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

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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. 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.

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 0.01058 g/g (7), the solvent contained 2.87 g (0.0048 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 6750 research chromatograph with a flame ionization detector and employing a 3% XBR column, 6 ft × ½ 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 by reacting 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
Retention Time [min.]

Figure 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).

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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**: H₂S → H⁺ + HS⁻
- **Addition**: HS⁻ + RCH = CHR' → RCHCHR'⁻ + SH
- **Chain transfer**: RCHCHR'⁻ + H₂S → RCHCH₂R' + HS⁻

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-butanol 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.

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

Figure 4. Sulfur content increase for H₂S-treated vegetable oils in presence and absence of 2,2’-azo-bis(isobutryronitrile) (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.