Kinetics of Inhibited Oxidation of Lipids in the Presence of 1-Octadecanol and 1-Palmitoylglycerol

Vessela D. Kortenska, Nedjalka Vl. Yanishlieva* and **Vitalii A. Roginskii**[1]
Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

The kinetics of initiated oxidation of sunflower oil methyl esters at 50°C in the presence of the phenolic inhibitor *p*-methoxyphenol are investigated. It is established that addition of 0.1 M 1-octadecanol and of 0.1 M 1-palmitoylglycerol leads to a 1.5- or 2.3-fold decrease of the rate constant of chain termination on the inhibitor, which proves the blocking of its effect due to the formation of a complex based on a hydrogen bond. The stronger effect of 1-palmitoylglycerol is explained by the presence of two hydroxyl groups in its molecule.

KEY WORDS: 1-Octadecanol, 1-palmitoylglycerol, inhibited oxidation, kinetics, lipids.

The problem of ensuring a high stability of lipids and lipid-containing products determines the interest in investigating the participation of hydroxy components (partial acyl glycerols and fatty alcohols) in lipid autoxidation (1). Previous studies have shown that the addition of fatty alcohols to inhibited lipid systems leads to a decrease in the induction period (2), and above a definite concentration of the additive the autoxidation proceeds as uninhibited. It is supposed that this effect is a result of the formation of a complex based on the hydrogen bond between the hydroxy compound (ROH) and the phenol antioxidant (PhOH) (3,4). As is known, the efficiency of the antioxidant is determined by the rate of its reaction with the peroxide radical (termination of the chain on the inhibitor).

There are no data in the literature concerning the role of lipid hydroxy components on the rate constant of chain termination.

The purpose of the present work was to use a model study performed in a regime of initiated oxidation in order to elucidate whether the fatty alcohol and the monoacylglycerol lead to a drop of the rate constant of this reaction. Methyl esters of sunflower oil were used as model lipid substrate.

EXPERIMENTAL PROCEDURES

The methyl esters of sunflower oil (MESO) were obtained according to Christie (5), purified from pro- and antioxidants by column chromatography (6) and stored in an inert atmosphere at −10°C.

1-Octadecanol (Merck, Darmstadt, Germany) was distilled under vacuum, while 1-palmitoylglycerol, 99% (Fluka, Buchs, Switzerland) was used without preliminary purification.

The inhibitor (*p*-methoxyphenol, *p*-OMePh) was subjected to repeated recrystallization, while the initiator (azobisisobutyronitril, AIBN) and the solvent (chlorobenzene) were purified by standard methods (7).

The fatty acid composition of MESO was determined by gas chromatography: Pye Unicam 304 apparatus, 2 m glass column, 11% DEGS on Supelcoport, temperature 200°C.

MESO have the following fatty acid composition in wt%: $C_{14:0}$,2.0%; $C_{16:0}$,8.8%; $C_{16:1}$,1.8%; $C_{18:0}$,6.8%; $C_{18:1}$,20.2%; $C_{18:2}$,58.6%; $C_{20:0}$,1.8%.

The oxidation was carried out in an initiated regime. The oxygen absorption kinetics was studied by a high-sensitivity capillary volumeter. The construction of the reaction vessel allowed introduction of samples during the experiment (8). The volume of the mixture being oxidized was 0.1–0.3 cm^3. The rate of initiated oxidation (W) was determined by the formula equation:

$$W = \alpha\,(dh/dt)/V \qquad [1]$$

where α is the reaction vessel constant determined experimentally ($\alpha = 2.25 \times 10^{-7}$ mol/mm); dh/dt is the oxygen absorption rate (mm/min), and V, the volume of the reaction mixture (cm^3).

The kinetic data presented in this paper are mean results from five independent experiments.

RESULTS AND DISCUSSION

At sufficiently high oxygen concentrations and constant rate of initiation W_i the oxidation process during its initial stage can be presented by the following reactions:

Initiation	$\xrightarrow{+O_2,\,LH}$ $LO_2^\bullet$	W_i
(2)	$LO_2^\bullet + LH \rightarrow LOOH + L^\bullet$	k_2
(6)	$LO_2^\bullet + LO_2^\bullet \rightarrow$ products	k_6
(7)	$LO_2^\bullet + PhOH \rightarrow LOOH + PhO^\bullet$	k_7
(8)	$LO_2^\bullet + PhO^\bullet \rightarrow$ products	k_8

The system of differential equations for the concentration of active particles can be written as (9):

$$d[LO_2^\bullet]/dt = W_i - k_6[LO_2^\bullet]^2 - k_7[LO_2^\bullet][PhOH] - k_8[LO_2^\bullet][PhO^\bullet]$$

$$[PhO^\bullet]/dt = k_7[LO_2^\bullet][PhOH] - k_8[LO_2^\bullet][PhO^\bullet]$$

$$-d[PhOH]/dt = k_7[LO_2^\bullet][PhOH]$$

$$-d[O_2]/dt = k_2[LH][LO_2^\bullet]$$

*To whom correspondence should be addressed at Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences, bl. 9, 1040 Sofia, Bulgaria.
[1]Present address: Institute of Chemical Physics, Academy of Sciences of the USSR, 117977 Moscow, USSR.

Taking into account the oxygen absorption rate W_o in the absence of an inhibitor (Equation 2):

$$W_o = k_2 k_6^{-1/2} [LH] W_i^{1/2} \quad [2]$$

the system of differential equations can be solved as follows (Equation 3):

$$F = \ln [(1 + W/W_o)/(1 - W/W_o)] - W_o/W = (k_7 W_o / k_2 [LH])t + c \quad [3]$$

where W_o and W are the rates of oxygen absorption in the absence and presence of an inhibitor (Ms^{-1}), respectively, and c is an integral constant.

Equation 3 describes the process in the regions of both linear and mixed (linear + quadratic) chain termination (9). In addition, the determination of k_7/k_2 does not require knowledge of initiation rate, induction period and absolute antioxidant concentration.

The results obtained during initiated oxidation of MESO at 50°C are shown in Figure 1, those in the presence of 0.1 M 1-octadecanol in Figure 2 and of 0.1 M 1-palmitoylglycerol in Figure 3. From the slope of curve 3, $k_7W_o/k_2[LH]$ is determined and, hence, k_7/k_2 is found. The concentration of the substrate being oxidized [LH] is in this case equal to that of methyl linoleate because, during the initial stage of MESO oxidation, only linoleate moieties are oxidized while the methyl esters of other acids present in MESO (*e.g.* saturated, oleic and palmitoleic acids) are practically inert (8,10), *i.e.* [LH] = 1.5M.

The following values are obtained for k_7/k_2: pure lipid substrate, 3.75×10^2; in the presence of 0.1 M 1-octadecanol, $k_7/k_2 = 2.50 \times 10^2$, while its value in the presence of 0.1 M 1-palmitoylglycerol is 1.65×10^2. The value obtained for k_7/k_2 in the absence of additives coincides with that determined for neat methyl linoleate under the same experimental conditions (8). The above data show that the addition of 1-octadecanol and 1-palmitoylglycerol leads to a 1.5- and 2.3-fold decrease, respectively, of the rate constant of chain termination on the inhibitor.

The kinetic effect observed proves the blocking of the action of the phenolic antioxidant (PhOH) in the presence of hydroxy compounds (ROH). This effect may be due to their solvating action, *i.e.* formation of a complex based on a hydrogen bond [3,4]:

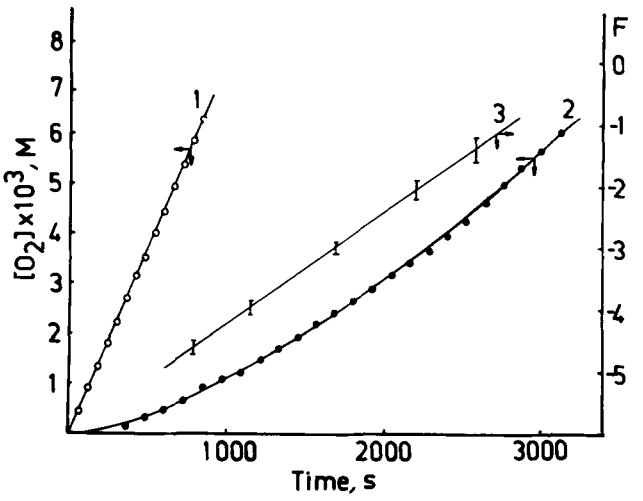

FIG. 1. Kinetic curves of oxygen absorption during oxidation of MESO at 50°C, [AIBN] = 2×10^{-2} M, (1) in the absence of an inhibitor and (2) in the presence of 7×10^{-5} M *p*-OMePh; (3) anamorphosis of curve (2) in coordinates of Equation 3.

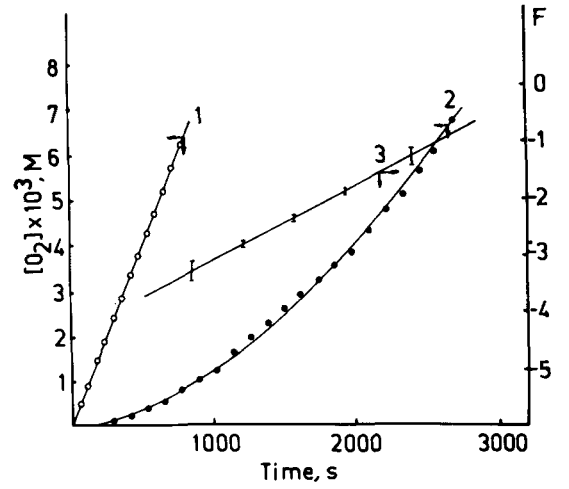

FIG. 2. Kinetic curves of oxygen absorption during oxidation of MESO in the presence of 0.1 M 1-octadecanol at 50°C, [AIBN] = 2×10^{-2} M, (1) in the absence, and (2) in the presence of 7×10^{-5} M *p*-OMePh; (3) anamorphosis of curve (2) in coordinates of Equation 3.

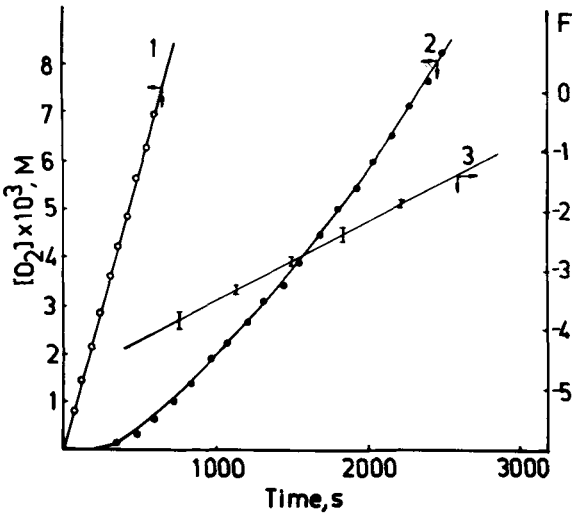

FIG. 3. Kinetic curves of oxygen absorption during oxidation of MESO in the presence of 0.1 M 1-palmitoylglycerol at 50°C, [AIBN] = 2×10^{-2} M, (1) in the absence and (2) in the presence of 7×10^{-5} M *p*-OMePh; (3) anamorphosis of curve (2) in coordinates of Equation 3.

$$PhOH + ROH \overset{K_o}{\rightleftharpoons} \left[PhOH \ldots . O \begin{matrix} H \\ R \end{matrix}\right]$$

$$(7') \left[PhOH \ldots . O \begin{matrix} H \\ R \end{matrix}\right] + LO_2^{\bullet} \rightarrow LOOH + PhO^{\bullet} = + ROH \quad k_7'$$

The activity of the complex is much lower than that of the inhibitor molecules, which do not participate in the complex. This is due to blocking of the active center of the inhibitor (4). In other words, additional energy for liberation of this center from the complex is needed to enable it to react with the peroxide radicals. As a result, the concentration of free inhibitor molecules decreases, which leads to a decrease in effectiveness of the inhibitor, and $k_7' < k_7$. From the above kinetic scheme for k_7' and W' (rate of inhibited oxidation in the presence of a hydroxy compound), one obtains (Equation 4):

$$k_7' = k_7/(1 + K_o[ROH]); \; W' = k_2 [LH] \; W_i/f \; k_7''[PhOH]_o \quad [4]$$

where f is the stoichiometric coefficient determining how many radicals perish in an inhibitor molecule; $[PhOH]_o$ is the initial concentration of the phenolic antioxidant (M).

The results obtained confirm the assumption (2), that fatty alcohols and monoacylglycerols participate in the reactions of chain termination on the inhibitor and reduce the rate constant of this reaction. The presence of two hydroxyl groups in the monoacylglycerol is the reason for the more pronounced decrease of the inhibitor's effectiveness compared to that of 1-octadecanol.

REFERENCES

1. Yanishlieva, N., and V. Kortenska, *J. Food Sci. Agric. 47*:215 (1989).
2. Yanishlieva, N., and V. Kortenska, *Fat Sci. Technol.*, in press.
3. Kortenska, V., and N. Yanishlieva, *Effect of the Lipid Substrate on the Role of Fatty Alcohols during Inhibited Oxidation of Lipids; International Conference on Regulation of Free Radical Reactions (Biomedical Aspects) Abstracts*, No. 86, Bulgaria, Varna, 13–16 September (1989).
4. Emanuel, N.M., G.E. Zaikov and Z.K. Maizus, *The Role of Environment in the Chain-Radical Oxidation Reactions of Organic Compounds*, Nauka, Moscow (in Russian), 1973, p. 205.
5. Christie, W.W., *Lipid Analysis*, Pergamon Press, New York, 1982, p. 52.
6. Popov, A., N. Yanishlieva and J. Slavceva, *Compt. Rend. Bulg. Acad. Sci. 21*:443 (1968).
7. Beljakov, V.A., R.F. Vassiliev and G.F. Fedorova, *Chemistry of High Energies 12*:247 (1978) (in Russian).
8. Roginskii, V.A., *Kinetics and Catalysis 31*:546 (in Russian), 1990.
9. Roginskii, V.A., *Phenolic Antioxidants—Reactivity and Efficiency*, Nauka, Moscow (in Russian), 1988, p. 53.
10. Yanishlieva, N., and A. Popov, *Rev. Franç. Corps Gras 20*:11 (1973).

[Received March 12, 1991; accepted July 22, 1991]