# Decomposition of Methyl Hydroperoxido Oleate

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THE first products of autoxidation of oleic and linoleic acids are hydroperoxides (1, 2). The products of decomposition of these hydroperoxides have not previously been identified. The results reported here indicate that one of the decomposition reactions of methyl hydroperoxido oleate is fission to produce α,β-unsaturated carbonyl compounds, one of which is 2-undecenal.

## Experimental

Methyl hydroperoxido oleate was prepared by a previously described method (3). It was observed that decomposition of the hydroperoxide at temperatures of 60°C., 90°C., and 150°C. yielded products whose absorption spectra in 95% ethanol exhibited maxima at 223-224 mμ and corresponding extinction coefficients, $E^{\mathrm{g./l.}}_{\mathrm{1\ cm.}}$ of 7.5, 10, and 14, respectively.

Identification of at least one of the substances responsible for the absorption at 223-224 mμ was accomplished as follows:

Methyl hydroperoxido oleate (20 g.) was decomposed by immersing it in an oil bath heated to 150°C. After about 3-4 minutes spontaneous decomposition occurred during which reaction the temperature of the sample rose rapidly to 260°C. and then decreased during the next 3-4 minutes to the approximate temperature of the bath.

The decomposition mixture (extinction coefficient at 223 mμ in 95% ethanol, $E^{\mathrm{g./l.}}_{\mathrm{1\ cm.}} = 13.9$) was fractionated to yield the following series of fractions: (1) Approximately 1 g. of product (extinction coefficient at 222 mμ, $E^{\mathrm{g./l.}}_{\mathrm{1\ cm.}} = 17.2$) which distilled at 95°-100°C. at *ca.* 17 mm. pressure; (2) *ca.* 2 g. of product (extinction coefficient at 222 mμ, $E^{\mathrm{g./l.}}_{\mathrm{1\ cm.}} = 29.8$) which distilled at 100°-150°C. at *ca.* 1 mm. pressure; and (3) *ca.* 2 g. of product (extinction coefficient at 224 mμ, $E^{\mathrm{g./l.}}_{\mathrm{1\ cm.}} = 22.5$) which distilled at 150°-160°C. at *ca.* 1 mm. pressure.

*2,4-Dinitrophenylhydrazone.* The 2,4-dinitrophenylhydrazone prepared for each fraction was a mixture of red crystalline substances. The first two distillate fractions yielded reaction products from which a 2,4-dinitrophenylhydrazone melting at 117°C. was separated by repeated crystallizations and chromatographic separations on columns of alumina. The absorption spectrum of the 2,4-dinitrophenylhydrazone melting at 117°C. exhibited a maximum at 373-377 mμ, and a molecular extinction of $\epsilon = 29{,}239$, calculated on the basis of a molecular weight corresponding to $C_{17}H_{24}O_4N_4$, which is in accord with recently published data (4) to the effect that the 2,4-dinitrophenylhydrazones of α,β-unsaturated carbonyl compounds have absorption spectra exhibiting a maximum at 377-379 mμ and a molar extinction, $\epsilon = 26{,}600$ to 29,200.

*Anal:* Calc'd for $C_{17}H_{24}O_4N_4$: C, 58.6; H, 6.9; N, 16.1. Found: C, 57.7; H, 6.8; N, 16.2.

*Semicarbazone:* A similar distillate fraction produced from another sample of thermally decomposed methyl hydroperoxido oleate was reacted with semicarbazide hydrochloride. The product was a crystalline semicarbazone melting at 159°-160°C.

*Anal:* Calc'd for $C_{12}H_{23}ON_3$: C, 64.0; H, 10.3; N, 18.7. Found: C, 63.0; H, 9.7; N, 19.0.

The aldehyde, which was regenerated by steam distillation of a 4% hydrochloric acid solution of the semicarbazone, gave a positive reaction with ammoniacal silver nitrate, Fehling's solution, and Schiff's reagent.

The regenerated oily product was converted to a 2,4-dinitrophenylhydrazone which melted at 112°-114°C. Insufficient material was available for further purification of the product. However, a 50:50 mixture of the product with the previously described 2,4-dinitrophenylhydrazone (m.p. 117°C.) melted at 114°-116°C.

*Reduction of the Semicarbazone of the Unsaturated Aldehyde.* The semicarbazone (m.p. 159°-160°C.) on hydrogenation with palladium as catalyst gave a crude crystalline product which melted at 94°-96°C. After two crystallizations from ethanol the product melted at 101°-102°C. A melting point of 103°C. has been reported for the semicarbazone of undecanal (5).

The melting point, 101°-102°C., of the semicarbazone was unchanged when admixed with an authentic specimen of the semicarbazone of undecanal, m.p. 103°C. Its melting point was depressed to 96°-97°C. when admixed with an authentic specimen of the semicarbazone of decanal, m.p. 102°C. A mixture of authentic semicarbazones of undecanal and decanal melted at 95°-96°C.

*Anal:* Calc'd for $C_{12}H_{25}ON_3$: C, 63.4; H, 11.0; N, 18.5. Found: C, 63.0; H, 10.9; N, 18.5.

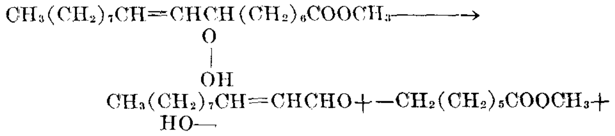
A second fraction obtained from the mother liquors melted at 97°-98°C.

*Anal:* Found: C, 62.4; H, 10.9; N, 18.5.

The above crystalline products, on hydrolysis in aqueous hydrochloric acid yielded an aldehyde which gave positive reactions with Schiff's and Tollen's reagents.

## Discussion

Farmer (1) and others (3, 6, 7) have shown that the autoxidation of methyl oleate results in the formation of a mixture of methyl 8- and 11-hydroperoxido-9-octadecenoic acids, or, more probably, this mixture and in addition, methyl 9-hydroperoxido-10- and 10-hydroperoxido-8-octadecenoic acids. It has been shown in the present work that the thermal decomposition of this mixture of oxidized ester produces α,β-unsaturated aldehydes as fission products, one of which has been identified as 2-undecenal. This aldehyde is probably produced according to the equation



$$\mathrm{CH_3(CH_2)_7CH{=}CH}\underset{\substack{\mathrm{O}\\|\\\mathrm{OH}}}{\mathrm{CH}}\mathrm{(CH_2)_6COOCH_3} \longrightarrow$$

$$\mathrm{CH_3(CH_2)_7CH{=}CHCHO + {-}CH_2(CH_2)_5COOCH_3 + HO{-}}$$

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Qualitative evidence has been obtained in the course of the isolation and purification of 2-undecenal of the presence of the decomposition mixture of analogs and homologs of this aldehyde. Aldehydes of the type represented by 2-undecenal readily undergo oxidation, reduction, and isomerization thus making it possible to account for many of the end products which have been qualitatively and quantitatively identified in various types of oxidizing fat systems.

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# The Hydrolysis of Soap Solutions. II. The Solubilities of Higher Fatty Acids

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IN studying the hydrolysis of soap systems, some investigators state that the fatty acid formed is in excess of its saturation value in certain concentrations; others state that it is always less. The first step is to determine what the saturation values actually are.

In general, there have been few available data for the solubilities of the higher fatty acids though some isolated values are given in the literature. In 1942 Ralston and Hoerr (1) determined the solubilities of the normal saturated fatty acids from $C_6$-$C_{18}$ in water and in a number of organic solvents at the temperatures 0, 20, 30, 45, and 60°C. Saturated solutions of the acids made with conductivity water were titrated with barium hydroxide, using phenolphthalein as indicator. The authors apparently made no correction for carbon dioxide, neglect of which would lead to high results.

### Experimental

The solubilities of capric, lauric, myristic, palmitic, and stearic acids in water were determined at 25° and 50°C., using a conductivity method. Saturated solutions of the pure Kahlbaum acids (except Eastman's capric and some Lepovsky's especially prepared myristic) were prepared by adding crystals of the acids to conductivity water in 100 ml. or 250 ml. Jena glass bottles. They were heated on a water bath to about 60-70°C. for half an hour or longer, with intermittent shaking, then allowed to stand, usually 24 hours or longer. Crystals of capric and lauric acids separated on cooling, leaving the solutions perfectly clear. Excess myristic, palmitic, and stearic acids in finely divided form often remained suspended in the solutions, making them appear cloudy.

The conductivity of these solutions was determined by use of a Grinnell Jones-Dyke type of bridge supplied by Leeds and Northrup, with an oil thermostat at 25°C. ± 0.01° and 50°C. ± 0.05°. Bottles of solution were allowed to come to the desired temperature in the thermostat, then the conductivity cell was filled. The reading was taken after about 15 minutes. The resistance did not remain constant but changed almost continuously even over a period of several hours. The values usually, but not always, increased with time, probably due to sorption of the dissolved acid. The cell was rinsed with acetone to remove any sorbed acid before refilling it for another trial.

The resistance given for the acids in Table I is the average of from 5 to 10 measurements, rounded off to two or three significant figures. Deviation from the mean ranged from 0.7% in the case of capric and lauric acids, to about 7% in the case of stearic and palmitic acids at 25°C. where the solubility is very low.

The equivalent conductivities for the acids at 25° and 50° were obtained from the values of Bunbury and Martin(2) and of Gonick (3). Some of the mobilities were known at 25° and at 90°C., and the values at 50° were calculated by linear interpolation. The equivalent conductivities used at 25 and at 50°C. were the following:

| | 25° | 50° |
|---|---|---|
| Hydrogen ion | 349.8 | 478 |
| Capric acid | 374.7 | 519.2 |
| Lauric acid | 373.3 | 517.4 |
| Myristic acid | 372.3 | 516 |
| Palmitic acid | 371.4 | 514.7 |
| Stearic acid | 370.7 | 513.6 |

The method of calculation was that used by McBain and Taylor (4). The following calculation for the solubility of palmitic acid at 50°C. illustrates the method used for all. The cell constant was 0.02895. The specific conductivity of water at 50° was $1.47 \times 10^{-6}$ (at 25°, it was $0.72 \times 10^{-6}$), and that of the saturated palmitic acid solution at 50°C. was $\frac{0.02895}{13{,}200} = 2.19 \times 10^{-6}$ mhos. The conductivity of conductivity water is assumed to be due to the $H^+$ and $HCO_3^-$ from dissolved carbon dioxide. Therefore the dissolved palmitic acid slightly increased the $H^+$ concentration and decreased the $HCO_3^-$ concentration. The difference between the increased hydrogen ion concentration, $C_{H^+}$, and the decreased $HCO_3^-$ concentration, $C_{HCO_3^-}$ would be equal to the concentration of the free palmitate ion, $C_{P^-}$. In the above measurements the conductivity of palmitic acid is $\frac{2.19}{1.47}$ times that of water. If $V_l$ is the volume in liters containing one mole of acid completely dissociated, and $\Lambda$ is the equivalent

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