Since most tall oils contain from 5-10% of sterol or other inert materials, a correction factor was introduced into the above equation. The average number of ethylene oxide groups in a sample of tall oil was obtained by subtracting the average molecular weight of the original tall oil from that obtained from the saponification equivalent determined above and dividing the difference by 44, *i.e.*, the molecular weight of ethylene oxide. Table II lists molecular weights on a number of polyethenoxy tallates prepared in this laboratory and varying in their tall oil composition from predominantly fatty acids to those containing mostly rosin acids. The molecular weights determined by the above saponification method are compared to molecular weights obtained from actual weights of tall oil and ethylene oxide used.

TABLE II
Molecular Weights of Various Samples of Polyethenoxy Tallates

Sample No.	From actual weights of tall oil and ethylene oxide	Determined by the saponification equivalent
1	864	830
2	864	865
3	879	887
4	867	890
5	1,200	1,250
6	900	972
7	873	825
8	873	898
9	906	905

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Application of Tracer Techniques to Studies on Autoxidation Reactions[1]

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THE autoxidation reactions of the fatty acids and esters involve intricate mechanisms, possibly of varied types. The voluminous literature (1) without much clarification of the picture for more than a century will add confirmation to the point. The actual advancement of our knowledge in this field may be attributed to the research carried on since 1936 by virtue of the advantages available to the present-day chemist, especially the tools from the school of physics and physical chemistry. Furthermore the approach to the studies on the mechanisms of autoxidation through reactions of oxygen with the simpler and known compounds, methyl oleate, linoleate, and linolenate, has facilitated such progress. Following these modern trends, it is felt that tagging of these simpler compounds with the suitable tracer isotopes may help to reveal some aspects of the mechanisms of autoxidation. However in the initial studies (2) autoxidation of methyl 9,10-dideutero-oleate gave results apparently contradictory to the general expectation, and no definite conclusions were reached. Contrary to expectations, dideutero-oleate showed a much longer induction period than oleate. It was not known whether the induction periods were due to trace impurities or were inherent properties of the compounds. The purification of these compounds through chromatography did not change such induction periods. Moreover deuterium contents of the water, volatiles, and residues of dideutero-oleate were unexpectedly uniform, calculated on a percentage basis. The purpose of the present paper is to show that these apparent contradictions are the indirect guides to the goals originally sought and may be correlated to the existing information on autoxidation of mono-olefinic substances.

Tracer techniques have been used in different chemical and biological reactions with good results but have not been used in autoxidation reactions before. The isotopes that can be used in the studies of autoxidation reactions of fatty acids and their esters are: deuterium, ($^2_1H \sim D$); heavy oxygen, $^{18}_8O$; stable carbon isotope, $^{13}_6C$; radioactive carbon isotope, $^{14}_6C$. Deuterium (99.0-99.5% pure) may be used for such studies. Heavy oxygen, to present knowledge, cannot be obtained in a purer state than 70 to 80% concentration and is used only in special cases involving decomposition of peroxides. When heavy oxygen in pure form becomes available, its use may throw some light on the intricate chemistry of the peroxides. The stable isotope C^{13} and the radioactive isotope C^{14} can play important roles in autoxidation studies, especially in locating the point of scission of the carbon chain during such reactions.

From the free radical mechanism of autoxidation reactions, the positions most involved are the carbon and H atoms of the double bond and of the methylene group alpha to the double bond. The methylenic group alpha to the carboxyl group, though very reactive in organic ionic reactions, has been neglected in autoxidation reactions. Tracer techniques may possibly detect these positions of reactivity. Two different alpha methylene C-atoms in the same molecule may be differentiated by incorporating radioactive C^{14} in one position and stable C^{13} in the other.

The methylenic group alpha to double bonds in methyl oleate or octadecene tagged with deuterium (3) C^{14} or C^{13} may be obtained from the 8-C ester via alcohol, bromides, etc. The other positional isomers may be synthesized by choice of proper fragments. Such synthesis has already been accomplished (4-7). The recent synthesis of linoleic acid by work-

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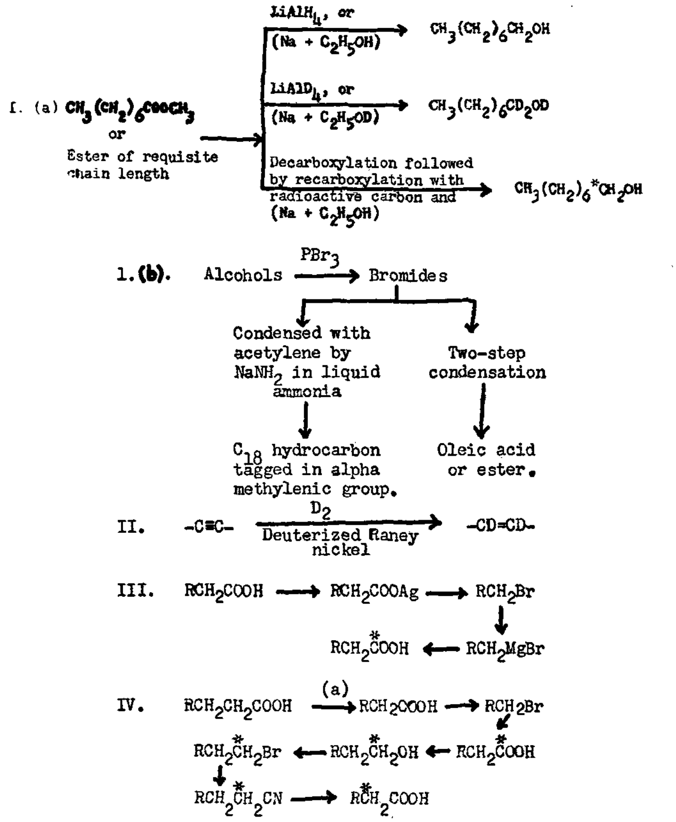
ers in this country (8) and in England (9) offers prospects for tagged derivatives of this dienoic acid also. The deuterium may be introduced into the double bond by selective deuteration of the corresponding acetylenic compound in the presence of deuterized Raney nickel (10). Through decarboxylation and recarboxylation the carboxyl group and its alpha methylene group may be labelled (11). The general reactions for synthesis may be represented as follows:



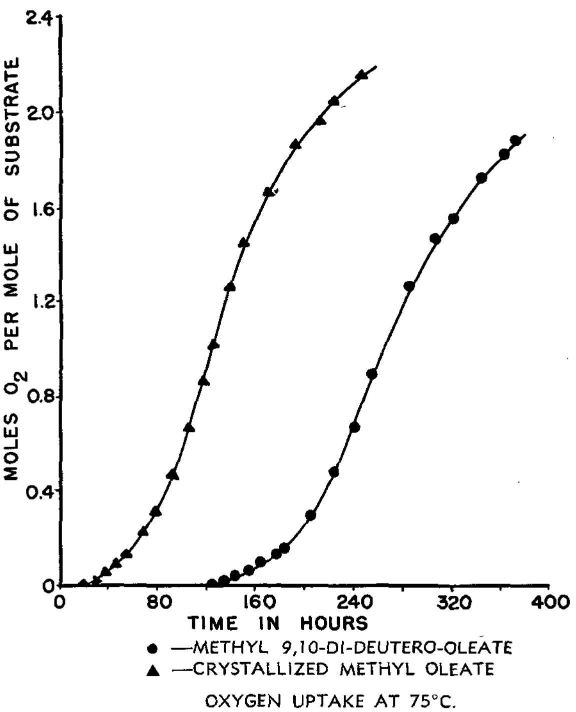
(a) This degradation may be accomplished by several standard methods for decreasing one carbon at a time in an aliphatic acid.

The use of radioactive compounds will be limited mainly by the elaborate precautions necessary for their safe handling. Most laboratories are not equipped to work with radioactive isotopes, but in the hands of workers who have access to proper facilities radioactive carbon C^{14} may be an effective tool for research in autoxidation reactions. However from the point of view of initial attack the replacement of alpha methylenic and double bond hydrogen atoms with deuterium should reveal some phases of the mechanics of autoxidation reactions. This, in combination with the availability of deuterium in pure form and the ease of handling and analysis by mass spectrography, led to the use of this isotope in preference to others already mentioned.

In the studies reported below autoxidation of methyl oleate and methyl 9,10-dideutero-oleate at 75°C. gave evidence of four distinct stages of reactions. Since the induction period is usually attributed to minor impurities, the substrates were passed through a chromatographic column with a view to removing these impurities. The points of attack by oxygen on substrates, formation of peroxides, and their decomposition giving rise to water and volatile products have been noted. An attempt at elucidation of these processes on the basis of the present knowledge of bond strength of the different atoms in the molecules involved has also been made.

Procedures

The 20 g. each of crystallized methyl oleate and methyl 9,10-dideutero-oleate (2) were separately dissolved as a 10% solution in n-heptane, which was freed of the unsaturated substances by treatment with fuming sulfuric acid twice, followed by washing with distilled water, drying with anhydrous calcium chloride, and finally by distillation. It was then passed through a 1 × 18″ column of alumina (dried at 400-450°C. and freed of oxygen by alternate suction by vacuum pump and flushing with oxygen-free nitrogen several times) and eluted with n-heptane until no product came through. The first two fractions and the last two fractions were rejected out of 16 fractions obtained and the middle fractions were combined (methyl oleate: b.p., 172-173° at 2 mm.; I.N., 85.5; n^{20}, 1.4521. Methyl 9,10-dideutero-oleate: b.p., 173-174° at 2 mm.; I.N., 84.9; n^{20}, 1.4518. Deuterium content, 5.05 atoms per cent of hydrogen plus deuterium) and were used for autoxidation reactions. For iodine number Wijs (½ hour) method was applied. The methods and techniques of autoxidation used were similar to those reported by Deatherage and Mattill (12) and Khan, *et al.* (2), in which oxygen is bubbled through the substrate at 75°C. and volatile materials are collected in dry ice traps. Each of the deutero-compounds was converted to water by micro-combustion (13). This water was decomposed into deuterium and hydrogen, which were subjected to mass spectrographic analysis to obtain the atom percentages of deuterium. The "memory effect" was avoided by a few extra runs in each of the above steps of deuterium analysis.

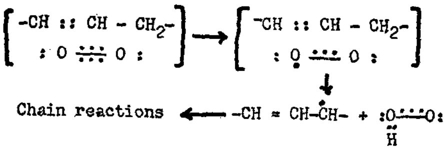


OXYGEN UPTAKE AT 75°C.

FIG. 1.

Results and Discussions

Figure 1 shows the trend of oxygen consumption by the two substrates, methyl oleate and methyl 9,10-dideutero-oleate. The separate stages of oxidation are easily recognized in both the substrates. If the minor impurities, highly polar in character, that may act as antioxidant may be assumed to be removed by chromatographic treatment, then the induction period (taken as period of time required for oxygen absorption to begin) may be an inherent property of these substances. As indicated by many authors, the induction period is the indication of a potential energy barrier in chemical reactions. This is either increased or decreased by the experimental conditions whereby the induction period is never found reproducible. In the present investigations this property was shown to be reproducible by keeping the experimental conditions constant as far as possible. No experimental evidence is so far available to throw any light on this phase of autoxidation. However, the simple replacement of hydrogen atoms on the double bond by deuterium atoms increases the induction by more than 100 hours (Fig. 1). This may point to the fact that the double bond plays some role in the stage of autoxidation. The physico-chemical concept of the acquisition of sufficient energy by collision of oxygen molecules with those of the substrate and subsequent formation of a complex by virtue of the electron concentrations at the double bond will possibly offer the best explanation of the induction period. The concept of electron clouds over the double bond and its adjoining atoms from the British school of electronics (13a) in order to indicate the olefinic character of a molecule may pave the way to understanding such complex formation. These complexes may change the energy relations and initiate the free-radical chain reactions involved in general autoxidation:

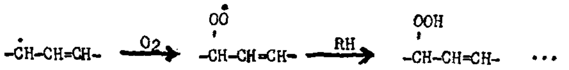


.... (A)

The idea of complex formation is not new but very well-known in the cases of copper-catalyzed oxidation and the reactions involving porphyrin enzyme systems. The isotopic effect of deuterium (maybe of the second order) delays such activation effect of the double bond and subsequent dissociation of alpha methylenic hydrogen. Such activation is so sensitive as to be effected even by functional groups, especially ester or acid in the substrates that may add to the polarity of the medium, not to speak of the antioxidants or the prooxidants. Hence a minute effect by deuterium may account for the lengthening of the induction period and point indirectly to the role of double bond in the initiation reaction and of the alpha methylenic group in the final autoxidation. The physico-chemical concept may be even preferable to Farmer's concept of the diradical (14). The diradical mechanism postulates the formation of an unstable system, and such a consequence is usually considered unfavorable in a reaction sequence from the kinetic point of view. The former provides gradual excitation of the oxygen molecule to break one of its three electron bonds (15) by complex formation with the substrate and the removal of one hydrogen atom from the alpha methylenic group. Both oxygen molecule and substrate result in free radicals stabilized by resonance (cf. reaction, A). Shifting of the double bond may occur by this resonance to explain the formation of the hydroperoxides at 8 through 11 positions during autoxidation reactions (16). Initial products formed during autoxidation of methyl oleate at 0°-25° with and without catalysis were found to be pure monohydro-peroxides with double bonds intact but shifted in position and cis-trans configuration through chemical and infrared analyses. Further confirmation of complex formation and acquisition of energy is added by the next stage of peroxidation period during autoxidation. In this stage oxygen absorption begins to be appreciable, increasing gradually to a maximum rate of main autoxidation. Thus 90-98% of the absorbed oxygen may be accounted for as forming peroxides. As soon as the critical amount of the peroxides is formed, the period of main autoxidation or steady state starts. Then the formation of peroxide is balanced by decomposition that adds energy to the system and leads to more chain formation and an increased rate of autoxidation. By stopping the main autoxidation reaction at an intermediate stage (about 1 mole of oxygen absorbed per mole of substrate, methyl oleate, or deutero-oleate (Figure 1) it is found that 90-95% of the total water obtained throughout the whole course of the autoxidation is formed during this initial period of steady state exactly after the peroxidation period, possibly from the decomposition of hydroperoxide. No appreciable amount of volatile organic matter is produced at such a stage. Consequently most of the volatile organic products are formed at a later stage of the steady state as a result of the scission of the main c-chain before the period of decline, when the rate of absorption of oxygen falls off due to a lack of available active centers in the substrate. The duration of the steady state is almost the same for both oleate and deutero-oleate and unaffected by any impurity, antioxidant, or prooxidant, and consequently reproducible. This may point to the common point of autoxidation in both the substrates which is evidently alpha methylenic group. The deuterium distribution among the different products from autoxidation of deutero-oleate in atoms percentage of hydrogen: water 5.5%, volatile organic matter 3.2%, and residue 4.5% remains the same, no matter how the autoxidation is started. This again lends support to one major pathway for autoxidation, dependent on the reactions of peroxides providing energy and the alpha methylenic group propagating chain reactions.

In order to locate points of scission and decomposition in the products of autoxidation reaction, it may be necessary to determine the possible weaker points. Table I records the bond strengths between different atoms in such molecules, as collected from different reliable sources. The C—H bond adjacent to a double bond is labile; its value of dissociation falls off due to resonance stabilization during the activated stage in autoxidation reaction and further decreases while it is in transition to the stable state of a free radical (cf. benzene ring). The C—H bond strength is very low in the natural linoleate system, and so the induction period of autoxidation is considerably low and sometimes undetectable. The values for O—O, O—H, and C—O bonds will indicate the point of scission of —CH OOH. The O—O bond strength is always low, and its easy dissociation has been proven by various workers by identification of the products. One bond in the $C{=}C$ bond is easy to break, but the resulting product is not stabilized; rather it is unstable. The weak C—C bond between carbons α and β to the double bond may bring forth some clues to the scission products. The knowledge of the bond strength and its dissociation energy will also indicate the importance of the applications of tracers to the autoxidation reactions. Evidently deuterium in the positions of labile hydrogen may indirectly determine the point of activity in a molecule by decreasing, by virtue of its isotopic effect, such lability and consequently the reactivity. Heavy oxygen may play the same role in scission of the O—O bond (17). However the distribution of these tracers among the different products of autoxidation may contribute to the disclosure of many facts about autoxidation reactions. In the case of studies on the scission of the main C chain, the radioactive C^{14} and the stable C^{13} isotopes may be of great importance. Their distribution among the different organic products along with the amount of their radioactivity may lead to identification of the products or at least to some idea about their molecular size and consequently their parent source.

The O—O bond strength and the formation of water during the period of maximum peroxide formation and decomposition will help trace the origin of such water formation. Infrared and chemical analyses showed that these initial peroxides are hydroperoxidic. The initiation reactions may form hydroperoxides:



$$-\dot{\mathrm{C}}\mathrm{H{-}CH{=}CH}- \xrightarrow{\mathrm{O_2}} -\overset{\mathrm{O\dot{O}}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH{=}CH}- \xrightarrow{\mathrm{RH}} -\overset{\mathrm{OOH}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH{=}CH}- \quad \cdots \quad \text{(B)}$$

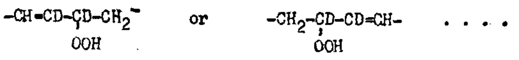
The hydroperoxides may then decompose during the propagation or the main autoxidation reactions as:

$$-\overset{\mathrm{OOH}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH{=}CH}- \longrightarrow -\overset{\dot{\mathrm{O}}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH{=}CH}- + \dot{\mathrm{O}}\mathrm{H} \quad \cdots \quad \text{(C)}$$

These free radicals may increase the rate of autoxidation, and the $\dot{O}H$ radical may at the same time contribute to the formation of water without scission of the carbon chain. This will also support the experimental observation that the formation of the major portion of water is not accompanied by that of the volatile organic scission products. Experimental evidence for such decomposition has been produced by Vaughan and his coworkers (18), Swift, *et al.* (19), Schepartz and Daubert (20), Martin, Schepartz, and Daubert (21), Brekke and MacKinney (22), Holman, *et al.* (23), Swift (24), and Kawahara and Dutton (25). The deuterium that is found in water may come from the deuterium atoms at 9 and 10 positions due to resonance:

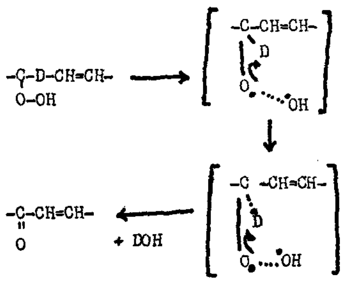
$$-\dot{\mathrm{C}}\mathrm{H{-}CD{=}CD{-}CH_2}- \longleftrightarrow -\mathrm{CH{=}CD{-}}\dot{\mathrm{C}}\mathrm{D{-}CH_2}- \quad \ldots\ldots \quad \text{(D)}$$

and consequent formation of the peroxides.



$$-\mathrm{CH{=}CD{-}}\underset{\mathrm{OOH}}{\underset{|}{\mathrm{C}}}\mathrm{D{-}CH_2}- \quad \text{or} \quad -\mathrm{CH_2{-}}\underset{\mathrm{OOH}}{\underset{|}{\mathrm{C}}}\mathrm{D{-}CD{=}CH}- \quad \ldots\ldots \quad \text{(E)}$$

Their decomposition through hydroxyl and carbonyl radicals may form deuterium-containing water. It may be reasonable to believe that hydroxyl radical may extract D-atom from the carbonyl radical as soon as it is formed without any time lag due to its excess energy involved (cf. Walsh, 26). This process may take place as follows:



Active intermediates
of carbonyl and
hydroxyl radicals

In the case of hydrogen compounds ordinary water (H_2O) will be formed by the above process. By consideration of all possible decomposition processes of these peroxides, the deuterium content in the water formed may be proved to be derived from this normal decomposition of hydroperoxide. Furthermore the findings of Holman, *et al.* (23) and Swift (24) related to the unsaturated carbonyl compounds may add some confirmation to the occurrence of such a process during the autoxidation reactions. These carbonyl compounds may be very unstable and also susceptible to autoxidation and elusive in respect to detection by chemical means. The formation of deutero-water by the oxidative attack or cleavage at the double bond (2) does not seem to occur in the case of free radical mechanisms for the monoethenoic substances to an extent sufficient to account for formation of such water during autoxidation. It may be an insignificant minor reaction, causing no appreciable change in the reaction products at the stage of water formation. Thus the period of the formation of water, the energy contents available in the system of the reactions, the dissociation energy of the O—O bond, the behavior of the free radicals, especially that of $\dot{O}H$ (26, 27, 28), all combine to show the hydroperoxides at 8 through 11 positions of methyl oleate are responsible for water formation. Hence hydrogen atoms at these positions may contribute to water, depending on the proportions of the stable hydroperoxides formed in each such position. In any case it must be remembered that the dissociation energy of a bond may be entirely different in an activated system where the highly energetic bodies like free radicals carry on reactions. Probably a neutral molecule, acquiring energy from a free radical by collision and subsequent dissipation, may need considerably lower energy for such dissociation at the vulnerable points noted.

Max, *et al.* (3) did not find deuterium in water by autoxidizing $(-CD_2-CH{=}CH-CD_2-)$ tetradeutero octadecene, since it is hard to initiate autoxidation through the α $-CD_2$ group. The C—D bond may be so strong that the labilizing effect of the double bond is not sufficient to bring down the value of this bond strength for such initiation. When the autoxidation was forcefully started, C—D still remained immune to the free radical attack, which may seek preferentially any other weaker points in the chain. It may be that other C—H bonds in the chain are weaker than this α C—D bond.

From the previous works (29-32) it may be shown that C—D bond strength exceeds C—H bond by *ca.*, 1.7-3.0 K cal., depending on its location and experi-

TABLE I

Free Radical Dissociation

Bond	Nature	Bond strength *(K. Cal)*
C—H	Ordinary as in CH_4 etc	99-100
C—H	Hydrocarbons	$p>s>t$
C—H	Ethylene	91
C—H	Labile adjacent to one double bond	80
C—H	Same as above but activated due to resonance	< 64
C—H	Doubly flanked by double bond	$\ll 64$
C—H	Adjacent to conjugated double bonds	> 64
O—O	In hydrogen peroxide (HO—OH)	64
O—O	In hydroperoxide (CO—OH)	66
O—O	Di-alkyl peroxide (CO—OC)	> 66
O—O	Di-acyl peroxides	< 64
O=O	In oxygen molecule	118
O—C	In peroxides	87
O=C	In aldehyde	174
O=C	In ketone	174
O—H	In H—O—H	110
O—H	In $H—O_2—H$	100
O—H	In $RO_2—H$	>100
—C=C—	Carbon to carbon double bond	145
—C=C—	—C—C— (one bond fission)	64
—C—C—	General	81
—C . . . C—C=C—	Bond between C-atoms, alpha and beta to double bond	< 81

mental conditions. This may account for the anomalous behavior of this compound. Their conclusion as to the alpha hydroperoxides not contributing to the formation of water may not be so valid because there may not be formed a sufficient amount of hydroperoxides at the alpha methylenic group with deuterium atoms. However the slow rate of autoxidation of this compound (1/6th the normal rate) and the failure to undergo normal course of autoxidation may give rise to the question: have the deuterium atoms in this compound blocked the points that help carry out the normal course of autoxidation? As a matter of fact, this is what may have happened (30), and consequently no appreciable amount of alpha hydroperoxides has been produced to contribute to any water formation. The isotopic effect of deuterium has thus indirectly located the vulnerable points during autoxidation. This may be a stumbling block in the studies on the general kinetics and the course of autoxidation by the use of deuterium as tracer in the methylenic group, alpha to the double bond. However deuterium, if properly incorporated in a molecule, may indicate the seat of the reactions, chemical or otherwise, by virtue of its isotopic effect.

Free radical mechanism prevalent in autoxidation reactions are very elusive. The same radical may behave differently under different experimental conditions. Following the suggestion of Remick (33), the free radical mechanism in the present investigation is based on the general trend of the chemical reactions and the possible identity of the products formed. Considering all points, it may be said that deuterium-tagging does not give direct clues to mechanism but indirectly hints to the many important facts related to the mechanisms involved. In the future, with the progress of our knowledge of radioactive and non-radioactive isotopes and of their behavior in different media, these tracers may help reveal the intricate mechanisms of the autoxidation reactions.

Summary

The tracers containing deuterium, carbon isotopes, and heavy oxygen that may be applied to the studies on autoxidation reactions are described. The autoxidation of the deuterated compounds formed by replacing hydrogen atoms on the double bond has given concrete experimental evidence for the following phenomena of autoxidation reaction: a) initial attack of oxygen at the double bond and the inherent induction period, b) the propagation of autoxidation by attack on the methylenic group, alpha to the double bond during the steady state, c) the presence of resonance in the free radicals formed and consequent shifting of the double bond, and d) the location of the hydrogen atoms contributing to the formation of the major portion of the water.

These investigations have led to the elucidation of some aspects of the mechanism of decomposition of peroxides and consequent formation of hydroxyl radicals, which attack the substrates at certain preferential points giving rise to water. They also provide the mechanisms of cleavage and formation of the volatile products.

Our experiments have also established four different and distinct stages of autoxidation. Water formation in autoxidation is shown to be the outcome of the primary decomposition of peroxides, mainly hydroperoxides, and the formation of the organic volatile products to be that of the secondary decomposition at a later stage. These processes have been correlated to the bond strengths of the different atoms in the substrates and the resulting products. The advantages and disadvantages of the application of these tracer techniques to autoxidation reactions in general are also discussed.

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Report of the Smalley Committee, 1952-53

FOLLOWING custom the reports of the four subcommittees of the Smalley Committee represent the complete report. These reports will be individually recorded, but before doing so the chairman would like to offer some general comments.

Some 3,215 samples were distributed and the results tabulated during the year. While the members of the committee and subcommittees have been fully cooperative and effective and the chairman expresses his thanks for their work and guidance, certain organizations and individuals merit special note.

The American Oil Chemists' Society and the fat and oil industry are indebted to the following for the preparation and distribution of the samples:

G. Conner Henry and Law and Company for the Oil Seed Meal and Oil Seed Samples.
J. P. Hewlett and the HumKo Company for the vegetable oil samples.
K. H. Fink and Armour and Company for the tallow and grease samples.

Special appreciation is also expressed to:

A. S. Richardson for tabulating the cottonseed oil results.
F. R. Earle for tabulating the soybean oil results.
R. T. Doughtie for tabulating and grading the oil seed results.
R. A. Decker for calculating the grades on the vegetable oils.

The chairman has been fortunate in having excellent committee support.

SMALLEY COMMITTEE
R. W. BATES, chairman

Subcommittee on Oil Seed Meal

We present herewith the 35th report of the subcommittee on Oil Seed Meal. This year 15 samples were distributed to 110 collaborators. The samples were sent to 27 states, 5 Canadian provinces, and 2 South American countries.

A graph has been prepared, showing the number of collaborators (based upon the percentage of the total) who were within the recognized tolerance of the accepted average. The general average of all samples was also calculated and the values of the past five seasons listed for comparison.

It will be noted that the moisture results were not quite as good this season, 52% being within the tolerance. The oil and nitrogen results were in line with past seasons, being 52.1 and 50.2%, respectively.

Sample No. 10 was a soybean meal, and there was a lack of knowledge on the part of some of the collaborators as to the method applicable for the determination of moisture. This resulted in poor agreement, and the collaborators were not graded on moisture results of this sample.

To eliminate ties for second place on the determination of moisture the results of those tied for second place were recalculated, using no tolerance.

Those collaborators with the highest grades this season were:

1. *On Oil and Nitrogen.* The American Oil Chemists' Society Cup for the highest proficiency in the determination of oil and nitrogen will be awarded to P. D. Cretien (#1) of the Texas Testing Laboratory, Dallas, Tex., with a grade of 99.985%. Mr. Cretien won the cup in 1951 and again in 1952 and, in accordance with custom, will be given permanent possession of the cup. He joins the select group consisting of The Battle Laboratories, E. H. Tenent Sr., D. B. McIsaac, the late W. F. Hand, and R. R. Haire who in years gone by have won the cup at least three times.

In second place was Edward R. Hahn (#8) of the Hahn Laboratories, Columbia, S. C., with a grade of 99.982%.

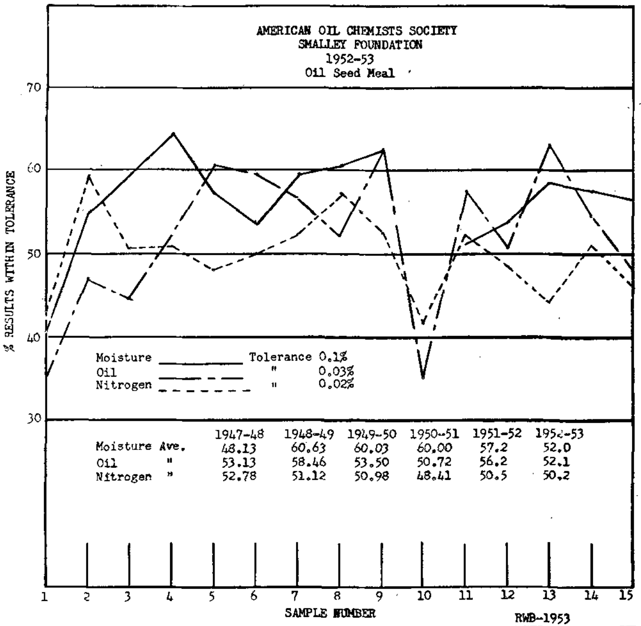
Honorable mention (no certificate) is given to R. C. Pope of the Pope Testing Laboratories of Dallas, Tex., with a grade of 99.971%.

2. *On Oil.* Two were tied for the highest standing in the determination of oil with grades of 100.0% proficiency. These were:

R. C. Pope (#22), Pope Testing Laboratory, Dallas, Tex.
E. R. Flack (#72), Allied Mills, Peoria, Ill.

Honorable mention is given to the following with grades of 99.988%:

P. D. Cretien, Texas Testing Laboratories, Dallas, Tex.
W. H. Kesler, Woodson-Tenent Laboratories, Little Rock, Ark.
W. F. Beedle, Geo. W. Gooch Laboratory, Los Angeles, Calif.



Geographical Distribution

Tex.	22	Iowa	2	Pa.	1
Ill.	9	Ohio	3	N.H.	1
Calif.	8	Ariz.	4	N.Y.	1
Ga.	6	Minn.	1		
Ala.	3	Kas.	2		
S.C.	5	N.C.	2	Canada	8
Mo.	4	Wisc.	1	Brazil	1
Miss.	5	Ind.	1	Argentina	1
La.	4	Conn.	1		
Tenn.	4	Wash.	1		
Ark.	3	Va.	1		
Okla.	4	Neb.	1		

Total 110