Free Radical Addition of Hydrogen Sulfide and Thiols to Linseed Oil and Methyl Oleate[1]

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Abstract

Free radical additions of hydrogen sulfide, ethanedithiol, and 1,6-hexanedithiol have been made to methyl oleate and linseed oil with ultraviolet radiation. Reactions were carried out in dichloromethane at −70C and in benzene at 25C. With the dithiols, a new dibasic ester has been prepared from methyl oleate in which bridging is accomplished through a dithiol moiety. Hydrogen sulfide has been added to linseed oil in suitable solvents at both −70C and 25C. It appears that zero-order kinetics control the additions at both temperatures. Infrared data show a linear relationship between mercapto absorption and the amount of sulfur incorporated. Nuclear magnetic resonance (NMR) spectra demonstrate a decrease in olefinic protons with an increase in sulfur content. Fair agreement on the extent of reaction exists between data from NMR, sulfur content, and infrared analyses. Hydrogen sulfide-treated linseed oil films air-dry slowly at room temperature; at 250C for 1 hr under a CO_2 atmosphere these oils cure to brown films with Sward Rocker values of 24 to 32 and pencil hardness values of five to greater than six. Pencil hardness and alkali resistance increased with sulfur content. The film from the 4.2% sulfur sample resisted alkali at room temperature for 24 hr.

Introduction

Although reactions of the hydrocarbon chain of unsaturated fatty acids have been investigated extensively (9), there are few references on the introduction of a mercapto group to the double bonds of fatty acids or triglycerides. An indirect method for the preparation of a mercapto fatty acid via an acetylthio derivative has been described by Koenig et al. (11). Fore and co-workers (7) studied the addition of mercaptoacetic acid to linoleic acid and methyl linoleate, but their products contained only sulfide groups. Several references (1,6,14,17,20) in the patent literature concern reactions of fatty materials with sulfur, hydrogen sulfide, mercaptans, sulfur halides, and phosphorus sulfides; however the reaction products are not well characterized. These products are claimed to be useful as lubricant additives, coatings, and rubber substitutes.

Mayo and Walling (13) found that mercaptans usually add abnormally (contrary to Markownikoff's rule) to olefins, but they showed no examples of abnormal addition with hydrogen sulfide. Vaughn and Rust (23–24) discovered that hydrogen sulfide adds to olefins abnormally when the reaction is conducted at room or lower temperatures under ultraviolet radiation. The *gamma*-radiation-induced addition of hydrogen sulfide to olefins was reported by Kenichi Sugimoto et al. (22) to yield thiols when an excess of hydrogen sulfide was used. Recently Oswald (15) has disclosed a direct synthesis of thiol-modified polybutadienes by using ultraviolet radiation.

Studies in this laboratory involved the free radical addition of hydrogen sulfide and thiols to methyl oleate and linseed oil. The products were characterized by chemical analyses, NMR, and infrared spectra. Film properties of the addition products from hydrogen sulfide and linseed oil cured under several conditions are described.

Experimental Section

Materials

Methyl oleate (99+%) was obtained from Applied Science Laboratories. Ethanedithiol, n_D^{20}, 1.5570, and 1,6-hexanedithiol n_D^{20}, 1.5110, bp 118–9/15 mm, were from Aldrich Chemical Company Inc. Hydrogen sulfide (CP grade) was received from The Matheson Company. Benzene was "Baker Analyzed" reagent grade. Dichloromethane, bp 39.5–40.5, was procured from Matheson, Coleman, and Bell.

Equipment

The apparatus used for UV irradiation is the same as described by Schwab et al. (18). A Hanovia lamp (type 8A36) was used in the irradiations. For experiments at 20–25C, tap water was circulated through a cooling chamber which was provided in the double-walled quartz immersion well. At higher temperatures the reaction vessel was mounted in a suitable bath heated to the desired temperature. For low-temperature work the reactor was mounted in a 4-qt Dewar flask containing isopropanol. Dry ice was added periodically to the isopropanol to maintain −70C. A magnetic stirrer provided the necessary agitation. The flow of hydrogen sulfide was controlled with a corrosion-resistant hydrogen sulfide regulator (Matheson Model 11–330, equipped with a check valve). Detection of mercapto, sulfide, and disulfide groups was made on a Beckman IR 8 infrared spectrophotometer. Unsaturation and olefinic groups were determined with a Varian A-60 NMR analytical spectrometer, 60 megacycle. A Rotovisco Haake rotating viscometer was employed to measure viscosity. Molecular weights were determined with a vapor pressure osmometer Model 301A (Mechrolab).

Methyl 9(10)-Mercaptostearate

Methyl oleate (7.4 g, 0.025 mole) was dissolved in 50 ml of dichloromethane in the quartz chamber of the UV apparatus. The stirred solution was cooled to −70C, and approximately 7 moles of hydrogen sulfide was introduced. The mixture was irradiated (not continuously) for 20 hr at −68 to −72C. After irradiation of the mixture, the solvent was removed on a steam bath with nitrogen bubbling through the solution. Hexane (10 ml) was added to the residue, and the solution was washed with two 10-ml portions of distilled water. An emulsion developed but broke on standing overnight. The separated oil layer was filtered through anhydrous sodium sulfate and

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vacuum-distilled at 1 mm Hg to yield 2.6 g of product, bp 210C.

Anal. Calcd. for $C_{19}H_{38}O_2S$: C, 69.0; H, 11.58; S, 9.7; M.W., 330. Found: C, 68.2; H, 11.78; S, 9.84; M.W., 358. NMR indicated no olefinic protons. Infrared absorption had a band at 3.90 mμ, characteristic of mercapto groups; $n_D^{25} = 1.4653$. Viscosity at 25C was 39.0 cp at 1873 sec^{-1} and 23.2 cp at 16860 sec^{-1} with a plate cone attachment on the Rotovisco Haake rotating viscometer.

Methyl oleate (8.0 g, 0.0269 mole) and 300 ml benzene were introduced into the UV apparatus previously described (18). The apparatus was assembled in a water bath maintained at 25C. Hydrogen sulfide was bubbled through the solution at a rate of approximately two bubbles per second. The Hanovia lamp was inserted in the quartz well, and the sample was irradiated for 1 week. After solvent removal and vacuum distillation at 1 mm Hg, a fraction resulted that distilled at 200–210C.

Anal. Calcd. for $C_{19}H_{38}O_2S$: C, 69.0; H, 11.58; S, 9.7. Found: C, 67.7; H, 11.4; S, 10.5. Infrared absorption showed mercapto groups and sulfide linkages. NMR indicated the presence of some olefinic protons.

In another experiment at 25C, methyl oleate in benzene was irradiated with UV light while hydrogen sulfide was bubbled into the solution as described above. Samples were withdrawn periodically and analyzed for sulfur content (Fig. 1). Fig. 1 also compares experiments conducted with an old and new lamp. Fig. 2 shows a plot of percentage of sulfur vs. infrared absorption of SH at 3.9 μ for the hydrogen sulfide-treated methyl oleate.

Reaction of Methyl Oleate and 1,6-Hexanedithiol. A mixture of methyl oleate (7.4 g, 0.025 mole), 1,6-hexanedithiol (1.9 g, 0.0125 mole), and 300 ml of benzene was introduced into the UV apparatus (18). The Hanovia lamp was inserted in the quartz well, and the irradiation apparatus, fitted with a reflux condenser, was placed in a bath maintained at 41 ± 2C. After three days of irradiation, solvent in the mixture was removed, and the residue was dissolved in 10 ml of hexane. This product was washed with water and dried over anhydrous sodium sulfate. An attempt to distill the dibasic ester at <1 mm was not successful, but the product was purified by passage through a Silica Gel G column with a hexane:diethyl ether solvent mixture (1:1) to yield 1.6 g of material, which analyzed as follows.

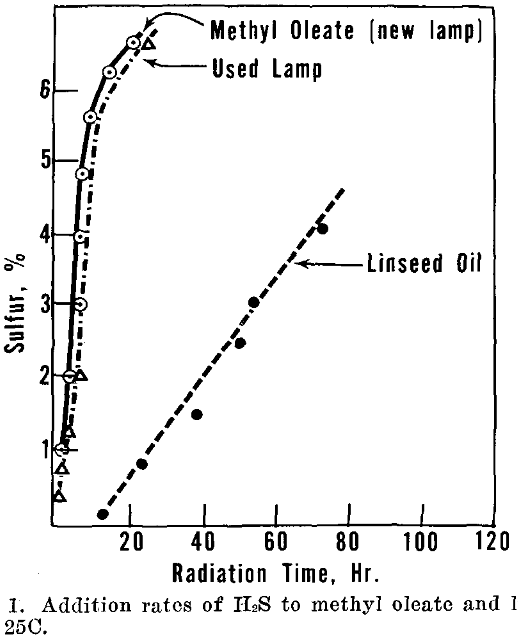

FIG. 1. Addition rates of H_2S to methyl oleate and linseed oil at 25C.

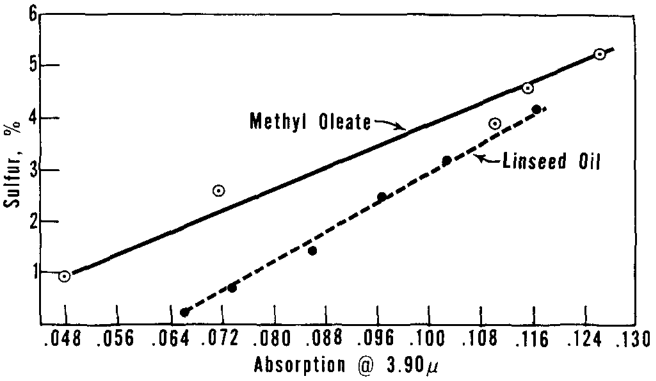

FIG. 2. Infrared absorption at 3.9 μ of hydrogen sulfide-treated samples at 25C.

Anal. Calcd. for $C_{44}H_{86}O_4S_2$: C, 71.10; H, 11.66; S, 8.63. Found: C, 70.99; H, 11.43; S, 8.49. An infrared spectrum showed absorption at 14.3 μ, characteristic of stretching vibrations of the sulfide linkage; no absorption was detected at 3.9 μ (SH band). Viscosity at 25C was 16.4 cp at 2810 sec^{-1} and 8.4 cp at 16860 sec^{-1}.

Reaction of Methyl Oleate and Ethanedithiol

Reaction conditions and purification procedures were similar to those with methyl oleate and 1,6-hexanedithiol. From 7.4 g of methyl oleate and 1.2 g of ethanedithiol was obtained 1.3 g of a fraction (from the Silica Gel G column), which analyzed as follows.

Anal. Calcd. for $C_{40}H_{78}O_4S_2$: C, 69.78; H, 11.44; S, 9.33. Found: C, 70.19; H, 11.58; S, 10.96. An infrared absorption band was noted at 14.3 μ; a weak absorption at 3.9 μ indicated a trace of mercapto groups. Viscosity at 25C was 40.6 cp at 2810 sec^{-1} and 21.4 cp at 16860 sec^{-1}.

Addition of Hydrogen Sulfide to Linseed Oil

In experiments at −70C, dichloromethane served as a solvent whereas in experiments, at room temperature and above, benzene was the solvent. Alkali-refined, bleached, linseed oil (20 g) was weighed into the quartz chamber, solvent (100 ml) was added, and the solution was stirred with a magnetic stirrer. Hydrogen sulfide was introduced into the solution from a compressed gas cylinder. The Hanovia lamp was the UV source. At −70C, experiments were conducted (not continuously) for 1 to 7 days to yield products containing 0.3 to 5.8% sulfur. At 25C, experiments were run continuously from 1 to 6 days to give products with 0.2 to 4.2% S. Addition of hydrogen sulfide (as determined by sulfur analysis) vs. time is shown in Fig. 1. In Fig. 2 infrared absorption at 3.9 μ, which is due to SH stretching, is plotted against percentage of sulfur for hydrogen sulfide-treated linseed oil at 25C. Table I is a comparison of the degree of reaction of hydrogen sulfide-treated linseed oil, based on sulfur content and NMR analysis.

Film Evaluation. Films (50% solids in toluene) were drawn down with a doctor blade to 4 mils of wet thickness on 4 × 6 × ¼ in. plate glass and on 6-in. diameter black iron discs (0.023 in. thick). Film hardness was determined with a Sward Rocker and

TABLE I

Sulfur and NMR Analyses of Hydrogen Sulfide-Treated Linseed Oils (25C)

Sulfur Analysis		NMR Analysis		
Sulfur, %	Reaction, % (based on sulfur)	Olefinic protons, %	Olefinic groups, C_{18} unit	Reaction, % (based on NMR)
Untreated	......	13.0	2.18	......
0.2	1.0	12.9	2.16	0.8
0.7	3.5	12.7	2.13	2.3
1.4	7.0	12.2	2.04	6.2
2.5	12.5	11.2	1.88	13.7
3.2	16.0	10.8	1.81	16.9
4.2	21.0	10.6	1.79	18.5

by the pencil method (8) on films drawn on plate glass. Dry-to-touch and tack-free times were determined at elevated temperatures by the method of Schwab, Teeter, and Cowan (19) on films cast on the black iron discs. Alkali-resistance tests were made on the films drawn on plate glass after the hardness tests were completed. In the alkali test, approximately 0.2 ml of a 5% NaOH solution was placed in two different locations on the film, then a watch glass (No. 1½) was inverted over each drop. The edge of each watch glass was sealed with wax to prevent evaporation. Observations were made hourly during the first 8 hr and at 24-hr intervals thereafter. Films were considered to have failed when they showed definite signs of solution.

Results and Discussion

To obtain some information on the nature of the reaction between hydrogen sulfide and unsaturated fatty esters, we treated methyl oleate with hydrogen sulfide under UV irradiation at −70C. Elemental analyses on the distilled product give an empirical formula of $C_{18.6}H_{38.2}O_{2.1}S$ compared with $C_{19}H_{38}O_2S$ for methyl 9(10)-mercaptostearate. Infrared spectra showed a band at 3.9 μ for –SH and no band at 14–16 μ for C–S–C. The NMR spectra showed no olefinic protons. The molecular weight of the distilled product was 358, within 10% of the calculated value of 330 for methyl mercaptostearate. The refractive index of 1.4653 was close to the reported value of 1.4648 for this compound prepared by another procedure (11). In contrast, when the reaction was conducted in benzene at 25C, the product contained both mercapto and sulfide linkages as well as some olefinic protons. Compounds in addition to methyl 9(10)-mercaptostearate were evidently present. Bell and Thacker (3) found that, although hydrogen sulfide reacts with olefins at temperatures from −35 to 150C, satisfactory production of mercaptans is achieved at temperatures near 0C. Eaton and Fenn (5) found that temperatures below −40C are advantageous since a larger yield of the desired mercaptan results.

The rates of addition of hydrogen sulfide to linseed oil and methyl oleate at 25C in benzene are shown in Fig. 1. Since radiation intensity from a UV lamp may vary with use, the methyl oleate reaction with hydrogen sulfide was run with both a new and a used lamp to ensure that differences which were observed in the rate of reaction between methyl oleate and linseed oil were real. Both curves suggest a zero-order reaction although in the methyl oleate run the reaction kinetics become more complex after 10 to 15 hr. The reaction of hydrogen sulfide and linseed oil gave only zero-order kinetics, probably because it was not carried as near completion (saturation of all the double bonds) as that with methyl oleate.

A zero-order reaction would be expected if the rate-determining step (reaction a) involved the absorption of UV radiation by hydrogen sulfide to form radical intermediates. The rate of addition of hydrogen sulfide to methyl oleate is more rapid than to linseed oil. One possible explanation for the faster reaction with methyl oleate is provided by the following multistep chain mechanism (2,10):

$$\text{a) } H_2S \xrightarrow{h\nu} H\cdot + HS\cdot$$

$$\text{b) } HS\cdot + RCH = RCH' \longrightarrow \underset{\displaystyle SH}{RCH} - \dot{C}HR' \qquad \text{(I)}$$

$$\text{c) } \underset{\displaystyle SH}{RCH} - \dot{C}HR' + H_2S \longrightarrow \underset{\displaystyle SH}{RCH}\,CH_2R' + HS\cdot$$

Reaction *a* in common with photochemical processes is slow and rate-determining. Studies with thiols and unsaturated compounds have shown that reaction *c* is usually slower than *b* and that the rate of *c* varies, depending on the resonance stabilization of I. Pallen and Sivertz (16,21) observed that radical I in the reaction of *n*-butanethiol and 1-pentene is not resonance-stabilized and reacts a thousand times faster with thiol than the corresponding radical in the butanethiol-styrene system. Similarly radical I in the methyl oleate-hydrogen sulfide system is not resonance-stabilized and would react faster than the resonance-stabilized radical from linoleate or linolenate in linseed oil. Thus reaction *c* would produce HS· radicals faster from oleate than from linseed oil. Since the HS· radicals from *a* and *c* are used in *b*, the hydrogen sulfide appears to form thiyl radicals more rapidly in the methyl oleate reaction than with linseed oil.

Cunneen (4) studied the addition of thiols to olefins and found the following order of reactivity: cyclohexene > dihydromyrcene > squalene > rubber. This order is in agreement with our observations. The infrared absorption of SH stretching at 3.9 μ plotted against percentage sulfur from the 25C runs (Fig. 2) gives a linear relationship and is evidence that the primary reaction products are thiols. Table I shows that, with linseed oil, a good correlation exists between the extent of reaction as calculated from the disappearance of olefinic protons (NMR data) and from the amount of sulfur incorporated (assuming only thiol formation).

Marvel et al. (12) studied radical additions of

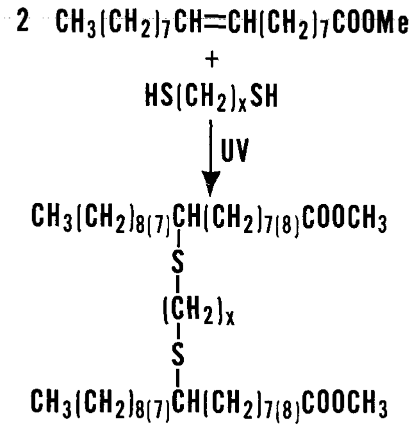

FIG. 3. Preparation of a new dibasic ester from methyl oleate.

TABLE II

Sand Trail Times[a] of Untreated and Hydrogen Sulfide-Treated Linseed Oil Radiated 6 hr at —70C

Oil	Dry-to-touch time, hr	Tack-free time, hr
Control (no H_2S)	1.0	22
Treated (1.2% sulfur)	0.33	5

[a] Oven temperature = 100C. Drier system = 0.03% Fe, 0.03% Zr.

dithiols to diolefins and found that the products are polymeric. The reaction of methyl oleate with ethanedithiol and 1,6-hexanedithiol gave two respective compounds that represent a new type of dibasic ester from methyl oleate (Fig. 3), in which bridging is accomplished through the dithiol moiety. Both these compounds were characterized by elemental and infrared analyses. The sulfur analysis for the ethanedithiol dimer was higher than theory and may indicate impurities. However reproducibility of sulfur determinations on this compound has been difficult, and variations of 0.5% and higher have been noted. Infrared spectra did show some mercapto groups although the absorption was weak. The 1,6-hexanedithiol dimer was easier to purify. Its elemental analysis agreed well with the calculated values. The infrared spectra indicated traces of mercapto groups present.

The sand trail data (Table II) demonstrate the effectiveness of the hydrogen sulfide treatment in improving drying characteristics of linseed oil. The control sample of linseed oil in this experiment received the same treatment as the hydrogen sulfide sample except that nitogen was used instead of hydrogen sulfide during the irradiation. Table III is an evaluation of baked films from hydrogen sulfide-treated linseed oils irradiated at 25C. Films from these oils air-dry slowly (requiring at least a week to 10 days), but these films can be cured much more rapidly at elevated temperatures. When baked at 250C for 1 hr under a cabon dioxide atmosphere, the color of the films varied from yellow to brown; the films with the higher sulfur content were darker.

TABLE III

Evaluation of Films[a] from Hydrogen Sulfide-Treated Linseed Oil (Irradiated at 25C)

Film	*Sulfur*, %	*Pencil* hardness	*Sward* Rocker	Resists 5% alkali, hr
Untreated oil	0	2	4	6
1	0.2	5	24	6
2	0.7	6	30	6
3	1.4	>6	28	6
4	3.2	>6	30	8
5	4.2	>6	32	24

[a] Baked 1 hr at 250C, CO_2 atmosphere.

Both pencil and Rocker hardness of sulfur-containing films were significantly better than the untreated film. The pencil hardness of films appears to increase with increasing sulfur content, but the Rocker values remain about 30 after the film contains 0.7% or more sulfur. Alkali resistance of the films improves with increasing sulfur content, and a significant increase in alkali resistance was observed in the film containing 4.2% sulfur. It is also significant that an untreated linseed oil film, baked under carbon dioxide, will resist alkali for 3 hr. Ordinarily linseed films, baked in air, will resist 5% alkali for only minutes.

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