

AUTOXIDATION RATE OF TRIOLEIN

YOSHINOBU KAWANO*, YASUO SAITO, KOICHIRO SHIOMORI AND YOSHINARI BABA

Dept. Materials Science, Miyazaki University, Gakuenkibanadai Nishi 1-1, Miyazaki 889-21

YASUO HATATE

Dept. Applied Chem. and Chem. Eng., Kagoshima University, Korimoto 1-21-40, Kagoshima 890

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Introduction

The formation of hydrogen peroxides in the oxida-

tive degradation of lipids has been studied for many years^{1, 6, 7)}.

A very small amount of peroxide in foods signifi-

* Received March 2, 1994. Correspondence concerning this article should be addressed to Y. Kawano.

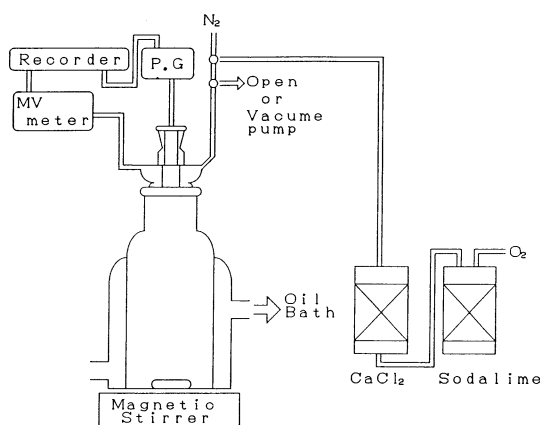


Fig. 1 Experimental apparatus and flow diagram

canfly affects human health. Furthermore, the oils and fats of our diet consist largely of mixtures of triglycerides³⁾.

Few studies have been reported for the kinetics of lipid autoxidation in spite of the actual importance to the food industry^{2, 8)}. In the previous work^{4, 5)}, degradation by the autoxidation for oleic acid and oleates was found to proceed autocatalytically by the peroxidation of oleic acid or its esters. For purposes of understanding the degradation, it is important to clarify the oxidation mechanism in induction period. In this paper, the autoxidation rate in the induction period of triolein was examined to understand the degradation of the oils and fats.

1. Experimental

1.1 Oxidation of triolein by oxygen

Triolein and methyl laurate, GR reagents were obtained from Wako Pure Chemical Co. and were used without further purification. The reactor for the oxidation of triolein was a double tubular type separable flask connected with a pressure gauge as shown in Fig. 1. Contaminants as peroxides in triolein were almost thermally decomposed until peroxide value (POV) of 0.2 was obtained before the oxidation. The concentration of triolein in the reaction solution was changed by adding methyl laurate which is not oxidized by oxygen⁵⁾. Oxygen was filled to 1070 hPa at first in the reactor containing the solution. The pressure of the oxygen in the reactor was measured continuously during the oxidation. The amount of oxygen consumed was assumed to be proportional to peroxide formation. POV in the solution could be continuously determined with an accuracy of ± 0.05 by measurement of the pressure change proposed in the study. In the determination of POV by the standard titration, a large quantity of the sample was required to obtain the same accuracy, and continuous measurement of POV is impossible. The initial and final state of POV in the solution were also determined by the standard titration method⁸⁾. The changes of concentrations of triolein in the solution agreed with those measured in volumetric methods.

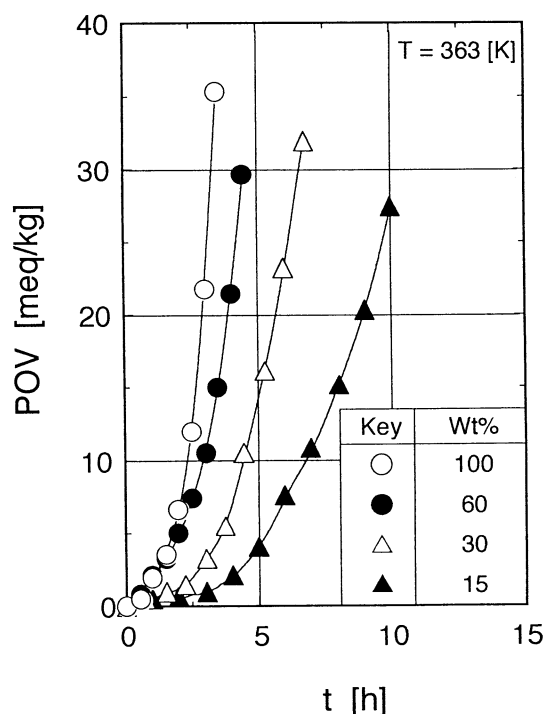


Fig. 2 Relationship between POV and reaction time at 365 K for various concentrations of triolein

2. Theory

The kinetics of triolein auto oxidation was modified from the one proposed for oleic acid⁴⁾. Each unsaturated double bond in triolein was assumed to have the same reactivity. Peroxide formations via intermediates, decomposition of peroxides and polymerizations were assumed to proceed in parallel. Considering the steady state approximation for all of the intermediates in the reactions, the rate of peroxide formation can be expressed by the following equation:

$$\frac{d(POV)}{dt} = K_0 [R_3 H_3] [O_2] + K_1 (POV)^{(1/2)} [O_2] / \{K_2 / [R_3 H_3] + [O_2]\} + k^*_d (POV) \quad (1)$$

where,

$$K_0 = (k^{\circ}_1 k^{\circ}_3 / k^{\circ}_2) \times 10^6 / \{d_s (11/12)\} \quad (2)$$

$$K_1 = K_{RH} K_i \times 10^6 / \{d_s (11/12)\} \quad (3)$$

$$K_2 = k^{\circ}_2 (k_2 + k_3) / k^{\circ}_1 k_1 \quad (4)$$

$$k^*_d = (k''_d / 2 + k'_d / 4 + k_d / 6) \times 10^6 / \{d_s (11/12)\} \quad (5)$$

k°_i , k_i ($i = 1, 2$ and 3), k_d , k'_d and k''_d are the rate constants for the elementary reactions reported previously⁴⁾. K_{RH} and K_i are constants; consists of rate constants⁴⁾. The concentration of oxygen in the solution of triolein at constant pressure was found experimentally to be almost independent of the weight fraction of triolein. The value of $[R_3 H_3]$ can be written as follows:

$$[R_3 H_3] = d_s f \times 10^6 / M_R \quad (6)$$

d_s varied from 900 to 850 kg/m³ according to the

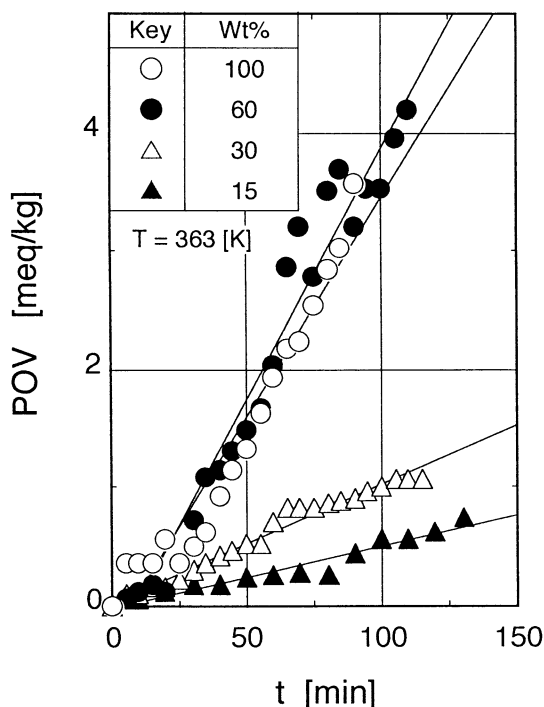


Fig. 3 Variation of POV with time at 365 K for various concentrations at low (POV)

concentration of triolein. To simplify the calculation, d_s was assumed to be constant. Eq. (1) can be written as follows:

$$d(POV)/dt = K'_0 + K'_1(POV)^{(1/2)} + k^*_d(POV) \quad (7)$$

where,

$$K'_0 = \{K_0 d_s f [O_2] \times 10^6\} / M_R \quad (8)$$

$$K'_1 = \{K_1 [O_2]\} / \{K_2 M_R / (d_s f \times 10^6) + [O_2]\} \quad (9)$$

The values of k^*_d for oleic acid and its oleates were very small^{4,5}. In the initial stages, where POV is low, the third term in Eq. (7) was assumed to be negligible compared with the first and the second terms. Consequently, the rate equation can be written as follows:

$$d(POV)/dt = K'_0 + K'_1(POV)^{(1/2)} \quad (10)$$

3. Experimental Results and Discussion

The experimental results for various concentrations at 363 K are shown in **Fig. 2**. The (POV) increases with time slowly in the initial steps and rapidly in the latter step of high POV. Similar results were observed at 353 and 373 K. In the initial steps of oxidation, the second term in Eq. (10) is negligible compared with the first term. By integration of Eq. (10), the following equation can be obtained:

$$(POV) = (POV)_0 + K'_0(t - t_0) \quad (11)$$

In **Fig. 3**, (POV) are plotted against time at 363 K. A linear relation between (POV) and time is observed in the initial

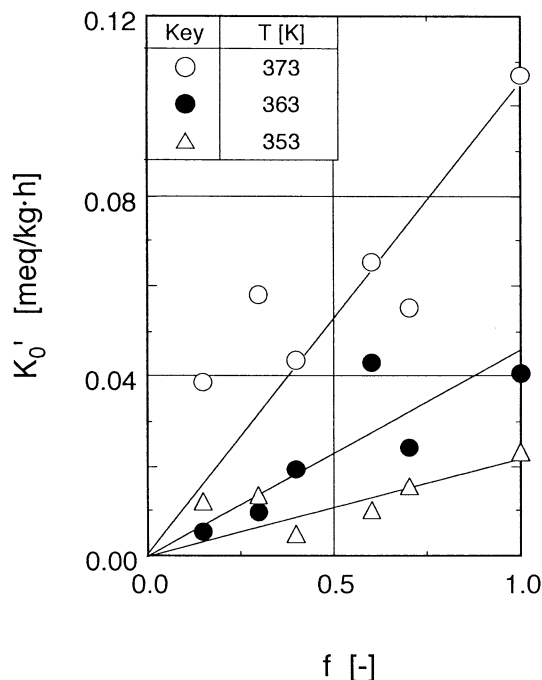


Fig. 4 Effect of weight fraction of triolein on the slope of the straight line in Fig. 3

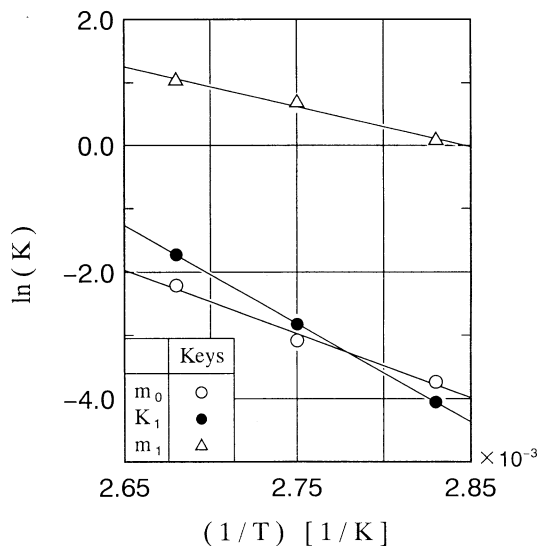


Fig. 5 Arrhenius plots for m_0 , K_1 and m_1

step. The values of K'_0 obtained by slopes of the straight lines are plotted against. The weight fraction of triolein, f , in **Fig. 4**. The values of K'_0 increased linearly with f although there was large scatter at each temperature. The slope of the lines in Fig. 4 correspond to a value of $K_0 d_s [O_2] \times 10^6 / M_R$ (denoted as m_0). The values of m_0 are plotted against $(1/T)$ in **Fig. 5**. In the range of POV where the second term in Eq. (10) is predominant compared with the first term, the following equation was obtained:

$$(POV)^{(1/2)} = 2K'_1 t + C \quad (12)$$

where C is a constant dependent on the initial conditions. In **Fig. 6**, $(POV)^{(1/2)}$ are plotted against time at 363 K. The slope corresponds to the value of $2K'_1$ in Eq. (12). The

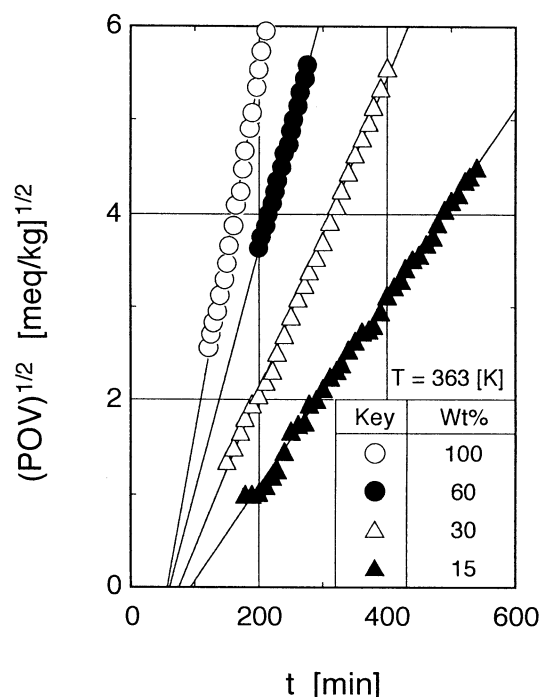


Fig. 6 Variation of $(POV)^{(1/2)}$ with time at 365 K for various concentrations in high (POV)

reciprocal of the slopes in Fig. 6 are plotted against $(1/f)$ in Fig. 7. The values of $K_2 M_R / (d_s [O_2] \times 10^6)$ (denoted as m_1) and K_1 are calculated from the slope and intercept as in Fig. 7, and are plotted against $(1/T)$ in Fig. 5. The linearities of the lines in Fig. 5 provide the following empirical equation for the autoxidation of triolein in the induction period:

$$d(POV)/dt = 2.34 \times 10^{11} \exp(-1.06 \times 10^4 / T) f + 1.08 \times 10^{17} \exp(-1.53 \times 10^4 / T) (POV)^{(1/2)} / \{1.68 \times 10^9 \exp(-7.50 \times 10^3 / T) / f + 1\} \quad (13)$$

Conclusion

Autoxidation of triolein was investigated in the induction period. The following results were obtained.

(1) Slow increases in POV at low POV and rapid increases in POV at high POV were found due to autoxidation of triolein.

(2) A new kinetic equation based on the autoxidation was determined for the triolein oxidation reaction in the induction period. The parameters in the proposed equation were functions of temperature and weight fraction of triolein.

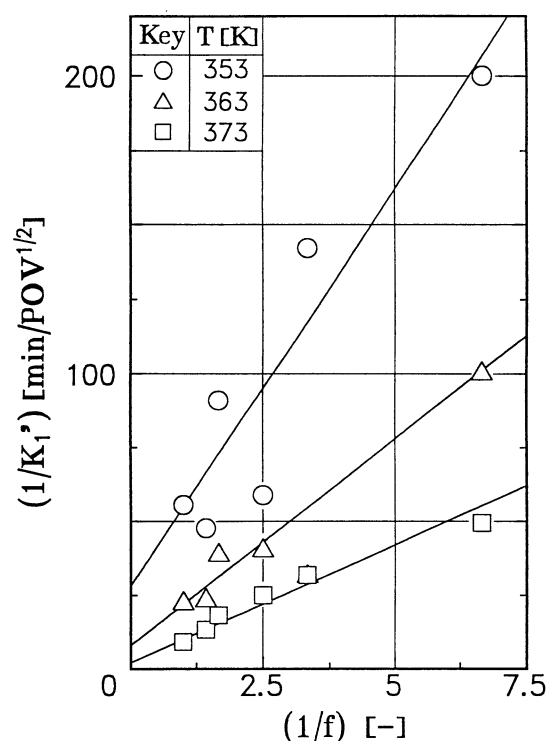


Fig. 7 Plot of $(1/f)$ versus the reciprocals of the slope of the straight lines in Fig. 6

Nomenclature

d_s	= density	[kg/m ³]
f	= weight fraction of triolein	[-]
H	= constant	[kmol/m ³ ·Pa]
K_i	= kinetic constant defined in Eq. (6)	
K'_i	= kinetic constant defined in Eq. (8)	
k_i, k'_i, k''_i	= kinetic constants for intermediate reactions	
k^o_i, k'^o_i, k''^o_i	= kinetic constants for intermediates reactions	
M_R	= molecular weight of triolein	[g/mol]
POV	= peroxide value	[meq/kg-oil]
$[R_3H_3]$	= concentration of triolein	[kmol/m ³]
T	= temperature	[K]
t	= time	[h]

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