# OZONOLYSIS OF UNSATURATED FATTY ACIDS

## I. OZONOLYSIS OF OLEIC ACID[1]

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## ABSTRACT

Ozonolysis of oleic acid in methanol, a reacting solvent, with subsequent decomposition of the ozonide products by hydrogen peroxide in formic acid, gives yields of principal dicarboxylic acid fission products exceeding 95% with a minimum of secondary acidic products. The method is highly reproducible and offers unique advantages in the total recovery of the dicarboxylic acids and the elimination of peroxidic materials. The principal non-acidic by-products were tentatively identified as the $C_9$ alcohols and their formyl esters.

## INTRODUCTION

The study of the position of the ethylenic double bonds in long-chain fatty acids is important in connection with the isolation of various naturally occurring fatty acids, and even more important in fields where the chemical treatment of the fatty acid by partial hydrogenation, alkali fusion, or other prototropic reactions leads to the formation of positional isomers. In the former instance, any reasonable yield of principal fission products resulting from the scission of the double bond is satisfactory for bond location, particularly as naturally occurring fatty acids are usually homogeneous in bond position and impurities will differ enough structurally to be recognized as such. In the case of mixtures of positional isomers, the over-all yield is less important than two other factors which must be considered. Firstly, the occurrence of abnormal fission products such as lower homologues of the principal fission products must be reduced to a minimum, and secondly, the method of recovery and analysis of the products must be such that the analysis reflects the true proportions of these products.

Scission of the double bonds is usually achieved by oxidative fission. Some work has been done to give aldehydes as primary products (1–9), but the more extensive application of this technique has always been in the direction of obtaining the more tractable acidic fission products. Ozonolysis is an attractive technique owing to the complete reaction of ozone with the starting material (8) and the simplicity of the reagents and procedures generally adopted. The chief disadvantages, other than the necessity of an ozone generator, have always been the nominal yields (70–85%) (10–16) of primary acidic fission products, the associated formation of carbonyl, peroxidic, and polymeric materials (1, 7, 17), and the presence of one or more secondary acidic oxidation products. The latter can cause considerable uncertainty where minor amounts of positional isomers are being determined, while by-products hinder both separation and analysis of the products (10, 18). Certain procedures do give high yields of products, but the silver oxide oxidation method of Asinger (3, 12, 19) and the procedure of Klenk and Bongard (20) are somewhat complex, while that of Pryde *et al.* (8) yields aldehydes as principal products.

The most common alternatively employed oxidizing agent, potassium permanganate, also gives only moderate yields of acidic products and considerable secondary oxidation (11, 12, 18, 21–24). The recently introduced permanganate-catalyzed periodate method of von Rudloff (3, 25–28) is much more attractive owing to the simplicity of the method

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and the very high yields of primary products. These techniques do suffer from a disadvantage in that recovery of the primary products, in particular the dicarboxylic acids, must be made by extraction from a highly mineralized aqueous solution, with consequent risk of losses of the more soluble lower dicarboxylic acids. In the past this factor has led to erroneous results in determining the relative proportions of positionally isomeric double bonds (13, 24, 29, 30).

If ozonolysis is to be considered as a useful method for the sensitive determination of double-bond position in long-chain fatty acids it must satisfy the following requirements:

1. the method should have a high yield of primary products and should give rise to the least possible amounts and variety of "abnormal" products;
2. the procedure of working-up should give the highest possible recoveries of related products even when these have differing physical properties;
3. the method should be simple and reproducible;
4. the method of analysis should be sensitive and accurate.

It was deemed desirable that the principal products should be acidic in order to capitalize on the stability and low volatility of the desirable dicarboxylic acids. The method outlined below, based on ozonolysis in methanol, a reacting solvent, with decomposition of the ozonide product with hydrogen peroxide in formic acid, satisfies the above requirements. The yield of principal dicarboxylic acid product averages 95%, accompanied by only 2–4% lower homologous dicarboxylic acids and 2–4% other materials. The principal non-dicarboxylic acid by-product has been tentatively identified as the alcohol formed from the principal acidic product through the loss of one carbon atom, occurring both as the alcohol and as its formyl ester. Since only volatile solvents and reagents are employed, and the monocarboxylic acids are removed by steam distillation, total recovery of the dicarboxylic acids present is possible. The method is relatively simple and while some variation is found in the proportion of non-dicarboxylic products to dicarboxylic acids, the ratio of total secondary dicarboxylic acid products to principal dicarboxylic acid product is remarkably stable. The mixture of products is readily analyzed with a high degree of accuracy by gas–liquid chromatography. The methanol – formic acid procedure is derived from that employed by Bailey (31, 32) for the production of adipic acid by ozonolysis of cyclohexene, by Perry (33) in the ozonolysis of norbornylene, and by Pryde *et al.* (8) in the ozonolysis of methyl oleate to give carbonyl products. Methanol has also been employed recently by other workers in the ozonolysis field (34–37), although not necessarily in exploitation of the same type of reaction.

## EXPERIMENTAL

Pure oleic acid was prepared from filbert oil (38) via the methyl esters by established procedures (39, 40). The following properties were determined: iodine value 91.2 (Wijs), 89.1 (by precision semimicro hydrogenation (41)) (calc. 89.9); $n_D^{25}$ 1.45785 (cf. $n_D^{25}$ 1.45792 (42)). Ultraviolet spectrophotometry showed no diene or triene content prior to alkali isomerization* and the latter procedure showed a diene content of 0.1% or less. Gas–liquid chromatography of the methyl ester showed only an oleate peak.

It has been reported that an oleic acid prepared from olive oil by standard methods contained appreciable amounts of positional isomers (29). The present and other studies (13, 14) have confirmed that oleic acid homogeneous in bond position can be readily

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**Modification of the method of Vandenheuvel and Richardson (43); 21%* KOH *in ethylene glycol, effective heating time 15 minutes.*

prepared. The ultimate criterion of purity in all cases must be the analysis of both mono- and di-carboxylic acid fission products. Thus the presence of small amounts of suberic acid in the dicarboxylic acid product does not signify the presence of octadec-8-enoic acid unless decanoic acid can be found in the complementary monocarboxylic acids. In the present studies the occurrence of both mono- and di-carboxylic acid products containing 10 carbon atoms has been noted in amounts of $\leqslant 0.1\%$. Thus the amounts of octadec-8- and octadec-10-enoic acids cannot have exceeded this level.

Ozone was furnished by a pyrex corona discharge tube (4). At an oxygen flow rate of 1.1 l./hr, the ozone content was determined as 2.2% (w/w) by decomposition of potassium iodide (44). A dry-ice trap supplemented chemical drying of the oxygen.

### *1. Ozonolysis in Methanol*

Pure oleic acid (ca. 1 g) was weighed in a long-necked, 100-ml standard taper flask. Absolute methanol (Fisher Spectrophotometric Grade, 40 ml) was added and the solution was chilled to −30° C and treated with ozone-containing oxygen until complete absorption ceased. The flask was fitted with a distilling head in order to admit a capillary tube (nitrogen) and was connected through a dry-ice trap to a mechanical vacuum pump system. The flask was immersed in water at room temperature and vacuum applied in stages until all the methanol was removed and the pressure was less than 1 mm. Formic acid (98%, 25 ml) was added to dissolve the syrupy residue and hydrogen peroxide (30 or 50% aqueous solution, 10 mole-equivalents) added. A reflux condenser was immediately fitted to the flask and gentle warming induced an exothermic reaction, on completion of which the mixture was heated for 1 hour on a steam bath. The peroxide and peracid content fell rapidly below measurable limits.

Water (20 ml) was added and the solution transferred to a continuous steam-distillation unit, a few drops of acetone serving as rinse. In this case, 200 ml of distillate was collected for recovery of the nonanoic and associated monocarboxylic acid products. The dicarboxylic acid solution was transferred to a distillation unit and evaporated nearly to dryness under aspirator vacuum. Toluene was added in small lots (ca. 10 ml) and removed under reduced pressure until the distillate was free of water and formic acid (45). Further vacuum treatment eliminated residual toluene. The product was dissolved in acetone (100 ml) and aliquots were taken for determination of yield by weight and titration. The balance of the material was freed of solvent and esterified with distilled diazomethane (18) in ether solution. The ether was removed and the product examined by gas–liquid chromatography. The results are presented in Table I.

The steam distillate was extracted with hexane (100 ml). The hexane solution was dried over sodium sulphate, and after removal of solvent the monocarboxylic acids were converted to methyl esters with diazomethane. Analysis of these methyl esters is presented in Table II.

The methanol in the cold trap was diluted with water and extracted with hexane. The bulk of the solvent was removed and the remaining solution examined by gas–liquid chromatography. Only traces of nonaldehyde were observed.

### *2. Ozonolysis in Acetic Acid and Other Solvents*

Ozonolyses were carried out as described above employing 40 ml of a mixture of acetic acid and methyl formate (3:1), acetone, or methyl formate, with cooling in an ice-water bath. After complete ozone absorption had ceased, aqueous hydrogen peroxide (30%, 5 ml) was added and the flask was fitted with a reflux condenser. After standing overnight at room temperature, the mixtures were heated on a steam bath for 1 hour.

TABLE I

Dicarboxylic acids obtained from ozonolysis of oleic acid and control oxidations

| Experiment | | | % yield | | Weight% dicarboxylic acid composition* | | | | | | | % other material‡ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run | Material | Solvent | Weight† | Titration† | $C_9$ | $C_8$ | $C_7$ | $C_6$ | $C_5$ | $C_4$ | $C_3$ | |
| 1-A | Oleic | $CH_3CO_2H$ | 96.2 | 77.5 | 70.6 | 7.1 | 6.1 | 3.8 | 4.7 | 6.9 | 0.8 | 24.1‖ |
| 1-B | Oleic | $(CH_3)_2CO$ | 83 | 73 | 86.8 | 8.2 | 1.2 | 1.1 | 1.1 | 1.6 | — | 20.7§ |
| 2-A | Oleic | MeOH | 100 | 93.5 | 97.2 | 1.9 | 0.4 | 0.2 | 0.2 | 0.1 | — | 5.6‖ |
| 2-B | Oleic | MeOH | 100 | 93.1 | 97.5 | 2.2 | 0.1 | 0.1 | 0.1 | — | — | 3.1‖ |
| 2-C | Oleic | MeOH | 100 | 95.5 | 98.7 | 0.9 | 0.1 | 0.1 | 0.1 | 0.1 | — | 1.8‖ |
| 2-D | Oleic | MeOH | 106 | 100 | 97.6 | 1.9 | 0.1 | 0.1 | 0.1 | 0.1 | — | 3.9‖ |
| 2-A | Oleic | MeOH | | | 96.0 | 2.5 | 0.6 | 0.3 | 0.3 | 0.3 | — | 5.4§ |
| 2-B | Oleic | MeOH | | | 95.4 | 2.9 | 0.7 | 0.4 | 0.2 | 0.4 | — | 4.2§ |
| 2-C | Oleic | MeOH | | | 97.9 | 1.5 | 0.1 | 0.1 | 0.2 | 0.2 | — | 0.7§ |
| 2-D | Oleic | MeOH | | | 97.8 | 1.5 | 0.2 | 0.2 | 0.2 | 0.1 | — | 1.5§ |
| 3-A | Azelaic | $HCO_2H$ | 97.7 | 98.2 | 98.9 | 1.0 | — | — | 0.1 | — | — | 1.1‖ |
| 3-A | Azelaic | $HCO_2H$ | | | 98.5 | 1.2 | 0.1 | — | 0.1 | 0.1 | — | 1.1§ |
| 3-B | Azelaic | $HCO_2H$ | 98.6 | 100.3 | 99.1 | 0.6 | 0.1 | — | 0.1 | 0.1 | — | 0.6§ |

*% of total dicarboxylic acids indicated by gas–liquid chromatography.
†Calculated as azelaic acid.
‡% of total volatile materials indicated by gas–liquid chromatography.
§Polyester substrate.
‖Silicone grease substrate.

TABLE II

Monocarboxylic acids from ozonolysis of oleic acid

| Run† | % monocarboxylic acids | Weight% monocarboxylic acid composition* | | | % other material‡ |
|---|---|---|---|---|---|
| | | $C_9$ | $C_8$ | $C_7$ | |
| 2-D | 95.8§ | 98.1 | 1.6 | 0.3 | 4.2 |
| | 95.7‖ | 98.4 | 1.2 | 0.4 | 4.3 |

*% of total monocarboxylic acids indicated by gas–liquid chromatography.
†Details set forth in Table I.
‡% of total volatile materials indicated by gas–liquid chromatography.
§Silicone grease substrate.
‖Polyester substrate.

Monocarboxylic acids were removed by extraction with hexane (100 ml) after addition of water (100 ml). The aqueous solution containing the dicarboxylic acids was freed of solvents and volatile acids as described above, yields were determined, and the product was converted to methyl esters. Gas–liquid chromatographic analyses of the products are presented in Table I for the acetic acid and acetone products. The methyl formate product did not differ appreciably from the acetone product.

### 3. *Control Oxidation of Azelaic Acid*

Pure azelaic acid (100% by gas–liquid chromatography of the dimethyl ester) was refluxed for $1\frac{1}{2}$ hours with hydrogen peroxide solution in formic acid in the proportions used in the ozonolysis procedure. After removal of the solvent the recovery was 97.7% by weight. The esters were examined by gas–liquid chromatography and gave dicarboxylic acid chromatograms almost identical with those obtained from ozonolysis (Table I). The only significant feature appears to be the lower amounts of pimelic and adipic acids formed and the absence of the alcohol by-product.

### 4. *Control Oxidation of Azelaic Acid Methyl Ester Semialdehyde Acetal*

Azelaic acid methyl ester semialdehyde was prepared from methyl oleate by ozonolysis in acetic acid and reduction with zinc (8, 9). After a preliminary distillation, a concentrate was converted to the acetal by refluxing with methanolic HCl (46). The acetal methyl ester was treated with sodium bisulphite solution and after removal of solvent was purified by preparative gas–liquid chromatography (47). The product was not completely pure (cf. ref. 8), but on treatment with hydrogen peroxide in formic acid, a vigorous exothermic reaction took place, and working-up of the products, as in section 2 above, gave a product the gas–liquid chromatogram of which was virtually identical with that obtained by oxidation of azelaic acid.

### 5. *Determination of Peroxidic Materials*

An aqueous solution of hydrogen peroxide (30%, 5 ml) was added to the solvent under consideration (40 ml) in a round-bottomed standard taper flask fitted with a reflux condenser. The solution was heated on a steam bath, aliquots being withdrawn at intervals for analysis. Determination of hydrogen peroxide was made with ceric sulphate, and of peracids, with potassium iodide and sodium thiosulphate (48). Only formic acid showed an appreciable peracid content at any time, and only with formic acid or mixtures containing formic acid was rapid destruction of all active oxygen evident.

### 6. *Gas–Liquid Chromatography*

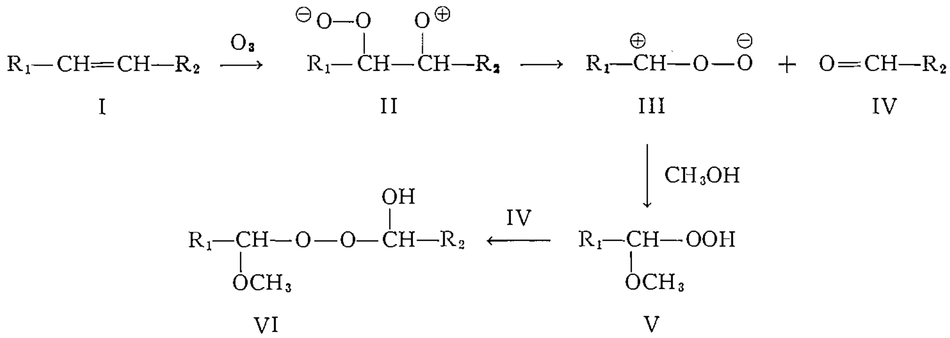
The apparatus employed was a Podbielniak Chromacon. Columns were 10 ft in length and $\frac{1}{4}$ in. in diameter, packed with 30% of either high-vacuum silicone grease (Dow Corning), especially treated (49), or diethylene glycol – adipic acid polyester (LAC-2-R-446), on 60–80 mesh Chromosorb. Analyses of monocarboxylic esters were carried out at 100° C with hydrogen flow rates of 55 ml/min for the polyester column and 100 ml/min for the silicone column. Dicarboxylic esters were analyzed at 160° with hydrogen flow rates of 85 ml/min for the polyester column and 38 ml/min for the silicone column. Areas were determined by a ball-and-disk-type integrator. The errors associated with the small peaks ($\sim$0.1%) may be ±30% owing to the few counts available (50).

The monocarboxylic acid chromatograms showed, in addition to minor amounts of octanoic and heptanoic methyl esters, three other components. The minor one was identified as nonanal and the others as octanol and octyl formate, the latter predominating. These identifications are assigned on the basis of complete coincidence of small additions of authentic materials added to the ozonolysis product, carried out on both polyester and silicone substrates.

In addition to a large number of very minor peaks, the dicarboxylic acid ester chromatograms showed one major non-dicarboxylic acid by-product. Methyl 8-hydroxyoctanoate was not available, but methyl 9-hydroxynonanoate was prepared by the method of Diaper and Mitchell (51). Calculations of the equivalent chain lengths (52) of methyl 8-hydroxyoctanoate were made from the retention times of methyl 9-hydroxynonanoate. These indicated that the retention times, relative to dimethyl azelate, would be 0.605 on the silicone column and 1.16 on the polyester column. Minor peaks were in fact observed at 0.610 and 1.20 respectively. The formyl ester of the alcohol methyl ester could be similarly shown to have relative retention times, calculated from those of the formyl ester of methyl 9-hydroxynonanoate, of 0.680 on the silicone grease column and 0.905 on the polyester column. These values correlate with the relative retention times of the major non-dicarboxylic acid product, 0.706 and 0.902 respectively. The value of the relative retention time for the by-product peak on the silicone grease column could not be accurately determined as it was overlapped by the dimethyl suberate peak. Mixed runs with small amounts of methyl azelaaldehyde (9) did not coincide with any component on either silicone or polyester analyses.

## DISCUSSION

The Criegee ozonolysis mechanism (1, 53, 54) suggests that the zwitterion (III) in the presence of a reacting solvent, in this case methanol, leads to a methoxy hydroperoxide (V). There is a possibility that this may then react with the aldehyde (IV) to give a hemiperacetal (VI). If the latter step were not complete (cf. ref. 33), some loss of volatile aldehyde would be expected when the methanol is removed under vacuum, whereas only a trace of free aldehyde (nonaldehyde) has been observed in this step. Reaction of the aldehydes with methanol to give hemiacetals or acetals is also a possibility (37).



$$R_1{-}CH{=}CH{-}R_2 \xrightarrow{O_3} R_1{-}\overset{\ominus O-O\qquad}{CH}{-}\overset{O^{\oplus}}{CH}{-}R_2 \longrightarrow R_1{-}\overset{\oplus}{CH}{-}O{-}\overset{\ominus}{O} + O{=}CH{-}R_2$$

I II III IV

$$\downarrow CH_3OH$$

$$R_1{-}\underset{OCH_3}{CH}{-}O{-}O{-}\overset{OH}{CH}{-}R_2 \xleftarrow{IV} R_1{-}\underset{OCH_3}{CH}{-}OOH$$

VI V

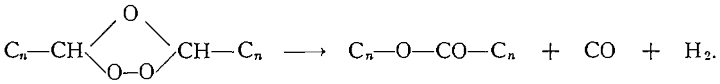
The decomposition of the hydroperoxides, hemiperacetals, hemiacetals etc. is readily accomplished by treatment with hydrogen peroxide and formic acid, the active agent probably being performic acid (55) formed *in situ*. Peracetic acid has been employed in similar cases (15, 16, 37). Performic acid decomposes readily on heating, ensuring the rapid destruction (31, 32) of all peroxidic materials, to leave inert products. Regardless of the nature of the material being oxidized, less than 1% nonaldehyde and only traces of azelaic semialdehyde are found in all cases. This can be taken as a reliable indication that oxidation is virtually complete.

The quality of the reagents is significant. Thus results 2-A and 2-B, Table I, where ordinary reagent grade methanol was employed, show slightly higher amounts of both dicarboxylic acid and non-dicarboxylic acid by-products than results 2-C and 2-D where spectrophotometric grade methanol was used.

The acidic composition of the monocarboxylic acid fraction (Table II) parallels, in certain respects, that of the dicarboxylic acid product. However, since the recovery is only about 90% and losses of lower materials are high, the results are less significant.

The close duplication of the ozonolysis results by the control oxidations of azelaic acid and azelaic acid methyl ester semialdehyde acetal (see Table I, also above), not only in terms of secondary dicarboxylic by-products, but also partly in the miscellaneous by-products, indicates that these materials result from true secondary oxidation by the hydrogen peroxide in formic acid, and do not form during the ozonolysis step.

The occurrence of the presumed alcohol by-products in both the monocarboxylic and dicarboxylic acid products suggests a symmetrical reaction characteristic of isolated double bonds, and since they are not found in the control oxidation reactions (see above), their formation must take place during the ozonolysis or decomposition of the ozonide. Two possible mechanisms may be considered. In the first instance Pasero *et al.* (56–58) have observed the formation of appreciable amounts of esters during the ozonolysis of monoethylenic acids, and ascribe this to simple decomposition of the ozonide:



Thus monooctyl azelate is one of the two potential products in the ozonolysis of oleic acid, and in the presence of formic acid and water, might be expected to hydrolyze or transesterify to give both octanol and octyl formate, together with azelaic acid.

Lefort *et al.* (59, 60) have observed the formation of similar esters ($C_n$—O—CO—$C_n$) when aliphatic peracids are heated, although under anhydrous conditions, suggesting a complex reaction of peracids during the ozonide decomposition with hydrogen peroxide in formic acid. On the present evidence either mechanism might be applicable.

Complete elimination of by-products is a highly desirable but rarely attained end in all oxidative fission procedures. The methanol – formic acid procedure reduces the by-product level to a point where gas–liquid chromatography is greatly facilitated, while at the same time retaining the advantage of total recovery of the dicarboxylic acids. The by-products do not, therefore, detract from the advantages of this technique, combined with gas–liquid chromatography, as a quantitative means of analysis of the position of ethylenic double bonds in long-chain monounsaturated fatty acids.

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