

Oxidation of Methyl Oleate Induced by ^{60}Co γ -Radiation

Part 1.—Pure Methyl Oleate

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The ^{60}Co γ -radiation-induced oxidation of pure methyl oleate at dose rates below 1.3×10^{18} $\text{eV l.}^{-1} \text{ sec}^{-1}$ has been shown to occur by a chain mechanism in which the O_2 absorbed is quantitatively converted to hydroperoxide at conversions up to about 8 %. The reaction has an overall activation energy of 6.4 kcal/mole, and involves a temperature-independent production of initiating radicals from methyl oleate with a G -value of 5.36. HO_2^{\cdot} radicals do not participate in the initiation reaction since the yield of radiolytic hydrogen ($G = 1.01$) from methyl oleate is unaffected by the presence of O_2 . The appearance of a peak in the absorption spectrum at $219 \text{ m}\mu$ is attributed to α, β -unsaturated ketones produced in the chain-termination reaction. The rate of oxidation of methyl oleate dissolved in methyl stearate, for which G_{radical} was 5.24, increases linearly with the solute concentration.

The oxidation of many organic liquids induced by ionizing radiation occurs under suitable conditions¹ by the hydroperoxide chain mechanism,² involving a temperature-independent initiation resulting from the radiolytic formation of radicals from the substrate.³ During the initial stages of the oxidation of cumene, cyclohexene and tetralin¹ the oxygen consumed is quantitatively converted into hydroperoxide at temperatures around 30°C. Moreover, the radiation-induced oxidation of methyl oleate produces the same isomeric hydroperoxides in essentially the same distribution as the autooxidation initiated by u.-v. light.⁴ However, in the oxidation of methyl oleate and oleic acid considerable yields of carbonyl compounds accompany the peroxides,⁵ and Burlakova *et al.*⁶ showed that the primary products of the radiolytic oxidation of methyl oleate include epoxides. In neither of these investigations^{5, 6} was the absorption of oxygen measured so that the data did not indicate whether a material balance had been obtained.

In view of this uncertainty and because methyl oleate is an important model compound for food lipids we have examined the ^{60}Co γ -radiation-induced oxidation of the carefully purified ester by measuring both the absorption of oxygen and the formation of hydroperoxides. This also provides a basis of comparison for a study of the radiolytic oxidation of methyl oleate emulsions which is described in the succeeding paper.⁷

EXPERIMENTAL

MATERIALS

The purification of methyl oleate (B.D.H. Ltd) was based on the procedure of Wheeler and Riemenschneider,⁸ which efficiently removes the more rapidly oxidizable polyunsaturated impurities. After drying with anhydrous CaSO_4 it was fractionated at pressures of about 3 torr in a 33 in. column packed with 1/16 in. Dixon gauze rings. The vapour pressure

data of Scott *et al.*⁹ were used to select the methyl oleate fraction, which was subsequently handled in an inert atmosphere. An acetone solution of the ester (0.1 g/ml) was kept at -37°C for 2 h and then filtered. The filtrate was diluted with half its volume of acetone and similarly crystallized at -60°C , the methyl oleate crystals being washed with cold acetone, melted, and the residual acetone distilled off. The resulting methyl oleate was subjected to the crystallization cycle again and the product passed through chromatographic alumina to give a colourless liquid. This was refractionated and collected in receivers (equipped with glass diaphragm break-seals) in which it was degassed and sealed off under vacuum. These receivers were stored in the dark and fitted directly to an automatic burette as required.

The above stages of the purification of methyl oleate were followed by gas chromatography using a 3-m 1/4 in. ext. diam. stainless steel column packed with 20 % diethylene glycol succinate polyester on 60-80 mesh Chromasorb P and operated at 200°C ¹⁰ in an F and M model 609 instrument equipped with a flame ionization detector. The final material was greater than 99.7 mole % methyl oleate and contained no detectable methyl linoleate ($<0.09\%$), methyl linolenate ($<0.06\%$), methyl palmitate ($<0.02\%$) or methyl stearate ($<0.05\%$), but did contain 0.13 % of an unidentified compound having a retention time between those of the palmitate and stearate. Retention times and calibration data for the above methyl esters dissolved in methyl oleate were determined with pure samples (Applied Science Laboratories, Inc., Pennsylvania). On operating the column initially at 75°C the acetone content of the purified methyl oleate was less than 0.01 mole %. Addition of acetone in amounts up to 1.7 mole % caused no detectable change in the oxidation rate at 30°C . The rate was measured at various stages of the purification and was found to decrease and become linear to a greater conversion as the polyunsaturated impurities were removed. Moreover, no significant change occurred in the content of the unidentified impurity on oxidation to 10 % conversion, so that it is probably a saturated compound and has no effect on the rate of oxidation. All of the batches of methyl oleate employed oxidized at the same rate, within experimental error, under a selected set of irradiation conditions.

The purified methyl oleate was free from conjugated diene impurities since the absorption spectrum showed no peak in the region of $230\text{ m}\mu$;¹¹ in Spectrosol cyclohexane solution $\epsilon_{230\text{ m}\mu}^{20.0^{\circ}} = 28.0$. The crystallization and alumina treatment both reduced the absorption in the u.-v. region. The density of the pure methyl oleate $\rho_{4^{20.0^{\circ}}} = 0.8733$ is in reasonable agreement with the data of Gouw and Vlugter,¹² from which the temperature coefficient was calculated.

Oxygen from a cylinder was passed through columns of silica gel and KOH and then through a trap at -78°C .

2,6-Di-*t*-butyl-*p*-cresol (Koch-Light Laboratories Ltd) was twice recrystallized from methanol and dried under vacuum at room temperature. The absorption spectrum of a methanol solution had a peak at $278\text{ m}\mu$ with $\epsilon_{278\text{ m}\mu}^{20.0^{\circ}} = 1.88 \times 10^3$ in agreement with published values.^{3, 13}

Methyl stearate (B.D.H. Ltd., specially pure) was recrystallized from acetone at -37°C as described above, to remove any methyl oleate present. This resulted in a 16 % decrease in the initial oxidation rate, which was unchanged on further recrystallization.

All other materials were of Analytical Reagent grade.

MEASUREMENT OF OXYGEN ABSORPTION

The rates of oxygen absorption at selected pressures were measured automatically in a constant pressure apparatus.¹⁴ Oxidations were performed in flat cylindrical glass reaction vessels of 30 mm int. diam. and 11 mm int. thickness, and having a 7 mm diam. side tube incorporating a diaphragm break-seal and a narrow bore side-arm fitted with a ground-glass joint. Weighed amounts of any additives required were introduced into the vessel prior to methyl oleate, which was added from an automatic burette through an adaptor which excluded contact with air. The samples, of approximately 5 ml total volume, were then degassed and sealed off under vacuum. The reaction vessel was immersed in a thermostat controlled to $\pm 0.02^{\circ}\text{C}$ and clamped at reproducible positions with respect to a

200 curie ^{60}Co source¹⁵ which was also immersed in the thermostat. To keep the liquid saturated with oxygen the reaction vessel was shaken at measured rates by means of a motor driving a Kopp Variator (Allspeeds Ltd.) connected, by an eccentrically mounted rod, to the bar supporting the reaction vessel. The latter was joined to the oxygen absorption apparatus via a flexible glass spiral. After evacuating the system and filling with oxygen to the required pressure, the break-seal was fractured by a glass-covered magnet, and the constant pressure apparatus controls set before introducing the ^{60}Co source to start the reaction.

HYDROPEROXIDE ANALYSIS

The formation of hydroperoxides was measured in the reaction vessels used for the oxygen absorption runs, but having a ground glass joint through which samples were withdrawn and oxygen introduced, the pressure being maintained at about 850 torr. The samples were analyzed immediately after removal from the reaction vessel by an iodometric method similar to that of Wibaut *et al.*¹⁷ with isopropanol added to keep the analytical mixture homogeneous. There is no addition of I_2 to methyl oleate under the analytical conditions since analyses of 99.8 % t-butyl hydroperoxide with or without the addition of methyl oleate gave identical results. Saunders *et al.*¹⁸ have shown that hydroperoxides constitute about 95 % of the peroxides determined by iodometric analysis of autoxidized methyl oleate.

FORMATION OF GASEOUS REACTION PRODUCTS

Methyl oleate (5 ml) was irradiated in the presence of excess oxygen in the vessels used for the oxygen absorption runs but having a bulb and greaseless stopcock added. The vessels, of known volume, were filled to measured pressures of oxygen and shaken during irradiation, after which they were connected to a modified Saunders-Taylor apparatus¹⁹ and measurements made of the total volume of gas obtained by repeated degassing at -80°C . This was then condensed in liquid hydrogen and the yield of H_2 measured volumetrically, after which the residual gases were transferred directly to a Perkin-Elmer model 452 gas chromatograph and analyzed on 2-m. columns of molecular sieve 5A and modified silica gel operated at 50.0°C using a thermistor detector. The gaseous products from degassed methyl oleate irradiated under identical conditions were similarly measured. The samples of "hydrogen" separated by the above procedure contained at least 98.1 % H_2 .

DOSIMETRY

The rates of energy absorption in the oxidizing samples were calculated on the basis of electron densities from measurements made at 20.0°C in the reaction vessels with 5 ml of ferrous sulphate dosimeter solution, taking $G_{\text{Fe}^{3+}} = 15.5$,¹⁶ and correcting for ^{60}Co decay.

RESULTS

In the oxidation of methyl oleate the maximum rates of oxygen absorption were encountered at the highest dose rate ($1.26 \times 10^{18} \text{ eV l.}^{-1} \text{ sec}^{-1}$) and temperature (59.9°C) used. Under these conditions the rate of oxygen absorption was independent of the oxygen pressure in the system over the range 354–1034 torr, and did not depend on the frequency at which the reaction vessel was shaken in the range 692–245 c/min, but decreased at lower shaking rates, being 32 % lower at 103 c/min. Runs were normally performed at a pressure of about 750 torr and a shaking rate of 540 c/min, where the measured rate of oxygen absorption is not controlled by the dissolution of oxygen and is therefore a true measure of the rate of the oxidation reaction. The evolution of H_2 and CH_4 may be neglected, being always less than 2 % of the rate of oxygen absorption.

Fig. 1 shows that at 30°C the absorption of oxygen and the formation of hydroperoxides were initially linear functions of the radiation dose, and coincided up to

about 8 % oxidation, after which the oxygen absorption accelerates slightly and diverges from the plot of hydroperoxide formation. At 30°C there was no detectable post-irradiation oxidation on removal of the radiation source, indicating that thermal decomposition of the hydroperoxides formed does not contribute to initiation of the oxidation at this temperature. Short induction periods were observed, the duration of which varied with the batch of methyl oleate used and decreased with increase of dose rate. Assuming the inhibition to be due to scavenging of peroxy radicals it was calculated that the inhibiting impurities were present at concentrations of about 1×10^{-5} M.

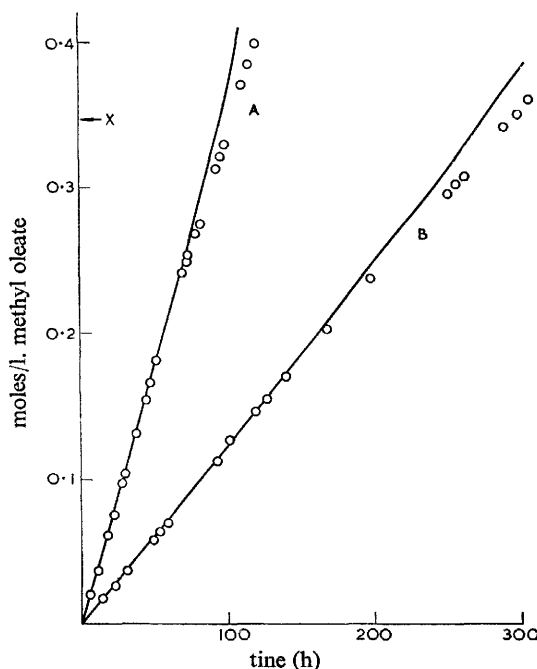


FIG. 1.—Oxygen absorption (—) and hydroperoxide formation (○) in the oxidation of methyl oleate at 30.0°C and dose rates of 8.69×10^{17} eV l.⁻¹ sec.⁻¹; (A), and 1.01×10^{17} eV l.⁻¹ sec.⁻¹; (B). X = 12.0 % oxidation.

The rate of oxidation was proportional to the square root of the dose rate over the range 2.11×10^{16} to 1.32×10^{18} eV l.⁻¹ sec.⁻¹ at 30.0°C (fig. 2), and *G*-values for oxygen absorption ranged from 465 to 60.3 respectively at these dose rates. To determine the activation energy of the oxidation the reaction rate was measured at temperatures from 30 to 60°C. At temperatures above 30°C post-irradiation oxidation occurred on removing the radiation source; consequently these runs were performed in four stages consisting of two periods of radiation-induced oxidation each followed by a measurement of the post-irradiation rate, the total conversion being approximately 2.8 %. Corrections equal to the mean rates of the appropriate thermal oxidations were subtracted from the rate of each radiation-induced stage. The close agreement of the two rates obtained by this procedure confirmed the validity of the corrections, and the average values of these rates at several dose rates are plotted in fig. 2. The square-root dependence on the dose rate holds at each temperature, and the rate constants k_{obs} obtained from the slopes of these lines

are summarized in table 1. An Arrhenius plot of these data leads to an overall activation energy of 6.4 kcal/mole.

The oxidation rates of mixtures of methyl oleate and methyl stearate were measured over the full range of concentrations and are shown in fig. 3. Each mixture prepared had a total volume of 5 ml and measurements were performed

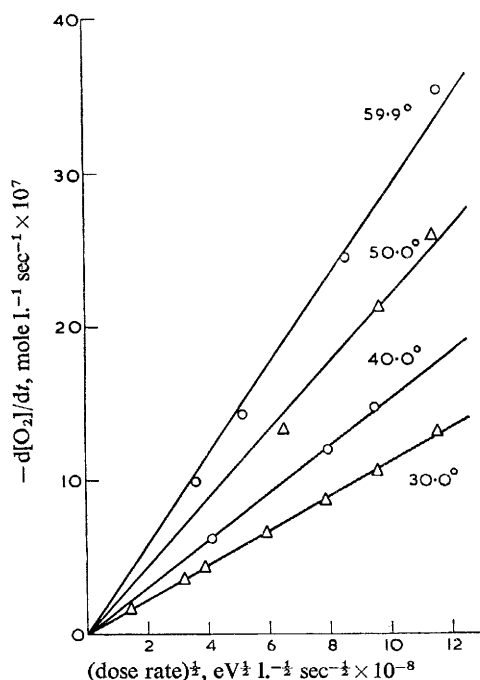


FIG. 2.—Effect of dose rate and temperature on the rate of oxidation of methyl oleate.

at 42.0°C, i.e., above the m.p. of the stearate. The highest point on the graph represents pure methyl oleate, and it is seen that the oxidation rate is proportional to the mole fraction of methyl oleate.

The rate of initiation of the oxidation was determined at several dose rates by introducing known amounts of 2,6-di-*t*-butyl-*p*-cresol and measuring the resulting

TABLE 1.—TEMPERATURE DEPENDENCE OF RATE CONSTANT FOR OXYGEN ABSORPTION

temp. °C	$k_{\text{obs}} \times 10^{15}$ mole eV ^{-1/2} l. ^{-1/2} sec ^{-1/2}	$k_7/(2k_8)^{1/2} \times 10^3$ l. ^{1/2} mole ^{-1/2} sec ^{-1/2}
30.0	1.13	1.31
40.0	1.54	1.78
50.0	2.22	2.57
59.9	2.92	3.38

induction periods. These were well defined and the subsequent rates of oxygen absorption were identical to those in the absence of the inhibitor. At each dose rate the plot of the induction period against the inhibitor concentration was linear, and the initiation rate was calculated from the slope of this line assuming that each inhibitor molecule scavenges two peroxy radicals.²⁰ Fig. 4 shows the linear dependence of the initiation rate on the dose rate at 30°C; the value measured at 44.8°

falls on the line, so that the initiation reaction has no measurable activation energy. The G -value for the production of peroxy radicals calculated from the slope of the line in fig. 4 is 5.36. The maximum concentration of inhibitor employed was 9.9×10^{-4} M because the reaction mechanism is uncertain at higher concentrations.³

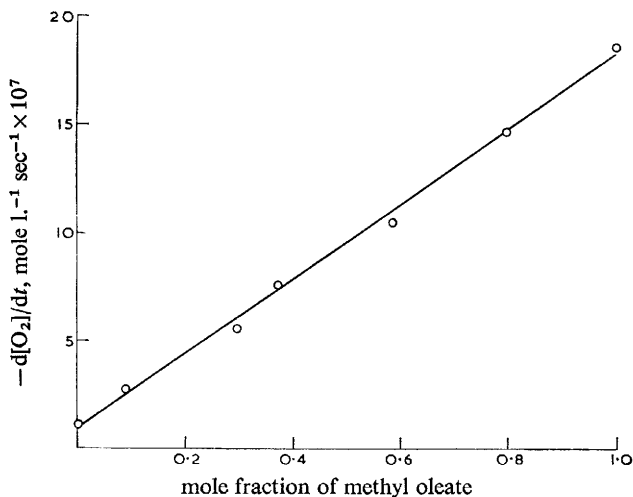


FIG. 3.—Rates of oxidation of methyl oleate + methyl stearate mixtures at 42.0°C. Dose rate = 1.08×10^{18} eV l.⁻¹ sec.⁻¹.

The above procedure was also used to measure the rate of production of peroxy radicals from methyl stearate at 55°C and gave a value of $G_{\text{radical}} = 5.25$, from data obtained at one dose rate (7.89×10^{17} eV l.⁻¹ sec.⁻¹).

The formation of gaseous products on irradiation of methyl oleate at 30°C was examined for samples containing excess oxygen and for degassed samples. In

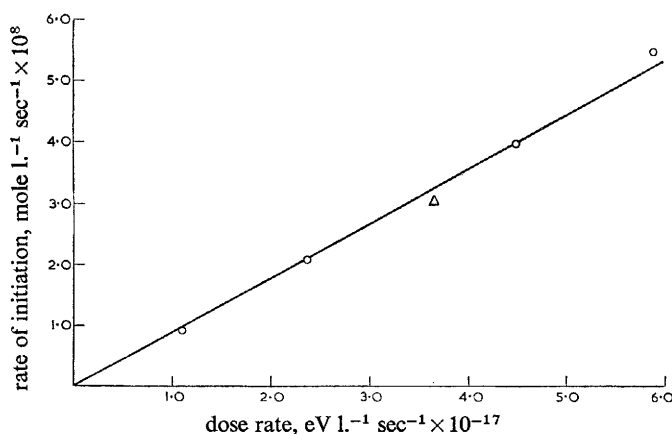


FIG. 4.—Effect of dose rate on the rate of initiation. ○, 30.0°C; △, 44.8°C.

both cases the major product was hydrogen; fig. 5 shows that the yields were linear with dose up to at least 3.0×10^{23} eV l.⁻¹, and were unaffected by the presence of oxygen. The results in fig. 5 and similar data obtained at a dose rate of 7.37×10^{16} eV l.⁻¹ sec.⁻¹ lead to a mean value for the yield of hydrogen of $G_{H_2} = 1.01$. CH₄ and CO were also produced both in the absence and presence of oxygen in a total

yield equal to about 20 % of that of the H_2 . In the absence of oxygen, C_2H_6 , C_2H_4 , and C_3H_8 were also obtained, each amounting to less than 5 % of the CH_4 yield.

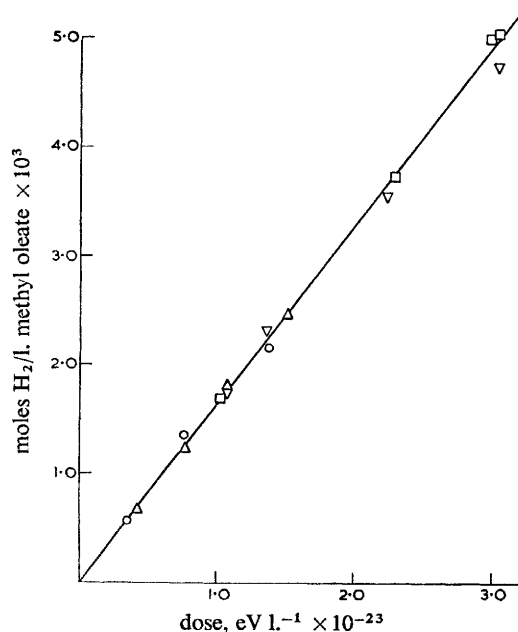


FIG. 5.—Yield of H_2 as a function of dose at 30.0°C. No O_2 present: □, 7.20×10^{17} eV l.⁻¹ sec⁻¹; ○, 2.41×10^{17} eV l.⁻¹ sec⁻¹. Excess O_2 present: ▽, 7.20×10^{17} eV l.⁻¹ sec⁻¹; △, 2.41×10^{17} eV l.⁻¹ sec⁻¹.

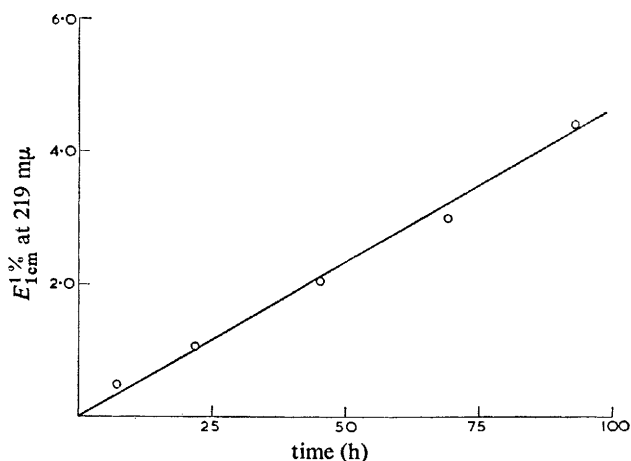


FIG. 6.—Variation of absorbance at 219 mμ with dose at 30°C. Dose rate = 8.52×10^{17} eV l.⁻¹ sec⁻¹.

The absorption spectra of samples of methyl oleate irradiated to various doses in the presence of oxygen showed the appearance of a peak at 219 mμ in Spectrosol cyclohexane solution. The peak absorption, corrected for that of unirradiated methyl oleate, is plotted in fig. 6, which shows it to be linear with dose up to about

10 % oxidation. Taking into account the effect of solvent on the peak wavelength,²¹ this peak may be assigned²² to the α,β -unsaturated ketones which appear as minor products in the oxidation of mono-olefins, and their concentration calculated assuming an extinction coefficient of 16,000^{21, 22} is 11.0×10^{-3} M after 45-h irradiation under the conditions given in fig. 6.

DISCUSSION

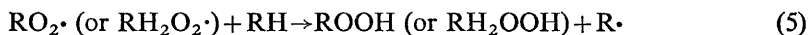
The high G -values for oxygen consumption compared with G_{radical} indicate that the reaction occurs by a chain mechanism. Since the rate of oxygen absorption is independent of the pressure, O_2 must be scavenging all of the available radicals by a process which is not rate-controlling. The concentration of O_2 in solution was about 8×10^{-3} M under the conditions normally used.²³

The radiolytic yield of H_2 from methyl oleate is independent of the dose rate, and is not decreased by O_2 so that $HO_2\cdot$ radicals, which might be formed by scavenging of H atoms, do not contribute to the initiation reaction. However, the following radical processes will probably occur in the radiolysis of olefins.²⁴



If the transient H atoms produced in reaction (1) undergo either addition (2) or abstraction (3) with methyl oleate they will produce radicals which may subsequently be scavenged by O_2 and therefore initiate oxidation. The reaction of H atoms with olefins of the type $RHC=CHR$ has a ratio of rate constants for abstraction and addition of 0.24.²⁵ Consequently, if the yield of H atoms is taken as $\frac{1}{2}G_{\text{radical}}$, i.e., $G_H = 2.68$, then the H_2 yield produced by reaction (3) is $G_{H_2} = 0.64$. The remainder of the H_2 observed ($G = 0.37$) probably results from molecular elimination processes since the reaction $H\cdot + H\cdot \rightarrow H_2$ does not contribute significantly to the radiolysis of liquid olefins under the conditions used in this work.^{24, 26} Howton and Wu²⁷ have shown that the predominant process in the γ -radiolysis of de-aerated oleic acid is dimerization of allylic radicals to give doubly unsaturated products. Their results indicate that dimerization of $RH_2\cdot$ radicals and their addition to $R\cdot$ radicals is insignificant, which implies that the rates of these inter-radical reactions are sufficiently low to permit efficient scavenging of the radicals by O_2 .

Reactions (2) and (3) will therefore be followed by

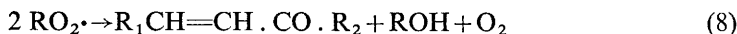


and since the oxygen absorbed is quantitatively converted to hydroperoxide in the initial stages of the oxidation then the normal propagating sequence² will occur:



The square-root dependence of the reaction rate on the dose rate indicates that termination is by bimolecular interaction of the chain-carrying peroxy radicals. The appearance of an absorption band attributable to α,β -unsaturated ketones agrees with the observation by Dugan and Landis⁵ who also found that for methyl oleate the absorbance increased linearly with dose. The latter fact implies that the

ketones do not arise mainly by radiolysis or thermal decomposition of the hydroperoxide formed during the oxidation since their rate of formation would then increase with the hydroperoxide concentration, i.e. with the dose. The observed linearity with dose is consistent with their formation in the termination step. The peroxy radicals derived from methyl oleate possess a secondary carbon atom, and according to Russell²⁸ their interaction will produce one molecule of α,β -unsaturated ketone ($R_1CH=CH \cdot CO \cdot R_2$) and one molecule of alcohol in each termination step which may be written :



Since under stationary conditions the rates of initiation and termination are equal, then the occurrence of reaction (8) implies that the rate of ketone production will be half of the initiation rate. Using the measured G_{radical} value, the concentration of ketone expected after 45 h irradiation under the conditions given in fig. 6 was calculated to be 6.4×10^{-3} M. Neither the hydroperoxide, nor the alcohol produced in reaction (8), will have absorptions in this region significantly different from that of methyl oleate. However, the discrepancy between the value calculated above and the experimentally observed concentration of 11.0×10^{-3} M may be due to the following: (i) some α,β -unsaturated carbonyl compounds may be formed by radiolytic decomposition of the hydroperoxide, (ii) the absorption at 219 $m\mu$ may contain a contribution from products such as conjugated dienes formed by loss of H_2 from methyl oleate, although this must be small since no peak appeared in the region of 230 $m\mu$ on irradiation, (iii) the extinction coefficient assumed may be inaccurate. The concentrations of ketone calculated from the values of $E_1^{1\%}$ obtained by Dugan and Landis⁵ for methyl oleate oxidized at 7.5°C are about 30 % of the corresponding concentrations of hydroperoxide formed. This is consistent with the fact that extrapolation of our data in fig. 2 to the conditions used by Dugan and Landis leads to a kinetic chain length of about 2.5.

Assuming stationary concentrations of the intermediate radicals, the rate of oxygen absorption may be expressed by

$$-\frac{d[O_2]}{dt} = \frac{R_i}{2} + \frac{k_7}{(2k_8)^{\frac{1}{2}}} R_i^{\frac{1}{2}} [RH],$$

when R_i is the rate of initiation, i.e., the total rate of production of radicals which take part in reaction (4), and is measured by G_{radical} . The kinetic chain length $-\frac{d[O_2]}{dt}/R_i = G_{-O_2}/G_{\text{radical}}$ will have a minimum value in the present work of 11.3

at a dose rate of 1.3×10^{18} eV l.⁻¹ sec⁻¹ at 30°C. The first term in the above equation is therefore negligible compared with the second term so that

$$-\frac{d[O_2]}{dt} = \frac{k_7}{(2k_8)^{\frac{1}{2}}} \left(\frac{G_{\text{radical}}}{100 N} \right)^{\frac{1}{2}} I^{\frac{1}{2}} [RH],$$

where I is the dose rate and N is Avogadro's number.

The experimentally measured rates of oxygen absorption varied with the square root of the dose rate and were directly proportional to the substrate concentration. This latter behaviour has not previously been verified for a radiation-induced chain oxidation, owing to the difficulty of obtaining solvents which are "inert". In the present system, methyl stearate behaves as an inert solvent since its rate of oxidation is low compared with that of methyl oleate, and the almost identical electron densities and radical yields of the components produce a rate of initiation which is independent of the composition. Moreover, methyl stearate is not aromatic so

that energy transfer effects may reasonably be expected to be absent, and indeed the results are consistent with this assumption.

The rate constant obtained from the slope of a plot of $-d[O_2]/dt$ against $I^{1/2}$ may therefore be written as

$$k_{\text{obs.}} = \frac{k_7}{(2k_8)^{1/2}} \left(\frac{G_{\text{radical}}}{100N} \right)^{1/2} [\text{RH}].$$

The ratios $k_7/(2k_8)^{1/2}$ calculated from this equation are shown in table 1, and are about 30 % higher than the corresponding value given by Bateman.^{2,23}

Burlakova *et al.*²⁹ obtained a G -value for peroxy radical production from methyl oleate of approximately 4 by an inhibitor method using diphenylamine at 20°C. They assumed each inhibitor molecule scavenged 2 radicals whereas use of the stoichiometry for diphenylamine²⁰ would lead to a radical yield of about 5.6 from their data, in closer agreement with our value of 5.36.

We have shown that the initiation reaction has zero activation energy, so that the measured overall activation energy is $E_A = E_7 - \frac{1}{2}E_8$. The experimental value of 6.4 kcal/mole is lower than the 7.7 kcal/mole which may be calculated from the data of Bateman.^{2, 23}

Since there is no significant post-irradiation thermal effect at 30°C the eventual acceleration of the oxygen absorption and its divergence from the hydroperoxide formation must be due to radiolysis of the hydroperoxide. This will give a higher yield of radicals³⁰ than the ester, and therefore increase the initiation rate. Burlakova *et al.*⁶ concluded that considerable yields of epoxides are also obtained as primary products of the radiolytic oxidation of methyl oleate at 70°C at a dose rate of 6×10^{17} eV l.⁻¹ sec⁻¹. Since we find the initial oxygen absorption and hydroperoxide formation to be equal at 30°C there are no significant amounts of other primary products formed at this temperature.

The oxidation rate of methyl oleate reported here may be compared with the measurements of Dugan and Landis.⁵ The initial rate of hydroperoxide formation calculated from their graph at 29° is about 10 % higher than the corresponding rate of oxygen absorption extrapolated from our data. Moreover, since the chain length calculated for their conditions is 5.3 then their results are equivalent to an initial rate of oxygen absorption about 20 % higher than we find. This may possibly be due to the more rapid oxidation of traces of linoleate originally present; however, they did not analyze the methyl oleate used. They oxidized methyl oleate to about 30 % conversion at 29°C, so that the non-linearity of the peroxide yield with time is due to its radiolytic decomposition and may also reflect the consumption of more readily oxidizable impurities.

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