Nucleophilic Addition of Hydrogen Sulfide to Methyl Oleate, Methyl Linoleate, and Soybean Oil[1]

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ABSTRACT

Hydrogen sulfide was added to methyl oleate, methyl linoleate, and soybean oil at -70 and 25 C in the presence of boron trifluoride. Major reaction compounds were identified by gas liquid chromatography and mass spectrometry. At -70 C with a 200 molar ratio of hydrogen sulfide to ester, the reactions were complete in 4 hr. Primary reaction product from methyl oleate was methyl 9(10)-mercaptostearate. Methyl linoleate gave ca. equal amounts of methyl 9-(2-pentyl-1-thiolan-5-yl) nonanoate and methyl 8-(2-hexyl-1-thiolan-5-yl) octanoate. At 25 C, the reaction of methyl oleate and linoleate with hydrogen sulfide was less complete, and more side reactions were noted. When equimolar amounts of methyl oleate and methyl 9(10)-mercaptostearate were reacted in the presence of boron trifluoride at 25 C, a new compound was formed, bis(methyl n-octadecanoate 9[10]-yl) sulfide. The addition of liquid hydrogen sulfide to soybean oil at -70 C in the presence of boron trifluoride yields a product which, upon saponification, acidification, and methylation analyzes by gas liquid chromatography as ca. 52% thiolan, 27% mercaptostearate, 10% palmitate, 6% stearate, and 5% unidentified compounds.

INTRODUCTION

The addition of hydrogen sulfide to olefins has been known for many years. Such adducts formed by electrophilic, nucleophilic, or free radical mechanisms (1) have found use in lubricants, synthetic rubbers, ore floatation collectors, fungicides, nonionic detergents, and chemical manufacture (2-6). Previously, we studied the free radical addition of hydrogen sulfide and mercaptans to unsaturated fatty esters and oils under UV radiation (7,8). However, yeilds of sulfur adducts tended to be low, and the polyunsaturated derivatives gave complex mixtures. We now have initiated a study of the boron trifluoride-catalyzed reaction of hydrogen sulfide with unsaturated fatty esters and oils. This paper reports on the work with methyl oleate, linoleate, and soybean oil.

EXPERIMENTAL PROCEDURES

Starting Materials, Preparative Gas Liquid Chromatography (GLC), and Analytical Procedures

Methyl oleate came from Applied Science Laboratories, State College, Pa., and methyl linoleate from The Hormel Institute, Austin, Minn. These materials were 99% pure by GLC analyses. Hydrogen sulfide and boron trifluoride were Matheson CP grades.

Hexane was redistilled Skelly B (bp 67-70) obtained from the Skelly Oil Co., Tulsa, Okla. Toluene was Fisher Certified A.C.S. T-324. The soybean oil was a freshly deodorized alkali refined and bleached commercial sample received from the C&T Refinery, Charlotte, S.C.

Samples separated by GLC were collected in 2 in. no. 14 Teflon tubes inserted at the exit port of a 7620 A Series Hewlett-Packard gas chromatograph. Column was 6 ft x 1/4 in. stainless steel packed with 12.5 g 3% JXR. Program runs were conducted at 180-300 C with a heating rate of 2 C/min and a helium carrier gas flow rate of 30 cc/min. This instrument was fitted with a microsplitter-collector, which provided a 1:10 split ratio (one part to the flame ionization detector and 10 parts to the collector tubes). Samples were rechromatographed to increase purity.

Mass spectra were measured on a Nuclide 12-90 DF mass spectrometer equipped with a probe inlet; source temperature, 200 C, and 70 V electron energy.

Addition of Hydrogen Sulfide to Methyl Esters and Soybean Oil

A 100 ml graduate with a Teflon-coated magnet was mounted in a propanol-dry ice bath inside a Dewar flask and the system cooled to -70 C. Hydrogen sulfide was introduced through a fritted glass sparger tube until ca. 20 ml collected. The magnetic stirrer was started, and a 1 g sample of the methyl ester dissolved in 20 ml hexane was added to the liquid hydrogen sulfide. Boron trifluoride was then introduced (at a rate of ca. one bubble/sec) from a compressed gas cylinder. After 4 hr, the boron trifluoride flow was stopped and the reaction mixture permitted to reach room temperature with stirring (usually stood overnight). After complete degassing, a yellow oil remained. Diethyl ether (50 ml) was added and the ether layer water-washed in a separatory funnel with 100 ml distilled water. The ether layer was separated and dried over anhydrous sodium sulfate. The ether was removed on the steam bath with nitrogen ebullition.

Soybean oil (1 g) was dissolved in 20 ml hexane and added to 20 ml liquid hydrogen sulfide at -70 C. After 5 hr of bubbling boron trifluoride into the solution, ca. 1 ml yellow oil had settled out. The product was isolated as previously described for the esters. For GLC analysis, ca. 0.15 g of this oil was saponified with 4 ml 0.5 N methanolic sodium hydroxide and then methylated with 5 ml methanolic BF_3 (14% w/v). Solubility problems were encountered when the soybean oil experiment was scaled up to a 10 g sample. It became necessary to use 150 ml toluene instead of hexane and to operate at -20 C for a clear solution. After 7 hr reaction, the sample was treated as previously described and analyzed by GLC.

For experiments at 25 C, the apparatus used at low temperatures was mounted in a constant temperature bath. The hexane solution was saturated with hydrogen sulfide before introducing the boron trifluoride. Solubility of hydrogen sulfide in hexane at 20 C is 0.0341 on a mole-fraction solubility basis (9). A 1 g sample of methyl oleate in 20 ml hexane saturated with hydrogen sulfide has a 2.6 to 1 mole ratio of hydrogen sulfide to methyl oleate. Hydrogen sulfide was bubbled into the solution along with boron trifluoride during the reaction.

Addition of Methyl 9(10)-Mercaptostearate to Methyl Oleate

Methyl 9(10)-mercaptostearate was prepared at -70 C as described under "Methyl Esters and Soybean Oil." GLC analysis showed a trace of methyl oleate along with ca. 8% of an unidentified product. This preparation was dissolved in 10 ml toluene along with methyl oleate (0.9 g). GLC
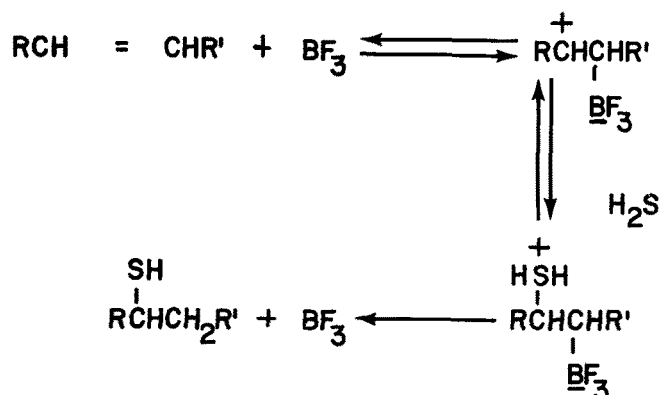
analysis showed approximate equiamounts of oleate and mercaptostearate. The reactor was placed in a bath at 25 C, and boron trifluoride was bubbled in (one bubble/sec) for 16 hr. The mixture then was water-washed and treated as previously described in the preparation of methyl 9(10)-mercaptostearate to yield 1.33 g.

RESULTS AND DISCUSSION

Methyl Oleate Adduct

The importance of low reaction temperatures and of a large excess of hydrogen sulfide for optimum yields of mercaptans was first observed by Eaton and Olin (10). They recommend temperatures of -60 C and a mole ratio of hydrogen sulfide to olefin of at least 5 to 1. We conducted the BF_3-catalyzed reaction of methyl oleate and hydrogen sulfide at -70 C for 4 hr with a 200 molar excess of hydrogen sulfide. A GLC analysis of the reaction mixture is shown in Figure 1A. The principal peak has the same retention time as an authentic sample of methyl 9(10)-mercaptostearate prepared from methyl oleate and thiolacetic acid (11). Addition of an internal standard (lauryl mercaptan) showed that more than 94% of the reaction product placed on the GLC emerged from the column.

Mass spectrometry confirmed that the product was primarily methyl 9(10)-mercaptostearate, but the presence of small peaks at 157 and 199 suggest that some mercapto groups are at the 8 and 11 positions, respectively. The high yield of methyl 9(10)-mercaptostearate by the BF_3-catalyzed reaction is in sharp contrast to the low yield by the photochemical reaction (8). Boron trifluoride is a strong Lewis acid, and the addition of hydrogen sulfide to methyl oleate quite likely proceeds by a heterolytic mechanism, such as:

$$RCH = CHR' + \underline{BF}_3 \rightleftharpoons \overset{+}{RCHCHR'}\underset{\underline{BF}_3}{|}$$

$$\underset{SH}{\underset{|}{RCHCH_2R'}} + \underline{BF}_3 \longleftarrow \overset{+}{\underset{\underline{BF}_3}{\underset{|}{RCHCHR'}}} \overset{H\,\overset{+}{S}H}{\underset{H_2S}{}}$$

In the first step, BF_3 complexes the olefin to form a carbonium ion. Hydrogen sulfide is a nucleophile which readily attacks the carbonium ion in the second step to form a sulfenium ion. The third step is the dissociation into the mercapto derivative and boron trifluoride. This mechanism is similar to that for the hydration of an olefin which proceeds through an oxonium ion (12). Another mechanism that involves a coordination compound of boron trifluoride and hydrogen sulfide is unlikely since these complexes exist only at lower temperatures (13).

GLC analysis of the BF_3-catalyzed addition of hydrogen sulfide to methyl oleate at 25 C for 7 hr is shown in Figure 1B. Unreacted methyl oleate is present along with some unidentified components (Table I). When making comparisons of the reaction products obtained at -70 and 25 C, temperature difference is not the only factor. At -70 C, the mole ratio of hydrogen sulfide to methyl oleate is 200:1, whereas at 25 C the ratio is 2.6:1.

Boron trifluoride-catalyzed reactions of methyl linoleate and hydrogen sulfide are more complete and have fewer side reactions than UV-irradiated reactions. With BF_3 at
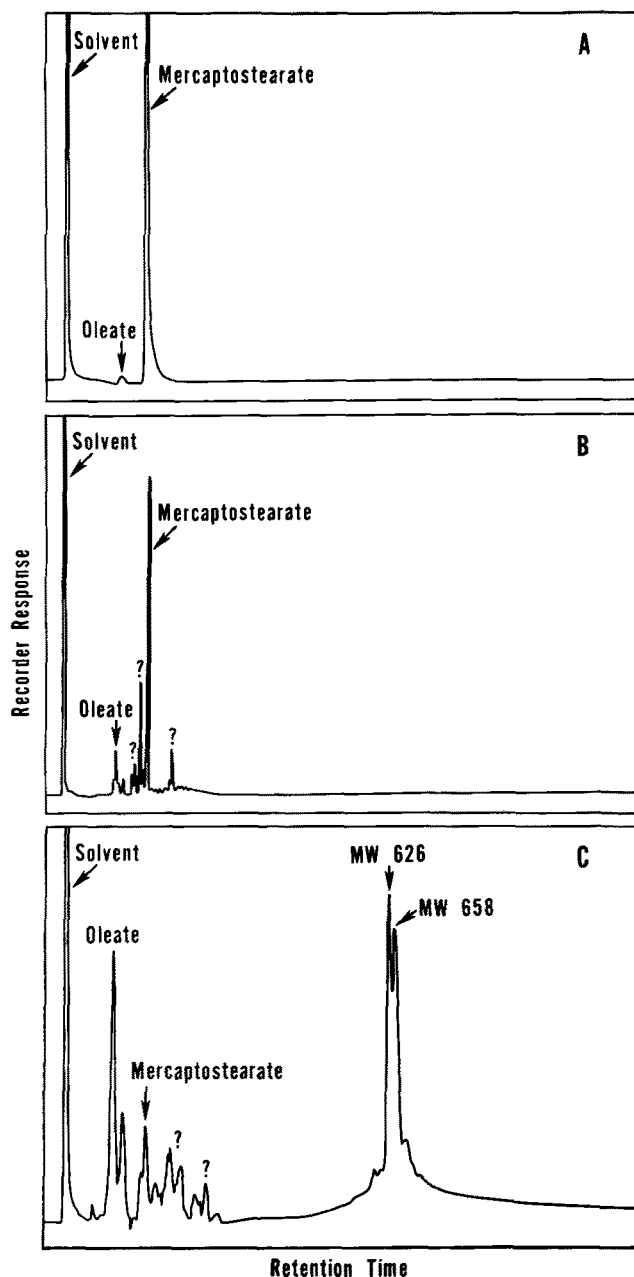

FIG. 1. Gas chromatograms of (A) product of methyl oleate at -70 C, (B) product of methyl oleate at 25 C, and (C) product of methyl oleate and methyl 9(10)-mercaptostearate at 25 C.

-70 C, less than 1% of the starting ester remained after 4 hr, and only 15% side products were noted (Table I). Addition of an internal standard (lauryl mercaptan) to the methyl linoleate product from the -70 C reaction showed 92% volatiles on GLC. More than 83% of the product appeared in one major peak. In contrast, the photochemical addition of hydrogen sulfide to methyl linoleate at 25 C had four major reaction products and considerable unreacted methyl linoleate (7). Mass spectra data of the principal product from the BF_3 reaction at -70 C were identical to the mass spectra obtained from one of the GLC-trapped samples of the UV-irradiated reaction product; namely, an approximate equal mixture of methyl 9-(2-pentyl-1-thiolan-5-yl) nonanoate and methyl 8-(2-hexyl-1-thiolan-5-yl) octanoate (7). At 25 C, the BF_3-catalyzed addition of hydrogen sulfide to methyl linoleate was not so complete after 7 hr as the -70 C addition (Table I). Side products were formed in somewhat greater amounts.

An experiment was conducted at 25 C with the addition

TABLE I

BF₃-Catalyzed Addition of Hydrogen Sulfide to Methyl Esters

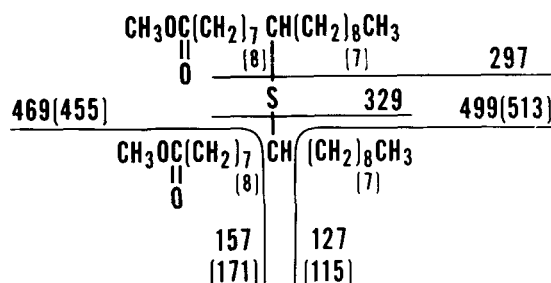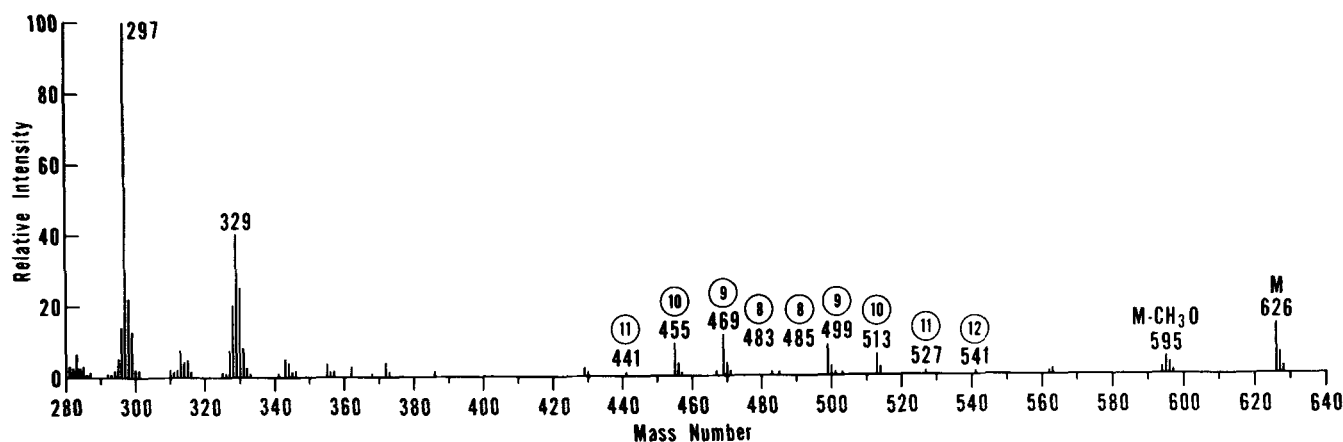| Ester	Solvent	Temperature, C	Time, hr	Composition (GLC)[a], %		
				Starting material	Main product	Side products
					Thiol	
Oleate	Hexane	-70	4	2.4	88.9	8.7
	Hexane	25	3	47.6	38.3	14.1
	Hexane	25	7	12.6	56.7	30.7
					Cyclic sulfide	
Linoleate	Hexane	-70	4	0.9	83.8	15.3
	Hexane	25	7	16.9	64.5	18.6
	Ether	-70	4	99.7	0.3	None

[a]GLC = gas liquid chromatography.

FIG. 2. Mass spectrum of bis(methyl n-octadecanoate 9[10]-yl) sulfide.

of 1.09% boron trifluoride etherate (based upon wt of methyl linoleate) in place of gaseous BF₃. No reaction had occurred after 8 hr. In a related experiment at -70 C, hexane was replaced with ether as solvent and after a 4 hr treatment with gaseous boron trifluroride essentially no sulfur products resulted (Table I). Inactivity in both experiments can be attributed to the BF₃ ether complex which does not coordinate the olefin.

Bis(methyl n-octadecanoate 9[10]-yl) Sulfide

An equal molar mixture of methyl oleate and methyl 9(10)-mercaptostearate was reacted in toluene at 25 C with the BF₃ catalyst. GLC analysis of the products is shown in Figure 1C. Unreacted methyl oleate and methyl 9(10)-mercaptostearate are present, but the major components are two products of mol wt 626 and 658. Preparative gas chromatography and mass spectroscropy indicate that the 626 mol wt product has the structure shown in Figure 2.

A parent mass of 626 is noted with fragmentation peaks at 595 due to loss of one methoxy and at 563 due to loss of two methoxy groups. Peaks at 513 and 499 are due to cleavage α to the sulfur branch and loss of the hydrocarbon

end of the fatty acid, whereas peaks at 469 and 455 are due to a similar cleavage but loss of the ester end. Small peaks at 527, 485, 483, and 441 suggest that all coupling is not through the 9 and 10 positions but that some sulfur is at the 8 and 11 positions and very probably at the 12 position (peak 541). Isomerization during the reaction may occur through either a cyclic sulfenium ion (14) or a carbonium ion (15). Peaks at 329 and 297 are due to cleavage of the carbon sulfur bonds joining the two fatty esters. In the preparation of methyl 9(10)-mercaptostearate, mass spectrometry has shown some 8- and 11-mercapto products present, and linkages in the sulfide at the 8 and 11 positions were expected.

Hydrogen Sulfide Adduct of Soybean Oil

The results of the nucleophilic addition of hydrogen sulfide to soybean oil are shown in Table II for a 1 g and 10 g batch of oil. The methyl esters from the 1 g sample of oil were analyzed by GLC, and their composition showed that oleate was converted primarily to mercaptostearate and linoleate to the thiolan. The minor constituents (palmitic and stearic) of soybean oil would not be expected to react

TABLE II

BF_3-Catalyzed Addition of Hydrogen Sulfide to Soybean Oil[a]

Sample size, g	Solvent	Temperature, C	Methyl ester composition (GLC)[b], %					
			Palmitate	Stearate	Mercaptostearate	Thiolan	Sulfide	Other
1	Hexane	-70	10.0	6.7	26.9	52.2	None	4.2
10	Toluene	-20	12.3	9.9	9.2	36.1	9.4	23.1

[a]Starting material: 10.3% palmitate, 5.4% stearate, 23.3% oleate, 51.9% linoleate, and 9.0% linolenate.
[b]GLC = gas liquid chromatography.

with hydrogen sulfide, but the other minor constituent (linolenic) could reaction with 2 moles of hydrogen sulfide. A net result would be 1 mole of hydrogen sulfide appearing to add to each acyl group in the glyceride. Sulfur analysis for the 1 g sample was 9.9%, which percentage is close to the calculated value of 9.7% for glycerol trimercaptostearate.

When batch size was increased to 10 g in 100 ml hexane, incompatibility was encountered. Toluene was a better solvent, but 150 ml/10 g oil was required, and the temperature had to be raised to -20 C. Data on the methyl esters from the 10 g batch (Table II) showed that the reaction led to a more complex mixture of products. An unidentified GLC peak (23.1%) could result from the alkylation of toluene with unsaturates. Work on the addition of hydrogen sulfide to soybean oil is continuing.

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