Hydrolytic, Reductive and Pyrolytic Decomposition of Selected Ozonolysis Products. Water as an Ozonization Medium[1]

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Abstract

Hydrolytic, reductive and pyrolytic decompositions of ozonolysis products formed in water were surveyed as potential preparative routes to aldehydes. Water is an effective ozonolysis medium and reacts with the transient zwitterion formed during ozonolysis in the same manner as participating solvents. Reductive decomposition proved to be superior to either hydrolytic or pyrolytic decomposition for the preparation of aldehydes. Pyrolytic decomposition, as carried out in the injection port of a gas chromatograph, gave varying amounts and types of products depending upon the type of ozonolysis product used. Interconversion of the various types of ozonolysis products, including ozonides, methoxy hydroperoxides, acetoxy hydroperoxides and hydroxy hydroperoxides, does not occur except under acid catalysis.

Introduction

OZONOLYSIS OF AN UNSATURATED fatty ester in a participating organic solvent and subsequent reductive decomposition have lead to the desired carbonyl compounds in high yields (17). If ozonolysis in such a solvent were scaled up to large batch quantities, certain problems in solvent removal and recovery would arise that suggest a better solvent system is needed. Because water handles more easily and costs less than organic solvents, it would be the preferred solvent. Several reports in the literature describe ozonolysis of selected unsaturated materials in water to yield acids or aldehydes, or both (4,6,10,15,16,18,20,27). Reported yields of acids varied from 8–100% and of aldehydes from 47–100%. The literature also reports the thermal hydrolytic decomposition of ozonolysis products from solvents other than water (5,7,12,19,26,28,29). Attempts were made to apply these procedures to unsaturated fatty esters. Because aldehyde yields were poor in original phases of the work, the structure and reaction of selected ozonolysis products of 1-decene were also investigated.

Experimental Procedures

Methyl oleate from Applied Science Laboratories contained 91% of its double bond in the C_9–C_{10} position as determined by oxidative cleavage (14). The methyl oleate also contained 15–16% *trans,* calculated as methyl elaidate, as determined by infrared. After distillation, butyl oleate from Swift & Co. contained 0.357 double bond equivalents per 100 g. 1-Decene came from Humphrey Chemical Company (100% C_{10} monoene) and 2,4,4-trimethyl-2-pentene (~95%), from Phillips Petroleum Company. Methyl linoleate was isolated from soybean methyl esters by liquid-liquid centrifugal extraction (2,3). All reagents were used without further purification.

GLC analyses were carried out on a Model 500 F & M gas chromatograph with a thermal conductivity detector (17) and an F & M Model 810 with a hydrogen flame detector. In the wet analysis for carbonyl, hydroxylamine hydrochloride (22) served as the reagent.

IR data were obtained on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Differential thermal analyses were carried out on a DuPont Model 900 analyzer and thermogravimetric analyses on a DuPont 950 analyzer.

Each ozonolysis was on a 10–20 mmole scale in a suitable size reaction flask with oxygen containing 2–3% ozone generated by a Welsbach Model T23 ozonator. The end point of the reaction was determined by monitoring the exit gases with a Welsbach Model C ozone meter. At the completion of ozonolysis oxygen and ozone were flushed out with nitrogen.

Hydrolytic Decomposition

Methyl Oleate in Water. A dispersion of methyl oleate (5.0 g, 0.017 mole) in water (distilled, unbuffered, pH 6.7, 25.0 g) was ozonized at 20 C (run 2, Table I). Upon completion of ozonolysis, the mixture was transferred to a distilling flask with 100 ml of water and a small amount of methanol. Water and methanol were removed slowly by distillation until 100 ml of distillate had been collected. The residue was adjusted to the methyl orange end point with concentrated HCl, and organic material was extracted with dichloromethane. After the solution

TABLE I
Hydrolytic Decomposition[a] of Compounds Ozonized in Water

Run	Substance ozonized	pH of water used	Hours at 100 C	Carbonyl yield, %			Acid yield, %	Total recovery, %
				$H_2NOH \cdot HCl$				
				Uncorrected[b]	Corrected	GLC		
1	Methyl oleate	6.7	2	69	44	....	20	64
2	Methyl oleate	6.7	2	66	54	....	28	82
3	Methyl oleate	6.7	11	63	37	....	29	66
4	Methyl oleate	1.0	11	13	11	....	74	85
5	Methyl oleate	9.0	11	38	30	....	78	78
6	Methyl linoleate	7.0	4	....	....	45	....	....
7	Methyl linoleate	7.0	....	....	....	43[c]	....	....
8	1-Decene	7.0	4	....	....	39	....	....

[a] Decomposition carried out under nitrogen atmosphere.
[b] Uncorrected for peroxide.
[c] Methanol added after ozonization and removed by distillation.

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[1] Presented in part at the AOCS Meeting, Philadelphia, October, 1966.

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TABLE II

Effect of *t*-Butanol as an Auxiliary Solvent in the Hydrolytic Decomposition of Ozonolysis Products

Run	Substance ozonized	pH of buffered water	Mole ratio, *t*-BuOH:H_2O	Carbonyl yield, %		Acid yield, %	Total recovery, %
				$H_2NOH \cdot HCl$[a]	GLC		
9	Butyl oleate	10.8	1.85:1	25	....	47	72
10	Butyl oleate	7.8	1.85:1	52	....	18	70
11	Butyl oleate	7.0	1.85:1	77	....	Trace	77
12	Butyl oleate	6.6	1.85:1	77	....	Trace	77
13	Butyl oleate	4.1	1.85:1	90	....	Trace	91
14	Methyl linoleate	11.0	0.25:1	....	21	....	....
15	Methyl linoleate	7.0	1.80:1	....	23	....	....

[a] Not corrected for peroxide.

was dried over Drierite, solvent was removed on a rotary evaporator under reduced pressure. Apparent carbonyl yield was 54% (hydroxylamine hydrochloride method); total recovery of product was 82% of theory based on starting material.

Similar runs repeated at other pH levels with phosphate buffers, as suggested by Brown and Sparks (6), are summarized in Table I.

Butyl Oleate in t-Butanol/Water. Butyl oleate (5.00 g, 0.0178 mole $>C=C<$) suspended in water (5.00 g) and *t*-butanol (37.0 g) was ozonized (run 13, Table II) in accordance with the procedure of Sturrock et al. (27).

After ozonolysis the reaction mixture was transferred to a distilling flask by means of phosphate buffered water (pH 4.1). *t*-Butanol was removed to a vapor temperature of 96 C; the residue was acidified to the methyl orange end point and then extracted with dichloromethane. After solvent was removed, the product gave a positive test for peroxide. Based upon a carbonyl yield of 90%, as determined by the hydroxylamine hydrochloride method (see Discussion), the apparent recovery of double bond cleavage products was 91%.

Similar runs were carried out at various other pHs and are summarized in Table II.

Catalytic Reduction

Methyl Oleate in Water. A dispersion of methyl oleate (5.03 g, 0.017 mole) in water (distilled, unbuffered, 5.00 g) (run 17, Table III) was ozonized at 45–50 C. Reduction was effected at 45 C by adding 0.12 g 10% Pd/C catalyst and by bubbling hydrogen through the ozonized mixture. A negative peroxide test using potassium iodide and glacial acetic acid was indicated when reduction was complete. After extraction of organic material with dichloromethane, the solution was dried over Drierite and then filtered to remove catalyst and drying agent; the solvent was evaporated on a rotary evaporator under reduced pressure to give carbonyl in a 53% yield.

Table III summarizes the catalytic reduction of ozonolysis products from solvent systems having water as one component.

Chemical Reduction

Methyl Oleate in Water. Methyl oleate (5.02 g, 0.017 mole) was ozonized in a water (distilled, unbuffered, 5.0 g) suspension at 45 C (run 26, Table IV). Upon completion of ozonolysis, zinc dust (5.0 g) and glacial acetic acid (5.0 g) were added in small increments with stirring and cooling so that zinc was always in excess and the reaction temperature was always below 45 C. When the peroxide test was negative, organic material was extracted with dichloromethane, and each extract was washed to remove acetic acid. The carbonyl yield by wet analysis was 79%. Results for chemical reduction appear in Table IV.

Ozonolysis of 2,4,4-Trimethyl-2-Pentene

The ozonolysis of 2,4,4-trimethyl-2-pentene (4.25 g) was carried out in purified pentane-hexane/water (35 ml/45 ml) at 35 C. The reaction mixture detonated near the end of the ozonolysis and completely destroyed the reactor. At the time of the explosion, approximately one third of the pentane-hexane was left in the reactor; the rest was volatilized and condensed in traps. Purified pentane-hexane had been used previously as a solvent without any problems. The explosion was apparently due to unstable ozonolysis products.

Ozonization-Pyrolysis

Samples of 1-decene (0.2–0.5 g) were ozonized at 5–10 C in acetic acid or in water at 25–30 C in a small reaction flask with a conical well into which the ozone inlet was placed. When ozonolysis was complete, the ozonolysis products were freed of solvent, and the internal standard, dimethyl azelate, was added. The mixture was injected directly into the hot injection port (250 C) of the chromatograph. Products were resolved (Fig. 1) on a 48 × ¼ in. aluminum column packed with 0.2% SF-96 methyl silicone fluid on 70–80 mesh glass beads, and a hydrogen flame detector was used to monitor the effluent. The column oven was programmed from 70–200 C at 10 C/min. Results of the modified

TABLE III

Catalytic Hydrogenation of Methyl Oleate Ozonolysis Products Obtained in Water With an Auxiliary Solvent

Run	Auxiliary solvent	Mole ratio, auxiliary solvent:water		Carbonyl yield,[b] %	Acid yield, %	Total recovery, %
		Ozonolysis	Hydrogenation[a]			
16	None	....	....	51	27	78
17	None	....	....	53	23	76
18	Methanol	....	0.2:1	60	39	99
19	Acetic acid	0.30:1	No change	57	....	....
20	Acetic acid	1.00:1	No change	58	....	....
21	1-Butanol	0.34:1	No change	70	....	....
22	1-Butanol:acetic acid		0.15:0.15:1.0	68	....	....
23	1-Butanol:acetic acid	0.34:1.34:1	No change	80	....	....
24	1-Butanol:acetic acid	0.34:0.34:1	No change	83	....	....

[a] Catalytic hydrogenation at 45 C with 10% Pd/C to a negative peroxide test.

[b] By the $H_2NOH \cdot HCl$ method.

TABLE IV
Decomposition of Ozonolysis Products Obtained in Water by Chemical Reduction and by Extraction Methods

Run	Substance ozonized	Method of decomposition	Auxiliary solvent	Carbonyl yield, %		Acid yield, %	Total recovery, %
				$H_2NOH{\cdot}HCl$[a]	GLC		
25	Methyl oleate	Zn + HOAc, 100 C	None	79	....	7	86
26	Methyl oleate	Zn + HOAc, 45 C	None	79	....	16	95
27	Methyl oleate	Zn + HOAc, 45 C	HOAc (1:1)	78	....	16	94
28	Methyl linoleate	Extraction	None	....	51	....	....
29	1-Decene	Extraction	None	....	49	....	....
30	1-Decene	Extraction	Pentane-hexane (1:1)	....	50	....	....

[a] Peroxides absent.

ozonolysis-pyrolysis (9) studies are summarized in Table V.

Interconversion of Ozonolysis Products

The product formed by ozonolysis of 1-decene in water was mixed with methanol containing 0.3 meq/ml of HCl. Samples were withdrawn from reaction mixture at various time intervals and dissolved in methylene chloride. HCl was neutralized with saturated sodium bicarbonate solution and the organic layer was separated, dried and evaporated on a rotary evaporator. Residues were then subjected to pyrolysis. The resulting products were aldehyde, dimethyl acetal, methyl ester and hydrocarbon (Fig. 2).

Thermal Analysis

Differential thermal analysis (DTA) was run on milligram samples in an inert nitrogen atmosphere with a programming rate of 10 C/min. Thermogravimetric analysis (TGA) was run on samples of 5–10 mg under a nitrogen atmosphere (40 cc/min) at a programming rate of 10 C/min. Data from thermal analyses appear in Table VI, and representative curves appear in Figure 3.

Results

Hydrolytic Decomposition

Two hydrolytic methods reported in the literature were investigated. In one, aldehyde yields as high as 96% from 1-octadecene ozonolysis products were described (6). Hydrolysis was carried out with buffered water at 100 C on the ozonolysis products obtained in pentane-water mixtures. Application of this method to methyl oleate, methyl linoleate and 1-decene resulted in only 30–50% yields of aldehyde (Table I). pH of the buffered water had a significant effect: on either side of neutrality, much higher amounts of acid were formed than at a pH of about 7. It seems probable that the report for 1-octadecene was in error because of undecomposed peroxides, which, like aldehyde, would consume hydroxylamine during wet analysis of the product. We find that reflux at 100 C in neutral water results in incomplete decomposition of ozonolysis products; further, that hydrogen peroxide reacts in 1:1 stoichiometry with hydroxylamine. Complete decomposition of the ozonolysis products under more stringent conditions would result in some additional aldehyde, but mostly acid (23).

In the second method, diphenaldehyde was reportedly prepared in high yield by ozonolysis of phenanthrene in a mixture of *t*-butyl alcohol and water (28). Upon application of this method to the ozonolysis of oleates and linoleates, we again found decomposition of the ozonolysis products to be incomplete. Apparent carbonyl yield by wet analysis was high, but actual aldehyde yield was low (Table II). It is probable that the ozonolysis medium consisting of *t*-butyl alcohol and water is uniquely applicable to cyclic systems such as phenanthrene and not generally applicable to acyclic, aliphatic olefins.

Extraction of hydrogen peroxide from various ozonolysis products has been reported (4,26). Our attempts to extract hydrogen peroxide were unsuccessful. Repeated extraction of methyl and butyl

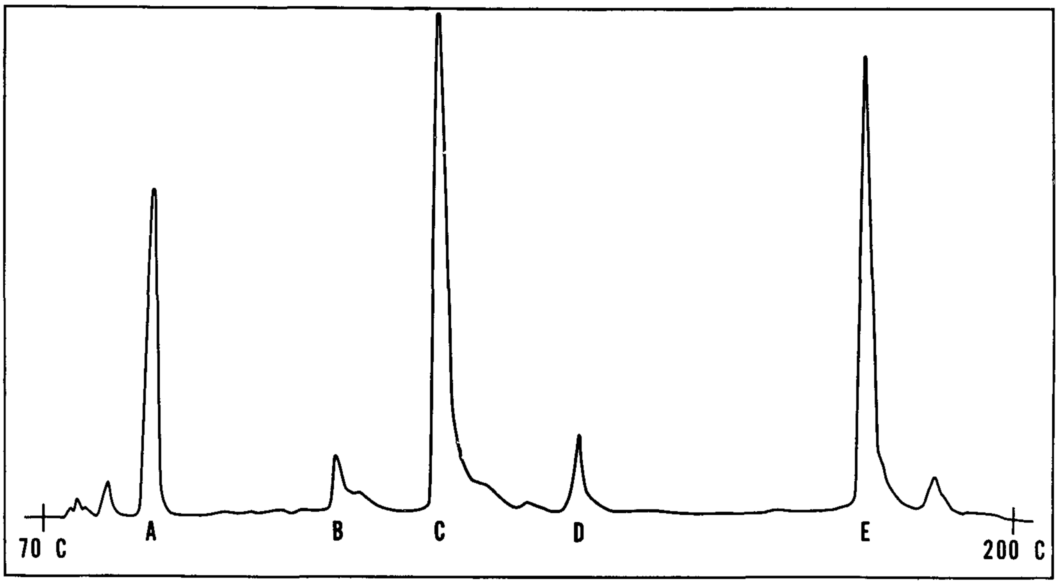


FIG. 1. Typical GLC analysis from ozonization-pyrolysis. Peak A, octane; B, 1-decene; C, nonanal; D, methyl nonanoate; E, dimethyl azelate.

TABLE V

Pyrolytic Decomposition of 1-Decene Ozonolysis Products in a Chromatographic Injection Port (Temperature = 250 C)

Run	Ozonization solvent	Subsequent treatment		Injection conditions	Product					
		Reactant	*Conditions*		Pelargonaldehyde		Octane		Methyl pelargonate	
					Wt, g	Yield, %	Wt, g	Yield, %	Wt, g	Yield, %
31	None	Carbon tetrachloride	Held for ½ hr	Carbon tetrachloride solution	0.0513	48	0.0043	5	0	0
32	None	None	....	Undiluted	0.0633	58	0.0220	25	0	0
33	None	Carbon tetrachloride	Injected immediately	Carbon tetrachloride solution	0.0573	53	0.0054	6	0	0
34	None	Carbon tetrachloride	Removed from run 33 after several hr	Undiluted	0.0618	57	0.0149	17	0	0
35	None	Carbon tetrachloride	Held for 24 hr	Carbon tetrachloride solution	0.0518	48	0.0041	5	0	0
36	None	Methylene chloride	Held for ½ hr	Methylene chloride solution	0.0528	49	0.0024	3	0	0
37	None	Chloroform	Held for ½ hr	Chloroform solution	0.0563	52	0.0060	8	0	0
38	None	Pentane	Held for ½ hr	Pentane solution	0.0437	41	0.0051	6	0	0
39	None	Methanol	Methanol removed after 1 hr	Undiluted	0.0636	...	0.0108	....	0	0
40	None	Water	Water removed after 1 hr	Undiluted	0.0695	....	0.0129	....	0	0
41	None	Acetic acid	Held for 1 hr	Acetic acid solution	0.0606	....	0.0054	....	0	0
42	Methanol	None		Undiluted	0.0286	14	0.0133	26	0.0306	12
43	Methanol	Carbon tetrachloride	Held for ½ hr	Carbon tetrachloride solution	0.0263	13	0.0081	16	0.0650	26
44	Methanol	Water	Removed after 1 hr	Undiluted	0.0264	13	0.0194	38	0.0324	13
45	Methanol	Acetic acid	Removed after 1 hr	Undiluted	0.0378	19	0.0103	20	0.0332	13
46	Water	None		Undiluted (1-decene still present)	0.1735	46	0.0756	4	0	0
47	Water	Carbon tetrachloride	Held for ½ hr	Carbon tetrachloride solution	0.2050	54	0.0593	4	0	0
48	Water	Methanol	Removed after 1 hr	Carbon tetrachloride solution	0.1820	48	0.0567	3	0	0
49	Water	Acetic acid	Removed	Carbon tetrachloride solution	0.2290	60	0.0503	3	0	0
50	Acetic acid	None		Undiluted	0.3625	41	0.0914	15	0	0
51	Acetic acid	Carbon tetrachloride	Held for ½ hr	Carbon tetrachloride solution	0.2405	28	0.0118	2	0	0
52	Acetic acid	Water	Removed after 1 hr	Undiluted	0.2750	31	0.0768	12	0	0
53	Acetic acid	Methanol	Removed after 1 hr	Undiluted	0.2690	30	0.0675	11	0	0

oleate, methyl linoleate and 1-decene ozonolysis products with distilled water resulted in only traces of peroxide in the extract.

Reductive Decomposition

Reductive decomposition of ozonolysis products was explored for the purpose of comparison with the hydrolytic method. Catalytic hydrogenation (Table III) and chemical reduction with zinc and acetic acid (Table IV) were carried out on methyl oleate ozonolysis products obtained either in water alone or in water with an auxiliary solvent.

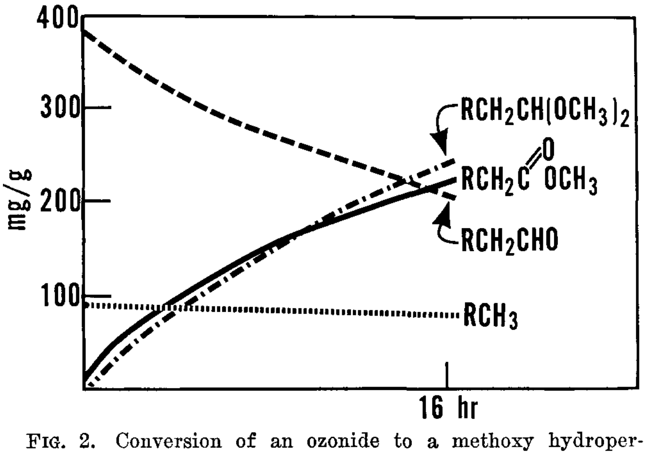


FIG. 2. Conversion of an ozonide to a methoxy hydroperoxide, catalyzed by HCl.

In these experiments, ozonolysis was carried out on the heterogeneous mixture of fatty ester and water at 45–50 C. The weight ratio between the water and ester proved to be critical. With a water-ester ratio greater than about 1, an oil-in-water dispersion formed, ozone absorption was incomplete, and the ozonolysis products collected in a gelatinous mass which could not be dispersed readily. When the water-ester ratio was about 1 or less, a water-in-oil dispersion formed, ozone absorption was complete, a gelatinous product was not formed, and reduction proceeded smoothly.

We found reductive decomposition to be superior to hydrolytic decomposition as a method for preparing aldehydes. Yields by chemical reduction were on the order of 80%. Variations such as order of addition of acetic acid and zinc had no effect. Yields by catalytic hydrogenation varied from 50–80% depending upon the presence and type of auxiliary solvent.

TABLE VI

Thermal Analysis of Various Ozonolysis Products

Ozonolysis medium	Ozonolysis product	Differential thermal analysis		Thermogravimetric Analysis		
		T_{ons}[a], C	T_{max}[b], C	T_{ons}[a], C	T_m[c], C	$\Delta W/\Delta T_{max}$[d], mg/degree
		1-Decene				
None added	Ozonide	78	127	81	195	>1
CH_3COOH	Acetoxy hydroperoxide	65	109	73	159	>1
CH_3OH	Methoxy hydroperoxide	46	128	65	124	>1
H_2O	Hydroxy hydroperoxide	74	102	73	107	0.11
		Methyl oleate				
None added	Ozonide	119	157	82	161	0.5
CH_3COOH	Acetoxy hydroperoxide	71	113	80	122	0.14
CH_3OH	Methoxy hydroyeroxide	65	118	75	122	>1
H_2O	Hydroxy hydroperoxide	102	127	38	144	0.057

[a] Temperature at onset of exotherm or weight loss.

[b] Temperature at exotherm peak maximum.

[c] Temperature at midpoint of range of maximum rate of weight loss.

[d] Slope at maximum rate of weight loss. At high values (>1), the pan was usually blown off the balance.

With water alone, catalytic hydrogenation resulted in 51–53% yields of aldehyde. Better yields (to 70%) were obtained if an alcohol was used as an auxiliary solvent. If an alcohol was present only during hydrogenation and not during ozonolysis, the yield was 60%. With both acetic acid and butanol present as auxiliary solvents during both ozonolysis and hydrogenation (17), yields rose to over 80%. With acetic acid as the sole auxiliary solvent, the yield was 58%.

Variation in solvent is only one of the several factors affecting results in the catalytic hydrogenation of ozonolysis products. Hydrogenation at 75 C and 300 psig in water alone of methyl soyate ozonolysis products has given superior results (13,30).

Pyrolytic Decomposition

Thermal decomposition of ozonolysis products usually leads to both aldehyde and acid (23). We wished to evaluate the effect of solvent on this method and to determine if it would be suitable as a preparative route to aldehydes. In order to carry out the tests as rapidly and conveniently as possible, the pyrolyses were carried out in the injection port of a gas chromatograph (Table V). The reactions were carried out with 1-decene as a model compound since formaldehyde, which would give little or no interference, and pelargonaldehyde are the products formed. The use of an internal standard made possible calculation of estimated yields. Formation of

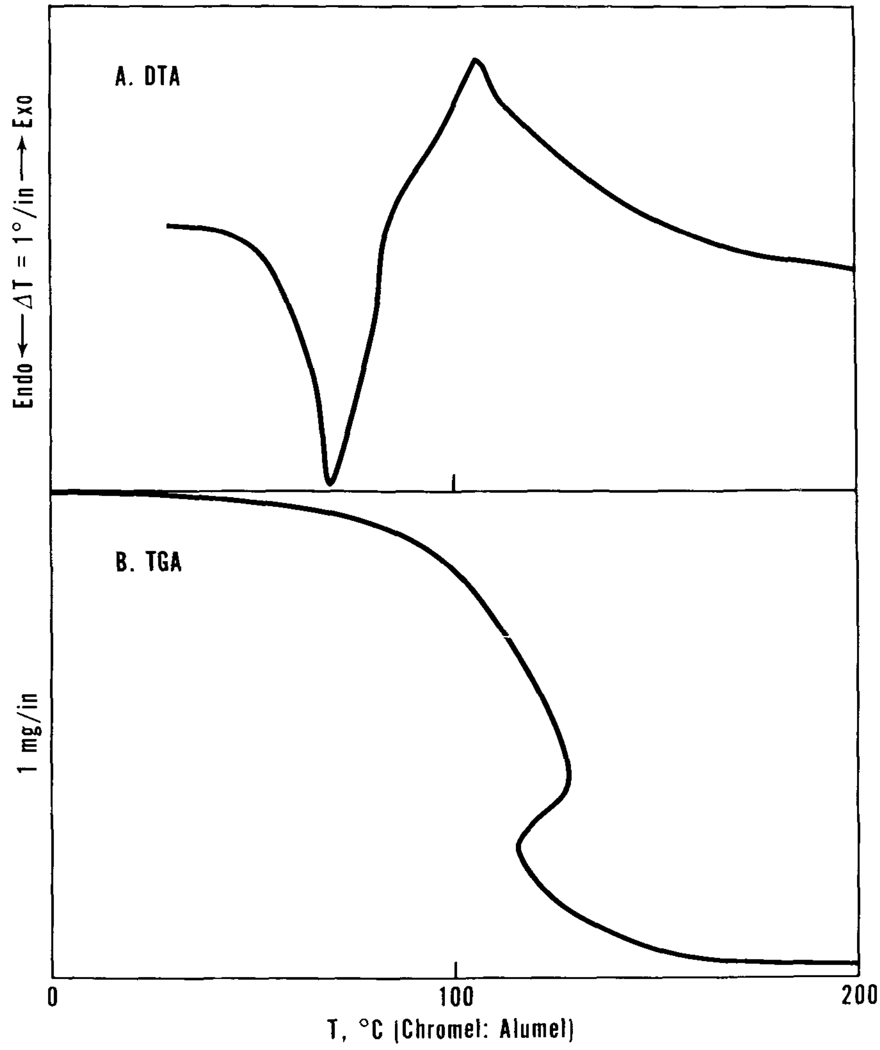


FIG. 3. Thermal analyses of 1-decene ozonolysis products: A, DTA of the ozonolysis product obtained in water, a white solid melting at 67 C as indicated by the endotherm; B, TGA of the ozonolysis product obtained in methanol.

carboxylic acid was not followed since acids were not eluted from the column.

The major products eluted from the chromatograph were pelargonaldehyde, octane and methyl pelargonate. The yields depended upon the type of ozonolysis medium used and also upon the presence or absence of a solvent used to facilitate transfer of sample to the injection port of the chromatograph. In all tests, the ozonolysis products were freed of any ozonolysis medium before pyrolysis. Pyrolysis was carried out either on the neat ozonolysis products or on solutions of the products in carbon tetrachloride, methanol or acetic acid.

The yield of pelargonaldehyde varied from 41–58% when the 1-decene was ozonized neat, from 13–19% with methanol as the ozonolysis medium, from 46–60% with water and from 28–41% with acetic acid. Comparison of pelargonaldehyde yields obtained by pyrolysis of neat ozonolysis products (runs 32, 42, 46 and 50) revealed the following preference in ozonolysis medium (in order of decreasing yield): none (58%), water (46%), acetic acid (41%) and methanol (14%).

Octane formation varied from 2–38% and was lowest when the ozonolysis products were formed in water, or when injected as a carbon tetrachloride solution regardless of the ozonolysis medium. Pyrolysis of the neat ozonolysis products gave the following preferred order of ozonolysis media with respect to octane formation: water (4%), acetic acid (15%), none (25%) and methanol (26%). The presence of solvents other than carbon tetrachloride during pyrolysis also reduced octane formation, but when the solvent was removed before injection the octane yield was again high. Treatment of the ozonolysis products with various neutral solvents which were removed before injection had little effect. Treatment with acetic acid had a small effect and gave somewhat reduced yields of both pelargonaldehyde and octane (run 41).

Methyl pelargonate was produced only if methanol was used for an ozonolysis medium and in 12–26% yields.

We conclude that pyrolytic decomposition is inferior to reductive but somewhat superior to hydrolytic decomposition as a preparative method for aldehydes. The low yield of pelargonaldehyde from pyrolysis of ozonolysis products formed in methanol indicates a relatively high degree of decomposition to carboxylic acid. Pyrolysis is best carried out on ozonolysis products formed in the absence of reactive solvents.

We noted that acetic acid had a small effect but neutral solvents had none on the characteristic behavior of ozonolysis products. Only if hydrochloric acid was present as a catalyst did methanol have a marked effect in changing the pyrolytic behavior of 1-decene ozonolysis products obtained in the absence of solvent. Increasing amounts of methyl pelargonate were formed, while hydrocarbon formation remained fairly constant (Fig. 2). Reactions of pelargonaldehyde with methanol in presence of the acid catalyst resulted in formation of the dimethyl acetal of pelargonaldehyde.

Thermal Analyses

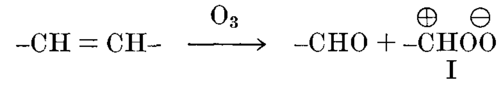
Each of the various ozonolysis products was characterized by DTA and TGA (Table VI and Fig. 3). DTA was not so good an indicator of stability as the rate of weight loss ($\triangle W/\triangle T$) determined by TGA. The $\triangle W/\triangle T$ values clearly show that the ozonolysis products obtained in water undergo a much milder exothermic reaction upon heating than do the others. Further, the values show that decomposition of the methyl oleate ozonolysis products is less vigorous than that of the 1-decene ozonolysis products.

Infrared Analyses

All samples were subjected to IR analyses as solutions in CCl_4. Bands reported for the ozonide structure were found in all samples. Run 50 had bands at 1,340–1,390 cm^{-1} and 1,230–1,250 cm^{-1} which were assigned to the methoxy group. All samples had bands in the 3,600–3,390 cm^{-1} region; indeed, in runs 43, 47 and 50, these peaks were quite large. No evidence was found for free aldehyde in any of the samples investigated. No interconversion of ozonolysis products was detected by IR analyses.

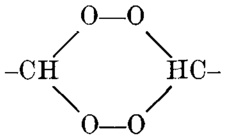
Discussion

Our results on hydrolytic, reductive and pyrolytic decomposition serve to emphasize the variety of ozonolysis products possible and to illustrate the different characteristics of each type. To explain the many types of ozonolysis products Criegee et al. postulate a zwitterion (I) as an intermediate in the ozonolysis of an olefin (8):

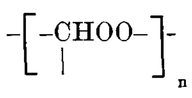


$$-CH=CH- \xrightarrow{O_3} -CHO + \underset{\text{I}}{-\overset{\oplus}{C}HO\overset{\ominus}{O}}$$

Criegee showed that the zwitterion reacts with an alcohol to produce an alkoxy hydroperoxide (II, Fig. 4), with an acid to produce an acyloxy hydroperoxide (III, Fig. 4), with an aldehyde to produce the ozonide (IV, Fig. 4), or with itself to produce peroxides (VI and VII):



VI



VII

Privett and Nickell (21) reported that the ozonide IV from methyl oleate is best formed (72% yield) in pentane. Other more polar solvents gave mixed ozonides and peroxides, as well as more aldehyde.

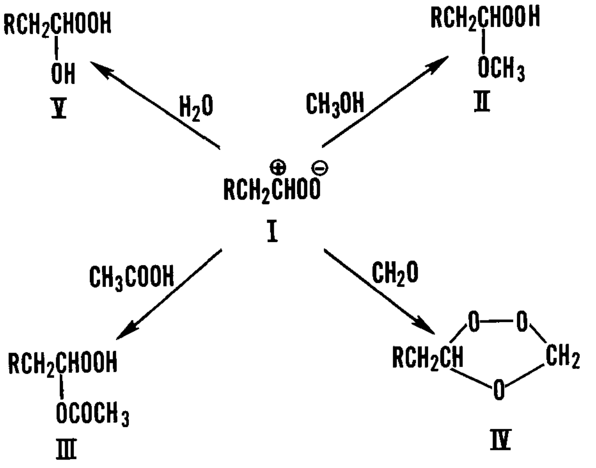


FIG. 4. Formation of various ozonolysis products from a zwitterion.

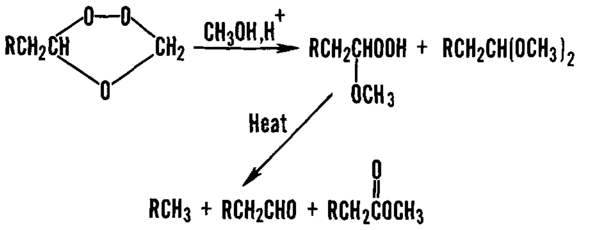
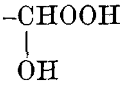


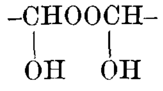
FIG. 5. Reaction of 1-decene ozonide with methanol in the presence of acid. The one carbon fragments are omitted for reasons of simplicity.

Each of these various ozonolysis products has a characteristic behavior when pyrolyzed. The ozonide (IV), formed in the absence of ozonolysis medium, gave 58% yield of pelargonaldehyde and 25% of octane. The methoxy hydroperoxide (II), formed in methanol, gave a 14% yield of pelargonaldehyde, 26% of octane and 12% of methyl pelargonate. The acetoxy hydroperoxide (III), formed in acetic acid, gave 41% yield of pelargonaldehyde and 15% octane. The ozonolysis product formed in water gave 46% pelargonaldehyde and 4% octane. Moreover, thermogravimetric analysis of the ozonolysis products showed that the one formed in water was the most stable of all.

We conclude that ozonolysis in a water-in-oil dispersion leads to formation of an ozonolysis product having the structure of a hydroxy hydroperoxide (VIII) or a dihydroxy peroxide (IX) (24):


$$\underset{\text{OH}}{\underset{|}{\text{-CH}}}\text{OOH}$$

VIII


$$\underset{\text{OH}}{\underset{|}{\text{-CH}}}\text{OO}\underset{\text{OH}}{\underset{|}{\text{CH-}}}$$

IX

The hydroxy hydroperoxide formed in the water-in-oil dispersion is analogous to the methoxy hydroperoxide formed in methanol. With too high a water-ester ratio, an oil-in-water dispersion formed which caused incomplete ozonization and a gelatinous ozonolysis product having the probable structure of an ozonide or a polymeric peroxide. The good results obtained with the water-in-oil dispersions are contrary to some previous reports which claim that water should be absent (5,7,11).

Since interconversion of ozonolysis products did not occur under neutral conditions, we further conclude that there are no equilibria between an ozonolysis product and the zwitterion or between types of ozonolysis products. The reactions involved in converting the ozonide to a methoxy hydroperoxide by acid catalysis are illustrated in Figure 5.

The formation of octane and the effect of solvents on the amounts formed can be explained as follows. Pyrolysis produces fragments in excited electronic states. An excited fragment with two oxygens could produce either an acid by rearrangement or a hydrocarbon by expulsion of carbon dioxide. An excited fragment with a single oxygen could produce an aldehyde or a hydrocarbon upon expulsion of carbon monoxide. Both carbon monoxide (23,25) and carbon dioxide (9,23,25) have been detected in the decomposition of ozonolysis products. In the presence of a solvent acting as an energy transfer medium, decomposition to the hydrocarbon is less likely to occur.

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[Received July 3, 1968]