

AUTOXIDATION RATES OF OLEIC ACID AND OLEATES

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Autoxidations of oleic acid, methyl oleate and ethyl oleate were carried out in the temperature ranges of 343–393 K, 358–378 K and 383–413 K, respectively, and in the oxygen partial pressure range of 0–0.1 MPa. The accumulation and decomposition rates of hydroperoxide were measured under the reaction control condition to obtain the following results. (1) Auto-acceleration in the formation rate of hydroperoxide was clearly observed in the initial stage of the oxidation. (2) A first-order dependence of hydroperoxide formation rate on oxygen partial pressure was found at low oxygen partial pressure, but the rate was almost independent of oxygen partial pressure at comparatively high oxygen partial pressures. (3) A semi-theoretical rate equation of hydroperoxide formation with four kinetic constants was developed to explain the autoxidation behavior of oleic acid and oleates.

Introduction

Degradation of lipids is caused mainly by autoxidation with oxygen in the air. The primary products of lipid autoxidation are hydroperoxides, which are considered deleterious when they accumulate above 30 meq/kg peroxide value (POV). Produced peroxides are easily decomposed by light and/or heat to produce radicals, key species in the polymerization that is a main secondary reaction by autoxidation. Considering the harmful effect of peroxides and polymers on health, it is very important to know the accumulation rate of peroxides. However, little work has been published so far done in this kinetic research area, although detailed information on products identification and autoxidation mechanisms has been published.

In the present study, autoxidation rates of oleic acid, one of the most important constituent fatty acids in vegetable fats, and of methyl oleate and ethyl oleate were measured under various operating conditions to develop a useful kinetic equation of autoxidation.

1. Experimental

1.1 Reagent

Oleic acid and oleates were purified by vacuum distillation and stored in the dark in an atmosphere of nitrogen before use.

1.2 Experimental apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. The reactor is a glass bubble column of 5 cm diameter and 15 cm height with a porous glass gas distributor covered with an aluminum sheet for shading. A sufficiently large rate of mass transfer of oxygen from gas phase to liquid phase was realized to measure the reaction-controlling rates of autoxidation, which are essential data for kinetic development. 1) Measurement of peroxide production rate About 60 cm$^3$ of oleic acid (or oleate) was poured into the reactor under a continuous calm bubbling of ultrapure nitrogen. An oil bath was used to heat the reactor. After reaching a desired temperature, blowing gas was changed from nitrogen to a gas mixture

![Fig. 1. Experimental apparatus](image-url)
containing a prescribed oxygen content to start the autoxidation reaction. Oxygen partial pressure was controlled by adjusting the flow rates of air and nitrogen or oxygen. Water vapor and carbon dioxide gas in the air stream were removed, using a silica gel tube and a soda lime tube respectively. Samples taken at given intervals were analyzed to obtain peroxide value (=POV) by titration and polymer product content* by gel permeation chromatography.5)

2) Measurement of decomposition rate of peroxide
At a given temperature, a prescribed amount of peroxide formed in the above-mentioned experiment was decomposed by changing the bubbling gas to ultra-pure nitrogen. Due to rapid desorption of dissolved oxygen by a violent mixing of blowing nitrogen, the observed consumption rate of peroxide would be equal to the true decomposition rate of peroxide.

2. Results and Discussion

From the practical viewpoint, conversion to polymer is limited to less than 10% in our kinetic study because such high conversion is considered to be complete degradation of lipids.

2.1 Oleic acid

Experimental conditions were in the temperature range of 343–393 K, and in the oxygen partial pressure range of 0–0.1 MPa.

1) Conditions for chemical reaction control. To obtain the true reaction rate in this system, mass transfer of oxygen from gas phase to liquid phase should be high enough to be under the control of chemical reaction. In a bubble column reactor, both the interfacial area between gas and liquid phases and the mixing intensity would increase with increasing gas flow rate. Hence, a reaction rate that is unchanged with increasing gas flow rate is considered to be the true reaction rate. In Fig. 2, time dependency of POV is shown at the reaction temperatures of 343, 373 and 393 K for various superficial gas velocities, satisfying the reaction rate-controlling conditions. The S-curve of the POV vs. time relation in the figure indicates typical autoxidation. Initial peroxide production rates at 343 and 393 K were 0.5 and 10 meq/kg in converted POV per min, respectively. Even at high temperature the peroxide accumulation rate is seen to be measured under the control of chemical reaction.

2) Effects of operating conditions on peroxide formation rate
The relations between POV and reaction time at various oxygen partial pressures are shown in Fig. 3 at reaction temperatures of 358, 373 and 393 K. The solid lines in these figures are explained later. It is obvious from these figures that the dependence of peroxide formation rate on oxygen partial pressure decreases with increasing oxygen partial pressure.

3) Determination of decomposition rate constant of peroxide
A representative result of peroxide decomposition at 393 K is shown in Fig. 4. Since dissolved oxygen would be purged just after changing the blowing gas to ultrapure nitrogen, only decomposition of peroxide occurs in the reactor. Assuming a first-order reaction for peroxide decomposition, the following equation is obtained.*

\[
\frac{POV}{POV_0} = \exp(-k_d t)
\]

(1)

Linearity in the relation between ln(POV/POV₀) and t was confirmed for all the data obtained. The Arrhenius plot of k_d values is shown in Fig. 5, from which the following equation was obtained for oleic acid.

\[
k_d = 3.65 \times 10^{-5} \exp(-67.3 \times 10^3/RT) \text{ s}^{-1}
\]

(2)

4) Derivation of kinetic equations
The observed

* Only a small amount of polymer was detected in the experimental runs for kinetics, so no effect of polymer on peroxide production rate was evident.
kinetic features of peroxide formation from oleic acid are auto-acceleration and decreasing dependency of oxygen partial pressure from first order to zero order with increasing oxygen partial pressure. A Michaelis-Menten type mechanism (Eq. (c), Table 1) is added to the common autoxidation mechanism (Eqs. (a), (b) and (d)) to explain the above mentioned kinetic characteristics. A proposed kinetic scheme is shown in Table 1. In this case, the main elemental reactions for peroxide formation are formations of primary and secondary intermediates. A primary intermediate formed from oleic acid (RH) with oxygen molecule (O₂) reacts with an active radical (R*) to form a secondary intermediate, and the latter decomposes to form peroxide (RO₂H). Finally, the following rate equation, which is consistent with the experimental findings, can be obtained for the peroxide formation rate using some approximations and assumptions. (see Appendix.)

\[
d[RO₂H]/dt = K₀[RH]²p_{O₂} + \{K₁[RO₂H]¹²/p_{O₂}\}/\{K₂/[RH]² + p_{O₂}\} - k_d[RO₂H]
\]

(3)

5) Determination of kinetic parameters The formation rate of [RO₂H] is equal to the first term of the right side of the rate equation in the absence of [RO₂H], so K₀ is obtained from the initial formation rate of peroxide. K₀-values obtained at \(p_{O₂} = 0.101\) MPa are 8.96 x 10⁻⁷, 2.78 x 10⁻⁶ and 1.44 x 10⁻⁵ (kmol/m³⁻¹ MPa⁻¹ s⁻¹) for 373 K, 358 K and 393 K, respectively. Hence, \(K₀\) is expressed as

\[
K₀ = 4.98 x 10^6 \exp(-87.0 \times 10^3/RT)
\]

(4)

Assuming low conversion to polymer, i.e. \([RH] = [RH]₀\), and a negligible \([RO₂H]\) formation rate by the reaction of RH with O₂ after the appreciable accumulation of RO₂H, Eq. (3) can be rewritten as

\[
d[RO₂H]/dt = \{K₁[p_{O₂}][RO₂H]¹²/[K₂/[RH]₀ + p_{O₂}]\} - k_d[RO₂H]
\]

(5)

Eq. (5) is integrated with the constant \(p_{O₂}\) and \([RH]₀\) to yield the following equation.

\[
[RO₂H]¹² = \{([K₁/k_d]p_{O₂})\}/\{1 - \exp(-k_d/2)\}/[K₂/[RH]₀ + p_{O₂}]
\]

(6)

Figure 6 shows a representative plotting of \(PO²¹/₂\) against \(1 - \exp(-k_d/2)\) at 393 K. The reciprocal of slope (S) of the line in Fig. 6 is expected to show a linear relation with \(1/p_{O₂}\) for each temperature investigated. The relation between \(1/S\) and \(1/p_{O₂}\) for each temperature is illustrated in Fig. 7. \(K₁\) and \(K₂\) are obtained from the intercept \((=k_d/K₁)\) and slope \((=K₂/k_d/K₁[RH]₀)\) of the line in Fig. 7. Arrhenius plots of \(K₁\) and \(K₂\) are shown in Figs. 8 and 9, respectively,
Fig. 6. Plot of $POV^{1/2}$ vs. $(1-\exp(-k_d/2))$ at 393 K for oleic acid

Fig. 7. Plot of $1/S$ vs. $1/p_{O_2}$ for oleic acid

Fig. 8. Arrhenius plot of $K_1$

Fig. 9. Arrhenius plot of $K_2$

Fig. 10. Effects of oxygen partial pressure and temperature on methyl oleate autoxidation

Fig. 11. Effects of oxygen partial pressure and temperature on ethyl oleate autoxidation

6) Comparison of calculated with observed $POV$
The lines in Fig. 3 are the calculated results from Eq. (3) assuming $[RH]=[RH_0]$. The comparatively good agreement shows that the $POV$ accumulation rate equation proposed in this work can be useful for predicting $POV$, at least under the conditions of $p_{O_2}=0-0.1$ MPa and temperature $=358-393$ K.

2.2 Methyl oleate and ethyl oleate

To verify the rate equation proposed here, the autoxidations of methyl and ethyl oleates were also investigated in the temperature range of 358–413 K, and in the oxygen partial pressure range of 0–0.1 MPa. However, an appreciable $POV$ was still detected even just after vacuum distillation. Since it is impossible to determine from the initial rate the rate constant $K_0$ of the reaction of $RH$ with $O_2$ in the presence of $RO_2H$, Eq. (5) is inspected in the place of Eq. (3).

1) Effects of operating conditions on peroxide formation rate

The relations between $POV$ and reaction time at various $p_{O_2}$ are shown in Figs. 10 and 11 for methyl oleate and ethyl oleate, respectively. The

$$K_1 = 7.12 \times 10^5 \exp(-67.9 \times 10^3/RT)$$  \hspace{1cm} (7)

$$K_2 = 2.13 \times 10^3 \exp(-31.1 \times 10^3/RT)$$  \hspace{1cm} (8)
Table 2. Kinetic constants for olate

<table>
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<tr>
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<th>Methyl oleate</th>
<th>Ethyl oleate</th>
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<tbody>
<tr>
<td>$k_d$ [s$^{-1}$]</td>
<td>$3.03 \times 10^5 \exp(-74.4 \times 10^5/RT)$</td>
<td>$2.89 \times 10^5 \exp(-97.7 \times 10^5/RT)$</td>
</tr>
<tr>
<td>$K_1$ [(kmol/m$^3$)$^{1/2}$s$^{-1}$]</td>
<td>$3.58 \times 10^5 \exp(-96.5 \times 10^5/RT)$</td>
<td>$2.17 \times 10^5 \exp(-96.3 \times 10^5/RT)$</td>
</tr>
<tr>
<td>$K_2$ [(kmol/m$^3$)$^2$MPa]</td>
<td>$5.48 \times 10^6 \exp(-61.5 \times 10^5/RT)$</td>
<td>$9.33 \times 10^6 \exp(-49.6 \times 10^5/RT)$</td>
</tr>
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POV vs. t curves in these figures show tendencies similar to those of oleic acid.

2) Determination of kinetic constants. The method mentioned above was also employed to determine $k_d$, $K_1$, and $K_2$ for each oleate. Figs. 5, 8 and 9 show Arrhenius plots for $k_d$, $K_1$ and $K_2$, respectively, for all species investigated. The kinetic constants obtained are listed in Table 2. The lines in Figs. 10 and 11 are the results calculated from Eq. (5), substituting kinetic constants in Table 2 and an observed value of POV. The good agreement shows that the kinetic rate equations presented can be useful for predicting POV of olate under various circumstances as well as for oleic acid. There is better agreement of calculated results for olate (Figs. 10 and 11) than for oleic acid (Fig. 3). This is considered to result from the difference of calculation method.

$k_d$ and $K_1$ represent the reactivity of each species. It is obvious from Figs. 5 and 8 that oleic acid and its peroxide are much more reactive and unstable than olate and their peroxides. Such quantitative results are consistent with previously published qualitative findings. Higher activation energies of olate than that of oleic acid would suggest the larger steric effects of olate. Direct application of these kinetic constants to the autoxidation of oleic acid and/or olate at ordinary temperature may involve some problems although the mechanism proposed is unchanged.

Conclusion

Actual autoxidation occurs heterogeneously. The rate depends generally on the physical transfer rate of oxygen and the true chemical reaction rate. In high chemical reaction rate conditions such as high temperature, presence of catalyst and high-energy irradiation, the oxygen transfer rate becomes very important.

In this study, autoxidation rates under the control of chemical reaction were obtained under various operating conditions of temperature and oxygen partial pressure for oleic acid, methyl olate and ethyl olate. A semi-theoretical rate equation of peroxide formation by autoxidation was developed in accordance with experimental findings, i.e. auto-acceleration and decrease in reaction order with respect to oxygen partial pressure as it increased.

The rate equation showed wide quantitative applicability to the degradation of each species.

Appendix

The active radical concentrations concerning $R^*$ are assumed to be proportional to [R] and [RH], giving the following equation.

$$[R^*] + [RH \cdot O_2 \cdot R^*] = K_R[R^*] + K_{RH}[RH]$$ (A-1)

where $K_R$ and $K_{RH}$ are constants ranging from zero to one, and $[RH] = \sum_{n=1}^{n} [RH_n]$.

Eq. (a) in Table 1 is assumed to hold at equilibrium, so

$$[RH \cdot O_2] = (k_0/k_2)[RH][O_2]$$ (A-2)

Assuming the quasi-steady state for $[RH \cdot O_2 \cdot R^*]$, [R] and [RH],

$$\frac{d[RH \cdot O_2 \cdot R^*]}{dt} = k_1[RH \cdot O_2][R^*] - (k_2 + k_3)[RH \cdot O_2 \cdot R^*] = 0$$ (A-3)

$$[R^*] = 2k_d/[RO_2H]/\left(k_3[RH]\right)$$ (A-4)

$$[RH\cdot O_2] = (2k_d/k_3)^{1/2}[RO_2H]^{1/2}$$ (A-5)

where $f$ represents the effective fraction of $R^*$ on the initiation polymerization. From Eqs. (A-1), (A-3), (A-4) and (A-5),

$$[RH \cdot O_2 \cdot R^*] = K_3[RH][O_2][RO_2H]/\left(K_m + [RH][O_2]\right)$$ (A-6)

where

$$K_3 = \frac{2k_dK_R}{k_3[RH]} + \frac{(2k_d)^{1/2}K_{RH}}{(k_3[RH])^{1/2}}$$

From Eqs. (b), (c) and (d),

$$\frac{d[RO_2H]}{dt} = k_3[RH \cdot O_2] + k_3[RH \cdot O_2 \cdot R^*] - k_d[RO_2H]$$ (A-7)

Using Eqs. (A-2) and (A-6),

$$\frac{d[RO_2H]}{dt} = \frac{k_0k^9}{k_2^9}[RH][O_2] + \frac{k_3K_3[RH][O_2][RO_2H]}{K_m + [RH][O_2]} - k_d[RO_2H]$$ (A-8)

Concerning $K_3$, the following two extreme cases are assumed.
Case 1. If $K_3 = 2k_d f K_R / (k_r[RH])$,
\[
\frac{d[R_2O]}{dt} = k_0^d k_2^O \frac{[RH][O_2]}{k_2^O} \frac{2k_d k_3 R_2O [O_2]^2}{K_m + [RH][O_2]} - k_d [R_2O] 
\]
(A-9)

Concerning the negligible effect of the first term of the right side of Eq. (A-9), $d[R_2O] / dt$ is proportional to $[R_2O]$. This is inconsistent with the experimental findings.

Case 2. If $K_3 = \frac{(2k_d f)^{1/2} K_{RH}}{(k_r[RH])^{1/2}}$
\[
\frac{d[R_2O]}{dt} = K_1^d K_2^O \frac{[RH][O_2]}{k_2^O} \frac{(2k_d f)^{1/2} K_{RH} k_3 k_4^{1/2}}{K_m + [RH][O_2]} - k_d [R_2O] 
\]
(A-10)

Eq. (A-10) was adopted in this study for consistency with the experimental results. The following relation between the dissolved oxygen mole fraction $x$ and oxygen partial pressure $p_{O_2}$ is established from Henry's law.
\[
x = p_{O_2} H 
\]
(A-11)

Since $x = [O_2]/[RH]$, $[O_2] = p_{O_2} [RH]/H$. Hence, Eq. (A-10) is expressed as
\[
\frac{d[R_2O]}{dt} = K_0 [RH]^2 p_{O_2} + \frac{K_2 [R_2O]^{1/2} p_{O_2}}{K_2/[RH]^2 + p_{O_2}} - k_d [R_2O] 
\]
(A-12)

where $K_0 = k_0 k_1^{0.5} k_3^{0.5}$, $K_1 = (2k_d f)^{1/2} K_{RH} k_3 k_4^{1/2}$, $K_2 = HK_m$

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Nomenclature

- $H$ = Henry's constant [MPa]
- $K_0$ = kinetic constant defined in Eq. (A-12) \([\text{kmol/m}^3]^{-1} \text{MPa}^{-1} \text{s}^{-1}\]
- $K_1$ = kinetic constant defined in Eq. (A-12) \([\text{kmol/m}^3]^{1/2} \text{s}^{-1}\]
- $K_2$ = kinetic constant defined in Eq. (A-12) \([\text{kmol/m}^3]^2 \text{MPa}\]
- $k_d$ = decomposition rate constant \([\text{kmol/m}^3]^{-1} \text{s}^{-1}\]
- $p_{O_2}$ = oxygen partial pressure [MPa]
- $POV$ = peroxide value [meq kg$^{-1}$]
- $R$ = gas constant \([\text{mol}^{-1} \text{K}^{-1}]\]
- $[RH]$ = concentration of oleic acid or oleate \([\text{kmol/m}^3]\)
- $[R_2O]$ = concentration of peroxide \([\text{kmol/m}^3]\)
- $S$ = slope of the line in Fig. 6 \([\text{kmol/m}^3]^{1/2}\]
- $T$ = absolute temperature \([\text{K}]\)
- $U_g$ = superficial gas velocity \([\text{cm} \cdot \text{s}^{-1}]\)
- $\rho$ = density \([\text{kg} \cdot \text{m}^{-3}]\)

Literature Cited