The Peroxidic Species Generated by Ozonolysis of Oleic Acid or Methyl Oleate in a Carboxylic Acid Medium

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The ozonolysis of oleic acid or methyl oleate in a carboxylic acid medium produces three major peroxidic species as well as aldehyde. These peroxidic compounds have been identified as 1-acyloxyalkyl-1-hydroperoxides, 1,2,4-trioxolanes, and bis(1-acyloxy-1-alkyl) peroxides. The bis(1-acyloxy-1-alkyl) peroxides have not been reported previously as oleic acid or methyl oleate ozonolysis products. A ^1H nuclear magnetic resonance examination of the ozonization products of oleic acid or methyl oleate in carboxylic acids, as well as methanol and iso-octane, led to the identification of the peroxidic compounds and aldehyde.

KEY WORDS: 1-Acyloxyalkyl-1-hydroperoxide, bis(1-acyloxy-1-alkyl) peroxide, ^1H NMR, methyl oleate, oleic acid, ozonization, 1,2,4-trioxolane.

The ozonolysis of commercial-grade oleic acid to prepare azelaic and pelargonic acid has been a successful industrial process for many years (1,2). Generally, the process is carried out in a carboxylic acid solvent. Modifications of this industrial process have been reported, but in general the basic procedure remains the same (3–7).

Information on the peroxidic compounds generated by ozonolysis of oleic acid in a carboxylic acid solvent is limited. It is known that ozonization of an olefin in a carboxylic acid will produce a 1-acyloxyalkyl-1-hydroperoxide (8). Consequently, it has been implied that oleic acid produces the same peroxidic species under similar conditions (2,6,9). The structure of the 1-acyloxyalkyl-1-hydroperoxide and its chemistry has been studied (10–14). However, nuclear magnetic resonance (NMR) data on these compounds are sparse. No NMR data were found in the literature on 1-acyloxyalkyl-1-hydroperoxides generated from oleic acid.

In this report, a detailed NMR study reveals that the expected ozonization products, 1-acyloxyalkyl-1-hydroperoxides and 1,2,4-trioxolanes, are not the only significant compounds generated from ozonolysis of oleic acid in carboxylic acids. ^1H NMR spectroscopy was an excellent non-destructive tool for functional group analysis of the numerous, complex, high-energy peroxidic compounds generated from oleic acid.

EXPERIMENTAL PROCEDURES

Materials. All carboxylic acids, methyl esters, and nonyl aldehyde were purchased from Aldrich Chemical Company (Milwaukee, WI). Deuterated chloroform was also purchased from Aldrich. Oxygen was purchased from AGA Gas, Inc. (Cleveland, OH).

Apparatus. The NMR spectra were generated in a Varian XL-200 NMR Spectrometer (Palo Alto, CA). A Welsbach T-23 Ozone Generator was used to produce ozone. All gas-liquid chromatography (GLC) work was performed on a Hewlett Packard 5880 Gas Liquid Chromatograph (Palo Alto, CA) with a Chrompack WCOT fused Silica FFAP-CB 25 m × 0.33 mm i.d. capillary column. The gas chromatograph oven was programmed to run at 100°C for 0.5 min followed by a 12°C/min linear ramp to a final temperature of 250°C held for 15 min. The injector and flame ionization detector operated at 270°C and 300°C, respectively. Helium was the carrier gas used with a 1:12.5 split ratio.

General ozonization procedure. A mixture of 5.00 g (17.7 mmoles) of pure oleic acid (99%) or 5.25 g (17.7 mmol) of methyl oleate (99%) in 10.0 g of solvent was stirred at 23°C and an ozone/oxygen mixture was sparged into the reaction mixture through a coarse sparge tube (ASTM 145-174u) at 0.27 mmole ozone/min. Generally, the ozonization was allowed to proceed for 2.5 to 3.0 hr, giving between 80–100% conversion to ozonide. Afterwards, nitrogen gas was sparged through the mixture for 15 min. A ^1H NMR sample of ~0.4 g was taken and diluted with 1.0 mL of $CDCl_3$. Alternatively, 50.0 g (177 mmoles) of oleic acid (99%) was ozonized in 50.0 g of carboxylic acid at 1.14 mmoles of ozone/min.

Reaction of oleic acid ozonolysis compounds with nonyl aldehyde. Nonyl aldehyde (2.0 mL, 11.6 mmol) was added to 5.00 g (1.38 mmol peroxide/g) of oleic acid ozonolysis compounds (generated in butyric or pelargonic acid) at once. The reaction mixture was stirred under N_2 at room temperature. After 0.50 hr, a sample was taken for ^1H NMR ($CDCl_3$) analysis and iodometric titration.

Analysis of peroxide functionality by iodometric titration. Samples of approximately 0.15 to 0.20 g of ozonide were weighed accurately to three decimal places in a small glass weighing cup and then dropped into a 125-mL iodine flask that was constantly purged with N_2. To this was added 10 mL of $CHCl_3$, 2.0 mL of saturated KI and 15 mL of glacial acetic acid. The N_2 purge was stopped and the flask was immediately stoppered and swirled. The flask was allowed to sit in the dark for 25 min, and then 50 mL of water was added. The mixture was then titrated with 0.0500M $Na_2S_2O_3$ while using a starch indicator. The following formula gives the number of mmoles of peroxide (*i.e.*, -O-O-)/gram sample:

$$\frac{\text{mmole peroxide (—O—O—)}}{\text{g sample}} = \frac{\text{V}(Na_2S_2O_3) \times 0.0500\ \text{M}\ (Na_2S_2O_3)}{2 \times \text{sample wgt.}}$$

Analysis of pelargonic and azelaic acid by GLC. Accurately weighed ozonide samples of approximately 0.2 g were immediately treated with 2.0 mL of dimethyl sulfide and allowed to stand at room temperature for no less than 3 hr. Afterwards, the excess dimethyl sulfide was removed under vacuum and the remaining oil was heated under reflux in 20.0 mL of 1.0 M HCl/methanol for 1.0 hr. The mixture was then cooled to room temperature, 1.00 mL of 0.0400 gram/mL of dimethyl phthalate in methanol (internal standard) was pipetted into the mixture, and a

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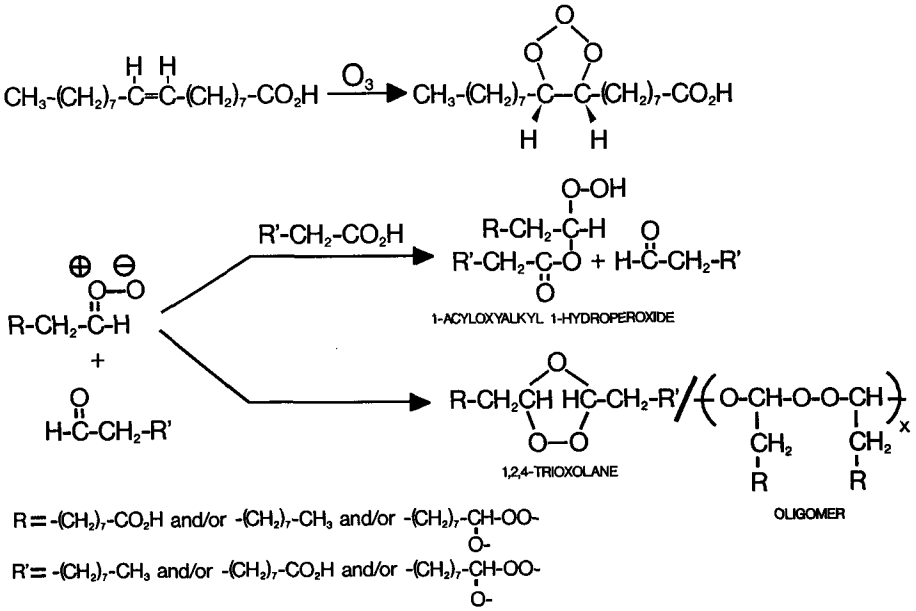
sample was taken for GLC analysis. Retention times (min) of pertinent compounds are given as follows: nonyl aldehyde (1.93), methyl azelaldehydate (6.91), methyl pelargonate (2.43), and dimethyl azelate (7.60).

RESULTS AND DISCUSSION

The Criegee mechanism for ozonolysis of the carbon-carbon double bond is generally accepted (15). According to this mechanism, oleic acid ozonolysis products formed in a participating carboxylic acid solvent should follow the route shown in Scheme 1.

Figure 1 shows a ^1H NMR of a mixture of 50.0 g (177 mmole) of pure oleic acid in 50.0 g of hexanoic acid that has been subjected to an O_3/O_2 stream until O_3 breakthrough was noted (saturated aqueous KI-soaked filter paper held at the gas exit showing positive oxidation). This same ^1H NMR pattern was observed when



SCHEME 1. Classic Criegee mechanism for ozonolysis.

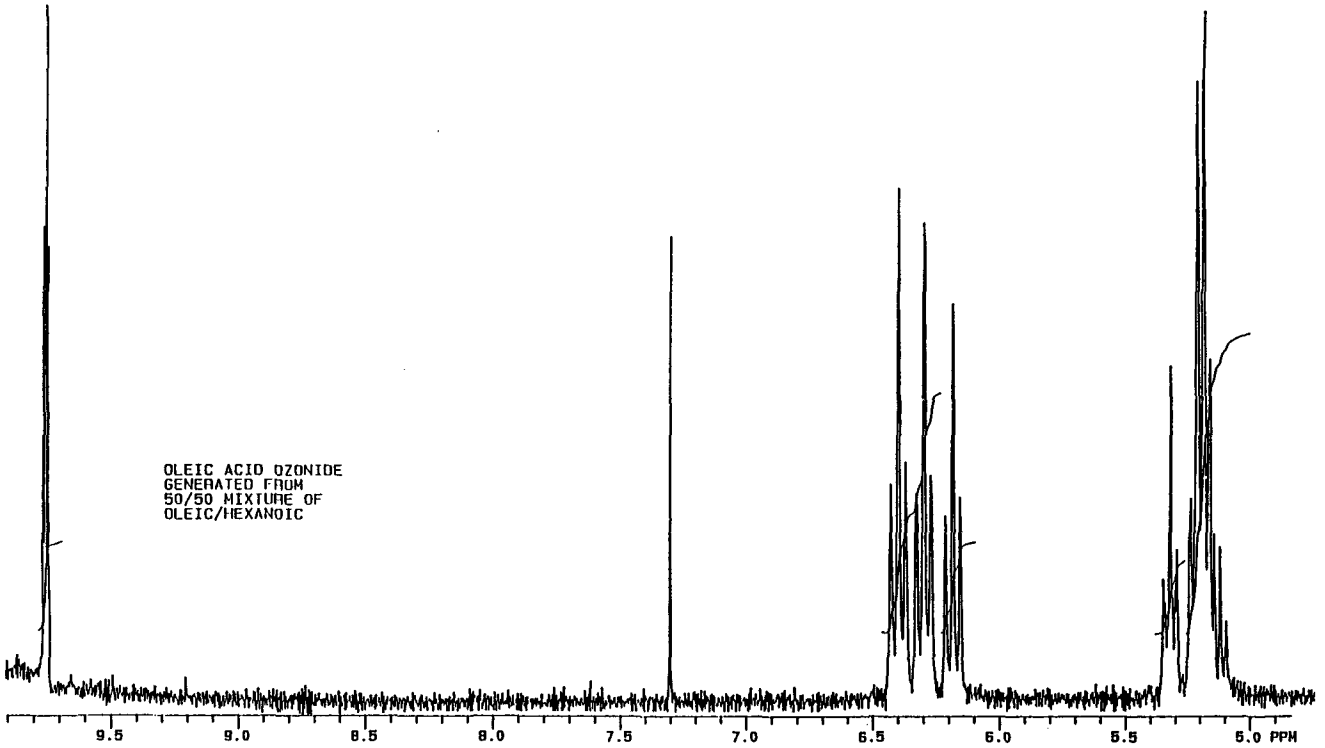
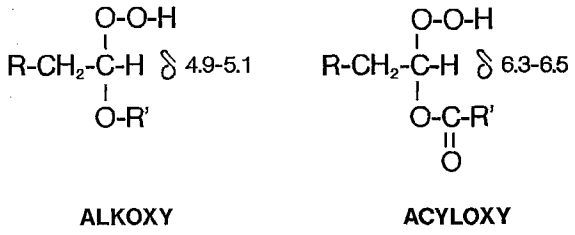


FIG. 1. ^1H NMR of the ozonolysis products from oleic acid and hexanoic acid.

oleic acid (or methyl oleate) was ozonized in other carboxylic acids, such as the series acetic through pelargonic acid, 2-ethylhexanoic acid and 2,2-dimethylbutyric acid.

According to the literature, the protons in the 1,2,4-trioxolane ring should resonate between δ4.85 and δ5.51 (16,17). For example, the ring protons of the 1,2,4-trioxolane generated from methyl oleate (ozonized in light petroleum) resonate at δ5.1 (18). In the case of 1-acyloxyalkyl-1-hydroperoxides, no report of the α-proton resonance was found. However, a value of δ6.39 for the α-proton of a 1-acyloxyvinyl-1-hydroperoxide has been reported (19).

Also a number of articles have shown that the 1-alkoxyalkyl-1-hydroperoxide α-protons resonate between δ4.9 and δ5.1 (20,21). A shift of +1.4 ppm is expected in going from alkoxy to acyloxy (22), and places the 1-acyloxyalkyl-1-hydroperoxide α-proton resonance between δ6.3 and δ6.5 as shown:



In this system it would be difficult to distinguish between the resonance of a 1,2,4-trioxolane and its oligomeric counterpart. Thus, in the ^1H NMR of Figure 1, the multiplets between δ5.1 and δ5.3 can reasonably be attributed to a 1,2,4-trioxolane or an oligomer, and the three triplets between δ6.1 and δ6.5 to acyloxy peroxy compounds. The small triplet at δ5.34 represents the vinyl protons of unreacted oleic acid, and the close-spaced triplet at δ9.74 represents the aldehyde associated with acyloxy hydro-peroxy compounds (see Scheme 1).

The assignment of the multiplets between δ5.1 and δ5.3 to a 1,2,4-trioxolane ring or an oligomer was further confirmed by the ^1H NMR analysis of the ozonide generated from methyl oleate in iso-octane. Iso-octane is a non-participating solvent and no hydroperoxy species should be formed by solvent interaction. In addition, use of the methyl ester of oleic acid was used to prevent any intra- or intermolecular interaction by an oleic carboxylic acid group. The ^1H NMR of the ring protons are shown in Figure 2. No other resonance was noted between δ2.5 and δ19 except for the methyl singlet at δ3.67. The exclusive resonance at δ5.15 is certainly due to the ring protons of the 1,2,4-trioxolane ring and confirms the original assignment of the δ5.1 to δ5.3 multiplets in Figure 1 to a 1,2,4-trioxolane/oligomer species. Note that the resonance in Figure 2 appears to be a pentet. In actuality, it is two triplets at δ5.13 and δ5.18 and possibly represents *cis* and *trans* isomers. Ozonization of oleic acid in iso-octane gave a ^1H NMR containing not only the trioxolane/oligomer protons, but also the three triplets between δ6.1 and δ6.5. The appearance of these three triplets reflects the significant intra- and intermolecular participation of the oleic acid carboxylic group in the ozonization process. The combined area of the triplets was slightly lower than the area under the δ5.1 to δ5.3 multiplets.

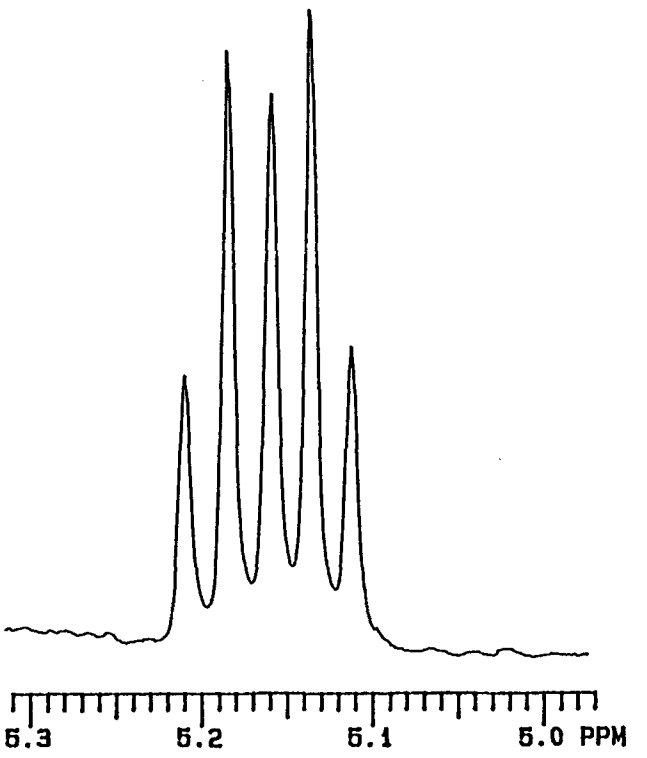


FIG. 2. ^1H NMR of the 1,2,4-trioxolane ring protons generated from methyl oleate.

A study of the peroxide compounds generated by ozonolysis of methyl oleate and oleic acid in methanol further confirms the original general structural assignments. In the case of methyl oleate, no peaks between δ6.1 and δ6.5, attributed to acyloxy peroxy compounds, were formed. Instead, the alkoxy counterpart, 1-methoxyalkyl-1-hydroperoxide, was formed and resonated between δ4.7 and δ4.9. The trioxolane/oligomer species can be found between δ5.1 and δ5.3 and is present in lower amounts than the methoxy hydroperoxides. That any trioxolane/oligomer compounds are formed at all is interesting because only methoxy hydroperoxy compounds are formed when cyclooctene (23), *trans*-3-hexene, *cis*-4-octene, and *trans*-5-decene (20) are ozonized in methanol. The oleic acid peroxides, generated in methanol, give a ^1H NMR spectrum similar to the spectrum of methyl oleate peroxides (Fig. 3). Note the small amount of acyloxyalkyl hydroperoxides generated by oleic carboxylic acid interaction. That the three triplets between δ6.1 and δ6.5 are absent in the methyl oleate peroxides, generated in methanol (trace amounts in the oleic acid case), and are replaced by a series of multiplets between δ4.7 and δ4.9, indicates that the acyloxyperoxides are formed in carboxylic acid and methoxy peroxides are formed in methanol. The original assignment of the three triplets between δ6.1 and δ6.5 to acyloxy peroxy compounds in Figure 1 appears to be justified.

However, it is unlikely that there would be three distinct triplets for 1-acyloxyalkyl-1-hydroperoxides differing in functionality seven $-CH_2-$ units away. The three triplets probably represent more than one type of peroxidic compound. This fact can also be surmised from an examination of Table 1. In Table 1, the oleic peroxidic compounds

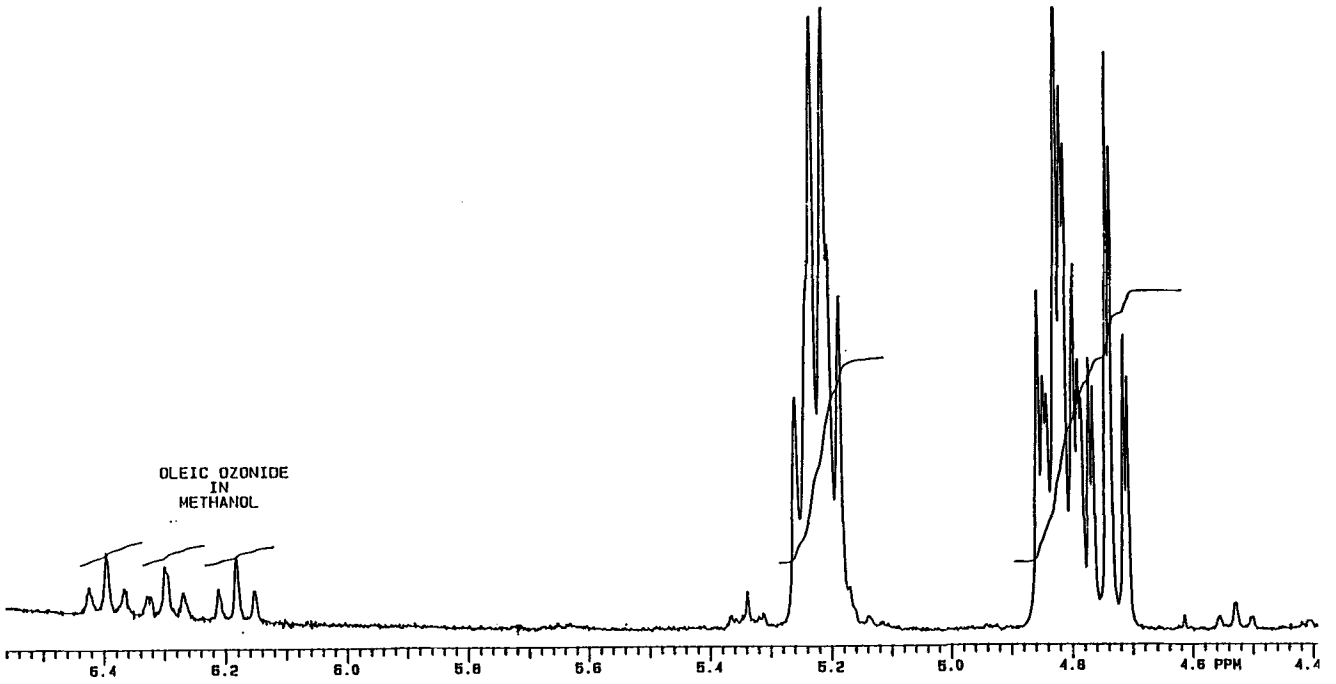


FIG. 3. ^{1}H NMR of oleic acid ozonized in methanol.

TABLE 1

Ozonization of Oleic Acid in Different Carboxylic Acid Solvents with Normalized ^{1}H NMR Area Percents (17.7 mmoles of Oleic Acid Ozonized in 10.0 g of Solvent)

Solvent	δ9.74	δ6.40	δ6.31	δ6.19
Pelargonic acid	22.9	27.2	27.2	22.7
Hexanoic acid	22.8	26.4	25.3	25.3
Valeric acid	20.0	28.2	27.1	24.7
Butyric acid	23.1	27.1	27.1	22.6
Average	22.3	27.2	26.8	23.6

generated in different carboxylic acids show that the aldehyde peak, δ9.74, is less than one-third the combined area between δ6.1 and δ6.5.

According to the Criegee mechanism, for every molecule of 1-acyloxyalkyl-1-hydroperoxide formed, an aldehyde must be formed as shown in Scheme 1. If the three triplets at δ6.19, δ6.31, and δ6.40 represent only 1-acyloxyalkyl-1-hydroperoxide, then the combined area between δ6.1 and δ6.5 would equal the area for aldehyde at δ9.74, which is not the case. It is conceivable that some of the aldehyde was converted to acid. A GLC analysis of the reaction mixture in pelargonic acid only showed a 3.3% conversion to azelaic acid.

Oleic acid ozonized in octanoic acid showed the same low yield of pelargonic (3.2%) as well as azelaic (3.7%) acid. Thus, conversion of aldehyde to acid does not account for the low aldehyde content. A cold-trap analysis of the ozone/oxygen out gas of ozonolysis showed no condensable organic material. Therefore, no aldehyde was "blown" out of the reaction mixture.

A re-examination of the normalized area percentages of the three triplets and the aldehyde resonance showed that the two peaks at δ6.31 and δ6.40 were nearly equal in area in all cases and that the δ6.19 and δ9.74 (aldehyde) peaks were close in area (the average aldehyde was generally slightly lower; this can be attributed to a small conversion to acid).

In a separate experiment, oleic acid was ozonized in different amounts of pelargonic acid. In more dilute solutions both the δ6.19 and δ9.74 (aldehyde) peaks were higher in area relative to the δ6.31 and δ6.40 peaks, as shown in Table 2. The one-to-one association of the δ6.19 and the aldehyde resonance upon dilution in pelargonic acid solvent fits the classic Criegee-type mechanism, which requires that for every free aldehyde produced an acyloxy hydroperoxide is formed. The δ6.19 triplet is, therefore, assigned to free 1-acyloxyalkyl-1-hydroperoxide:

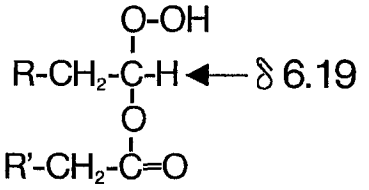
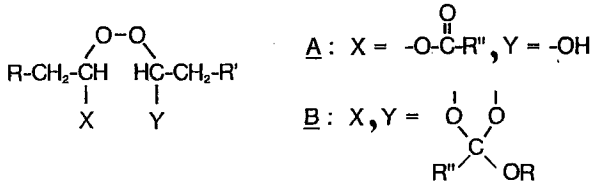


TABLE 2

Change in Normalized ^{1}H NMR Peak Areas Upon Dilution in Pelargonic Acid (17.7 mmoles of Oleic Acid Ozonized in Pelargonic Acid)

Pelargonic acid	δ9.74	δ6.40	δ6.31	δ6.19
63 mmol	22.9%	27.2%	27.2%	22.7%
166	27.2	21.6	22.3	28.1
253	28.6	20.4	20.4	30.6

It is reasonable to assign the δ6.31 and δ6.40 triplets to the same molecule because they were equal in area (or nearly so) in all cases studied. The position and splitting pattern of the peaks suggests a 1,1′-disubstituted peroxide as a likely structure:

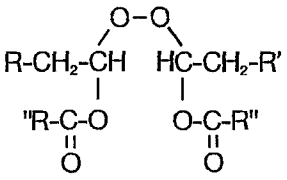


It has been reported in the literature that 1-acyloxyalkyl-1-hydroperoxides react with aldehydes to form 1-acyloxyalkyl-1′-hydroxyalkyl peroxides (Compound A) (12). Although this appears to be reasonable in a carboxylic acid system, a proton α to the hydroxy, peroxy functionality is expected to resonate in the δ4.8 to δ5.3 region (24–26). This resonance is not observed in the present system. The multiplets between δ5.1 and δ5.3 are due almost exclusively to the protons of a 1,2,4-trioxolane or oligomer. Any significant amount of hydroxy peroxide (which would resonate in this region) would cause an unequal area distribution of the δ6.31 and δ6.40 triplets.

In a separate attempt to generate 1-acyloxyalkyl-1′-hydroxyalkyl peroxide in the present system, an excess of nonyl aldehyde was added to oleic acid ozonolysis products generated separatedly in butyric and pelargonic acid. The results are shown in Figure 4 and Table 3. It is immediately obvious that the 1-acyloxyalkyl-1-hydroperoxide, δ6.19, reacted to form more trioxolane/oligomer and more of the compound responsible for the peaks at δ6.31 and δ6.40. No hydroxyperoxides were detected. The formation of the 1,2,4-trioxolane from a transient 1-acyloxyalkyl-1-hydroperoxide and an aldehyde has been reported in the literature (14), but no hydroxyperoxide intermediate was implied.

A cyclic peroxyorthoester (compound B shown above) was ruled out as the species responsible for the δ6.31 and δ6.40 peaks, because no peaks associated with an orthoester were found in a ^{13}C NMR-APT experiment (there were a series of inverted peaks between δ99 and δ102, which is indicative of -CH-O-O-).

The peroxy species that best fits the position of resonance, splitting pattern, and the equal area of the δ6.31 and δ6.40 resonance peaks (α-protons) is a bis(1-acyloxy-1-alkyl) peroxide:



Although it is curious that these two triplets are not magnetically equivalent ($\Delta\delta = 0.09$ ppm), an analogy can be found with bis(1-hydroxy-1-alkyl) peroxides. For example, the two protons α to the peroxy function in bis(1-hydroxy-1-propyl)peroxide display two triplets at δ5.06 and δ5.13 (27).

Table 4 shows the percent molar composition of the peroxides responsible for the ^1H NMR shown in Figure 1. Included in Table 4 is the aldehyde functionality at δ9.73, because aldehydes are also a direct product of ozonolysis. As mentioned before, this ^1H NMR pattern was repeated for reactions run in different straight and branched-chain carboxylic acid solvents. However, the mole percent of each species varied somewhat at different dilution levels and carboxylic acid chain lengths. The combination of iodometry (see Experimental Procedures for details) and ^1H NMR gave good results on a mole basis for peroxides generated. Accuracies were checked by calculated weight gains from ozone incorporation combined with NMR values of unreacted oleic acid.

Although no run-away reactions or explosions occurred during this study, it is advisable to take the necessary safety precautions when handling any peroxidic compounds.

TABLE 3

Reaction of Oleic Peroxidic Compounds with Nonyl Aldehyde[a]

	Butyric acid media		
^1H NMR	Before aldehyde addition mmole	After aldehyde addition mmole	Change in mmole
δ6.40 & δ6.31	2.27	2.61	+0.34
δ6.19	2.29	0.89	−1.40
δ5.19	2.94	3.80	+0.86
	Pelargonic acid media		
^1H NMR	Before aldehyde addition mmole	After aldehyde addition mmole	Change in mmole
δ6.40 & δ6.31	2.27	2.55	+0.28
δ6.19	1.48	0.53	−0.98
δ5.19	3.15	4.10	+0.95

[a]The number of mmoles of each peroxidic compound was determined by iodometry combined with a normalized area percent of each resonate peak associated with a peroxidic linkage.

TABLE 4

Peroxide Composition of ^1H NMR Shown in Figure 1

Position of resonance	Normalized mole %	Species responsible
δ9.74	19.6	Aldehyde
δ6.40 and δ6.31	26.7	Bis(1-acyloxy-1-Alkyl) peroxide
δ6.19	20.1	1-Acyloxyalkyl-1-hydroperoxide
δ5.12	33.5	1,2,4-Trioxolane/oligomer

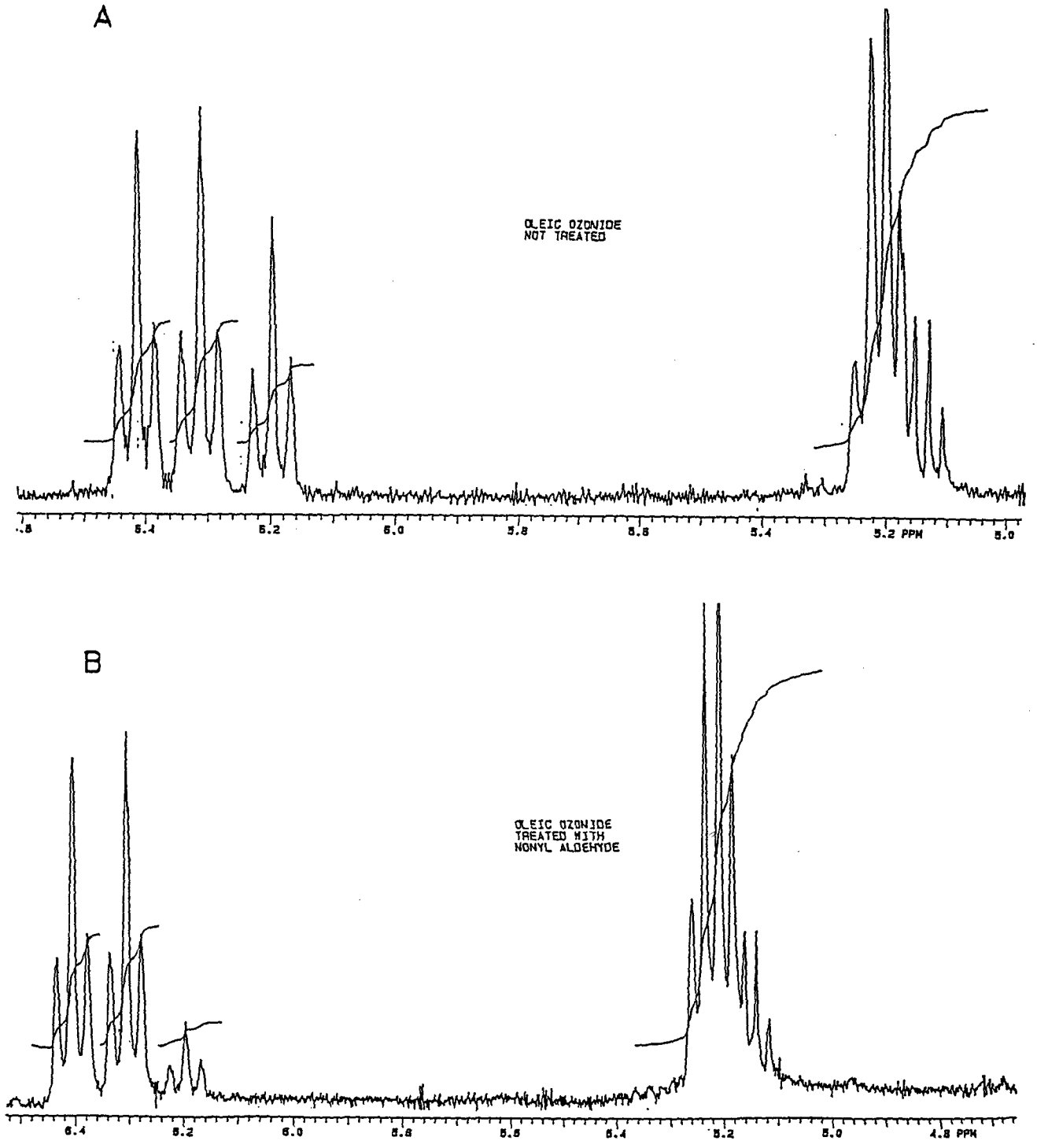


FIG. 4. A, Oleic peroxidic compounds, untreated; B, oleic peroxidic compounds, treated with aldehyde.

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