Free Radical Addition of Hydrogen Sulfide to Conjugated and Nonconjugated Methyl Esters and to Vegetable Oils[1]

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Abstract

The rate of addition of hydrogen sulfide to high purity methyl oleate, methyl linoleate, methyl linolenate, methyl 9,11-trans,trans-octadecadienoate and methyl β-eleostearate was investigated at 25 C with UV irradiation. A similar study was carried out with soybean, linseed and tung oils in the absence and presence of 2,2′-azo-bis(isobutyronitrile) with UV photolysis. Initially the reaction of hydrogen sulfide with methyl esters appears to follow pseudo-zero-order kinetics although as the reaction proceeds the kinetics of the polyunsaturated ester reactions become more complex. For nonconjugated systems the overall rate is determined by the initiation step, whereas the overall rate of addition to conjugated systems is a function of the stability of the resonance-stabilized addition radical in the chain transfer step. For methyl esters the following order of reactivity appears to hold:

Methyl oleate ≅ methyl linoleate ≅ methyl linolenate >> methyl 9,11-trans,trans-octadecadienoate > methyl β-eleostearate. Using 2,2′-azo-bis(isobutyronitrile) with UV photolysis markedly increases the rate of addition of hydrogen sulfide to nonconjugated vegetable oils.

Introduction

Vaughn and Rust (1) in 1942 used UV irradiation for adding hydrogen sulfide to olefins, and it is still one of the best methods for preparing mercaptans (2). Although high energy radiation, such as X-rays, γ-rays and β-rays, have been tried, it promotes secondary reactions and gives mercaptan in low yield. UV radiation at 3000 Å possesses energy of 95.3 kcal/mole (3) and exceeds the bond dissociation energy of 88 kcal/mole, which Darwent and Roberts (4) found in their studies on the photochemical decomposition of hydrogen sulfide into hydrogen and thiol radicals.

Previously we showed that under UV irradiation hydrogen sulfide added faster to methyl oleate than to linseed oil (5). So the mechanism of this photochemical reaction at 25 C was studied with high-purity methyl linoleate, methyl linolenate, methyl 9,11-trans, trans-octadecadienoate, methyl β-eleostearate and soybean, linseed and tung oils. The reaction of oils with hydrogen sulfide was examined with and without 2,2′-azo-bis(isobutyronitrile) (AZBN).

Experimental Procedures

The source of irradiation in our photochemical apparatus, described previously (6), was a medium pressure mercury vapor lamp (Hanovia 8A36). The reaction vessel was charged with 300 ml (264 g) of thiophene-free benzene and saturated with hydrogen sulfide (Matheson CP grade). Since the solubility of hydrogen sulfide in benzene at 25 C is 0.01088 g/g (7), the solvent contained 2.87 g (0.084 mole) of hydrogen

sulfide. Between 5 and 10 g of pure esters or oils was used in the irradiations. For 8 g (0.0269 mole) of methyl oleate, there is approximately a threefold excess of hydrogen sulfide in solution. When used, AZBN amounted to 0.1% of the weight of the oil. Hydrogen sulfide was bubbled in continuously (2 bubbles/sec) during the experiment to maintain a saturated solution. Samples were removed periodically for mercaptan and sulfur analyses. Mercaptan sulfur was determined potentiometrically by Karchmer's method (8). Gas liquid chromatography (GLC) analyses were performed on an F&M model 5750 research chromatograph with a flame ionization detector and employing a 3% JXR column, 6 ft × ¼ in. Programmed runs were conducted at 180–300 C with a heating rate of 4 deg/min and a flow rate of 30 cc/min with helium as the carrier gas. A Beckman IR 8 spectrophotometer was used to detect trans,trans-conjugated and trans-isolated double bonds.

Methyl linoleate and linolenate were obtained from The Hormel Institute; methyl oleate, from Applied Science Laboratories, Inc. These materials were 99% pure based on GLC analysis. trans,trans-9,11-Octadecadienoic acid was prepared by the method of Schneider et al. (9), and the methyl ester was prepared from the acid by reacting with 2,2-dimethoxy propane in acidic methanol (10). β-Eleostearic acid was obtained from tung oil by the procedure of Hoffmann et al. (11) and methyl β-eleostearate was prepared from the acid with 2,2-dimethoxy propane. GLC analysis: 92% methyl β-eleostearate, 4.7% methyl α-eleostearate, 1.8% methyl palmitoleate, 1.4% methyl stearate and traces of methyl palmitate and methyl oleate.

Dry-to-touch and tack-free times were measured by the method of Schwab et al. (12) on films cast on black iron discs.

Results and Discussion

The rates of thiol formation are plotted in Figure 1 for methyl oleate, linoleate, linolenate, 9,11-trans-trans-octadecadienoate and β-eleostearate adducts. Initially all curves indicate a zero-order reaction and
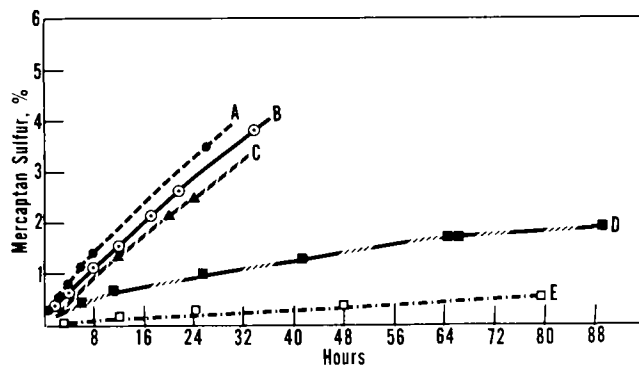

FIG. 1. Formation of mercaptan sulfur from conjugated and nonconjugated methyl esters UV treated with H₂S. Adducts from: A, methyl oleate; B, methyl linoleate; C, methyl linolenate; D, methyl 9,11-trans,trans-octadecadienoate; E, methyl β-eleostearate.
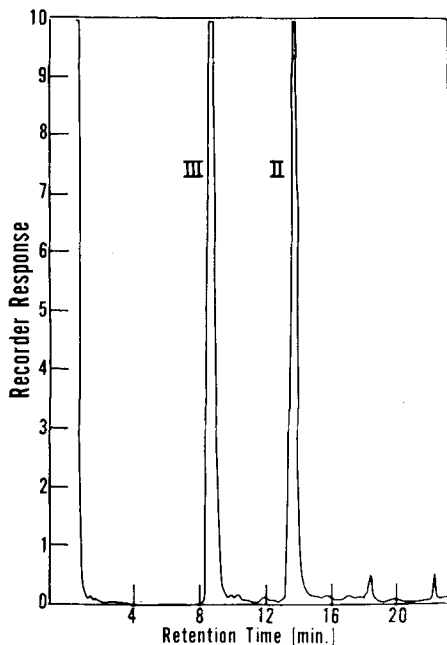
FIG. 2. Gas liquid chromatographic analysis of H₂S-treated methyl oleate after 26 hr UV irradiation at 25 C shows a mixture of methyl 9(10)-mercaptostearate (II) and methyl oleate and elaidate (III).

the following order of reactivity appears to hold: Methyl oleate ≅ methyl linoleate ≅ methyl linolenate >> methyl 9,11-trans,trans-octadecadienoate > methyl β-eleostearate.

These data show a significant difference in the rate of thiol formation between conjugated and nonconjugated systems with hydrogen sulfide. A reaction sequence producing thiols would be expected to proceed via a multistep radical chain mechanism:
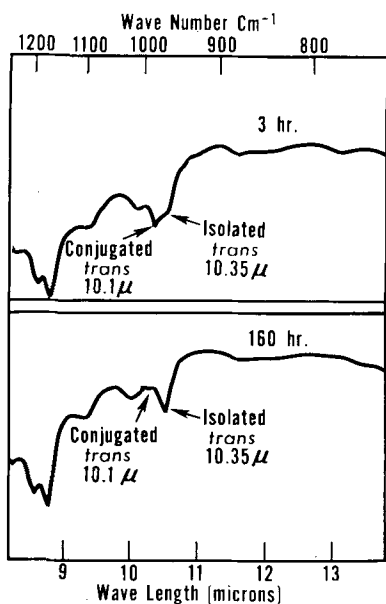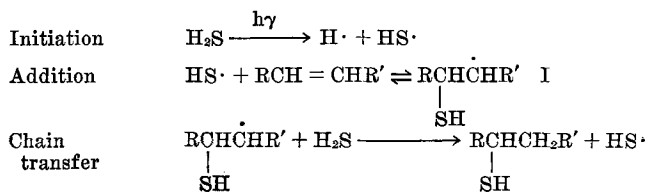
Initiation $H_2S \xrightarrow{h\gamma} H\cdot + HS\cdot$

Addition $HS\cdot + RCH = CHR' \rightleftharpoons R\overset{\cdot}{C}HCHR'$ I
                                                                        |
                                                                        SH

Chain $R\overset{\cdot}{C}HCHR' + H_2S \xrightarrow{\hspace{1cm}} RCHCH_2R' + HS\cdot$
transfer | |
                    SH   SH

FIG. 3. IR absorption of H₂S-treated methyl 9,11-trans,trans-octadecadienoate after 3 hr and 160 hr of UV irradiation.

The reaction is perpetuated by two consecutive steps; the addition of the thiol radical to the double bond followed by a transfer of the radical to hydrogen sulfide. With conjugated esters, chain transfer would be the rate-controlling step because the radical (I) would be resonance stabilized (13). Because radical I from the trienoate, eleostearate, would be more stable than the corresponding radical from octadecadienoate, the reaction with hydrogen sulfide is slower for the former.

The addition of hydrogen sulfide to methyl oleate and nonconjugated esters to form thiols was more rapid due to the lack of resonance stabilization in I. Sivertz (13) observed a similar effect on reactivities of double bonds from a study on the addition of n-butanethiol to styrene and 1-pentene. Sugimoto et al. (14) found that the radiation-induced addition of hydrogen sulfide was substantially slower to butadiene than to nonconjugated olefins.

Figure 2 is a programmed GLC curve of hydrogen sulfide-treated methyl oleate after 26 hr irradiation. The two primary components observed from GLC data were methyl 9(10)-mercaptostearate (II) and a mixture of methyl oleate and elaidate (III). The addition of a weighed amount of internal standards [n-octadecyl mercaptan and methyl 9(10)-mercaptostearate] to the reaction mixture before GLC analysis demonstrated that most of the reaction products separated on the column and were accounted for by compounds II and III.

The reaction of hydrogen sulfide with 9,11-trans, trans-octadecadienoate was more complicated. A GLC analysis (program run 180–300 C) demonstrated several products. IR absorption curves on samples after 3 hr and 60 hr of irradiation are drawn in Figure 3. After 3 hr, a shoulder at 965 cm⁻¹ represents a small amount of isolated trans esters, but the sample is largely trans,trans conjugated (989 cm⁻¹). After 160 hr, however, no trans,trans conjugation was evident; instead, a strong absorption for isolated trans developed (965 cm⁻¹). These data along with mercaptan sulfur analysis show that as conjugated trans,trans ester disappears, mercaptan sulfur and isolated trans unsaturation appear. Attempts were made to determine sulfide sulfur by the method of Hastings (15), but results were not reproducible. Undoubtedly, sulfides are present in these samples, as well as polymeric materials. We intend to do more work on the identification of these products.
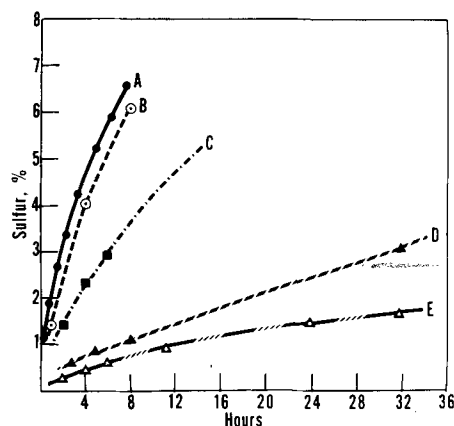

FIG. 4. Sulfur content increase for H₂S-treated vegetable oils in presence and absence of 2,2'-azo-bis(isobutyronitrile) (AZBN) with UV photolysis. Soybean and linseed oils without AZBN, C and D, respectively. Soybean, linseed and tung oils with AZBN, A, B and E, respectively.

TABLE I

UV-Irradiated Linseed Oil [0.1% 2,2'-Azo-bis(isobutyronitrile)]

Time, hr	Mercaptan sulfur, %	Total sulfur, %	Mercaptan sulfur, % / Total sulfur, %
1	1.14	1.44	0.79
4	3.70	4.06	0.91
8	5.14	6.01	0.86
24	6.86	8.22	0.89
32	7.10	8.88	0.80
51	8.28	9.79	0.85
74	9.03	10.62	0.85

TABLE II

Drying Properties of Polythiocarbamate Films From Mercapto Linseed Oils and Tolylene Diisocyanate

% S	Tack-free time, hr	Dry-to-touch, hr
0	22	12
2.3	9.5	7
4.4	9	7
5.7	9	7
8.8	7	6

After 176 hr of irradiation at 25 C in the presence of hydrogen sulfide, methyl esters of tung oil showed more than 90% of products volatile on the GLC column. This program run was made at 125–300 C with a heating rate at 4 deg/min. Chromatographs of the tung ester reaction up to 8 hr showed little evidence of sulfur compounds. At a 32 hr reaction time GLC showed largely mono sulfur adducts, but after 176 hr the chromatograph revealed a complex mixture and significant quantities of compounds containing two or more sulfur atoms.

The reaction with oils is also complex. Figure 4 is a plot of percent sulfur vs. time for hydrogen sulfide-treated soybean, linseed and tung oils under UV radiation with and without 0.12% (based on weight of oil) of AZBN. Since Lewis and Matheson (16) discovered that AZBN decomposed under UV irradiation, we used their technique to generate free radicals at 25 C. Data in Figure 4 demonstrate that AZBN markedly increases the rate of addition of hydrogen sulfide to nonconjugated oils. This increase is consistent for a mechanism where the rate of reaction is controlled by the initiation step. Because AZBN does not significantly increase the rate of addition to tung oil, evidently the stability of RCH(SH)ĊHR' in the chain transfer step controls the rate of reaction.

Table I lists the percentages of mercaptan and total sulfur of hydrogen sulfide-treated linseed oil in the presence of AZBN with UV photolysis. Most of the sulfur in these derivatives is present as mercaptan, and after an 8 hr reaction the mercaptan-to-total-sulfur ratio remains constant at about 0.85. Films from these mercapto derivatives dry slowly at room temperature but cure at 250 C under carbon dioxide to

produce yellow to brown coatings having Sward Rocker values ranging from 24 to 32 and pencil hardness values of 5 to greater than 6 (5). Perhaps the most outstanding property of these films is their alkali resistance. Cured films are unaffected by 5% sodium hydroxide after 7.5 hr but swelling develops on overnight standing. A control film of untreated linseed oil swells within 15 min under similar conditions.

Four mercapto linseed oils were treated with tolylene-2,4-diisocyanate in toluene with catalytic amounts of tri-n-butylamine catalyst to form polythiocarbamates. Drying properties of films from these products are given in Table II, along with those of a film from untreated linseed oil. Drying times were shorter as the sulfur content increased. Films dried significantly better than the linseed oil containing no sulfur.

REFERENCES

1. Vaughn, W. E., and F. F. Rust, J. Org. Chem. 7, 472 (1942).
2. Stacey, F. W., and J. F. Harris, "Organic Reactions," Vol. 13, Edited by A. C. Cope et al., John Wiley and Sons, Inc., New York, 1963, p. 194.
3. Daniels, F., "Outlines of Physical Chemistry," Third Printing corrected, John Wiley and Sons, Inc., New York, 1948, p. 598.
4. Darwent, B. de B., and R. Roberts, Proc. Roy. Soc. London 216A, 344 (1953).
5. Schwab, A. W., L. E. Gast and J. C. Cowan, JAOCS 45, 461 (1968).
6. Schwab, A. W., J. A. Stolp, L. E. Gast and J. C. Cowan, Ibid. 43, 30 (1966).
7. Seidell, A., and W. F. Linke, "Solubilities of Inorganic and Organic Compounds," Supplement to the Third Edition, D. Van Nostrand Co., New York, 1952, p. 232.
8. Karchmer, J. H., Anal. Chem. 30, 80 (1958).
9. Schneider, W. J., L. E. Gast and H. M. Teeter, JAOCS 41, 605 (1964).
10. Brown, J. H. and N. B. Lorette, U.S. 2,978,469 (April 4, 1961).
11. Hoffmann, J. S., R. T. O'Connor, D. C. Heinzelman and W. E. Bickford, JAOCS 34, 338 (1957).
12. Schwab, A. W., H. M. Teeter and J. C. Cowan, Ibid. 36, 275 (1954).
13. Sivertz, J., J. Phys. Chem. 63, 34 (1959).
14. Sugimoto, K., W. Ando and S. Oae, Bull. Chem. Soc. Japan 38, 221 (1965).
15. Hastings, S. H., Anal. Chem. 25, 420 (1953).
16. Lewis, F. M., and M. S. Matheson, J. Amer. Chem. Soc. 71, 747 (1949).

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