Sulfation with Sulfur Trioxide: Ethenoxylated Long-Chain Alkylphenols

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SULFATED ethenoxylated long-chain alkylphenols are of increasing interest as detergents because of high foaming power, excellent detergency, and low skin-sensitization (2, 11). The preparative procedure (2, 14, 15) involves reaction of a long-chain alkylphenol with any desired ratio of ethylene oxide to form a mixture of polyether alcohols, which is then sulfated and neutralized for use. The raw material of major industrial interest has been nonylphenol condensed with four moles of ethylene oxide. Recently dodecylphenol plus six moles of ethylene oxide has been considered.

A variety of sulfating agents was employed in the early work (5, 15) on these materials. These included sulfuric acid, oleum, and chlorosulfonic acid, all of which were used either alone or with solvents, such as ethyl ether, liquid sulfur dioxide, or chlorinated hydrocarbons. Sulfamic acid became the preferred reagent on a commercial scale (5). Recently sulfur trioxide vapor has achieved commercial acceptance, following promising tests on a pilot-plant scale (1). This reagent is commercially available from stabilized liquid sulfur trioxide, marketed under the trademark "Sulfan" (4). No data are available on the relative suitability of these various reagents for this type of sulfation. The purpose of the present study is therefore to compare sulfamic acid with sulfur trioxide vapor, especially for the sulfation of nonylphenol-4 ethylene oxide. Such a comparison is of economic interest since a unit weight of sulfamic acid costs about seven times as much as the equivalent sulfur trioxide obtained from "Sulfan." A similar study, recently reported (6) by the present authors, compared sulfur trioxide vapor and chlorosulfonic acid for the sulfation of ethenoxylated long-chain alcohols.

Raw Materials

Samples used in the present study, as obtained from four different commercial sources, are listed in Table I. Samples C-1-0 and C-1-1 represent separate batches of the same material obtained at different times. It is noted that in all cases the molecular weights, per hydroxyl values obtained during the present study, compare well with the theoretical.

Experimental Procedure

Sulfation. Sulfur trioxide vapor (6%), diluted with dry air (94%), was applied by the method previously used by the authors for sulfating lauryl alcohol (7) and ethenoxylated long-chain alcohols (6). The change (200–250 g.) was preheated to 60°C. before sulfation and kept at 70–80°C. during reaction by application of external cooling as needed. Mechanical agitation at 1,400 r.p.m. was maintained during the 20-min. sulfation period. Weight loss was less than 1% of the total weight of both reagents.

Sulfamic acid was applied in 5% molar excess, using the standard sulfation procedure (5, 10, 12) with a 200–250 g. charge. Addition of the acid took 45 min., followed by a 75-min. digestion period. Both were conducted at 120–30°C. in a nitrogen atmosphere as recommended (10). Weight loss was nil.

TABLE I
Data on Raw Materials Studied

Sample	Alkyl group on phenol	Moles ethylene oxide	Molecular weight	
			Theoretical	Found [a]
A	Nonyl	4	396	395
B	Nonyl	4	396	400
C-1-0	Nonyl	4	396	402
C-1-1	Nonyl	4	396	402
C-2	Nonyl	9	616	625
D-1	Octyl	3	338	348
D-2	Octyl	5	426	424
D-3	Octyl	12	734	733
E-1	Dodecyl	6	526	515

[a] Per hydroxyl values obtained in this study.

Neutralization. To avoid gelation, the acid sulfates were neutralized in aqueous ethanol. Typically, 225 g. of acid sulfate prepared with sulfur trioxide and 92 g. of 10% aqueous ammonia were added concurrently to 135 g. of 41% ethanol to pH 9. The resulting solution contained about 50% ammonium organic sulfate. A sulfamic-based product (271 g.) was mixed with 255 g. of 40% ethanol and adjusted to pH 9 with 12 g. of 10% aqueous ammonia.

Product Analysis. Color values were determined on 20% aqueous solutions in a Klett-Summerson Photoelectric Colorimeter, Test Tube Model, using No. 42 filter. The lower the number, the lighter the color (0 = colorless; 200 = light yellow). Colors were measured immediately after preparation since the samples bleach spontaneously on standing exposed to light.

Active-ingredient content, used as the basis for yield calculation of sulfamic-based products, was obtained by quaternary titration by the method of Epton (3) except that a 0.0054 molal solution of Hyamine 1622 [1] (13) was substituted for cetyl pyridinium bromide, which is less stable.

Yield determination for the sulfur trioxide-based materials is complicated by the side reaction of phenolic ring sulfonation, which does not occur with sulfamic acid. Some molecules therefore contain sulfonate as well as sulfate groups, both of which can probably react with the quaternary reagent. (Quaternary titration of disulfonates has not been reported in the literature; it was found during the present study that both sulfonate groups of disulfonated dodecyldiphenyloxide [2] titrate normally.) The yields reported herein for sulfur trioxide-based products are therefore apparent figures useful only for comparison since they were determined by quaternary titration for lack of a more precise procedure.

Degree of phenolic ring sulfonation occurring with sulfur trioxide was determined by the method of House and Darragh (9) for analyzing sulfonates and sulfates in the presence of each other. This factor is expressed as mole percentage based on starting organic compound. Since this determination is also based on quaternary titration, the figures are approximate and primarily of comparative value.

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[1] Rohm and Haas Company, Philadelphia, Pa.

[2] Dowfax 2A1, Dow Chemical Company, Midland, Mich.

Unsulfated (nonionic) material was determined by passage through a two-component (cation-anion) exchange column (8). Values obtained by this procedure were three to four times those obtained by five-fold countercurrent extraction with hexane.

Experimental Results

Experimental data are given in Figures 1 and 2. Conclusions were drawn as follows:

Color. Both reagents and all samples of nonylphenol-4 ethylene oxide gave colors considered acceptable for household use. There was considerable variation among samples from different companies and even from the same company (C-1-0 and C-1-1). These materials as a class are remarkably color-stable to increasing mole ratios of sulfur trioxide, therein differing from the ethenoxylated long-chain alcohols (6). Sulfamic acid gave darker colors than sulfur trioxide with all samples studied. A concerted effort to improve product color with sulfamic acid, involving changes in reaction times and temperatures and in the grade and degree of subdivision of the reagent gave no improvement.

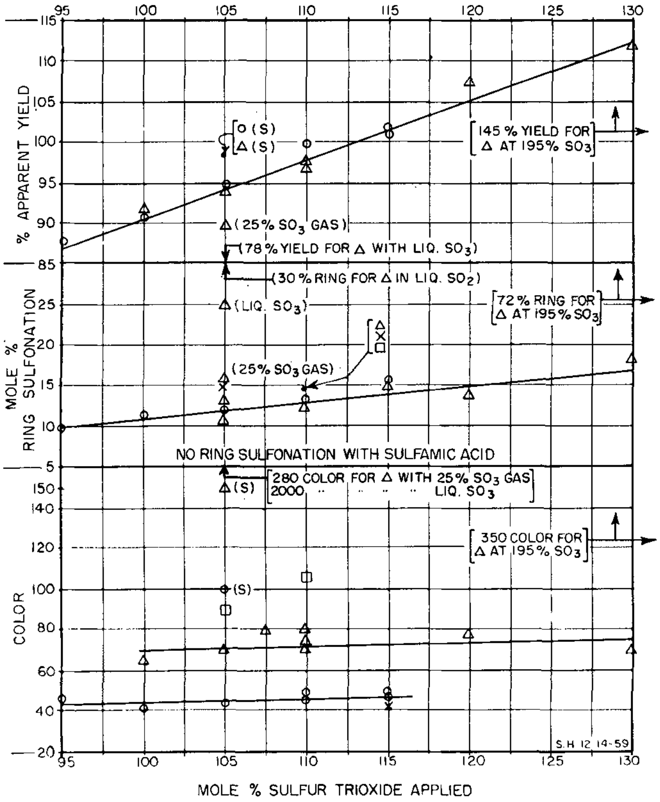

FIG. 1. Sulfation of various commercial samples of nonylphenol-4 ethylene oxide at 75°C. with varying ratios of sulfur trioxide vapor.

○ = C-1-0; ○(S) = prepared with sulfamic acid
△ = C-1-1; △(S) = prepared with sulfamic acid
□ = A
X = B

Degree of Ring Sulfonation. No ring sulfonation occurred with sulfamic acid, but it was always noted with sulfur trioxide. Increasing ring sulfonation resulted from a) increasing the mole ratio of sulfur trioxide; b) decreasing the length of the polyether chain; c) decreasing stirrer speed; d) using liquid (as opposed to gaseous) sulfur trioxide (even when employing liquid SO_2 solvent); and e) increasing the percentage of sulfur trioxide in the carrier gas. Efforts to eliminate ring sulfonation by variation in reaction conditions were without success.

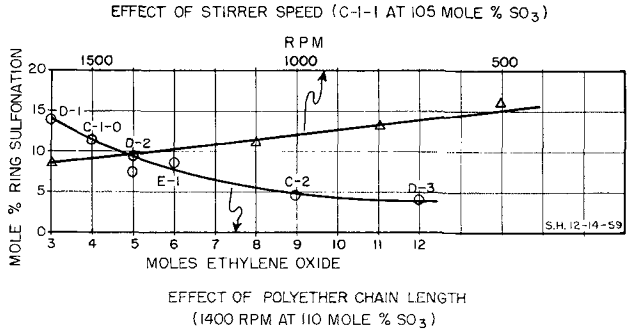

FIG. 2. Two factors affecting extent of ring sulfonation.

Unsulfated Material. Eight to 10% by weight of sample C-1-0 was recovered as unsulfated material after sulfation with 110% sulfur trioxide. Sulfamic acid, on the other hand, gave a recovery of 1.7%.

Sulfation Temperature. Below about 55°C. stirring becomes difficult, resulting in poor and uneven gas absorption and leading to a drop in yield and a slight increase in color. Above about 85°C. color and yield again begin to deteriorate. The temperature range 70 to 80°C. was therefore chosen as optimum.

Decrease in Percentage of Carrier Gas. An increase in the percentage of sulfur trioxide in the vapor over the usual 6% would result in increased operating efficiency. Unsatisfactory results were obtained at 25% since the color was dark, yield was reduced, and ring sulfonation increased (Figure 1).

Direct Addition of "Sulfan." This would constitute a preferred operating procedure since vaporization is obviated. With sample C-1-1, at 75°C. using 105 mole per cent, the yield was poor (78%), ring sulfonation was high (25%), and the color was prohibitively dark (2,000). It therefore appears that liquid sulfur trioxide is too disruptive in its action on these materials, as with most other organic compounds (7).

Liquid Sulfur Dioxide as Solvent. This is an excellent sulfonation medium for many organic compounds. Addition of 105 mole per cent "Sulfan" (dissolved in two volumes liquid sulfur dioxide) to sample C-1-1 (dissolved in one volume liquid sulfur dioxide) at reflux (−10°C.), followed by removal of sulfur dioxide *in vacuo* at a maximum temperature of 50°C., gave a product of 55 color in 94% yield with 30% ring sulfonation. This yield is normal, but the color is lighter and the per cent ring sulfonation is much higher (*cf.* Figure 1) than obtained with sulfur trioxide vapor.

Performance Tests

Comparative performance data are summarized in Table II. It is noted that with sample C-1-1, a typical nonylphenol-4 ethylene oxide, the sulfamic-based product and the three materials made from 100 to 110% sulfur trioxide are similar respecting wetting time, foaming power in distilled water, detergency in hard water at both concentrations, and in distilled water at 0.1%. Detergency at 0.05% in distilled water for all three sulfur trioxide-based materials is about half that of the sample prepared with sulfamic acid. Hard-water foaming power appears somewhat higher with sulfur trioxide materials. Sulfa-

TABLE II

Summary of Performance Data[a]

Sample	Reagent	Per cent reagent	Wetting time[b]	Foaming power		Detergency[e]			
						DW[f]		HW[g]	
				DW[c]	HW[d]	0.05	0.1	0.05	0.1
C-1-1	Sulfamic	105	17	155	170	20	36	36	35
C-1-1	SO_3	100	20	160	190	11	32	29	36
C-1-1	SO_3	105	18	160	210	10	33	34	36
C-1-1	SO_3	110	20	160	220	9	32	33	36
C-1-1	SO_3	195	171	125	200	4	8	5	14
D-2	Sulfamic	105	26	120	210	2	17	15	31
D-2	SO_3	110	28	185	210	5	17	16	27
E-1	Sulfamic	110	26	145	130	32	20	34	38
E-1	SO_3	110	32	140	140	38	36	38	40

[a] All samples showed excellent resistance to 15° hard water at 0.2%.
[b] Draves (Synthron Tape Method) in seconds at 25°C., 0.1% solution.
[c] Ross-Miles in distilled water at 0.05%.
[d] Ross-Miles in 15° hard water at 0.1%.
[e] Expressed as percentage of brightness increase of wool in Launder-Ometer.
[f] In distilled water at percentages given.
[g] In 20° hard water at percentages given.

tion with 195% sulfur trioxide strongly impairs all properties except hard-water foaming power. With octylphenol-5 ethylene oxide (D-2) the two reagents give sulfates of very similar performance except that the sulfur trioxide-based material has considerably better distilled water-foaming power. In general, this sulfate is a less effective detergent and wetting agent than that derived from nonylphenol-4 ethylene oxide regardless of reagent used. In the case of sample E-1 (dodecylphenol-6 ethylene oxide) the two reagents show similar performance, with possibly slightly better detergency and slightly greater wetting-time for sulfur trioxide.

Comparison of the performance data obtained in the present study with that reported recently by the present authors for the sulfated ethenoxylated long-chain alcohols (6) shows the alkylphenol-based products to advantage. Two of the alcohol-derived sulfates (B and D) gave nearly the same foaming-power as those made from the alkylphenol, but wetting time and detergency were considerably inferior. The third alcohol-based sulfate (E) showed substantially better detergency than the other two (but still lower than the alkylphenol-derived material); however it had comparatively poor foaming-power and wetting time.

Sulfating Agents Compared

The major conclusions from this study may be summarized as follows. Per unit weight of sulfur trioxide introduced, sulfur trioxide costs approximately one-seventh as much as sulfamic acid and involves about one-sixth of the reaction time. Sulfur trioxide gives lighter product color and allows formation of any desired-product salt while sulfamic acid gives the ammonium salt, which can be converted to other salts (*e.g.*, sodium) only with difficulty. On the other hand, sulfur dioxide gives appreciable foaming during sulfation while sulfamic acid gives none. Sulfur trioxide must be vaporized while sulfamic acid is added directly. Ring sulfonation with sulfur trioxide is appreciable, but none occurs with sulfamic acid. Product performance with the two reagents appears comparable however.

Acknowledgments

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Pure Oleic Acid from Olive Oil

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IN THE PAST 23 years a number of new techniques have been developed for the preparation of oleic acid from olive oil. Both olive oil acids and methyl esters have been submitted to purification. The use of low-temperature (−60°C.) solvent crystallization for this purpose, combined with fractional distillation, is described in "Biochemical Preparations" (1), where earlier literature references are given.

The discovery of urea inclusion compounds in 1949—a general review, as applied to fatty acids, is given by Schlenk (2)—provided yet another tool for fatty acid (or ester) fractionation. It was used by Schlenk