Thermal Oxidation of Mono-Unsaturated Short Chain Fatty Acids: II. Methyl Hexenoate, Hexenoic Acid, and Octenoic Acid

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ABSTRACT

Samples of methyl 3-hexenoate, methyl 2-hexenoate, 3-hexenoic, and 3-octenoic acid were oxidized and their decomposition products analyzed. Certain aldehydes, ketones, shorter chain acids or esters, hydroxy-derivatives, and dimers were found among the oxidation products of all four substrates. Epoxy-esters and 4-oxo-derivatives were major products from the esters but absent in the case of the acids. 3-heptene and 5-undecene were unique for 3-hexenoic and 3-octenoic acids, respectively. Reaction mechanisms are proposed for the formation of these products.

INTRODUCTION

The purpose of this work was to investigate the oxidation mechanisms of short chain fatty acids. Although such acids are present in natural fats in relatively small quantities, they can be formed by oxidative breakdown of the more abundant higher mol wt fatty acids (1), and they can themselves undergo further oxidation. In a previous publication (2), the identification of oxidation products from ethyl 3-hexenoate and ethyl 2-hexenoate was reported. Epoxy-esters, unsaturated keto- and hydroxy-esters, and dehydrodimers were among the major products formed. Aldehydes, short chain esters, and ketones were produced less abundantly. The results appeared to indicate that these compounds arise from the decomposition of both hydroperoxide and epoxy intermediates and that both the 2-hexenoates and the 3-hexenoates favor hydroperoxide formation in the 4-position which allows conjugation of the double bond and the ester carbonyl.

In the present study, the thermal oxidation of some 6-carbon and 8-carbon acids and their methyl esters is examined.

EXPERIMENTAL PROCEDURES

Samples of purified methyl 3-hexenoate, methyl 2-hexenoate, 3-hexenoic acid, and 3-octenoic acid were thermally oxidized under identical conditions and their decomposition products analyzed. Half-gram samples were oxidized in a glass tube which was heated in an oil bath at 130 C for 8 hr (occasionally at 150 C for 6 hr). Methods of identification were exactly the same as those described previously (2).

RESULTS AND DISCUSSION

At the end of the oxidation period, the peroxide value of the esters reached ca. 80 while that of the free acids was 40 meq/kg. The acids developed a red-brown color within 1 hr of oxidation, as compared to the esters which took 6 hr or longer to develop the dark color. The oxidation products identified from each of the four substrates are listed in Table I. All contain aldehydes, ketones, shorter

TABLE I

Products Identified from Thermal Oxidation of Short Chain Mono-Unsaturated Fatty Acids and Esters

Me 3- hexenoate	Me 2-hexenoate	3-Hexenoic acid	3-Octenoic acid
Me 3,4-epoxy hexanoate	Me 2,3-epoxy hexanoate		
Me 4-oxo-2-hexenoate	Me 4-oxo-2-hexenoate	4-hydroxy-2-hexenoic acid lactone	4-hydroxy-2-octenoic acid lactone
Me 4-hydroxy-2-hexenoate	Me 4-hydroxy-2-hexenoate		
Me 3-Et-4-oxohexanoate	Me 3-Et-4-oxohexanoate		
Ethanal	Ethanal	Propanal	Propanal
Propanal	Propanal	Butanal	Butanal
Butanal	Butanal		Pentanal
			Hexanal
			2-hexenal
2-pentanone		2-pentanone	
3-hexanone	3-hexanone	3-hexanone	2-hexanone
3-heptanone	3-heptanone	3-heptanone	2-heptanone
4-heptanone	4-heptanone	4-heptanone	4-heptanone
3-penten-2-one	3-penten-2-one	3-penten-2-one	
		4-octen-3-one	
Me propanoate			
Me butanoate	Me butanoate		
Me pentanoate	Me pentanoate		
Me crotonate	Me crotonate		
Me hexanoate	Me hexanoate		
Propanoic acid	Butanoic acid	Acetic acid	Butanoic
		Propanoic acid	Pentanoic
		Butanoic acid	Hexanoic
		3-heptene	5-undecene
Dehydrodimers	Dehydrodimers	Dimer acids	Dimer acids

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chain acids or esters, hydroxy-derivatives, and dimers. Epoxy esters and 4-oxo-derivatives are major compounds from the esters but absent in case of the acids. The compounds 3-heptene and 5-undecene are unique for 3-hexenoic and 3-octenoic acids, respectively.

As with the ethyl hexenoates (2), many of the same compounds produced from methyl 3-hexenoate were also found in the oxidation products of methyl 2-hexenoate. According to Farmer's theory, four isomeric hydroperoxides can form upon autoxidation of methyl 3-hexenoate. These are the 4-, 2-, 5-, and 3-hydroperoxy intermediates. In the case of methyl 2-hexenoate, α-methylenic abstraction can occur only at position 4, giving rise to only two isomers, the 4- and 2-hydroperoxy esters. In both cases, however, hydroperoxidation in position 4 is favored since the double bond and the carbonyl would be in conjugation. The other three hydroperoxide isomers are probably produced but in much less quantities. Consequently, the 4-alkoxy radical $R\text{-}\underset{\underset{O\cdot}{|}}{CH}\text{-}CH{=}CH\text{-}COOR$ is the predominant intermediate, regardless of whether the double bond was originally located in 2- or 3-position. This is substantiated by the fact that, for all four substrates (Table I), the oxo- and hydroxy-derivatives and the lactones are substituted in the 4-position.

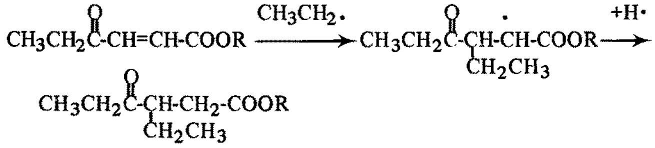
Typical of the decomposition of the 4-alkoxy radical is the formation of propanal from the six carbon substrates and pentanal from octenoic acid. Cleavage on the hydrocarbon side of the 4-hydroperoxy group would produce ethyl and butyl radicals from the hexenoates and octenoates, respectively. These may form the corresponding hydrocarbons which are too volatile for detection by the present methods. However, such alkyl radicals may play a significant role in the further production of other decomposition products. The ethyl radical, for example, may form acetaldehyde via a primary hydroperoxide, according to Bell and co-workers (3):

$$CH_3CH_2\cdot \xrightarrow{O_2,\ H\cdot} CH_3CH_2OOH \xrightarrow{-OH\cdot} CH_3CH_2O\cdot \xrightarrow{-H\cdot} CH_3CHO$$

Similarly, the butyl radical from octenoic acid would form butanal. Also, the ethyl and butyl radicals appear to be involved in a variety of recombination reactions. For example, a mechanism which involves thermal decarboxylation (4,5), followed by recombination with the ethyl radical, would explain the production of 3-heptene from 3-hexenoic acid:

$$CH_3CH_2CH{=}CHCH_2COOH \xrightarrow[-H\cdot]{-CO_2} CH_3CH_2CH{=}CHCH_2\cdot \xrightarrow{CH_3CH_2\cdot} CH_3CH_2CH{=}CH\text{-}CH_2CH_2CH_3$$

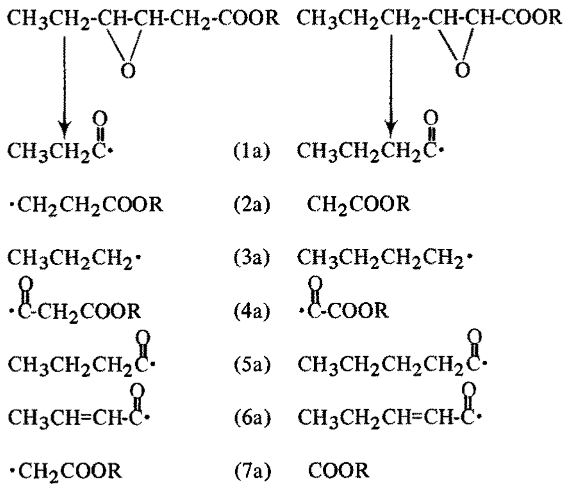
Such mechanism would also account for the formation of 5-undecene from octenoic acid. In addition, the ethyl radical is probably involved in the formation of the 3-ethyl-4-oxo-esters from the 3-hexenoates via direct attack on the double bond:



$$CH_3CH_2\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH\text{-}COOR \xrightarrow{CH_3CH_2\cdot} CH_3CH_2\overset{O}{\overset{\|}{C}}\text{-}\underset{CH_2CH_3}{\underset{|}{C}H}\text{-}\dot{C}H\text{-}COOR \xrightarrow{+H\cdot} CH_3CH_2\overset{O}{\overset{\|}{C}}\text{-}\underset{CH_2CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}COOR$$

The methyl 3- and methyl 2-hexenoates formed relatively large amounts of the 3,4- and 2,3-epoxy-esters, respectively, indicating that a direct attack on the site of the double bond is also involved. No epoxy-acids, however, were found among the oxidation products of the free acids. Epoxy-acids are very reactive and decompose readily. Koley (6) has shown that reaction of the oxirane with carboxylic acids yields dimers, and Ellis (7) reported that autoxidation of oleic acid at 65 C yields nearly 20% epoxy-acid, while at 100 C very little epoxy-acid is obtained because most of it reacts with free acids to form diol monoesters. Furthermore, α,β-unsaturated oxo-acids, found in considerable amounts at the lower temperature, were present only in small quantities at 100 C because they combined to form dimers and colored, resinous higher polymers. This observation is in accord with the results of the present study since the α,β-unsaturated oxo-derivatives were formed upon oxidation of the esters but were absent in the case of the free acids.

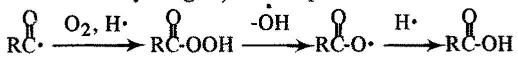
The oxirane group undergoes various ring-opening reactions to relieve the strain of the ring (8). This is particularly true in the presence of even small amounts of acids. The formation of free radicals by pyrolysis, photolysis, and free radical attack has been reviewed by Rosowsky (9). Accordingly, the 3,4-epoxy and 2,3-epoxyhexanoate would produce the following radicals:



$CH_3CH_2\text{-}CH\text{-}CH\text{-}CH_2\text{-}COOR$ (O bridging) $CH_3CH_2CH_2\text{-}CH\text{-}CH\text{-}COOR$

(1)	$CH_3CH_2\overset{O}{\overset{\|}{C}}\cdot$	(1a)	$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\cdot$
(2)	$\cdot CH_2CH_2COOR$	(2a)	CH_2COOR
(3)	$CH_3CH_2CH_2\cdot$	(3a)	$CH_3CH_2CH_2CH_2\cdot$
(4)	$\cdot\overset{O}{\overset{\|}{C}}\text{-}CH_2COOR$	(4a)	$\cdot\overset{O}{\overset{\|}{C}}\text{-}COOR$
(5)	$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\cdot$	(5a)	$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}\cdot$
(6)	$CH_3CH{=}CH\text{-}\overset{O}{\overset{\|}{C}}\cdot$	(6a)	$CH_3CH_2CH{=}CH\text{-}\overset{O}{\overset{\|}{C}}\cdot$
(7)	$\cdot CH_2COOR$	(7a)	$COOR$

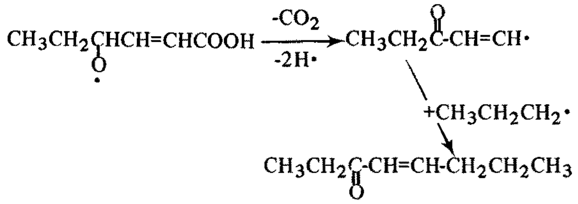
Radicals 1 and 1a derived from the epoxy esters could abstract a hydrogen to produce propanal and butanal from the 3- and 2-hexenoates, respectively. Similarly, pentanal and hexanal can be produced from 3-octenoic acid. Radicals 5 and 5a would produce butanal and pentanal. In the case of 3-octenoic acid, radical 7 would form hexanal. Radicals 3 and 3a would be expected to produce propane and butane. However, the methods used here preclude detection of such short chain hydrocarbons. Interestingly, the 3-esters produced considerable amounts of propanoic acid while the 2-esters produced butanoic acid. These could come from oxidation of propanal and butanal, of course, but the absence of acids corresponding to the other aldehydes produced suggests a more specific mechanism. The formation of primary hydroperoxides from radicals 1 and 1a, followed by their decomposition to alkoxy radicals which abstract a hydrogen, would produce these acids.



$$R\overset{O}{\overset{\|}{C}}\cdot \xrightarrow{O_2,\ H\cdot} R\overset{O}{\overset{\|}{C}}\text{-}OOH \xrightarrow{-\dot{O}H} R\overset{O}{\overset{\|}{C}}\text{-}O\cdot \xrightarrow{H\cdot} R\overset{O}{\overset{\|}{C}}\text{-}OH$$

The absence of the 4-oxo-derivatives from the oxidation products of hexenoic and octenoic acids is probably due to the much faster oxidation of the free acids as compared to their esters.

It can be seen that breakdown of the epoxy esters and the 4-hydroperoxy intermediates produces a pool of free radicals leading to the formation of a variety of decomposition products. To a lesser extent, the 2-hydroperoxide (from the 2- or 3-hexenoates) and that of the 3- and 5-hydroperoxides (only from the 3-hexenoates) would also contribute to the free radical pool. A variety of possible combinations between these free radicals can explain the formation of many of the ketones and esters identified. Thus, propanoates may form by combination of the $\cdot CH_2COOR$ radical (from the 3-hydroperoxy intermediates) and a methyl radical (from the 5-hydroperoxy intermediates). This mechanism accounts for ethyl and methyl propanoate produced from ethyl 3- and methyl 3-hexenoate, propanoic acid from 3-hexenoic acid, and pentanoic acid from 3-octenoic acid. As predicted, however, no methyl propanoate was formed from methyl 2-hexenoate. The recombination of an ethyl radical with radical 2 and 2a would produce pentanoates from the 3-esters and butanoates from the 2-esters, respectively. Butanoates could also form by combination of a methyl radical with radical 2, a propyl radical with 7a, or an ethyl radical with 7. Similarly, many of the ketones found to be common to all substrates can be formed by combination of alkyl and acyl radicals. The compound 4-octen-3-one produced only from 3-hexenoic acid may arise from the 4-alkoxy radical via decarboxylation and combination with a propyl radical.



$$CH_3CH_2\underset{\underset{\bullet}{O}}{C}HCH{=}CHCOOH \xrightarrow[-2H\cdot]{-CO_2} CH_3CH_2\overset{\overset{O}{\|}}{C}\text{-}CH{=}CH\cdot$$

$$+CH_3CH_2CH_2\cdot \longrightarrow CH_3CH_2\underset{\underset{O}{\|}}{C}\text{-}CH{=}CH\text{-}CH_2CH_2CH_3$$

No aldehyde-esters were found in the oxidation products of any of the substrates studied. Perhaps under the conditions of oxidation used and due to their short chain length, they underwent further degradation. The formation of dehydrodimers from ethyl 3- and ethyl 2-hexenoates was discussed in some detail previously. As expected, dimers appeared in the oxidation products of all four substrates examined in the present study.

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