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[Received August 2, 1954]

Reactions of Fatty Materials with Oxygen. XVII.[1] Some Observations on the Secondary Products of Autoxidation of Methyl Oleate[2]

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THE PRIMARY PRODUCTS of autoxidation of methyl oleate, as well as other fatty materials, are the subject of intensive study both in this laboratory and elsewhere (2,8,9,10,14,15,17,19). Even in the earliest stages of autoxidation however it is evident (14) that secondary products are being formed concurrently although to only a limited extent. Secondary products of autoxidation have received considerable attention but largely from the standpoint of their separation (4,5,6,11,16,18). At best, this is an intricate, tedious, and often inefficient process in view of the variety of products formed.

The most obvious method for ascertaining the nature and quantity of secondary products and at the same time for eliminating product isolation is determination of the composition of autoxidation mixtures analytically. Although this sounds as though it would be a simple procedure, it has only been within the past few years that reliable chemical, spectroscopic and other physical methods have become available. In an earlier investigation (9) we applied to methyl oleate autoxidized at 35°, 70°, and 100° analytical methods whose reliability had been checked with known mixtures the composition of which simulated that of autoxidized methyl oleate (13). In this initial analytical study (9) much useful and new information was collected, but it was concluded that a more productive approach would involve fractionation of the autoxidation products followed by an analytical investigation of the fractions.

This paper describes some of the results obtained in elaborating the composition of autoxidized methyl oleate by examining fractions obtained by urea complex separations. The results of this study have permitted us a) to reevaluate and reinterpret the analytical results on unfractionated methyl oleate reported earlier (9), b) to obtain a more reliable concept of the composition of autoxidized methyl oleate, c) to understand better why methyl oleate cannot be directly autoxidized to a peroxide content in excess of about 35-40%, and d) to develop a procedure for converting autoxidized methyl oleate (or oleic acid) to a relatively simple system having potential commercial value. Details of this last point are the subject of the following paper in this series (3).

[1] Paper XVI is reference 14.
[2] Presented at the Fall Meeting of the American Oil Chemists' Society, Minneapolis, Minn., Oct. 11-13, 1954.
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Experimental

Starting Material. The preparation of pure methyl oleate has been described (12). It contained 97-99% methyl oleate, less than 0.2% polyunsaturates, and was free of *trans* isomers.

Oxidation Procedure. Oxidations at or above 70° were conducted in the dark in Pyrex flasks. A vigorous, finely dispersed stream of pure oxygen was passed through the methyl oleate, and samples were withdrawn at intervals for analysis or fractionation.

Analytical Methods. These have already been described (13).

Urea Complex Separations. The procedure of an earlier paper was employed (2).

Typical Autoxidation and Fractionation Procedure. Methyl oleate was autoxidized in the dark at 80° until the peak in peroxide content (38%) had been passed and the material contained about 33% peroxide (peroxide oxygen content 1.60%). This required about 96 hours. One hundred and fifty-five grams were added to a hot solution of 728 g. of urea in 2,080 ml. of methanol. The solution was cooled to room temperature and filtered. From the filtrate, 90 g. of pale-yellow oil were recovered; from the precipitate, 62 g. (Table I).

This autoxidation-fractionation procedure was applied to many of the samples described in our previous paper (9). Those particularly studied contained from 5% peroxide to peak peroxide values (35-40%) and from the peak down to 10%. Analytical data similar to that in Table I were obtained but are not given here because of their large number and complexity. The data in Table I are most noteworthy, and the other data are briefly discussed in "Results and Discussion."

Results and Discussion

The motivation for a more detailed study of the secondary products of autoxidation of methyl oleate stemmed from a desire on our part to autoxidize methyl oleate directly to a peroxide content in excess of 35-40%, the maximum usually obtained (9). Various hypotheses to account for this levelling off had

TABLE I

Analyses of (1) Methyl Oleate Autoxidized at 80° Past Its Peak Value to 33% Peroxide Content, (2) Urea Complex-Forming Fraction, and (3) Non-Complex Forming Fraction

Material Analyzed	Wt. Balance[a]	Peroxide Content, %	Hydroxyl Compounds, %	Oxirane Compounds, %	Carbonyl Compounds, %	Iodine Number	α,β-Unsaturated Carbonyls, %[c]
A. M. O.[b]	100%	33	26	24	15[d]	Not detd.[e]	15
Complex-Forming Fraction	40%	3	9	49	34	25	23
Non-Complex-Forming Fraction	58%	41	45	17	7[f]	Not detd.[e]	Not detd.

[a] From 155 g. of autoxidized methyl oleate, 62 g. (40%) were obtained as urea complex and 90 g. (58%) did not form a complex (See Experimental).
[b] A. M. O. = autoxidized methyl oleate.
[c] Determined spectrophotometrically.
[d] Carbonyl oxygen cannot be determined by the chemical method on materials containing peroxides. This value is taken from the last column and is a minimum value.
[e] These values cannot be determined on materials containing peroxides.
[f] Calculated back from carbonyl analysis on the reduced sample.

suggested themselves. First, it was thought that the free acid which formed and accumulated as methyl oleate was progressively oxidized was catalyzing peroxide decomposition. Some support was given to this idea by the fact that oleic acid could be autoxidized to a maximum peroxide content of only about 10-15%. Second, it was considered possible that traces of metals present in or picked up during the purification of methyl oleate were acting as catalysts for peroxide decomposition.

Although dozens of experiments were conducted from 25-100° in the presence of acid neutralizing agents (pyridine, quinoline, sodium bicarbonate, sodium carbonate, etc.) and metal deactivating agents (salts of ethylene diamine tetraacetic acid, phosphoric acid, citric acid, ascorbic acid), in only rare cases did the peroxide content exceed 40% and never exceeded 45%. It soon became evident that the relative rate of decomposition and formation of peroxides was the overriding factor in determining the maximum value. Although this study did not accomplish its objective, it demonstrated that an autoxidation temperature of about 80° afforded the best compromise of reaction time, maximum peroxide content, and ease of control.

In addition to following the formation of peroxides with time, sufficiently large samples were withdrawn periodically and treated with urea (2) to separate peroxides (non-complex-forming) from non-peroxidic material (complex-forming). It was hoped that the most efficient enhancement of concentration of peroxide would take place at or near the peak in peroxide value since this would represent the most effective way to utilize methyl oleate for preparing peroxides. Surprisingly, an interesting and highly significant trend was noted in the composition of both the precipitate and filtrate fractions.

When the autoxidized methyl oleate contained not more than about 15% peroxides, the urea treatment gave a clean-cut separation of peroxides from non-peroxidic material. The peroxide concentrate contained about 90% peroxide, and the yield was substantially quantitative. At the peak of peroxide content (35-40%), but not past this value, the maximum peroxide content which could be obtained in the non-complex fraction was only about 70%. After the peak in peroxide value had been reached however and the peroxide content was decreasing, the urea separation was unsatisfactory in separating peroxides in every case. In a typical experiment autoxidized methyl oleate containing about 33% peroxides could be concentrated to only about 41%.

Analysis of the precipitate fractions obtained in the above separations revealed that these also differed markedly in composition as the autoxidation proceeded. In the first case (autoxidation to a peroxide content of 15%) decomposition of the urea complex yielded a product which was substantially peroxide-free, and contained no *trans*-isomers and only traces of oxirane, carbonyl, hydroxyl, and α-glycol oxygen. It was, in fact, substantially pure methyl oleate and, on distillation, it gave the pure product in high yield. On the other hand, decomposition of the complex from methyl oleate autoxidized to its peak value (35-40%) yielded products which were rich in oxirane, carbonyl, and hydroxyl oxygen and contained only small amounts of methyl oleate (estimated to be about 25% maximum). The comparable material from autoxidized methyl oleate (peroxide content 30-20%), whose peroxide content was declining from its peak value, contained little, if any, unoxidized methyl oleate. This last conclusion, which as we shall see later is inescapable, was originally suggested by the fact that a large increase in peroxide content would have been obtained in the non-complex (filtrate) fraction if any significant amount of methyl oleate had still been present. Complete analysis of the complex and non-complex fractions confirmed this conclusion. These results are shown in Table I.

The values given in the vertical columns of Table I for the content of the various types of oxygenated compounds are based on the hypothesis that the autoxidized material (and fractions obtained from it) contain only one oxygen-containing group in the alkyl chain. This hypothesis is based on the assumption that after the alkyl chain of methyl oleate is attacked by oxygen or methyl oleate peroxides to introduce oxygen (for example, oxirane, hydroxyl, carbonyl, or hydroperoxide), further attack is markedly reduced. Confirmation of the assumption of single attack on the chain in the autoxidation of methyl oleate is based on the following experimentally determined facts: a) up to the peak peroxide value and slightly beyond it, the sum of the various kinds of oxygen-containing compounds plus unoxidized methyl oleate equals 100 ± 10%; b) for a considerable period after the peak in peroxide value and between a peroxide content of about 30-20%, analysis indicates that methyl oleate is absent and the oxygen-containing compounds add up to 100 ± 10%; c) only in truly advanced stages of autoxidation, when the peroxide content has dropped to about 10%, does the sum of the oxygen-containing compounds exceed 110%, showing that multiple attack can occur but probably only after all of the methyl oleate has been singly attacked; and d) during the autoxidation period described in b) when peroxide content is decreasing, the sum of the oxygen-containing compounds in both the complex and non-complex fractions approximate 100%.

The last point is of special significance and requires additional amplification. Let us assume that the A.M.O. of Table I (which corresponds to the stage of autoxidation described in d) of the preceding paragraph) contained a fortuitous balance of methyl oleate, singly attacked methyl oleate, and doubly attacked methyl oleate. Analysis of the material for oxygen-containing functional groups would suggest, of course, that it consisted entirely of singly attacked material. Since methyl oleate forms a urea complex readily in high yield however, the sum of the oxygen-containing compounds in the complex (precipitate) fraction would be substantially less than 100%. Furthermore the urea separation would have resulted in a considerable increase in peroxide content in the non-complex fraction. Doubly attacked methyl oleate, if present, would concentrate in the non-complex (filtrate) fraction since increase in the number of substituents on a long-chain reduces complex-forming ability, and analysis would show a content of oxygen-compounds (computed on the basis of single attack) well in excess of 100%.

The facts are that both the precipitate and filtrate fractions from the urea treatment show a content of oxygen-containing compounds of about 100%. It can be stated unequivocally therefore that the A.M.O. of Table I (and numerous other samples of similar treatment which we have examined) must contain only limited quantities of unoxidized and doubly attacked methyl oleate. After this work had been completed, the brief report by Benton and Wirth (1) came to our attention. These investigators showed that, in the liquid phase autoxidation of n-decane at 145°, a) 80% of the functional groups introduced were in monofunctional compounds, and b) autoxidative attack was approximately equally distributed among the CH_2-groups with only minor oxidation occurring at the terminal CH_3-groups. Since methyl oleate contains the allylic system which is much more susceptible to autoxidative attack than the rest of the molecule, it would be anticipated that even more than 80% of the functional groups introduced would be in monofunctional compounds. This appears to be the case. Also the rather high temperature used with n-decane might be favorable to multiple attack of the molecule.

It is well known that at best analysis of autoxidation mixtures is subject to some error, and the conclusions reported in this paper must be evaluated with this in mind. As will be discussed in a subsequent paper, evidence based on a more elaborate fractionation process suggests that small amounts of methyl oleate can survive lengthy periods of autoxidation and double attack of the chain is detectable even before the maximum in peroxide content is reached. Furthermore, during autoxidation under the mild conditions described in this paper, small amounts of cleavage products and esters (estolides?) appear to be formed throughout. Also, when autoxidation is conducted for prolonged periods until the peroxide value falls almost to zero, polymers can be isolated in substantial quantities, especially when a metal salt catalyst is employed (18).

Also of interest is the content of α,β-unsaturated carbonyl compounds in autoxidized methyl oleate. These have been reported and isolated by Ellis (6, 7). As Table I shows, the bulk of the carbonyl compounds present in autoxidized methyl oleate are α,β-unsaturated carbonyls. These concentrate almost exclusively in the complex fraction. Most likely they are formed by the loss of water from an α-methylenic hydroperoxide. The content of α,β-unsaturated carbonyls in our materials is in the same range reported by Ellis in the oxidation of oleic and elaidic acid, employing a cobalt catalyst and a different method of analysis.

Acknowledgment

The authors wish to thank C. Roland Eddy for the ultraviolet spectrophotometric analyses for α,β-unsaturated carbonyls.

Summary

Methyl oleate, autoxidized for short and long periods of time, has been fractionated with urea. Up to a peroxide content of about 15% the autoxidation mixture can be cleanly separated into a peroxide concentrate containing 90% peroxide and unoxidized methyl oleate. From about 15% peroxide to the maximum peroxide content (35-40%) concentration to only about 70% peroxide can be obtained, and the remaining material is largely a mixture of oxygenated compounds and residual methyl oleate.

If the autoxidation is conducted beyond the peak value in peroxide content, little, if any, concentration of peroxide can be obtained. Also, beyond the peak in peroxide value and in the range of 30-20% peroxide, methyl oleate is substantially absent and the autoxidation mixture consists almost entirely of oxygenated compounds containing only one functional group in the chain.

Evidence is presented which shows that in the autoxidation of methyl oleate substantially all of it undergoes single attack by oxygen (or peroxides) before any significant quantity of multiple attack occurs.

α,β-Unsaturated carbonyl compounds are among the important secondary products of autoxidation.

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[Received August 9, 1954]