On the Kinetics of the Autoxidation of Fats. II. Monounsaturated Substrates

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The autoxidation of methyl oleate and oleic acid shows some differences as compared to the autoxidation of linoleate, *e.g.*, the formation of water at an early stage. Linearization of experimental data on the autoxidation to high oxidation degrees of methyl oleate and other monounsaturated substrates shows that the rate equations previously derived for methyl linoleate in the range of 1–25% oxidation are valid, provided the correct expression for the remaining unreacted substrate is used. With monounsaturated substrates, part of the oxygen is consumed by a secondary oxidation reaction almost from the beginning, and only a certain constant fraction α of the total O_2 consumption is consumed in hydroperoxide formation. The fraction α is different for methyl oleate, oleyl alcohol, oleic acid and *cis* 9-octadecene, but the rate constant for the hydroperoxide formation is the same for all of them when experimental conditions are the same. The main difference between oleate and linoleate autoxidation is the much faster decomposition of the oleate hydroperoxides relative to their slow formation.

KEY WORDS: Autoxidation, kinetics, linoleate, monounsaturated, oleate, oleic acid, rate equation, secondary oxidation.

Early experimental studies of fat autoxidation (1-3) concerned monounsaturated fats, the preferred substrate being methyl oleate (MeOl) or oleic acid (HOl), while later studies dealt with polyunsaturated fats, the preferred substrate being methyl linoleate (MeLi) or linoleic acid (HLi). The rates of autoxidation of the latter substrates are greater by an order of magnitude than for monounsaturates, which makes the experiments more convenient. Also, the increased consumption of polyunsaturated fats has made the autoxidation of MeLi and HLi more interesting.

The two types of fat differ not only with respect to the rate but, apparently, also with respect to the oxidation reactions. Franke and Jerchel (4) found that the yield of peroxide with HLi at 37°C in the presence of cobalt nitrate remained 100% of the O_2 consumed in the range 0-0.3 mole O_2 per mole substrate, whereas with HOl under the same conditions the peroxide yield decreased almost from the beginning. Similar results have been reported (1,3). Furthermore, with EtLi at 45°C and up to 0.4 mole O_2/mole substrate, Bolland (5) found that hardly any H_2O was formed, only about 0.01 mole of H_2O per mole of O_2 consumed, whereas Hamilton and Olcott (1) with MeOl at 80°C found 0.13 mole H_2O/mole O_2 at this oxidation degree. At 1.5 moles O_2 per mole MeOl, 0.4-0.5 mole H_2O/mole O_2 was found by other investigators (1,2,6).

Brimberg (7) in Part I and also in Reference 8 treats the autoxidation of MeLi and HLi. This second part treats the autoxidation of MeOl and other monounsaturated substrates.

METHODS

Experimental rate data from the literature are linearized, and the exact mathematical form of the rate equation is thereby identified as in previous studies (7,8). This requires that the data are accurate enough and span sufficient ranges of the variables. In all cases treated here, the oxidation was followed by measuring O_2 consumption at constant O_2 pressure.

The basic rate equation presented earlier (7,8) is

$$dx/dt = k\,[O_2]\,(1 - x/n)\,f'(t) \qquad [1]$$

where x is the number of moles of O_2 consumed at time t per initial mole of substrate, $[O_2]$ is the O_2 concentration in the substrate, $(1 - x/n)$ is the amount of unreacted substrate at time t and n is the number of O_2 molecules that can react with one molecule of substrate. For MeLi and HLi, n = 2. For MeOl, oleyl alcohol and *cis*-9-octadecene, also n = 2, as evidenced by O_2 absorption curves up to about 2 moles O_2/mole substrate (2,6). It is also indicated by the fact that autoxidation occurs symmetrically about the double bond (9). For oleic acid, n = 1 as treated below. Function f′(t) is the derivative of a function f(t), which is to be determined by linearization of the data.

The autoxidation proceeds in three stages. At low values of x

$$x = k_1\,f(t) + a \qquad [2]$$

where $f(t) = (t - t_o)^2$ or $f(t) = t - t_o$. In the second, the exponential stage,

$$dx/dt = k(A + x)\,(1 - x/n) \qquad [3]$$

which after integration becomes:

$$\ln[(A + x)\,(1 - x/n)^{-1}] = k_2 t + b \qquad [4]$$

In the last oxidation stage

$$dx/dt = K\,(1 - x/n) \qquad [5]$$

or, after integration,

$$-\ln\,(1 - x/n) = k_3 t + c \qquad [6]$$

RESULTS AND DISCUSSION

Autoxidation of MeOl at 60, 70 and 80°C. Kern and Willersinn (10-12), who made an extensive investigation of the kinetics of the autoxidation of MeLi referred to earlier (7,8), also presented data for the autoxidation of MeOl (13). The O_2 consumption at an O_2 pressure of 1 atm was

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measured up to x = 0.08. Their data are linearized with the same rate equations as found for MeLi. Figure 1 shows dx/dt = $(1 - x/2)^{-1}$ against x, Equation 3. The lines give the values of A in Equations 3 and 4. Figure 2 shows the data points, plotted as $\ln[(A + x)(1 - x/2)^{-1}]$ against t, Equation 4. Except for the first points, the data give straight lines of slope k_2. Figure 3 shows ln k_2 against 1000/T. The activation energy is 18 kcal/mole, the same as found for MeLi (7). Figure 3 also shows ln A against 1000/T. Its activation energy is −4 kcal/mole. This is of the same order of magnitude as the heat of solution for O_2 in the substrate (7).

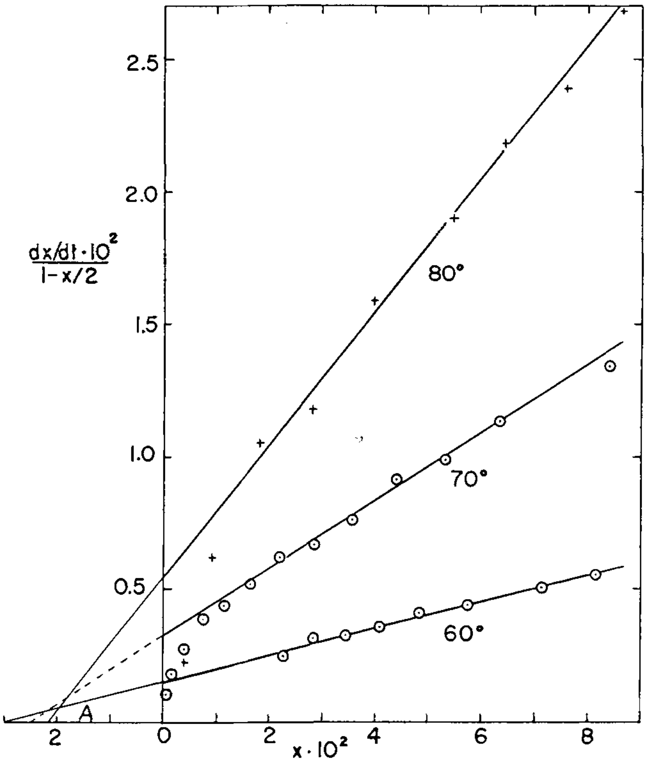

FIG. 1. Oxygen absorption x during the autoxidation of methyl oleate (MeOl) at 60, 70 and 80°C and 1 atm O_2; x in moles O_2 per initial mole MeOl, t in hours. dx/dt • $(1 - x/2)^{-1}$ • 10^2 against x • 10^2, Equation 3. Data from Kern *et al.* (11; Fig. 1 therein).

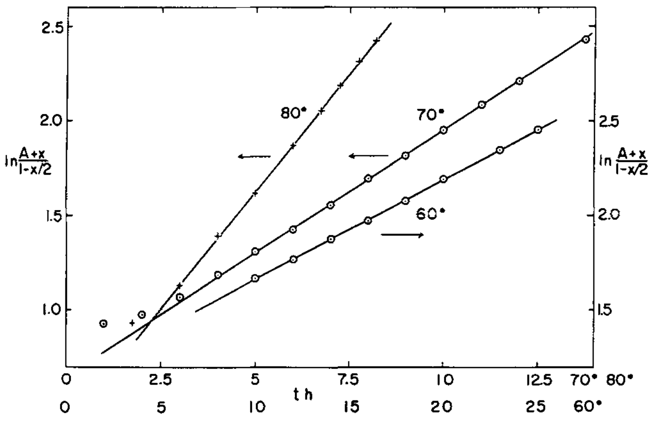

FIG. 2. Same data as in Figure 1. $\ln[(A + x)(1 - x/2)^{-1} \cdot 10^2]$ against t, Equation 4. A = $3 \cdot 10^{-2}$, $2.4 \cdot 10^{-2}$ and $2.15 \cdot 10^{-2}$ at 60, 70 and 80°C, respectively. x and A in moles O_2 per initial mole MeOl, t in hours.

This investigation by Kern *et al.* (13) thus shows the same kinetics for MeOl and MeLi in the range of 0–8% oxidation, except that the rate was much smaller for MeOl than for MeLi. The rate curves for MeLi by Kern *et al.* (10) usually ended at x = 0.2 to 0.25. The experiments with MeOl were terminated already at x = 0.08, probably because H_2O formation disturbed the O_2 measurement. Their apparatus had no cold traps to eliminate H_2O.

Autoxidation of MeOl, oleyl alcohol, cis-*9-octadecene and oleic acid.* Deatherage and Mattill (2) oxidized the substrates by bubbling O_2 through them to high degrees of oxidation. The volatile products were collected in dry-ice traps. The O_2 consumption was measured. The plots of their data as −ln (1 − x/n) against t, Equation 6, are given in Figure 4. They are linear from x = 0.1 through 0.25 up to about x = 0.8, but then the points deviate more and more upwards from the line. This deviation could indicate that O_2 is also consumed by some other reaction.

In Equation 1, the amount of unreacted substrate per mole of initial substrate at time t is (1 − x/n), which is valid when all O_2 consumed is converted into hydroperoxides (HP) as for MeLi up to at least x = 0.25. If a constant fraction α of the O_2 is converted to HP, and $(1 - \alpha)$ is consumed by some secondary reaction, which does not produce HP nor consumes substrate, the amount of unreacted substrate is $(1 - \alpha x/n)$, and the equation for the last oxidation stage is

$$-\ln(1 - \alpha x/n) = k_3 t + d \qquad [7]$$

The secondary reaction could be a reaction of O_2 with the HP already formed or with some decomposition product thereof.

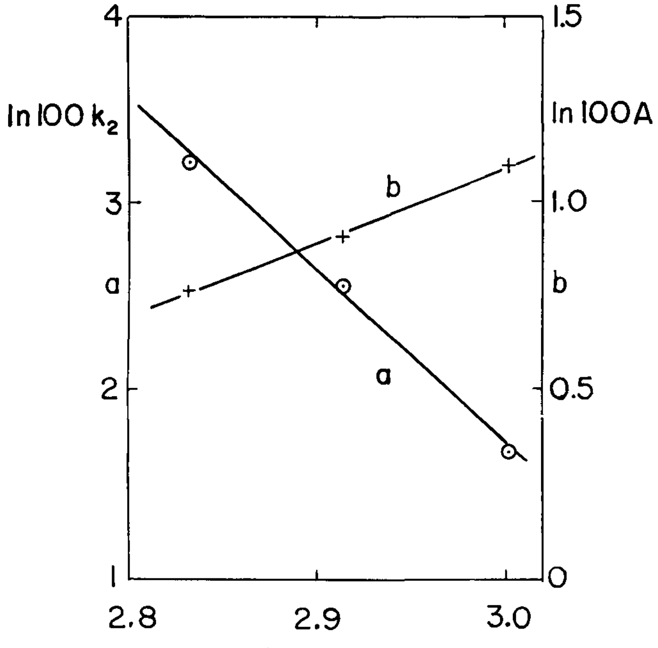

FIG. 3. Same data as in Figure 1. (a) ln $100k_2$ against 1000/T; (b) ln 100A against 1000/T.

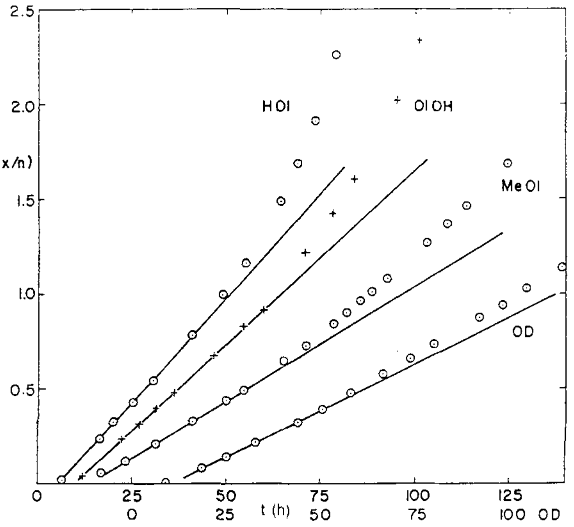

FIG. 4. Oxygen absorption x during the autoxidation of oleyl alcohol (OlOH), methyl oleate (MeOl), oleic acid (HOl) and *cis*-9-octadecene (OD) at 75°C in 1 atm O_2; $-\ln(1 - x/n)$ against t. For OlOH, MeOl and OD, n = 2; for HOl, n = 1; x in moles O_2 per initial mole substrate, t in hours. Data from Deatherage and Mattill (2; Table 1 therein).

Hargrave and Morris (14) found 81% HP from the O_2 consumed when oxidizing MeOl at 55°C. The same yield of HP was found by Saunders *et al.* (15) when oxidizing MeOl at 60°C up to $x = 0.2$. Therefore, I tried $\alpha = 4/5$ on the data of (2). When $-\ln(1 - 0.4x)$ is plotted against t for MeOl, a straight line is obtained in the range from $x = 0.3$ to the end of the experiment at $\alpha x = 1.3$ or $x = 1.63$ (Fig. 5). The data of Deatherage and Mattill (2) for MeOl follow Equation 7, the last oxidation stage, over almost their entire range. Only a few early points belong to the two first stages.

When no direct determination of α, as those for MeOl (14,15) is available, it is possible to determine α from the O_2 consumption after different times, provided the data give a long enough last oxidation stage.

Derivation of Equation 7 gives

$$d(\alpha x)/dt = \alpha dx/dt = k_3 n(1 - \alpha x/n) \qquad [8]$$

Thus, $dx/dt \cdot (1 - \alpha x/n)^{-1}$ is a constant, $k_3 n/\alpha$, and the value of α can be found by calculation of dx/dt from the experimental data as $(x_{n+1} - x_n)/(t_{n+1} - t_n)$, with the corresponding x being $(x_{n+1} + x_n)/2$. Then different values of α are tried until an α is found that makes $dx/dt \cdot (1 - \alpha x/n)^{-1}$ a constant. This is shown in Figure 6. For MeOl, the value of $dx/dt \cdot (1 - 0 \cdot 4x)^{-1}$ is fairly constant. Differentiated data always scatter more than the original data.

When the same value, $\alpha = 4/5$, is tried on the data of Deatherage and Mattill (2) for oleyl alcohol (OlOH), $-\ln(1 - 0.4x)$ against t is not linear, and $dx/dt \cdot (1 - 0.4x)^{-1}$ is not a constant. However, with $\alpha = 2/3$, $dx/dt \cdot (1 - x/3)^{-1}$ is fairly constant, as shown in Figure 6. The values with $\alpha = 4/5$ are also shown for comparison. The plot of $-\ln(1 - x/3)$ against t gives a straight line (Fig. 5) from $x = 0.28$ to the end of the experiment at $\alpha x = 1.33$ and $x = 2$. This line turned out to be parallel to the line for MeOl.

The values for *cis*-9-octadecene (9-OD) show less deviation from Equation 6 than do MeOl and OlOH (Fig. 4). For 9-OD, $\alpha = 8/9$ gives a fairly constant value of $dx/dt \cdot (1 - 4x/9)^{-1}$ (Fig. 6), and $-\ln(1 - 4x/9)$ against t is a straight line for all data points except for the first ones (Fig. 5). The line is parallel to the lines for MeOl and OlOH. For comparison, the same data points, but with $\alpha = 4/5$ as for MeOl, are shown. These points do not fall on a straight line at the end of the experiment.

For MeOl, OlOH and 9-OD, the O_2 absorption curves of Deatherage and Mattill (2; Fig. 2 therein) give $n = 2$. The curves consist of a single branch until the end of the experiment at about $x = 2$. With HOl, however, Figure 2 in Reference 2 shows that the oxidation rate decreases

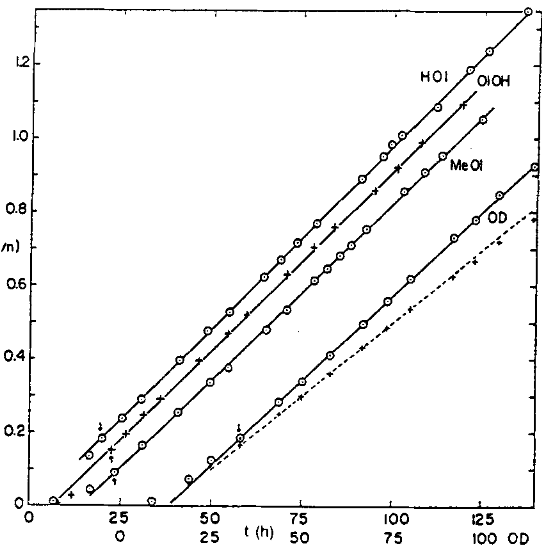

FIG. 5. Same data and abbreviations as in Figure 4; $-\ln(1 - \alpha x/n)$ against t. The values of α/n are: OlOH, 1/3; MeOl, 0.4; HOL, 0.6; OD, 4/9; and OD (dotted line), 0.4.

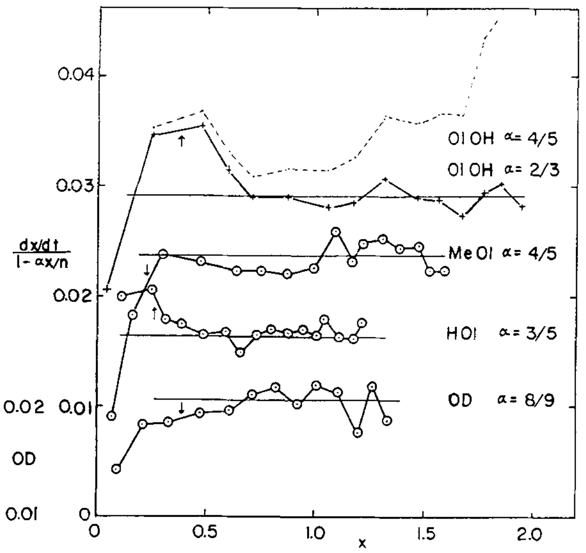

FIG. 6. Same data and abbreviations as in Figure 4; $dx/dt \cdot (1 - \alpha x/n)^{-1}$ against x.

earlier, and that the O_2 consumption will never reach $x = 2$ but tends toward $x = 1.7$. Thus, for HOl, $n = 1$. The value $\alpha = 3/5$ makes $dx/dt \cdot (1 - \alpha x)^{-1}$ fairly constant (Fig. 6), and $-\ln(1 - 0.6x)$ against t is a straight line, parallel to the other lines in Figure 5. The first point of each line in Figure 5 is marked with an arrow, and the corresponding points are marked in Figure 6. The horizontal lines in Figure 6 are drawn at k_3n/α, with k_3 found in Figure 5.

Thus, when the correct expression for the remaining unreacted substrate, $(1 - \alpha x/n)$, is used, autoxidation of monounsaturated substrates follows the same rate equations as autoxidation of MeLi. The HP formation is rate-determining, and this reaction has the same rate constant k_3 for MeOl, OlOH, 9-OD and HOl, if the experimental conditions are the same. It is remarkable that α remains constant over such a great oxidation range. This indicates a relation between HP formation and secondary O_2 consumption.

Other data for the O_2 consumption at 80°C, published by Hamilton and Olcott (1), could be linearized by Equation 7 with $\alpha = 4/5$ for MeOl. Because each entry represents a separate run, the data points scatter more than those of Deatherage and Mattill (2).

Hamilton and Olcott (1) also determined the amount of H_2O formed in each experiment and the amount of peroxides (PO) in the oxidized substrate. If the O_2 that is consumed by secondary oxidation reacts to give H_2O, the amount of H_2O formed should be equal to $2(1 - \alpha)x$. Figure 7a shows the amount of H_2O in moles/mole MeOl against 0.4x. The dotted line corresponds to H_2O/O, the theoretical line. The data by Hamilton and Olcott (1) indicate that this could possibly be the case, but not at the beginning and not above $x = 1.75$. If H_2O is formed at decomposition of HP, there ought to be a relation between the amount of H_2O formed and the amount of decomposed HP, $0.8x - PO$. Figure 7b shows this relation. The data points scatter too much to give a clear indication.

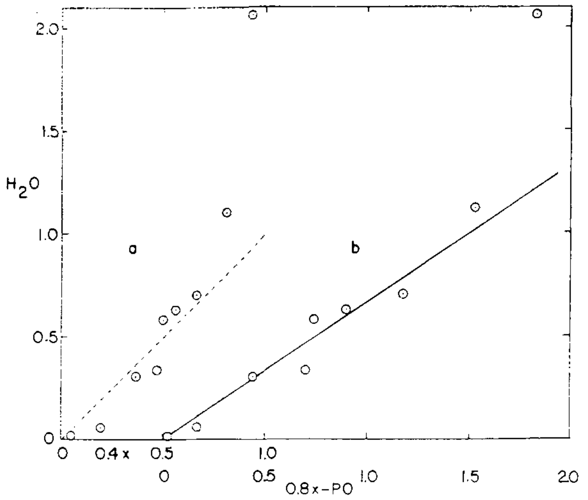

FIG. 7. Moles of water formed per initial mole substrate in the autoxidation of methyl oleate at 80°C in 1 atm O_2. (a) H_2O against $2(1 - \alpha)x = 0.4x$; (b) H_2O against decomposed peroxides = αx − peroxides (PO), where x is moles O_2 absorbed per initial mole substrate, $\alpha = 4/5$, and PO represents analyzed peroxides.

Autoxidation of MeOl and Me-9,10-Dideuterooleate. Khan *et al.* (6) studied the role of olefin H and D in the formation of water during the autoxidation of fats. Their methods, techniques and temperature, 75°C, were the same as those of Deatherage and Mattill (2). Their rate curves comprise all three oxidation stages, whereas those of Deatherage and Mattill (2) mainly show the last stage (Fig. 5). Possibly, the substrates of Khan *et al.* (6) contained less contaminating metals, which catalyze HP decomposition and thereby decrease the duration of the exponential stage. Furthermore, Khan *et al.* (6) have more data points in the early oxidation stage. The first stage, in this case with $f(t) = (t - t_o)^2$, is plotted as $\sqrt{x}$ against t (Fig. 8A). With MeOl, the O_2 consumption started without delay, but with methyl 9,10-dideuterooleate (MeD_2Ol), not until after 105 h.

Figure 8B shows the plot of $d(\alpha x)/dt \cdot (1 - \alpha x/2)^{-1}$ against αx. Since α was found earlier to be 4/5 for MeOl and the experimental conditions were the same, this value was used here too. Lines a in Figure 8B show the exponential stage,

$$d(\alpha x)/dt \cdot (1 - \alpha x/n)^{-1} = k\,(A + \alpha x) \qquad [9]$$

before the horizontal line, the last stage, is obtained at about $x = 0.7$. The determination of A in Equation 9 from lines a gives a value of about 0.02, which is the value found in Figure 1. Integration of Equation 9 gives

$$\ln[(A + \alpha x)\,(1 - \alpha x/n)^{-1}] = k_2t + e \qquad [10]$$

Figure 9 shows the plot of $\ln[(A + 0.8x)(1 - 0.4x)^{-1}]$ against t (lines a) and $-\ln(1 - 0.4x)$ against t (lines b),

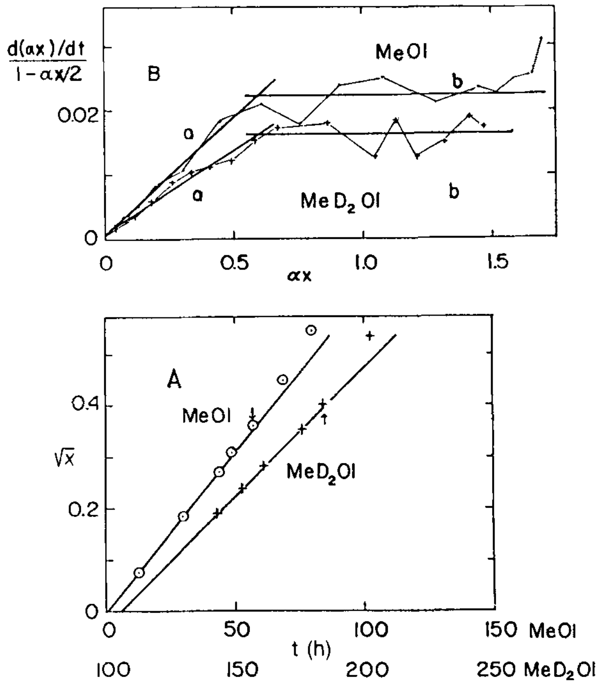

FIG. 8. Oxygen absorption x during the autoxidation of methyl oleate (MeOl) and methyl 9,10-dideuterooleate (MeD_2Ol) at 75°C and 1 atm O_2; x in moles O_2 per initial mole substrate, t in hours. (A) $\sqrt{x}$ against t, Equation 2; (B) $d(\alpha x)/dt \cdot (1 - \alpha x/2)^{-1}$ against αx, Equation 9; $\alpha = 4/5$. Data from Khan *et al.* (6; Figs. 2 and 3 therein).

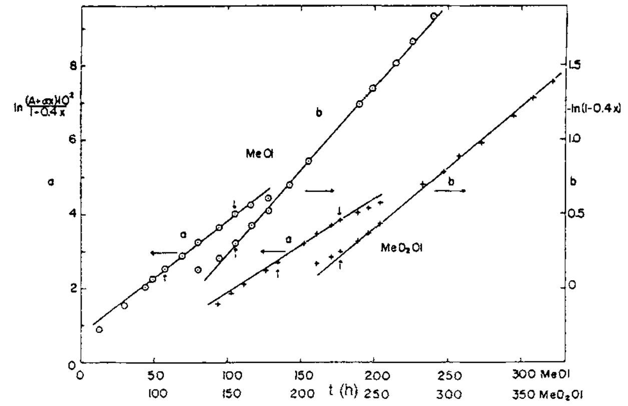

FIG. 9. Same data and abbreviations as in Figure 8; (a) ln [(A + αx) (1 − αx/2)$^{-1}$ • 10^2] against t, Equation 10; (b) −ln (1 − αx/2) against t, Equation 7, α = 4/5. A = 0.02 mole O_2/mole substrate. The last point of stage 1 and stage 2 are marked by arrows.

according to Equation 7. Autoxidation of MeOl and deuterated MeD_2Ol follows the same equations, but the rate constants are slightly lower for the deuterated ester.

The most conspicuous influence of D, however, is the long delay before O_2 consumption starts. This indicates that H is removed from the catalyst (the glass wall) possibly by exchange with D in the substrate. It is known that there is an exchange of H and D, *e.g.*, between CH_4 and CD_4, in the presence of a metal catalyst until an equilibrium with mixed products is obtained (16). The great influence of D on the start of O_2 uptake indicates the importance of H for initiation of the autoxidation.

Thus, the different behavior of oleate and linoleate, commented upon in the introduction, is caused by the different relative magnitudes of the rates of HP formation and decomposition. Probably, the decomposition rate is more or less the same for HP of MeOl and MeLi, but the HP formation rate for MeOl is only about 1/10 of that for MeLi. This reduces accumulation of HP in the case of oleate before the HP starts to decompose. With MeLi, some 30% HP accumulates before the decomposition becomes noticeable, as shown by the curves of Franke and Jerchel (4). At x > 0.3 for HLi, Figure 5 in Reference 4 shows a steady decrease of the HP yield, as found for HOl almost from the beginning (Fig. 3 in Reference 4). Possibly, the more general basic rate equation

$$d(\alpha x)/dt = k[O_2]\,(1 - \alpha x/n)\,f'(t) \qquad [11]$$

is valid for the linoleate as well, with $\alpha = 1$ up to about $x = 0.3$ and $\alpha < 1$ at higher oxidation degrees, but I have found no experimental data in the literature to confirm this.

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