On the Kinetics of the Autoxidation of Fats

Ulla I. Brimberg*
Alfa Laval AB, Tumba, S-14780 Sweden

The mechanism of fat autoxidation is elucidated from the rate data. All the data treated here and in an earlier publication follow the same basic rate equation, including the time function f(t) empirically derived for heterogeneous oxidation. Metals and glass (the wall of the reaction vessel) are catalysts. Depending on the state of the catalyst, f(t) = t^2 or f(t) = t. When f(t) = t, the kinetics are first-order as found for monolayer autoxidation, but in bulk phase they are complicated by a transient stage caused by the solubilization of O_2 into the hydroperoxide micelles produced in the exponential ("autocatalytic") part of the oxidation. Certain additives, such as inhibitors, affect the catalyst and thereby f(t). The kinetics, as determined by O_2 consumption or by analysis of the remaining unreacted substrate, show the first oxidation step. It is unaffected by further chemical changes of the primary oxidation products, *e.g.*, decomposition of hydroperoxides and trimerization in the autoxidation of 9,11-octadecadienoic acid methyl ester.

KEY WORDS: Autoxidation, catalyst, conjugated double bonds, inhibitor, kinetics, mechanism, rate equation.

Autoxidation and rancidity of fats have been the subject of research for more than 100 years. Browne (1) in 1925 said "A good review of the literature before 1890 is given by Ritsert" (2). Reviews of more recent work are given by Richardson and Korycka-Dahl (3), Allen and Hamilton (4) and Frankel (5). The kinetics have been reviewed by Labuza (6).

The main subject of this paper is the mechanism of autoxidation of fats as derived from the kinetics. In a recent paper (7) the rate formulae were derived. The formulae and direct observations show that autoxidation is a heterogeneous oxidation that is catalyzed by metals, especially Fe and Cu, and also by the glass wall of the reaction vessel. In presentations at annual meetings of the Deutsche Gesellschaft für Fettwissenschaft (DGF) the subject was extended to the effects of pro- and antioxidants. The first outline of the mechanism was presented (Nuernberg, 1990), whereas the case of conjugated double bonds was treated subsequently (Braunschweig, 1991).

This paper presents a summary of (7) and the two DGF presentations and also some supplementing results. The basic rate equation found empirically 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, by the substrate 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 linoleic acid and its esters n = 2, as found by analysis of the data. A function of time is f(t), derived empirically by Berg (Ref. 8 and unpublished work) and depends upon the state of the catalyst (metals and glass).

The measured event starts at t = t_o with a period where

$$f(t) = (t-t_o)^2 \qquad [2]$$

Then follows, usually to the end of the experiment, a steady state with

$$f(t) = t-t_o \qquad [3]$$

In some cases, branch [2] may be over before the first measurement. The function f(t) is treated further below.

The hydroperoxide yield from the autoxidation of ethyl linoleate at 55°C accounts for 98% of the O_2 uptake (9). Thus, in this case all O_2 consumed (within the error of analysis) is transformed into hydroperoxides.

An experiment by Kern and Dulog (10), where the substrate methyl linoleate was degassed before the experiment, showed a rapid initial absorption of O_2 until saturation of the substrate with O_2, whereupon followed O_2 consumption at a normal rate. Usually, the measurement of O_2 consumption, x, is started after this rapid saturation of the substrate with O_2.

METHODS

Experimental rate data in the literature are linearized, and the exact mathematical form is identified. In all cases except the monolayer oxidation of linoleic acid, LiH (11), the process was followed by measuring the O_2 consumption. This method is accurate and suitable for determination of the kinetics.

In some cases, the autoxidation process has been followed by determination of the peroxide value (PV), which is less accurate than O_2 measurement. Furthermore, after some time there is no longer a correspondence between the O_2 consumption and the PV, as illustrated by Labuza (6 and Fig. 2 therein).

In the presence of gels, the O_2 consumption method fails, *e.g.*, in the monolayer oxidation on silica gel. The gel absorbs gases, and this property is used in the BET method for the determination of the surface area of gels.

RESULTS AND DISCUSSION

Oxidation mechanism. According to the basic mechanism for heterogeneous oxidation given by Berg (Ref. 8 and unpublished work), the oxidation is initiated by the decomposition of H_2O, adsorbed on the surface of a hydrogen-replacing metal, *e.g.*, Fe or glass. Glass seems to react like such a metal. Robertson and Waters (12) suggested catalysis by "active spots on the surface of the reaction vessel" during the initial stage. Adsorbed H_2O is always present on a glass surface. The absorbed H_2O decomposes according to the formula

$$H_2O_{ads} \rightarrow H_{ads} + OH_{ads} \qquad [4]$$

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*Address correspondence at Backavägen 18, Hedesunda, S-81040 Sweden.

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H_{abs} is absorbed into the catalyst and OH_{ads} remains on the surface. The reaction proceeds to the extent that OH_{ads} is removed, *e.g.*, by reaction, and is replaced by H_2O_{ads} that decomposes. Finally, an equilibrium is attained where the catalyst is saturated with H_{abs}. It was shown by Wieland (13,14) already that O_2 reacts with H on a metal saturated with H to give H_2O_2

$$O_2 + 2H_{abs} \rightarrow H_2O_{2ads} \qquad [5]$$

The presence of H_2O_2 in aqueous extracts of oxidizing fats is referred to by Browne (1). Holm *et al.* (15) mention, without giving references, "the observations of a number of investigators that hydrogen peroxide is found when oxidation occurs."

The H_2O_2 reacts with the substrate to give hydroperoxides or peroxides, depending upon the substrate. When the catalyst has attained the steady state, no more H is required for continued oxidation

$$O_2 + 2H \rightarrow H_2O_2 \qquad [6]$$

$$H_2O_2 + RH \rightarrow ROOH + 2H \qquad [7]$$

$$O_2 + RH \rightarrow ROOH \qquad [8]$$

The importance of H_2O in the initiation of the autoxidation is evident from some experiments reported by Ingold (16). He measured the O_2 absorption in tetralin at 119°C without and with added dehydrating agents, such as $CaSO_4$, P_2O_5 and conc. H_2SO_4. Without a drying agent, 0.2 moles of O_2 per mole substrate was absorbed (20% oxidation) in 2855 s. The drying agents "completely inhibited the oxidation of tetralin for at least 5000 s." All of the H_2O present was bound by the drying agent, so that none could decompose on the catalyst.

Cu does not decompose H_2O, but it can take up H from other catalysts that do, *e.g.*, the glass wall of the reaction vessel. It catalyzes the oxidation in small amounts and usually from the start of the process. Cu becomes saturated with H_{abs} at a low level of H_{abs}. However, in the presence of large amounts of Cu, it takes time to reach even this low saturation level, and the consumption of O_2 is then delayed.

When the O_2 pressure is kept constant, $[O_2]$ of the substrate is constant according to Henry's law, and the integration of [1] gives a general formula

$$F(x) = K\,f(t) + a \qquad [9]$$

In the course of the process, F(x) assumes three different forms corresponding to the three oxidation stages, which will be shown and discussed below.

The initial oxidation stage. At small values of x, (1−x/n) is close to 1. The integration of [1] at constant $[O_2]$ and with $f(t) = (t-t_o)^2$ gives

$$x = k\,(t-t_o)^2 \text{ or } \sqrt{x} = \sqrt{k}\,(t-t_o) \qquad [10]$$

The value of t_o is determined by plotting $\sqrt{x}$ against t. The intersection of this line with the t-axis gives t_o. Integration of [1] with f(t) = t gives

$$x = k_1\,t + a \qquad [11]$$

where a is an integration constant.

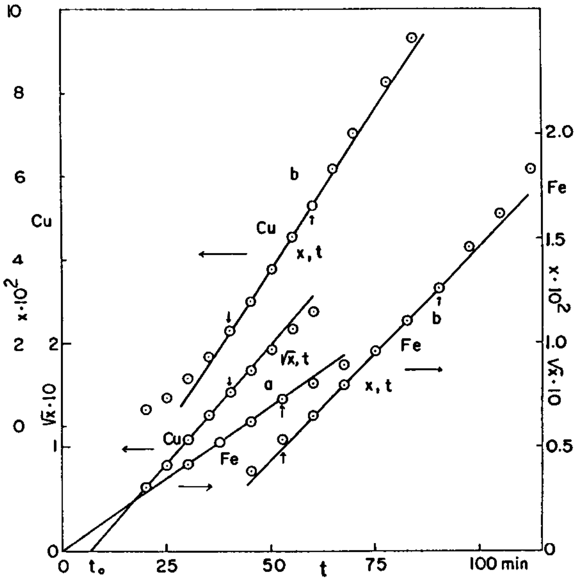

FIG. 1. Oxygen absorption x during the autoxidation of methyl linoleate (MeLi) at 50°C and 1 atm O_2 in the presence of $3 \cdot 10^{-4}$ moles Fe or Cu per mole MeLi; x in moles O_2/mole MeLi, t in minutes. a. $\sqrt{x} \cdot 10$ against t, [10]. b. $x \cdot 10^2$ against t, [11]. Data from Kern and Willersinn (17), Abb. 1.

Figure 1 shows the initial branches of the oxidation of methyl linoleate, MeLi, by O_2 at 50°C in the presence of $3 \cdot 10^{-4}$ moles of Cu per mole of ester (about 60 ppm of metal). For comparison, the corresponding curve for Fe is also shown in Figure 1. [Data from Kern and Willersinn (17).] With Fe, O_2 consumption starts at t = 0, but with Cu there is a delay of 7 min, as seen from Figure 1. The line for $\sqrt{x}$ cuts the t-axis at $t_o = 7$ min. This delay is also pointed out by Kern and Willersinn (17). In both cases, the curve is composed of line a, branch [10] and line b, branch [11]. The steady state of the catalyst is not reached at once, hence the branch according to [10]. The linearization of the continued process is shown in Figure 3 and discussed below.

Figures 1 and 4 (shown later) give examples of both [10] and [11]. Figure 2 shows a case where the attainment of catalyst saturation and the steady state were rapid. The first measured points, line b, follow [11]. After 3 h, the data show accelerated O_2 consumption, the exponential stage.

The exponential ("autocatalytic") stage. Several investigators of the autoxidation of fatty acid esters under constant O_2 pressure (18,19) have shown a linear increase of the oxidation rate dx/dt with the amount of O_2 consumed, x, but the straight line does not pass through the origin because this stage is preceded by the stages [10] and [11]. There is an extrapolated oxidation rate (18), v_o, at x = 0, $dx/dt - v_o = k\,x$ or

$$dx/dt = k\,(x + v_o/k) = k\,(x + A) \qquad [12]$$

With correction for the consumed substrate and with f′(t) = 1, [3], we obtain

$$dx/dt = k\,(A + x)\,(1 - x/n) \qquad [13]$$

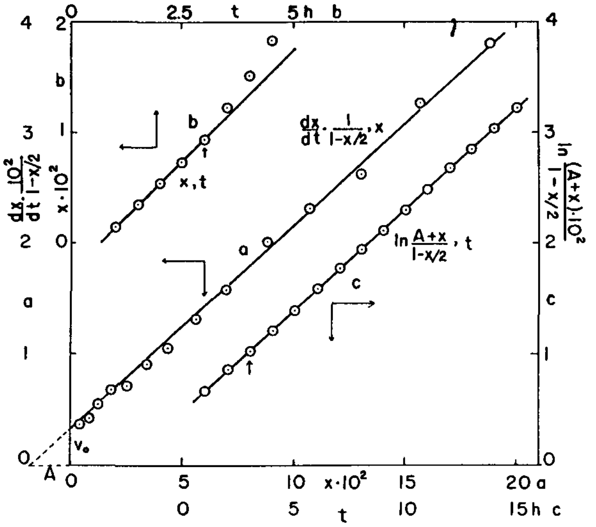

FIG. 2. Oxygen absorption x during the autoxidation of methyl linoleate at 50°C and 1 atm O_2. a. $dx/dt \cdot (1-x/2)^{-1} \cdot 10^2$ against $x \cdot 10^2$, [13]; b. $x \cdot 10^2$ against t, [11]; c. ln $[(A+x)(1-x/2)^{-1} \cdot 10^2]$ against t, $A = 1.8 \cdot 10^{-2}$, [14]. x and A in moles O_2/mole MeLi, t in hours. Data from Kern and Willersinn (19), Abb. 1.

In Figure 2, line a, $dx/dt \cdot (1-x/2)^{-1}$ is plotted against X for the oxidation of MeLi at 50°C under 1 atm O_2. [Data from Kern and Willersinn (19)]. The plot gives the value of A. Integration of [12] gives

$$\ln[(A+x)(1-x/2)^{-1}] = (A/n+1)\,k\,t+b = k_2t+b \qquad [14]$$

Figure 2, line c, shows ln $[(A+x)(1-x/2)^{-1}]$ against t for the same data. Equation [14] is valid to the end of the experiment at 20% oxidation.

After the initial stage, according to [11], line b, dx/dt increases as if $[O_2]$ were increasing, *e.g.*, by solubilization of O_2 into the hydroperoxide micelles formed in the substrate. The hydroperoxide, HP, molecule with its hydrophobic hydrocarbon chain and the hydrophilic —OOH group complies with the characterization of surface-active molecules, as given elsewhere (20). Surface-active agents form micelles when their concentration is above the critical micelle concentration (CMC). Here, O_2 is not solubilized until the CMC of the HP in the substrate, c′, is reached. The amount of O_2 solubilized is proportional to the number of micelles (21,22). Hence,

$$[O_2] = [O_2]_o + k'(x-c') = k'([O_2]_o/k' - c' + x) = k'(A+x) \qquad [15]$$

with

$$A = [O_2]_o/k' - c' \qquad [16]$$

Insertion of [15] in [1] gives

$$dx/dt = kk'(A+x)(1-x/n)\,f'(t) \qquad [17]$$

which, for $(1-x/n)$ near 1 and with $f'(t) = 1$, gives the empirical equation [12]. Figure 2, line b, indicates a value of c′ of about $1 \cdot 10^{-2}$ moles HP/mole MeLi.

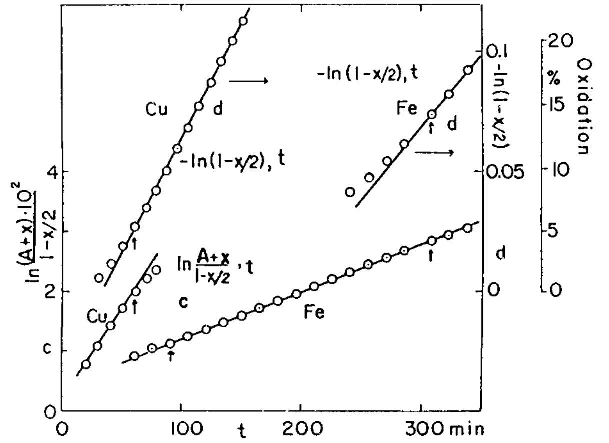

FIG. 3. As in Figure 1. c. ln $[(A+x)(1-x/2)^{-1} \cdot 10^2]$, against t, $A = 1.8 \cdot 10^{-2}$ [14], d. $-\ln(1-x/2)$ against t, [19]. x and A in moles O_2/mole MeLi, t in min.

The last oxidation stage. Oxidation experiments show an upper limit for the solubilization, above which $[O_2]$ is constant again but higher than $[O_2]_o$. Thus,

$$dx/dt = K(1-x/n)\,f'(t) \qquad [18]$$

with $K = k[O_2]$. Integration of [18] with $f(t) = t$, [3], gives

$$-\ln(1-x/n) = k_3\,t+c \qquad [19]$$

There is another difference between Fe and Cu as catalysts besides the one already discussed. Figure 3 shows the linearization according to [14] and [19] of the oxidation of MeLi with added Fe or Cu beyond the range of [11] in Figure 1. Under these experimental conditions, the transition from [14] to [19] is at 14% oxidation for Fe, but at 5% for Cu. With no added catalyst, the transition is not within the range of oxidation studied, up to 20% oxidation. It is well known that HP is decomposed more rapidly in the presence of metals, especially of Cu. Hence, above 14 and 5% oxidation, respectively, the number of micelles no longer increases because the HP is decomposed as rapidly as it is formed. Decomposition of the HP does not affect the kinetics in any other way. Equation [19] is valid to the end of the experiment, about 20% oxidation.

Equation [19] represents first-order kinetics. Wu *et al.* (11) followed the autoxidation of a monolayer of linoleic acid, LiH, on silica gel by measuring the amount of unreacted LiH after different times. They found no delay of the oxidation, and the kinetics remained first order, *i.e*, according to [19], over the entire range of 0–85% oxidation. The reason is that no micelles can be formed in a monolayer. In bulk-phase oxidation, the exponential stage is just a transient deviation from the first-order kinetics, caused by the solubilization of O_2 into micelles of HP.

Influence of added surface-active agents. Recently, Kortenska *et al.* (23) studied the "kinetics of inhibited oxidation of lipids in the presence of 1-octadecanol and 1-palmitoylglycerol." Their substrate was a mixture of the methyl ester of sunflower oil and small amounts of *p*-methoxyphenol (an inhibitor) and azobisisobutyronitril

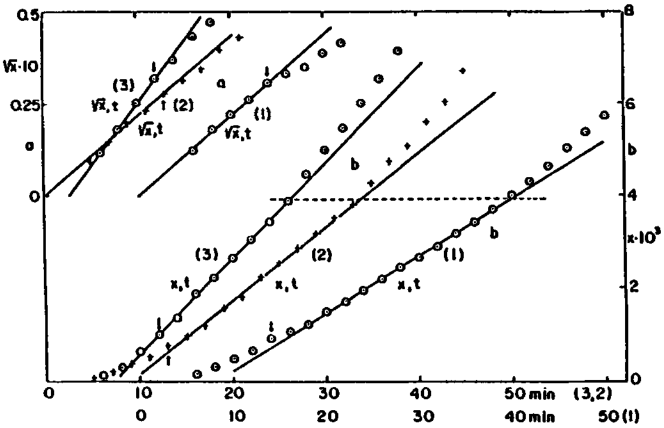

FIG. 4. Oxygen absorption x during autoxidation of the methyl ester of sunflower oil, mixed with $2 \cdot 10^{-2}$ M AIBN and $7 \cdot 10^{-5}$ M *p*-methoxyphenol, (1) no further addition, (2) 0.1 M 1-octadecanol added, (3) 0.1 M 1-palmitoylglycerol added. a. $\sqrt{x} \cdot 10$ against t, [10]; b. $x \cdot 10^3$ against t, [11]; x in moles $O_2 \cdot 10^{-3}$, t in minutes. Data from Kortenska *et al.* (23).

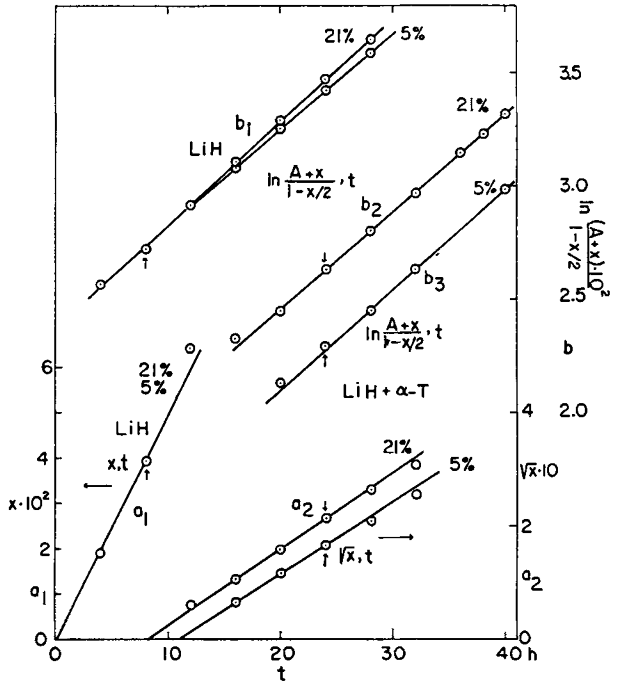

FIG. 5. Oxygen absorption x during autoxidation of an aqueous emulsion of linoleic acid (LiH) in the absence and presence of 0.005% of α-tocopherol; oxidation at room temperature in air, 21% O_2, or O_2-N_2 mixture with 5% O_2. a_1 $x \cdot 10^2$ against t, [11]; $a_2 \cdot \sqrt{x} \cdot 10$ against t, [10]; b. ln $[(A+x)(1-x/2)^{-1} \cdot 10^2]$ against t, [14]; b_1: $A = 11 \cdot 10^{-2}$, b_2: $A = 9 \cdot 10^{-2}$, b_3: $A = 7 \cdot 10^{-2}$. x and A in moles O_2/mole LiH, t in hours. Data from Marcuse and Fredriksson (Ref. 24, and Fig. 12 therein).

(an initiator). O_2 consumption at 50°C was measured. Their data, linearized in Figure 4, show that the two additives 1-octadecanol and 1-palmitoylglycerol increased the rate as compared to that of the substrate alone. Both additives are surface-active. The increased oxidation rate can be attributed to the solubilization of O_2 into the micelles of the additives. Their concentration was 0.1 M, which should be well above their CMC in the substrate.

Figure 4 shows that the oxidation started according to [10], probably as an effect of the inhibitor. Then, it followed the line according to [11]. The accelerated oxidation thereafter started at the same O_2 consumption, marked by the dotted line, in all three cases. It appears that no mixed micelles are formed by the additives and the HP formed.

The solubilization of gases by surfactants in oils has, to my knowledge, not yet been investigated, only solubilization of gases in aqueous solution (21,22). Micellization and solubilization in nonaqueous liquids is briefly treated (20), but not the solubilization of gases.

The function f(t). While the catalyst is unsaturated with H_{abs}, H cannot react with O_2, and no O_2 is consumed. MeLi is not oxidized by single OH_{ads} as formed by the decomposition of H_2O, but it is oxidized by H_2O_2. Ordinarily, the catalyst, the glass wall, becomes saturated quickly. There is no measurable delay in O_2 consumption, and f(t) quickly becomes f(t) = t, as is shown in Figure 2. However, additions to the substrate may affect the state of the catalyst and thereby f(t).

Effects of inhibitors on f(t). Inhibitors of the phenolic type, *e.g.*, hydroquinone and tocopherol, have been investigated by Marcuse and Fredriksson (24). Some of their data for the oxidation of LiH at room temperature with added α-tocopherol, α-T, are presented in linearized form in Figures 5 and 6. The substrate was an emulsion of LiH in a buffer solution. It was held in a glass vessel. The volume of the liquid was the same in all cases, and therefore, the surface area of the glass in contact with the liquid was the same. The concentration of α-T was 0.005% in Figure 5 and 0.01% in Figure 6. The concentration of LiH was 0.07 M in Figure 5 and 0.28 M in Figure 6. The atmosphere was air at 21% O_2 or N_2 with 5% O_2. The amount of O_2 absorbed by the liquid at a constant gas pressure was measured.

The curve for the case without added α-T is shown for comparison in Figure 5. It consists of two branches, both with f(t) = t. The first branch, line a_1, starts at t = 0 according to [11]. This means that the catalyst was saturated almost at once. The first branch drawn on the data for 0.005% α-T in Figure 5, lines a_2, starts at $t_o = 8$ h at 21% O_2 and at $t_o = 11$ h at 5% O_2. In this case, $f(t) = (t-t_o)^2$, [10]. Thus, the added α-T caused a delay of the attainment of catalyst saturation, possibly by being adsorbed onto the catalyst surface (the glass wall) and by reacting with OH_{ads} on the surface. The added α-T also reduced the value of A in [14].

During the first branch with $f(t) = (t-t_o)^2$, α-T is gradually oxidized and desorbed from the catalyst surface. Thus, the active catalyst surface area gradually increases, hence there is no steady state. When all α-T is oxidized and desorbed, the steady state with f(t) = t is attained, and rapid oxidation sets in. That the total consumption of α-T coincides with the onset of rapid oxidation of methyl linoleate is shown by Yamauchi *et al.* (25) and Terao (26). Reducing the O_2 content of the gas from 21% to 5% has a negligible effect on the rate constants of the different oxidation stages, but in the presence of α-T the delay, t_o, is increased and A in [14] is reduced. The oxidation system is complicated, containing a large amount of water, emulsifier and buffer chemicals. In spite of this, it follows

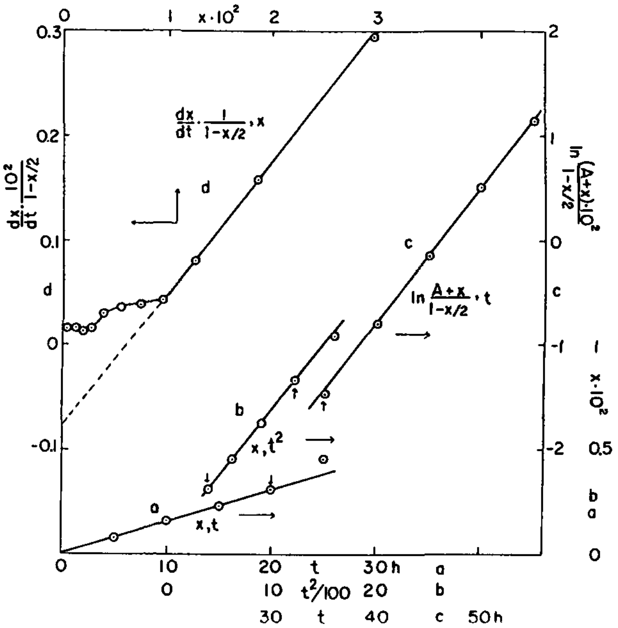

FIG. 6. Oxygen absorption x during autoxidation in air of an aqueous emulsion of linoleic acid in the presence of 0.01% α-tocopherol at room temperature. a. $x \cdot 10^2$ against t, [11]; b. $x \cdot 10^2$ against $t^2/100$, [10] with $t_o = 0$; c. ln $[(A+x)(1-x/2)^{-1} \cdot 10^2]$ against t, $A = -0.6 \cdot 10^{-2}$, [14]; d. $dx/dt \cdot (1-x/2)^{-1} \cdot 10^2$ against $x \cdot 10^2$, [13]; x and A in moles O_2/mole LiH, t in hours. Data from Marcuse and Fredriksson (Ref. 24, and Fig. 3 therein).

the rate equations found for the simple system MeLi in O_2.

When α-T is added in larger amounts, it becomes prooxidative in the sense that there is no delay in O_2 consumption. Figure 6 shows this case: x was linear against t, as in [11], from the beginning (line a). Evidently, the catalyst (the glass wall) was quickly saturated with H_{abs}. The oxidation rate, however, was only 1/8 of the rate without added α-T (not shown in Fig. 6). Thus, 7/8 of the catalyst's surface was quickly covered by adsorbed α-T. The steady state, f(t) = t, indicates that the surface coverage with α-T did not change. When one molecule of α-T was oxidized and desorbed, a new molecule of α-T from the substrate was adsorbed onto the vacant site. This can go on as long as the substrate still contains α-T. When the α-T of the substrate is consumed, the remaining α-T on the catalyst surface is gradually oxidized and desorbed and f(t) changes to t^2, as shown in Figure 6, line b. This branch was followed by line c according to [14], as in Figure 5. The three parts of the oxidation are conspicuous in the plot of $dx/dt \cdot (1-x/2)^{-1}$ against x according to [13], as shown in curve d of Figure 6.

Inhibitors thus seem to affect the oxidation in two ways: diminishing the active catalyst surface area by adsorption and delaying the attainment of the saturation of the catalyst.

Effect of conjugated double bonds. Kern *et al.* (27,28) investigated the autoxidation of fatty acid esters and hydrocarbons with conjugated double bonds. In one case (28), the methyl ester of 9,11-octadecadienoic acid (9,11-MeODD) was oxidized at 70°C to more than 90% oxidation at a constant O_2 pressure. In this process, one mole of O_2 was bound per mole of substrate, *i.e.*, n = 1 in [1].

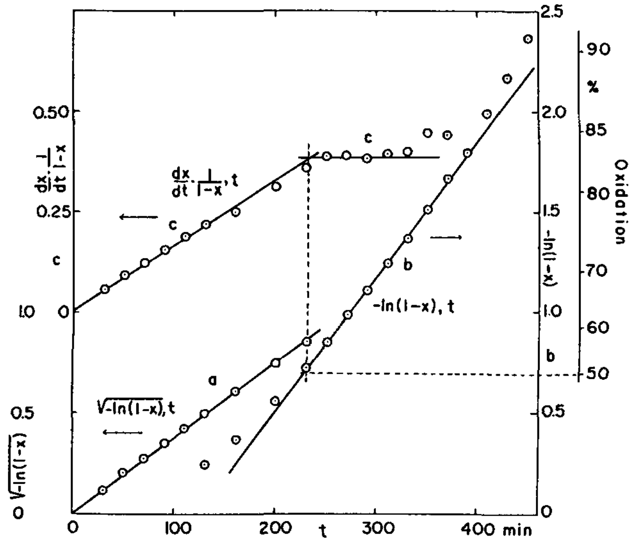

FIG. 7. Oxygen absorption x during autoxidation of 9,11-octadecadienoic methyl ester (MeODD) at 70°C in 1 atm O_2. a. $[-\ln(1-x)]^{1/2}$ against t, [21]; b. $-\ln(1-x)$ against t, [22]; c. $dx/dt \cdot (1-x)^{-1}$ against t, [20]; x in moles O_2/mole MeODD, t in minutes. Data from Kern *et al.* (28), Abb. 1.

A trimeric peroxide was formed, possibly with a ring structure. One double bond per molecule of oxidized substrate disappeared. Peroxides are not surface-active, and, therefore, no micelles are formed, and there is no exponential oxidation stage. The two lines c of Figure 7 show that the event follows

$$dx/dt = k\,(1-x)\,f'(t) \qquad [20]$$

with f′ (t) = t from 0 to 240 min and then f′ (t) = constant. The integrated formula with $f(t) = t^2$ (t_o=0) is

$$(-\ln(1-x))^{1/2} = \sqrt{k}\,t \quad \text{(line a)} \qquad [21]$$

and with f(t) = t it becomes

$$-\ln(1-x) = k\,t + c \quad \text{(line b)} \qquad [22]$$

If a trimeric peroxide were formed according to $3\ O_2 + 3\ S \rightarrow (s'\text{-O-O-})_3$, where S is the substrate molecule with two double bonds and S′ contains only one double bond, the rate equation might be

$$dx/dt = k\,[O_2]^N\,(1-x)^N\,f'(t) \qquad [23]$$

with N=3 in this case. When x is small and (1−x) near 1, it is not possible to check if the experimental data follow [23], but at larger values of x, it is evident from Figure 7 that they follow [1] where N = 1. The trimerization step, thus, is not part of the rate-determining step. Instead, the rate-determining step is the first step and the same as in the autoxidation of MeLi with the formation of HP. A possible mechanism is the initial formation of HP and the saturation of one double bond with H from the catalyst, as indicated by $f(t) = t^2$. The second step is the more rapid trimer formation, $3\ HP \rightarrow (\text{-S'-O-O-})_3 + 3\ H$. As part of this process, the H in -OOH is returned to the catalyst. As long as the amount of unreacted 9,11-MeODD is larger than the amount of reacted MeODD, the catalyst does not reach the steady state and $f(t) = t^2$. When the amount of unreacted MeODD is smaller than the amount of reacted MeODD, enough H is returned to keep the catalyst in the steady state. Hence, $f(t) = t^2$ turns into $f(t) = t$ at 50% oxidation, as shown in Figure 7.

The experimental values deviate from line b above 85% oxidation. If some of the O_2 is consumed by some other reaction, $(1-x)$ appears too small and $-\ln(1-x)$ falls above line b, as in Figure 7.

The small technique, linearization of rate data and identification of their mathematical form, has been applied previously to bleaching of vegetable oils (29,30), to crystallization of high-melting glycerides in oils (31) and to melting and phase transitions of cocoa butter (32). In all these cases, the time function was found to be $f(t) = (t-t_o)^2$ and $f(t) = (t-t_o)^{1/2}$, thus partly different from the functions found above.

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