Studies on the Ozonization of Methyl Oleate[1, 2]

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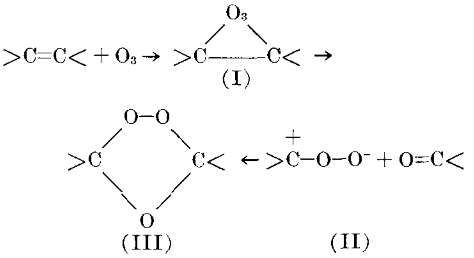
Abstract

The ozonides of methyl 9-octadecenoate, 9-octadecene and methyl 9-octadecendioate (along with pelargonyl aldehyde, methyl azelaaldehydate and a fraction which appears to consist mainly of hydroperoxy-ozonides) were isolated from ozonizations of methyl oleate in pentane and methylene chloride at −65C. The relative amounts of these compounds were determined in ozonizations of methyl oleate in pentane, methylene chloride and ethyl acetate.

Present concepts of the mechanism of the reaction are elaborated on the light of new information on the products of the ozonization of methyl oleate and related compounds under various conditions.

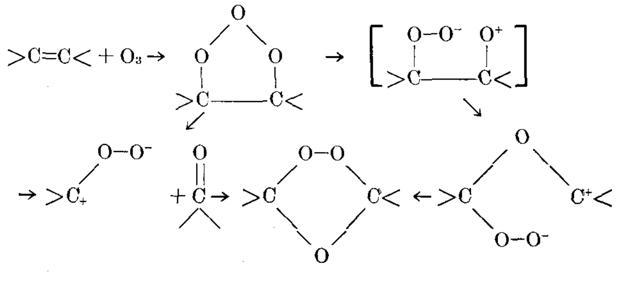
Introduction

THE REACTION of ozone with olefinic linkages is generally believed to occur by the following mechanism (1):

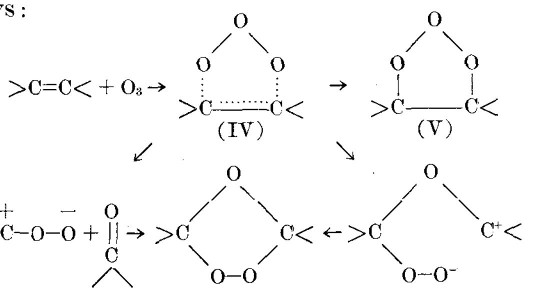


In addition to ozonides (III), other products may be formed via reactions of the intermediate zwitterion (II). According to Criegee (1), all products of the ozonization of olefins can be explained on the basis of reactions in which the zwitterion (II) is an intermediate. Bailey (2) has reviewed the application of this concept to the interpretation of the products of the ozonization of a large variety of compounds.

The formation of ozonides by mechanisms which do not involve a complete breakdown of the molecule have also been postulated (2,3,4). Recently, with good evidence for the formation of the initial I (5), and stereoisomer formation on the ozonization of di-*tert*-butylethylene, Criegee (6) considered the possibility of a second pathway for the formation of ozonides via a mechanism which involves a rapid rearrangement or decomposition of the initial ozonide. The overall mechanism may be represented as follows:



Bailey et al. (7) proposed that ozonide formation may occur via a concerted rearrangement of a quasi 5-membered intermediate ozonide (IV) as well as by the intereaction of zwitterion and aldehyde as follows:



Presumably, the initial ozonide (V) also decomposes into zwitterions and aldehydes which combine into ozonides.

The Criegee mechanism (1,2) involves a complete dissociation of the primary ozonide (I), followed by a recombination of aldehyde with zwitterion (II). Thus asymmetrical olefins should give not one but a mixture of ozonides as a result of a random interreaction of the intermediates. The failure to find such a mixture of ozonides when 3-heptene or a mixture of 4-octene and 3-hexene were ozonized was explained by Criegee (1) on the basis that the reaction occurred in a "solvent cage". Random interreaction of intermediates was believed to be restricted in this manner.

It was also concluded that geometric isomers of ozonides would not be formed (1). However, in a recent study (8), we isolated and identified the geometric isomers of the ozonides of methyl oleate and methyl elaidate and Schröder (9) has demonstrated the formation of *cis* and *trans* ozonides from *cis*-di-*tert*-butylethylene. Another anomaly observed in early work (2) was that the zwitterion reacted with foreign aldehydes only when they were added to ozonization reactions in large excess. Moreover, only highly reactive short-chain aldehydes were observed to undergo such interreactions (2).

In this investigation, the products of the ozonization of methyl oleate and related compounds were studied in order to clarify these and other facets of the mechanism of the reaction.

Experimental

Materials. Highly purified methyl oleate and methyl linoleate were obtained from The Hormel Foundation. Pelargonyl aldehyde (nonanal) was obtained from Matheson, Coleman and Bell and purified by distillation at about 40C under high vacuum. The distillate of nonanal was collected by condensation in a dry ice trap. The final product was chromatographically pure by TLC and GLC.

Methyl azelaaldehydate was prepared from methyl oleate by reductive ozonolysis (10). It was isolated by TLC and purified by recrystallization of its bisulfite derivative, followed by distillation at 40C under high vacuum. The final product was collected as a distillate in a dry ice trap. Its identity and purity were established from its infrared spectrum and GLC analysis.

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[1] Supported in part by Grant no. AM-05018, U.S. Public Health Service, National Institutes of Health.

[2] Presented at the AOCS meeting in Atlanta, 1963.

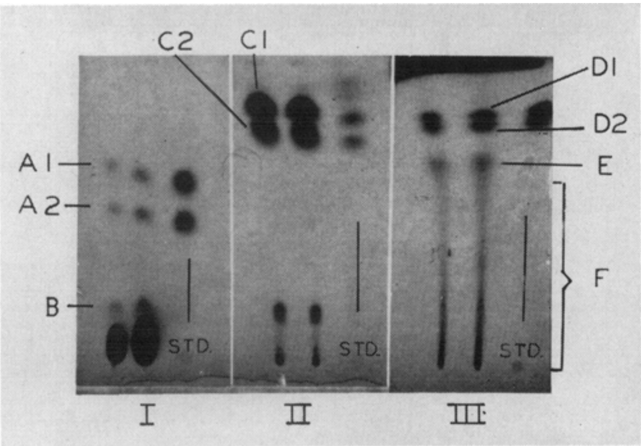


FIG. 1. TLC of products of the ozonization of methyl oleate in pentane and corresponding standard ozonides. Section I, 0.6%; section II, 10%; section III, 25% diethyl ether in petroleum ether. A_1, *trans*-9-octadecene ozonide; A_2, *cis*-9-octadecene ozonide; B, pelargonyl aldehyde; C_1, *trans*-methyl-9-octadecenoate ozonide; C_2, *cis*-methyl-9-octadecenoate ozonide; D_1, *trans*-methyl-9-octadecendioate ozonide; D_2, *cis*-methyl-9-octadecendioate ozonide; E, methyl azelaaldehydate; F, hydroperoxy-ozonide fraction. Three times as much sample was chromatographed in sections I and III as in II.

9-Octadecene was prepared as described by Deatherage et al. (11), except that reduction of the ester was carried out with $LiAlH_4$ (12) and unreacted ester was saponified and separated in the form of its salt. The final product consisted of about 95% 9-octadecene based on its infrared spectrum and analysis by reductive ozonolysis (10).

Methods. Details of the procedure for ozonization and catalytic reduction of ozonides have been previously described (10). Briefly, ozonization was carried out by introducing about 50 mg sample, dissolved in 1 ml solvent, into 20 ml of the same solvent containing 0.0006–0.0008 moles ozone at about −65C. The ozone solution was prepared by bubbling oxygen containing about 3% ozone from a Bonner ozone generator through purified pentane at −65C for about 10 min at 100 ml per min. After a reaction time of about one min, the excess ozone and oxygen were removed by evaporation of a portion of the solvent under vacuum from a water aspirator as the solution warmed up to room temperature.

Catalytic reduction of the ozonides was carried out with the Lindlar catalyst (13) at 0C in methylene chloride. Analysis of the aldehyde fragments was performed by GLC using an F&M Model 609 flame ionization instrument, with temp programming and a 14 x 12 in. column packed with 30% silicone on Chromosorb W as previously described (10).

IR and near-IR spectra were determined with a Perkin Elmer Model 21 and Beckman DK2 spectrophotometers, respectively. The IR spectra were determined with 10% carbon disulfide solutions and the near-IR spectra were determined with 10% carbon tetrachloride solutions.

TLC was performed with glass plates coated with Silica Gel G (according to Stahl) with various concentrations of diethyl ether in petroleum ether (B.P. 35–60C). For qualitative analysis, the spots were detected by spraying the chromatoplates with dichlorofluorescein and viewing them under UV light. Only the outside edges of the plates were sprayed when TLC was used for the isolation of ozonides to avoid contamination of the compounds with the spray reagent. It was necessary to extract the Silica Gel G thoroughly with diethyl ether prior to chromatography to remove organic contaminants.

TABLE I

Analysis of the Products of the Ozonizations of Methyl Oleate

	Designation	Pentane	Methylene chloride	Ethyl acetate
	(Fig. 1)			
Trans-9-octadecene ozonide	A_1	1.0	7.5	2.8
Cis-9-octadecene ozonide	A_2	1.0	5.6	1.9
Pelargonyl aldehyde	B	1.9	5.6	26.6
Methyl *trans*-9-octadecenoate ozonide	C_1	48.4	29.6	10.5
Methyl *cis*-9-octadecenoate ozonide	C_2	42.2	24.3	8.8
Methyl *trans*-9-octadecendioate ozonide	D_1	2.1	11.6	1.3
Methyl *cis*-9-octadecendioate ozonide	D_2			1.1
Methyl azelaaldehyate	E	1.7	5.5	24.6
Hydroperoxy-ozonides and acids	F	1.7	10.3	22.4

Quantitative TLC was carried out by densitometry of the spots obtained by charring. The general application of this technique to the analysis of lipids will be reported separately (14). Briefly, the spots were charred by heating the plates at 180C for 20 min after spraying them with chromicsulfuric acid (15). The density measurements were made with a Photovolt Densitometer (Photovolt Corp., New York) equipped with a special stage for holding chromatoplates. No filter was used and the measurements were made with a slit just longer than the diam of the largest spot. A peak was given by each spot and the areas under the peaks were used to determine the proportions of the components, by reference to a standard curve of each compound and with respect to the amount of total sample spotted on the plate. The amount of the most polar fraction, whose composition was largely undefined, was estimated by difference.

The elemental analyses were performed by the Microanalysis Laboratory, Wilmington, Del.

Results

The products of the ozonization of methyl oleate were separated into 9 components by TLC. Since the products of the reaction had widely different Rf values, they were chromatographed in 0.6,10 and 25% diethyl ether in petroleum ether (B.P. 35–60C). Also, since the concentration of the products varied greatly, the amount of sample chromatographed in each solvent system was varied accordingly. Each TLC analysis was carried out on a single 20 x 20 cm plate, which was divided into three sections by scoring the adsorbent layer with a pencil. The least polar products were developed in the first section with 0.6% diethyl ether in petroleum ether. Then the plate was removed from the chromatographic jar and the adsorbent was scraped off the base of this section to a height above the level of the solvent in the developing chamber. Another sample was spotted in the middle section and it was developed with 10% diethyl ether in petroleum ether. The adsorbent layer was scraped from the base of this section of the plate also and another sample was chromatographed in the last section with 25% diethyl ether. Duplicate samples were spotted along with samples of ozonides, isolated as described below, to serve as references. Figure 1 shows the analysis of the products of the ozonization of methyl oleate in pentane. Similar analyses were carried out on the products of the ozonization of methyl oleate in methylene chloride and in ethyl acetate. The relative amounts of each component formed in these solvents varied greatly, as shown in Table I.

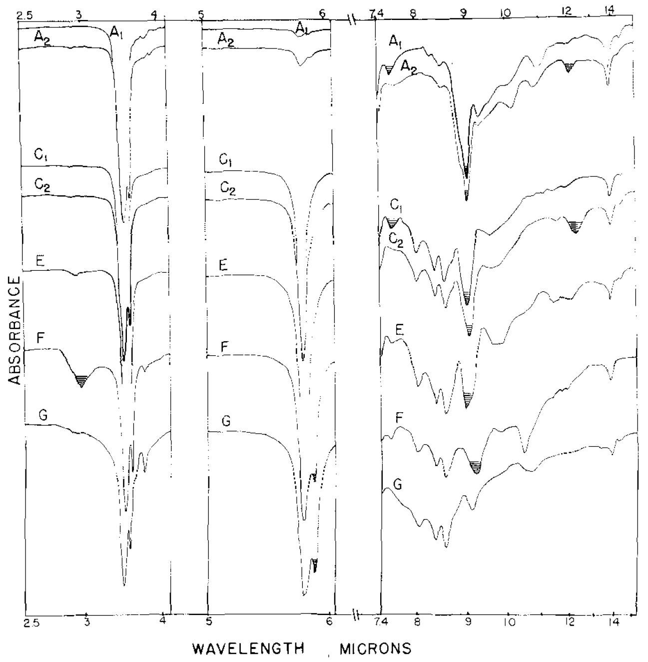


FIG. 2. IR spectra, 10% carbon disulfide products of the ozonization of methyl oleate. A_1 and A_2, *trans* and *cis* isomers of 9-octadecene ozonide, respectively; C_1 and C_2, *trans* and *cis* methyl-9-octadecenoate ozonides, respectively; E, methyl-9-octadecendioate ozonide; F, hydroperoxy-ozonide fraction; G, hydroperoxy-ozonide fraction after catalytic reduction.

Isolation of reaction products. The products of reaction were isolated by TLC from a number of 20 x 20 cm chromatoplates. About 80 mg sample was chromatographed on each plate with the same solvent systems, used above (Fig. 1). After the plates were developed, the positions of the spots were located by spraying the outside edges of the plate with dichlorofluorescein. The separated compounds were then scraped in a band of adsorbent from the middle of the plate only, thus avoiding contamination with spray reagent, and recovered by extraction with a 1:1 (v/v) mixture of diethyl ether and petroleum ether (B.P. 35–60C). Each compound was purified by rechromatographing it several times.

The isolated compounds were identified on the basis of elemental analysis, IR and near-IR spectra and the products of their catalytic reduction. Each ozonide separated into two spots on TLC with the appropriate solvent system, as shown in Figure 1. A previous study (8) showed that the two spots for the ozonides of methyl oleate and elaidate represented *cis* and *trans* isomers. Thus, an extensive analysis of the individual isomers of each ozonide was not carried out in the present study.

9-Octadecene ozonide. The *trans* and *cis* forms of this ozonide are designated as A_1 and A_2, respectively, in Figure 1 and Table I. This compound was isolated from the ozonization of methyl oleate in methylene chloride and from 9-octadecene in pentane. Calculated for $C_{18}H_{36}O_3$; C,72.0; H,12.0; 0,16.0; found: C,72.01; H,11.84; 0,16.09 (direct) for the former and, C,72.24; H,11.98; 0,15.96 (direct) for the latter. The IR spectra of the *trans* and *cis* isomers of this ozonide are presented in Figure 2. The *trans* form has a band at 7.6 μ, which is absent in the spectrum of the *cis* form, and the *cis* form has a band at 12.2 μ, which is absent in that of the *trans* form. Otherwise, the two spectra are identical. The peak of the ozonide band is at 9.0 μ. Catalytic reduction of this ozonide gave only pelargonyl aldehyde.

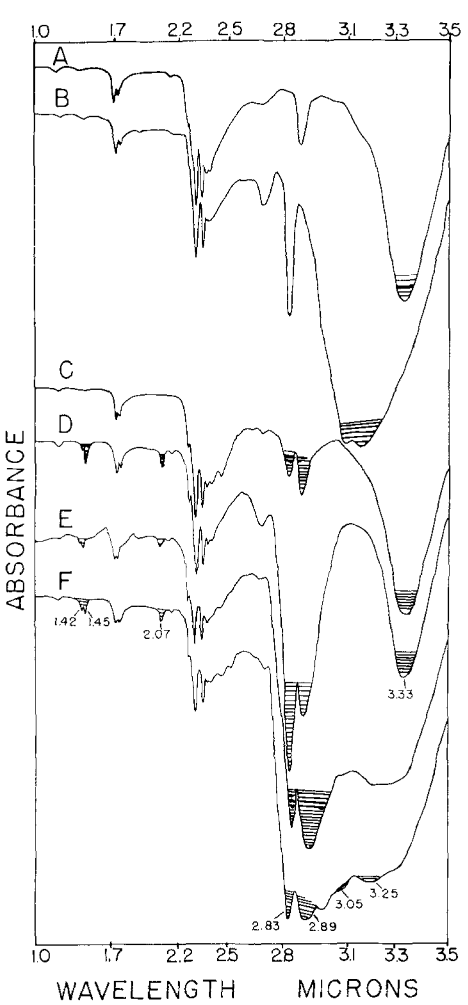


FIG. 3. Near-IR spectra in 10% carbon tetrachloride. A, methyl oleate; B, oleic acid; C, methyl-9-octadecenoate ozonide; D, methyl oleate hydroperoxide; E, hydroperoxy-ozonides of methyl oleate; F, products of the ozonization of methyl oleate in ethyl acetate.

Methyl 9-octadecenoate ozonide (C_1 and C_2, Fig. 1 and Table I.) The *trans* (C_1) and *cis* (C_2) forms of this compound were isolated previously, from the products of the ozonization of methyl oleate and of methyl elaidate in pentane (8). The same compounds were isolated from the ozonization of methyl oleate in methylene chloride in this study. The IR spectra of the *trans* and *cis* isomers of this compound are also presented in Figure 2. The peaks of the bands peculiar to the *cis* and *trans* forms and the ozonide groups are shaded to facilitate their identification. Catalytic reduction of this ozonide gave methyl azelaaldehydate and pelargonyl aldehyde. Calculated for $C_{19}H_{36}O_5$: C,66.4; H,10.5; 0,23.2; found: C, 66.36; H,10.45; 0,23.15 (direct).

Methyl 9-octadecendioate ozonide (D_1 and D_2, Figure 1 and Table I). This compound was also present in the form of *trans* (D_1) and *cis* (D_2) isomers, as evidenced by the two spots it gave on TLC (Fig. 1). The individual isomers were not analyzed separately. The infrared spectrum of this compound is also presented in Figure 2 (Spectrum E). Catalytic reduction of this compound gave only methyl azelaaldehydate. Calculated for $C_{20}H_{36}O_7$: C,61.8; H,9.3; 0,28.9; found: C,61.82; H,9.25; 0,28.93 (difference).

Pelargonyl aldehyde (B, Figure 1 and Table I) and methyl azelaaldehydate (E, Figure 1 and Table

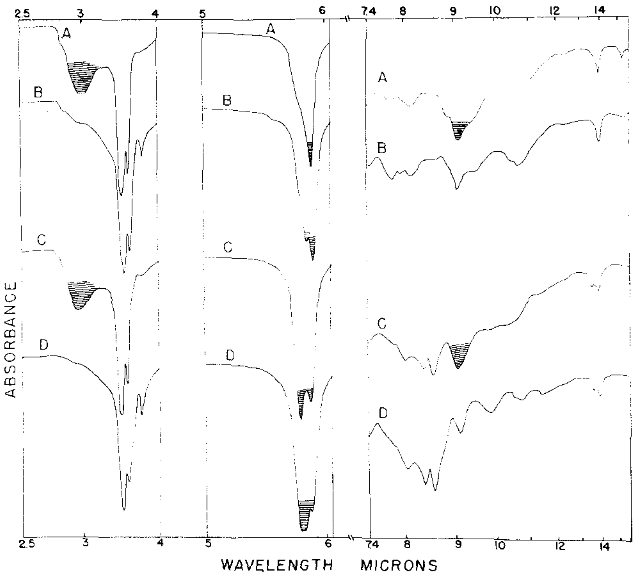


FIG. 4. IR spectra (10% carbon disulfide). A, Products of the ozonization of 9-octadecene in ethyl acetate; B, Products of the catalytic reduction of A; C, Products of the ozonization of methyl oleate in ethyl acetate; D, Products of the catalytic reduction of C.

I). These compounds were identified by comparison of their GLC and TLC properties with those of reference compounds.

Fraction F (Figure 1 and Table I). This fraction consists of a mixture of compounds, some of which are unstable, as evidenced by the streaking of the sample on the chromatoplate. It was isolated from the products of the reaction of methyl oleate in methylene chloride by recovering everything with an Rf value below that of methyl azelaaldehydate in samples chromatographed with 25% diethyl ether in petroleum ether. The IR spectra of the crude fraction (recovered from a single chromatography), before and after catalytic reduction, are shown in Figure 2, curves F and G, respectively. The near-IR spectrum of this fraction (Fig. 3,E) shows that the O-H stretching absorption is due to hydroperoxide groups since the band at 1.46 μ in the near-IR is specific for these compounds (16). The near-IR spectrum also shows that this fraction contains appreciable amounts of free acid, by comparison with the spectrum of oleic acid (Fig. 3,B).

Since ozonizations in ethyl acetate gave over 20% Fraction F (Table I). The IR spectra of the products of the ozonization of methyl oleate and 9-octadecene in this solvent (Fig. 4) are similar to that of Fraction F (Fig. 2). The near-IR spectrum of the product of the ozonization of methyl oleate in ethyl acetate (Fig. 3,F) also shows that the hydroxyl groups in these compounds existed chiefly in the form of hydroperoxides.

Catalytic reduction of the products of the ozonization of methyl oleate and 9-octadecene in ethyl acetate, as well as Fraction F, gave acids, as well as aldehydes, and eliminated the hydroperoxides as shown by the IR spectra (Figures 2,G and 4).

The fatty acids obtained on the reduction of the products of the ozonization of methyl oleate in ethyl acetate consisted mainly of pelargonic acid and the monomethyl ester of azelaic acid. Small, but appreciable, amounts of other acids were also detected. The detection of these fatty acids among the products of the reaction was carried out by GLC of the methyl esters prepared by esterification of the acids

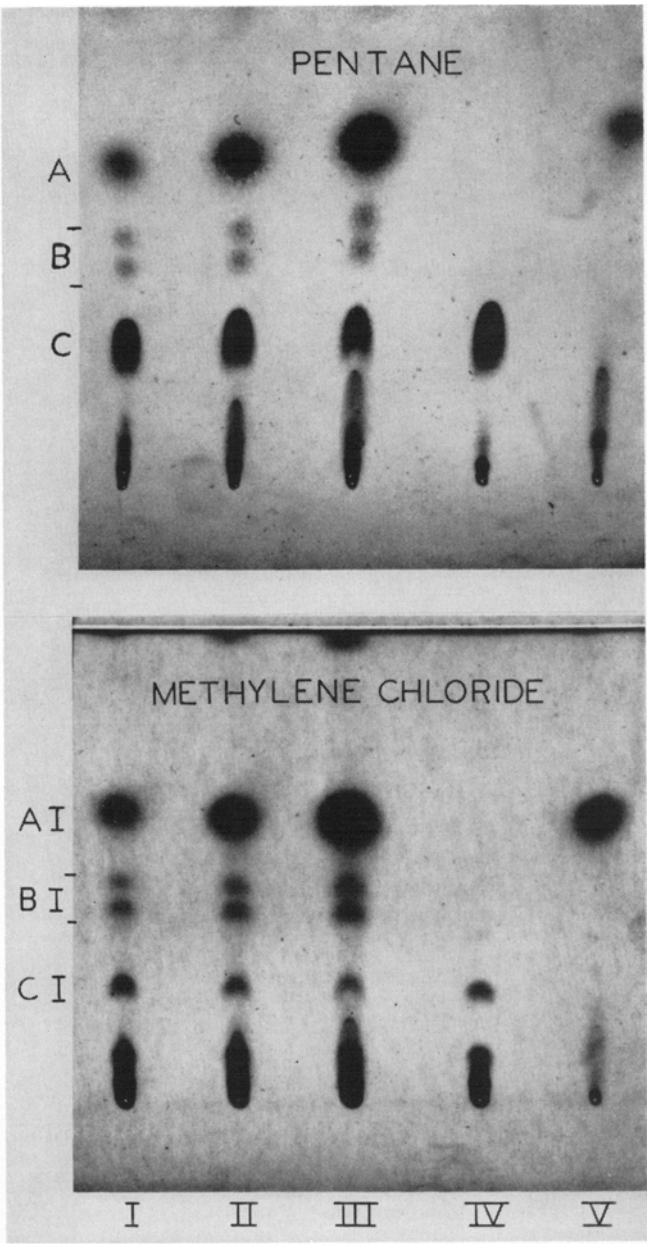
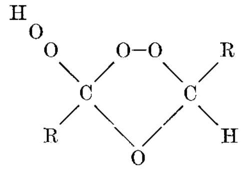


FIG. 5. Chromatoplates of the TLC analyses of the products of the ozonization of mixtures of methyl linoleate and pelargonyl aldehyde in pentane and methylene chloride. I,II and III, 1:1,1:2 and 1:4 mixtures of methyl linoleate to pelargonyl aldehyde; IV, methyl linoleate; V, pelargonyl aldehyde. Solvent system = 10% ethyl ether in petroleum ether. A and AI = pelargonyl aldehyde; B and BI = methyl oleate ozonide; C and CI = methyl linoleate ozonide.

with diazomethane after removal of the aldehydes in the form of their bisulfite adducts.

The above data indicate that Fraction F (Fig. 1, Table I) consists largely of hydroperoxy-ozonides. Since the reduction of this fraction gave acids and aldehydes instead of hydroxyl groups, the major compounds of this fraction were assigned the following structure:



Further evidence that the hydroperoxide group is affixed to the same carbon as the ozonide group is

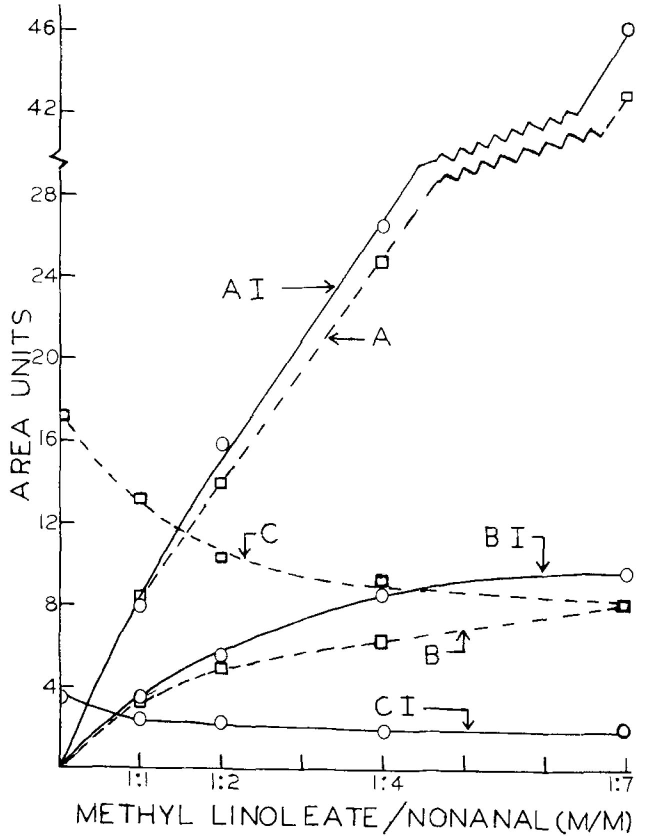
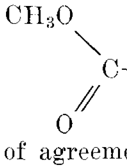


FIG. 6. The relationship between the incorporation of pelargonyl aldehyde into ozonides by the formation of methyl oleate ozonide, the formation of methyl linoleate ozonide, and the consumption of pelargonyl aldehyde on the ozonization of mixtures of methyl linoleate and pelargonyl aldehyde. A and AI, pelargonyl aldehyde in pentane and methylene chloride, respectively; B and BI, methyl oleate ozonide in pentane and methylene chloride, respectively; C and CI, methyl linoleate ozonide in pentane and methylene chloride, respectively.

provided by its instability since normal hydroperoxides can be chromatographed without decomposition (16). The band in the IR spectrum at 9.0 μ also indicates that these compounds contain an ozonide group.

The CHO analysis of the isolated fraction F was; C,60.6; H,8.75; 0,30.44. The theoretical values for a random mixture of hydroperoxy-ozonides, where R in the above structure is either $CH_3-(CH_2)_7-$ or



$CH_3O-C(=O)-(CH_2)_7-$, is: C,60.9; H,9.7; 0,29.4. Lack of agreement with the theoretical values is probably due to the presence of acids in this fraction formed as a result of decomposition of these and other compounds perhaps peracids and alkylidene peroxides which also may be formed.

Ozonization of mixtures of methyl linoleate and pelargonyl aldehyde. In order to clarify the role of aldehydes and obtain more information on the mechanism of the reaction, the extent of the incorporation of pelargonyl aldehyde into ozonides was determined on the ozonization of mixtures of it with methyl linoleate in pentane and methylene chloride. This pair of compounds was selected because interreaction or incorporation of the pelargonyl aldehyde into ozonides was readily detected by the formation of methyl oleate ozonide among the reaction products as illustrated in Figure 5.

The relative amounts of methyl oleate ozonide and methyl linoleate ozonide were determined in the ozonization of four mixtures of methyl linoleate and pelargonyl aldehyde (1:1, 1:2, 1:4, 1:7, mol/mol) by densitometry of the charred spots. The results (Fig. 6) showed that the amount of methyl oleate and linoleate ozonides formed became nearly independent of the amount of pelargonyl aldehyde in the mixture. Moreover, this relationship was the same in both pentane and methylene chloride, despite the formation of about five times as much methyl linoleate ozonide in pentane as in methylene chloride. As might be expected, a greater amount of methyl oleate ozonide was produced in methylene chloride than in pentane in the mixtures containing the higher ratios of pelargonyl aldehyde.

The ozonizations of mixtures of methyl linoleate with 9-octadecene also gave methyl oleate ozonide (in addition to other products) and demonstrated that interreaction of intermediates also occurred during the ozonizations of mixtures of olefins, as well as between intermediate fragments of the same olefin.

Discussion

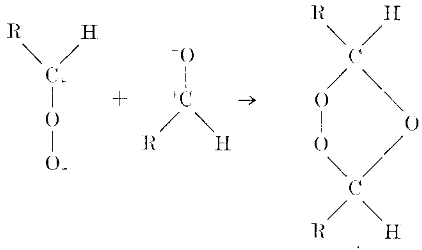
In contrast to early studies on the products of the ozonization of olefins, reviewed by Bailey (2), this investigation demonstrates that the interreaction of intermediates takes place during the formation of ozonides in accordance with the Criegee mechanism (6). Furthermore, the interreaction of "foreign aldehydes" with zwitterions is not limited to highly reactive short-chain aldehydes. However, unless the aldehydes added as "foreign aldehydes" to a reaction are highly purified, this interreaction does not appear to take place presumably because the impurities in such aldehyde preparations are highly reactive and compete more successfully for the zwitterion.

The present studies demonstrate well Criegee's mechanism by virtue of the isolation of ozonides of mixtures of intermediates and by the incorporation of pelargonyl aldehyde into ozonides of methyl oleate (Fig. 6).

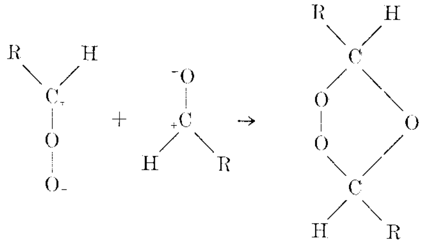
That another pathway for the formation of ozonides may exist is indicated by the pronounced influence of solvent polarity on the reaction and the influence of pelargonyl aldehyde on the products of the ozonization of methyl linoleate.

The influence of polarity may be solely that of the stabilization of the zwitterions which permits their interreactions in other ways in addition to the formation of ozonides of the parent molecule. On the other hand, since there is evidence that the reaction involves the formation of a primary ozonide or possibly a related quasi 5-membered ring intermediate, as proposed by Bailey et al. (7), it is also possible that the role of the solvent involves the degree of dissociation of these compounds. Both of these effects are related to the polarity of the solvent and thus are hard to distinguish. However, the experiments on the ozonization of the mixtures of pelargonyl aldehyde and methyl linoleate indicate that its incorporation into ozonides is related to the extent of the "availability" of the zwitterions. The availability of the zwitterions could be related to the degree of dissociation of the primary ozonide as well as to its stability since the proportion of linoleate ozonide formed on the ozonization of mixtures of pelargonyl aldehyde and methyl linoleate was not further decreased on increasing the concentration of the pelargonyl aldehyde beyond ca. a 3-M excess. Otherwise, the linoleate ozonide, especially the small amount detected in methylene chloride, should not have been formed had the availability been due solely to a stabilization of the completely dissociated zwitterion by the solvent. Furthermore, it may be noted that the interreactions between intermediates goes well beyond that expected of a random interreaction of aldehydes and zwitterions with a preponderance of hydroperoxy-ozonides and like compounds being formed as the polarity of the solvent in increased. Therefore, it seems entirely possible that there is a second pathway for the formation of ozonides, which does not involve a complete breakdown of the molecule. Presumably the extent of each reaction is related to the degree of dissociation of the primary ozonide as effected by the solvent.

The formation of *cis* and *trans* ozonides is not incompatible with either mechanism. In accordance with the Criegee mechanism, their formation may be visualized as a dipole-dipole interreaction simultaneously with a nucleophylic attack on the aldehyde as follows:



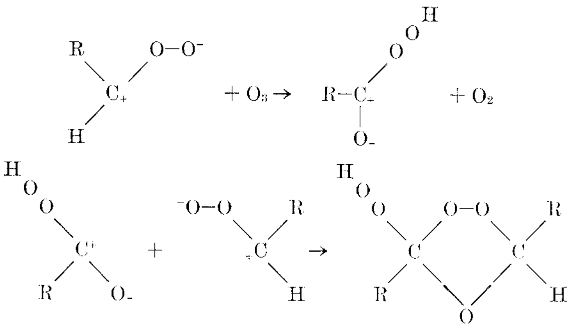
cis



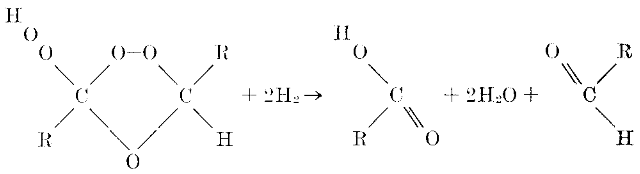
trans

The formation of *cis* and *trans* isomers depends on the orientation of the molecules at the time of their reaction. Roughly, equal amounts of each isomer should be formed from methyl oleate by such a mechanism and this is in accord with the experimental findings.

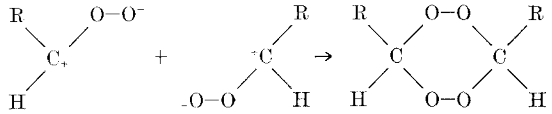
Hydroperoxy-ozonides may be formed by the following mechanism:



This reaction is based on the observation that ozone does not attack pre-formed ozonides on subjecting them to ozone under the conditions which they are formed; that is, ozonization in a dilute solution of methylene chloride at −65C. The formation of acids and aldehydes on catalytic reduction may be visualized as follows:



Peracids have essentially the same properties as those determined on the proposed hydroperoxy ozonides. They should exhibit a hydroperoxy band in the near-IR and IR regions of the spectrum and give acids on catalytic reduction. IR absorption indicates the presence of carboxyl groups in the polar fraction, and peracids may well be present in this fraction. However, the acid structure appears to arise from decomposition reactions and since the compounds in the polar fraction also contain ozonide groups which alone do not explain their high polarity, they are believed to be in the same molecule. Moreover, pelargonic acid which should be formed by decomposition of peracids cannot be readily detected on the chromatoplates by the charring technique because unlike aldehydes being fairly stable they evaporate before they are oxidized. Aldehydes are oxidized to acids by ozone under certain conditions but little oxidation of pelargonyl aldehyde occurred during ozonization in these experiments as evidenced by TLC analysis of this compound after treatment with ozone (Fig. 5). Acids may be formed by the decomposition of hydroperoxy-ozonides. They may also be formed from the decomposition of alkylidene peroxides. In fact, the inability to find alkylidene peroxides among the products of the reaction may be explained on this basis because if dissimilar zwitterions recombine, the same zwitterion may be expected to react with itself as follows:



Diacetone is a fairly stable compound (3). However, the stability of alkylidene peroxides depends on their substituent group (3,17,18). One of the substituents in the alkylidene peroxide peroxide of methyl oleate being a hydrogen atom may make it relatively unstable. On the other hand, the possibility must be considered that the alkylidene peroxides went undetected since all of the products of the reaction were not identified.

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