldehydic compounds will then be considered.

### Ozonization of Methyl Oleate

*Effect of Solvent.* Reductive decomposition of the ozonolysis products obtained from methyl oleate gives the products pelargonaldehyde and methyl azelaaldehyde. This reaction has been known and used for many years, but results were complicated by the presence of side reaction products and yields have been generally low (41). The best preparative method gave 60-70% yields, and consisted of ozonization in

acetic acid followed by reaction with zinc (25). Distillation of either freshly prepared or stored reaction product gave residues which were apparently the aldehyde trimers.

Recently, Criegee and coworkers elucidated the mechanism of the ozonization reaction and the types of products obtained in different solvents (16). This work has been reviewed in a general review of the ozonization of organic compounds (5). Alcohols, particularly methyl and ethyl alcohols, as participating or reactive solvents are apparently to be preferred.

In our investigations with methyl oleate, methanol proved to be the best solvent (Table I) (31). Methanol reacts somewhat with ozone, and this secondary reaction accounts for the 21% in excess of theory ozone consumed. The products of this secondary reaction do not interfere in the oximation analyses for carbonyl or isolation of carbonyl compounds (24); however, they apparently do interfere in chromatographic analyses (9). The ozone uptake is essentially quantitative, only 1-2% escaping near the end of the reaction. As measured before isolation of products, the conversion of unsaturation to carbonyl compounds was 92-93% of theory. Temp of the ozonization within the range of -20 to +25C had little effect. The yield of crude product after isolation by distillation was 94%, and its purity was in excess of 90%. The principal impurity was dimethyl acetal of methyl azelaaldehyde. In other runs where care was taken to minimize acetal formation, purities were even higher.

With acetic acid a product of high purity was obtained but in low yields. The low yield may have resulted from the presence of acidic compounds during isolation of the products by distillation. We found in several preparations that all traces of acidity must be removed to prevent high residues resulting from distillation.

The superiority of methanol as a medium for ozonization has also been demonstrated when oxidative cleavage is used for analytical purposes (1). Not more than 3-5% chain degradation occurred, in contrast to the large amount of degradation that occurred with other solvents.

The explanation for the superior results obtained in methanol depends on the Criegee mechanism for ozonization (Fig. 1). The primary ozonide, evidence for which exists only for *trans* di(*tert*-butyl)-ethylene (18), immediately forms a transient intermediate called a zwitterion (I) and a carbonyl compound. The zwitterion may then react in any one of several dif-

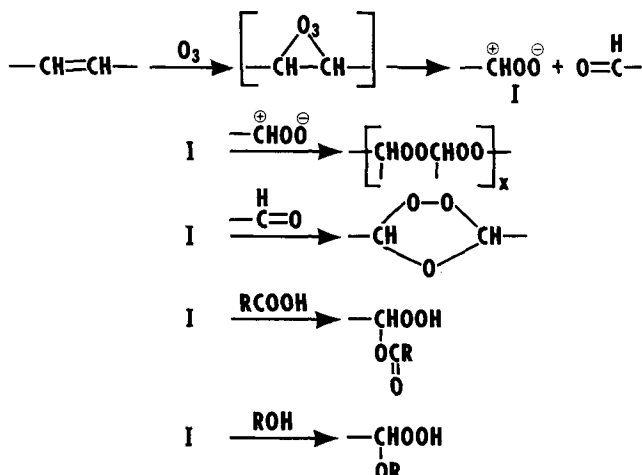


Fig. 1. Criegee mechanism for ozonization.

<sup>1</sup> Presented by E. H. Pryde.

<sup>2</sup> A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.