Oxidation Kinetics of β-Carotene in Oleic Acid Solvent with Addition of an Antioxidant, α-Tocopherol

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ABSTRACT: Oxidation experiments with β-carotene were performed in oleic acid solvent with addition of an antioxidant, α-tocopherol. A kinetic model was proposed based on a reaction mechanism consisting of the oxidation of β-carotene, oleic acid, and α-tocopherol; the antioxidation reactions of β-carotene and oleic acid by α-tocopherol; the cross-reaction of β-carotene and oleic acid; and the radical-exchange reaction of β-carotene and α-tocopherol. The model quantitatively described the oxidation behavior of β-carotene over a wide range of temperatures, oxygen compositions, and initial antioxidant concentrations. The model simulated well the time over which β-carotene was almost totally consumed under practical storage conditions at room temperature in air.

Paper no. J10672 in *JAOCS 81,* 389–394 (April 2004).

KEY WORDS: Antioxidant, β-carotene, kinetic model, oleic acid, oxidation, α-tocopherol.

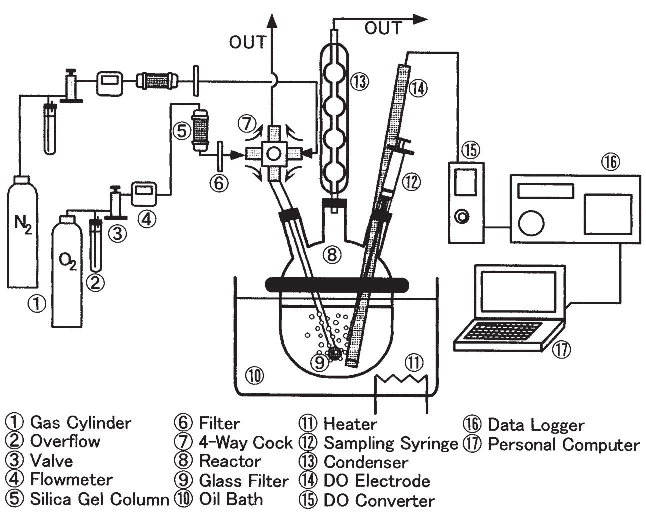
β-Carotene, having biological activity as an active oxygen quencher, is commonly dissolved in a lipid when used as a food additive because of its high solubility therein. β-Carotene is easily oxidized in air, resulting in a loss of activity. A lipid is also easily oxidized; hence, β-carotene oxidation in a lipid solvent proceeds *via* a co-oxidation mechanism accompanying the lipid oxidation. To prevent oxidation during processing and long-term storage in a food system, an antioxidant such as α-tocopherol is usually added to the system. In a practical food system, β-carotene, lipid, and antioxidant co-exist, so that not only the co-oxidation of β-carotene in lipid solvent but also protection of β-carotene and lipid by the antioxidant occur. To determine the amounts of antioxidant required to protect β-carotene in a practical system, one must understand the mechanism of oxidizing β-carotene in the lipid solvent to which antioxidant is added so as to construct a kinetic model based on the oxidation mechanism. Only a few studies have been made on oxidation kinetics in the presence of β-carotene, lipid, and antioxidant (1,2). In those studies, the antioxidative effect of α-tocopherol and β-carotene on lipid oxidation was discussed, and lipid oxidation was reported to be suppressed by adding α-tocopherol together with β-carotene. However, the mechanism for oxidation of β-carotene in a lipid solvent in the presence of antioxidant is still not elucidated, and a kinetic model has never been constructed.

In our previous study (3), we proposed a kinetic model for the co-oxidation of β-carotene in oleic acid as a lipid solvent based on a reaction mechanism that consisted of β-carotene oxidation, oleic acid oxidation, and the cross-reaction of β-carotene and oleic acid. A model for β-carotene oxidation in the presence of the antioxidant α-tocopherol also was constructed, in which not only the antioxidation of β-carotene by α-tocopherol but also the co-oxidation and radical-exchange reaction of β-carotene and α-tocopherol were incorporated (4).

In this study, a kinetic model describing β-carotene oxidation in oleic acid solvent with addition of α-tocopherol was proposed by combining the previous two models (3,4). Validity of the proposed kinetic model was verified by comparing the experimental and calculated results. The effect of the initial α-tocopherol concentration on the β-carotene oxidation under practical storage conditions at room temperature in air was simulated by the model.

EXPERIMENTAL PROCEDURES

β-Carotene and α-tocopherol were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Oleic acid, kindly provided by the NOF Co. (Tokyo, Japan), had a purity of 92.3%. Other chemicals were of reagent grade and were used without further purification. A schematic diagram of the experimental apparatus (3–6) is shown in Scheme 1. The reaction vessel was made of stainless steel, and its volume was



SCHEME 1

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5.0×10^{-4} m^3. The working volume was 3.0×10^{-4} m^3, and the initial β-carotene concentration was 0.75 mol·m^{-3}. The aeration gas—N_2 or a mixture of O_2 and N_2—was supplied by bubbling through a porous filter at the rate of 1.7×10^{-6} m^3·s^{-1} at atmospheric pressure. A condenser was installed at the gas outlet to reduce the loss of solvent due to evaporation. Before initiating the reaction, the reaction solution in the vessel was sufficiently aerated by inert N_2 gas to purge dissolved oxygen, and the vessel was immersed in an oil bath. After the solution temperature had reached a given constant value, the reaction was started by supplying the reaction gas mixture in place of the N_2 gas. An initiator was not used in this study. The reaction was stopped when β-carotene conversion reached 90%. The initial α-tocopherol concentration, the reaction temperature, and the oxygen composition in the supplied gas were regulated between 3.8 and 7.5×10^{-3} mol·m^{-3}, 323 and 343 K, and 20 and 40 mol%, respectively. The dissolved oxygen (DO) concentration was measured *in situ* by using a monitoring system with a DO electrode (OET-8350; TOA Electronics, Ltd., Tokyo, Japan). Sample solutions were withdrawn at specific time intervals. The β-carotene concentration in the sample was measured spectroscopically at 450 nm. Some experiments were repeated two times under the same condition. Relative errors from the replicated experiments were less than about 6%, and the reproducibility of the data was good.

RESULTS AND DISCUSSION

Figure 1 shows an experimental result for the oxidation of β-carotene in oleic acid solvent with addition of α-tocopherol. The temperature and the oxygen composition in the supplied gas were 333 K and 40 mol%, respectively, and the initial α-tocopherol concentration was 3.8×10^{-3} mol·m^{-3}.

The result for the same oxidation experiment in oleic acid without α-tocopherol (3) and that in *n*-decane with α-tocopherol (4) are also shown in this figure for comparison. In Figure 1A, the β-carotene concentration gradually decreased under any condition. The time for which β-carotene was almost consumed in oleic acid with α-tocopherol was longer than that without α-tocopherol, but was shorter than that in *n*-decane with α-tocopherol. The former fact suggested that β-carotene oxidation in oleic acid was suppressed by α-tocopherol. The latter fact arose for the following reasons. The solvent, oleic acid, itself was also oxidized, and the radical generated by the oxidation contributed to the increase in the oxidation rate of β-carotene (3). The antioxidant, α-tocopherol, was consumed for the protection of oleic acid as well as β-carotene, so that the consumption rate of α-tocopherol in oleic acid was faster than that in *n*-decane.

In Figure 1B, the DO concentration in *n*-decane rapidly increased during the first 15 min and then approached a constant value asymptotically. The DO concentrations in oleic acid initially increased, as is the case in *n*-decane, but they began to decrease after 4 h. At the end of the experiment using oleic acid with α-tocopherol, the concentration fell to 70% of the asymptotically constant value in *n*-decane. The decrease in the DO concentration seemed to be caused by the oxidation of the solvent, oleic acid, itself. The time course of the α-tocopherol concentration was not given because the α-tocopherol concentration in oleic acid could not be measured by HPLC.

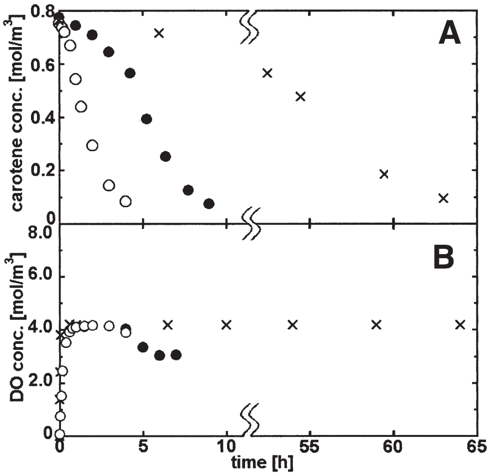

FIG. 1. Experimental results for β-carotene oxidation obtained at 333 K and 40 mol% of oxygen composition. (A) β-Carotene concentration, (B) dissolved oxygen (DO) concentration: (●) in oleic acid with addition of 3.8×10^{-3} mol·m^{-3} α-tocopherol; (○) in oleic acid without α-tocopherol; (×) in *n*-decane with addition of 3.8×10^{-3} mol·m^{-3} α-tocopherol.

CONSTRUCTION OF A KINETIC MODEL

The previously proposed co-oxidation mechanism of β-carotene in oleic acid (3) and the antioxidation mechanism for the protection of β-carotene by α-tocopherol (4) were combined, and the antioxidation of oleic acid by α-tocopherol is newly incorporated in the present reaction system.

As previously reported (5), the oxidation of β-carotene itself proceeds by a multistep autocatalytic free-radical chain reaction mechanism as

$$\mathrm{AH} + \mathrm{O_2} \xrightarrow{k_{\mathrm{I1,A}}} \mathrm{A\cdot} + \mathrm{HO_2\cdot} \qquad [1]$$

$$\mathrm{A\cdot} + \mathrm{O_2} \underset{k_{-\mathrm{P1,A}}}{\overset{k_{\mathrm{P1,A}}}{\rightleftharpoons}} \mathrm{AO_2\cdot} \qquad [2]$$

$$\mathrm{AO_2\cdot} + \mathrm{AH} \xrightarrow{k_{\mathrm{P2,A}}} \mathrm{AOOH} + \mathrm{A\cdot} \qquad [3]$$

$$\mathrm{AO_2\cdot} + \mathrm{AO_2\cdot} \xrightarrow{k_{\mathrm{T1,A}}} \text{nonradical stable product} \qquad [4]$$

$$\mathrm{A\cdot} + \mathrm{AO_2\cdot} \xrightarrow{k_{\mathrm{T2,A}}} \text{nonradical stable product} \qquad [5]$$

$$\mathrm{AOOH} + \mathrm{O_2} \xrightarrow{k_{\mathrm{I2,A}}} \mathrm{AO_2\cdot} + \mathrm{HO_2\cdot} \qquad [6]$$

Here, AH is β-carotene, A· and AO_2· are carbon-centered and peroxyl radicals derived from β-carotene, respectively, and AOOH is β-carotene hydroperoxide. Equation 1 is the chain initiation ($I1_A$), Equations 2 and 3 are the propagations ($P1_A$, $P2_A$), Equations 4 and 5 are the terminations ($T1_A$, $T2_A$), and Equation 6 is the secondary initiation ($I2_A$).

The oxidation of oleic acid itself is reported to proceed by a multistep autocatalytic free-radical chain reaction mechanism (6) as

$$LH + O_2 \xrightarrow{k_{I1,L}} L\cdot + HO_2\cdot \qquad [7]$$

$$L\cdot + O_2 \xrightarrow{k_{P1,L}} LO_2\cdot \qquad [8]$$

$$LO_2\cdot + LH \xrightarrow{k_{P2,L}} LOOH + L\cdot \qquad [9]$$

$$LO_2\cdot + LO_2\cdot \xrightarrow{k_{T1,L}} \text{nonradical stable product} \qquad [10]$$

$$LOOH + O_2 \xrightarrow{k_{I2,L}} LO_2\cdot + HO_2\cdot \qquad [11]$$

$$LOOH + LOOH \xrightarrow{k_{I3,L}} LO_2\cdot + LO\cdot + H_2O \qquad [12]$$

Here, LH is oleic acid; L·, $LO_2\cdot$, and LO· are the oleic acid-derived carbon-centered, peroxyl, and alkoxyl radicals, respectively; and LOOH is oleic acid hydroperoxide. Equation 7 is the chain initiation ($I1_L$), Equations 8 and 9 are the propagations ($P1_L$, $P2_L$), Equation 10 is the termination ($T1_L$) and Equations 11 and 12 are the secondary initiations ($I2_L$, $I3_L$). In the previous co-oxidation model (3), oleic acid oxidation remained in the initial stage of the chain reaction and only Equations 7 and 8 were included. As described in the Results and Discussion section, the DO concentration in this system decreased further than that in the previous system (3). Oleic acid oxidation is considered to proceed over the initial stage of the chain reaction so that Equations 9 and 10 should be incorporated. The hydroperoxide of β-carotene has a higher reactivity than that of oleic acid; hence, instead of Equations 11 and 12, the secondary initiation ($I2_{LA}$) of the oleic acid hydroperoxide with β-carotene hydroperoxide is taken into account as

$$LOOH + AOOH \xrightarrow{k_{I2,LA}} LO_2\cdot + AO\cdot + H_2O \qquad [13]$$

$LO_2\cdot$, having a high reactivity, also reacts with β-carotene, and this reaction contributes to the increase in the oxidation rate of β-carotene. Thus, similarly to the previous co-oxidation model (3), the cross-reaction (CR_{LA}) of β-carotene and oleic acid is included as

$$LO_2\cdot + AH \xrightarrow{k_{CR,LA}} LOOH + A\cdot \qquad [14]$$

α-Tocopherol, EH, is known to react with a peroxyl radical and to change itself to the stable α-tocopheroxyl radical, E· (7). The peroxyl radical, involved with the chain propagation, decreases by this reaction so that the chain oxidation of β-carotene is suppressed. In this system, not only β-carotene but also oleic acid are oxidized; hence, two antioxidation reactions by α-tocopherol (Inh_{EA}, Inh_{EL}) should be incorporated as

$$EH + AO_2\cdot \xrightarrow{k_{Inh,EA}} E\cdot + AOOH \qquad [15]$$

$$EH + LO_2\cdot \xrightarrow{k_{Inh,EL}} E\cdot + LOOH \qquad [16]$$

The reactivity of oleic acid is much lower than that of α-tocopherol, and oleic acid does not take part in the α-tocopherol oxidation. Thus, the α-tocopherol oxidation in oleic acid is considered to proceed by the same multistep autocatalytic free-radical chain reaction mechanism as that in *n*-decane (4), or

$$EH + O_2 \xrightarrow{k_{I1,E}} E\cdot + HO_2\cdot \qquad [17]$$

$$E\cdot + O_2 \underset{k_{-P1,E}}{\overset{k_{P1,E}}{\rightleftharpoons}} EO_2\cdot \qquad [18]$$

$$EO_2\cdot + AH \xrightarrow{k_{P2,EA}} EOOH + A\cdot \qquad [19]$$

$$EO_2\cdot + AO_2\cdot \xrightarrow{k_{T1,E}} \text{nonradical stable product} \qquad [20]$$

$$EO_2\cdot + AO_2\cdot \xrightarrow{k_{T2,EA}} \text{nonradical stable product} \qquad [21]$$

$$EOOH + AH \xrightarrow{k_{I2,EA}} EO\cdot + A\cdot + H_2O \qquad [22]$$

$$EOOH + AOOH \xrightarrow{k_{I3,EA}} EO_2\cdot + AO + H_2O \qquad [23]$$

$$EO\cdot + A\cdot \xrightarrow{k_{T3,EA}} \text{nonradical stable product} \qquad [24]$$

$$AO\cdot + A\cdot \xrightarrow{k_{T4,EA}} \text{nonradical stable product} \qquad [25]$$

Here, $EO_2\cdot$ and EO· are the α-tocopherol-derived peroxyl and alkoxyl radicals, respectively, and EOOH is α-tocopherol hydroperoxide. AO· is the β-carotene-derived alkoxyl radical. Equation 17 is the chain initiation ($I1_E$), Equations 18 and 19 are the propagations ($P1_E$, $P2_{EA}$), Equations 20 and 21 are the terminations ($T1_E$, $T2_{EA}$), and Equations 22 and 23 are the secondary initiations ($I2_{EA}$, $I3_{EA}$). Equations 24 and 25 are the terminations ($T3_{EA}$, $T4_{EA}$) concerned with the radicals generated by the secondary initiations.

When two resonance-stabilized radicals are present, an exchange reaction between the radicals is known to occur (8). Like the previous antioxidation model (4), the reversible exchange reaction (EX_{EA}) is taken into consideration as

$$E\cdot + AH \underset{k_{-EX,EA}}{\overset{k_{EX,EA}}{\rightleftharpoons}} EH + A\cdot \qquad [26]$$

Summarizing the forgoing, the oxidation of β-carotene in oleic acid solvent with addition of α-tocopherol proceeds by a series of mechanisms that consist of the β-carotene oxidation, Equations 1–6; the oleic acid oxidation, Equations 7–10 and 13; the cross-reaction of β-carotene and oleic acid, Equation 14; the antioxidation reactions by α-tocopherol, Equations 15 and 16; the α-tocopherol oxidation, Equations 17–25; and the radical-exchange reaction of β-carotene and α-tocopherol, Equation 26.

By assuming steady state for the concentrations of the respective radicals, A·, $AO_2\cdot$, AO·, E·, $EO_2\cdot$, EO·, L·, and $LO_2\cdot$, in the system, the rates of change in the concentrations of β-carotene, oleic acid, and α-tocopherol and the initial conditions are

$$\frac{dC_{\mathrm{AH}}}{dt} = -k_{\mathrm{I1,A}}C_{\mathrm{AH}}C_{\mathrm{O2}} - k_{\mathrm{PT,A}}C_{\mathrm{AH}}r_1^{\ 1/2} - k_{\mathrm{I2,EA}}C_{\mathrm{EOOH}}C_{\mathrm{AH}} - r_{\mathrm{II}} - k_{\mathrm{CT,LA}}C_{\mathrm{AH}}r_{\mathrm{III}}/2 \qquad [27]$$

$$\frac{dC_{\mathrm{LH}}}{dt} = -k_{\mathrm{I1,L}}C_{\mathrm{LH}}C_{\mathrm{O_2}} - k_{\mathrm{PT,L}}C_{\mathrm{LH}}r_{\mathrm{III}}/2 \qquad [28]$$

$$\frac{dC_{\mathrm{EH}}}{dt} = -k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} - k_{\mathrm{IT,EA}}C_{\mathrm{EH}}r_{\mathrm{I}}^{\ 1/2} - k_{\mathrm{IT,EL}}C_{\mathrm{EH}}r_{\mathrm{III}}/2 \qquad [29]$$

initial condition (i.c.) $t = 0$;

$$C_{\mathrm{AH}} = C_{\mathrm{AH}}(0),\ C_{\mathrm{LH}} = C_{\mathrm{LH}}(0),\ C_{\mathrm{EH}} = C_{\mathrm{EH}}(0), \qquad [30]$$

The initiation rates, r_{I}, r_{II}, and r_{III}, and the kinetic constants, $k_{\mathrm{PT,A}}$, $k_{\mathrm{IT,EA}}$, $k_{\mathrm{IT,EL}}$, $k_{\mathrm{CT,LA}}$, and $k_{\mathrm{PT,L}}$, in Equations 27–29 are given as

$$r_{\mathrm{I}} = \frac{1}{1 + k_{\mathrm{R1,A}}/C_{\mathrm{O_2}} + C_{\mathrm{EH}}/(k_{\mathrm{R2,EA}}C_{\mathrm{AH}}) + C_{\mathrm{EH}}^2/(k_{\mathrm{R3,EA}}C_{\mathrm{AH}}^2)} \times (k_{\mathrm{I1,A}}C_{\mathrm{AH}}C_{\mathrm{O_2}} + k_{\mathrm{I2,A}}C_{\mathrm{AOOH}}C_{\mathrm{O_2}} + k_{\mathrm{I1,L}}C_{\mathrm{LH}}C_{\mathrm{O_2}} + k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} - r_{\mathrm{III}}^{\ 2}/4) \qquad [31]$$

$$r_{\mathrm{II}} = k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} + k_{\mathrm{I3,EA}}C_{\mathrm{EOOH}}C_{\mathrm{AOOH}} + k_{\mathrm{IT,EA}}C_{\mathrm{EH}}r_{\mathrm{I}}^{\ 1/2} + k_{\mathrm{IT,EL}}C_{\mathrm{EH}}r_{\mathrm{III}}/2 - \left(\frac{C_{\mathrm{EH}}}{2k_{\mathrm{R2,EA}}C_{\mathrm{AH}}} + \frac{C^2_{\ \mathrm{EH}}}{k_{\mathrm{R3,EA}}C_{\mathrm{AH}}^2}\right)r_1 \qquad [32]$$

$$r_{\mathrm{III}} = [(k_{\mathrm{IT,EL}}C_{\mathrm{EH}} + k_{\mathrm{CT,LA}}C_{\mathrm{AH}})^2 - 4(k_{\mathrm{I1,L}}C_{\mathrm{LH}}C_{\mathrm{O_2}} + k_{\mathrm{I2,LA}}C_{\mathrm{LOOH}}C_{\mathrm{AOOH}})]^{1/2} - (k_{\mathrm{IT,EL}}C_{\mathrm{EH}} + k_{\mathrm{CT,LA}}C_{\mathrm{AH}}) \qquad [33]$$

$$k_{\mathrm{PT,A}} = \frac{k_{\mathrm{P2,A}}}{(2k_{\mathrm{T1,A}})^{1/2}} \qquad [34]$$

$$k_{\mathrm{IT,EA}} = \frac{k_{\mathrm{Inh,EA}}}{(2k_{\mathrm{T1,A}})^{1/2}} \qquad [35]$$

$$k_{\mathrm{IT,EL}} = \frac{k_{\mathrm{Inh,EL}}}{(2k_{\mathrm{T1,L}})^{1/2}} \qquad [36]$$

$$k_{\mathrm{CT,LA}} = \frac{k_{\mathrm{CR,LA}}}{(2k_{\mathrm{T1,L}})^{1/2}} \qquad [37]$$

$$k_{\mathrm{PT,L}} = \frac{k_{\mathrm{P2,L}}}{(2k_{\mathrm{T1,L}})^{1/2}} \qquad [38]$$

The kinetic constants, $k_{\mathrm{R1,A}}$, $k_{\mathrm{R2,EA}}$, and $k_{\mathrm{R3,EA}}$, in Equations 31 and 32 are

$$k_{\mathrm{R1,A}} = \frac{k_{\mathrm{T2,A}}k_{\mathrm{-P1,A}}}{k_{\mathrm{T1,A}}k_{\mathrm{P1,A}}} \qquad [39]$$

$$k_{\mathrm{R2,EA}} = \frac{k_{\mathrm{T1,A}}k_{\mathrm{P1,A}}k_{\mathrm{-P1,E}}k_{\mathrm{EX,EA}}}{k_{\mathrm{T2,EA}}k_{\mathrm{-P1,A}}k_{\mathrm{P1,E}}k_{\mathrm{-EX,EA}}} \qquad [40]$$

$$k_{\mathrm{R3,EA}} = \frac{k_{\mathrm{T1,A}}k_{\mathrm{P1,A}}^2k_{\mathrm{-P1,E}}^2k_{\mathrm{EX,EA}}^2}{k_{\mathrm{T1,E}}k_{\mathrm{-P1,A}}^2k_{\mathrm{P1,E}}^2k_{\mathrm{-EX,EA}}^2} \qquad [41]$$

In this system, the decrease in the DO concentration was observed experimentally. Therefore, the change in the DO concentration should be considered in the model. The mass-balance equation for oxygen in the solution and the initial condition are expressed as

$$\frac{dC_{\mathrm{O_2}}}{dt} = -k_{\mathrm{L}}a(C_{\mathrm{O_2}}^* - C_{\mathrm{O_2}}) - r_{\mathrm{O_2}} \qquad [42]$$

$$\text{i.c.: } t = 0;\ C_{\mathrm{O_2}} = 0 \qquad [43]$$

Here, $k_{\mathrm{L}}a$ is the volumetric mass-transfer coefficient and $C_{\mathrm{O_2}}^*$ is the saturated DO concentration. $r_{\mathrm{O_2}}$ is the oxygen consumption rate by the reaction and given as

$$r_{\mathrm{O_2}} = k_{\mathrm{I1,A}}C_{\mathrm{AH}}C_{\mathrm{O_2}} + k_{\mathrm{I2,A}}C_{\mathrm{AOOH}}C_{\mathrm{O_2}} + 2k_{\mathrm{I1,L}}C_{\mathrm{LH}}C_{\mathrm{O_2}} + k_{\mathrm{PT,L}}C_{\mathrm{LH}}r_{\mathrm{III}}/2 + k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} \qquad [44]$$

APPLICATION OF THE KINETIC MODEL

There are 17 unknowns including the constants for the oxygen mass transfer and the gas–liquid equilibrium, respectively, $k_{\mathrm{L}}a$ and $C_{\mathrm{O_2}}^*$; the kinetic constants for the β-carotene oxidation, $k_{\mathrm{I1,A}}$, $k_{\mathrm{PT,A}}$, $k_{\mathrm{I2,A}}$, and $k_{\mathrm{R1,A}}$; for the reaction between β-carotene and oleic acid, $k_{\mathrm{I1,L}}$; for the α-tocopherol oxidation, $k_{\mathrm{I1,E}}$; for the reaction between β-carotene and α-tocopherol, $k_{\mathrm{I2,EA}}$, $k_{\mathrm{I3,EA}}$, $k_{\mathrm{IT,EA}}$, $k_{\mathrm{R2,EA}}$, and $k_{\mathrm{R3,EA}}$; and for the reactions between β-carotene, oleic acid, and α-tocopherol, $k_{\mathrm{I2,LA}}$, $k_{\mathrm{IT,EL}}$, $k_{\mathrm{CT,LA}}$, and $k_{\mathrm{PT,L}}$ in the model. $k_{\mathrm{L}}a$ and $C_{\mathrm{O_2}}^*$ were previously reported to be 1.3×10^{-3} $\mathrm{s^{-1}}$ and 10.2 $\mathrm{mol \cdot m^{-3}}$, respectively (3), and these values were used in this study. The kinetic constants for the β-carotene oxidation (5), for the reaction between β-carotene and oleic acid (3), for the α-tocopherol oxidation, and for the reactions between β-carotene and α-tocopherol (4) were reported separately and those values were used. Table 1 lists the reported values of each kinetic constant.

Four kinetic constants, $k_{\mathrm{I2,LA}}$, $k_{\mathrm{IT,EL}}$, $k_{\mathrm{CT,LA}}$, and $k_{\mathrm{PT,L}}$, concerned with the reactions of Equations 9, 10, 14, and 16, are newly estimated. Like the previous studies (3–6), the constants are expressed using the pre-exponential factor, B_i, and the activation energy, E_i, as

$$k_{\mathrm{I2,LA}} = B_{\mathrm{I2,LA}}\exp(-E_{\mathrm{I2,LA}}/RT) \qquad [45]$$

$$k_{\mathrm{IT,EL}} = B_{\mathrm{IT,EL}}\exp(-E_{\mathrm{IT,EL}}/RT) \qquad [46]$$

$$k_{\mathrm{CT,LA}} = B_{\mathrm{CT,LA}}\exp(-E_{\mathrm{CT,LA}}/RT) \qquad [47]$$

$$k_{\mathrm{PT,L}} = B_{\mathrm{PT,L}}\exp(-E_{\mathrm{PT,L}}/RT) \qquad [48]$$

TABLE 1
Reported Values of Kinetic Constants (3–5)

	$k_i = B_i\exp(-E_i/RT)$	
Constants	Pre-exponential factor, B_i	Activation energy, E_i (J·mol)
$k_{I1,A}$	5.82×10^{10} ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	1.38×10^5
$k_{PT,A}$	2.30×10^4 ($\text{mol}^{-1/2}\cdot\text{m}^{3/2}\cdot\text{s}^{-1/2}$)	2.78×10^4
$k_{I2,A}$	5.30×10 ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	6.60×10^4
$k_{R1,A}$	2.02×10^3 ($\text{mol}\cdot\text{m}^{-3}$)	1.87×10^4
$k_{I1,L}$	2.03×10^{-7} ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	3.16×10^4
$k_{I1,E}$	4.96×10^{-1} ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	4.48×10^4
$k_{I2,EA}$	7.83×10^2 ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	2.61×10^4
$k_{I3,EA}$	7.77×10^{21} ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	1.29×10^5
$k_{IT,EA}$	8.91×10^6 ($\text{mol}^{-1/2}\cdot\text{m}^{3/2}\cdot\text{s}^{-1/2}$)	3.57×10^4
$k_{R2,EA}$	4.27 (–)	3.63×10^4
$k_{R3,EA}$	7.04×10^{12} (–)	1.35×10^5

These constants, B_i and E_i, were estimated by fitting Equations 27 and 42 with five sets of the experimental results for the β-carotene oxidation in oleic acid solvent with addition of α-tocopherol. The fitting procedure was the same as that reported previously (3–6).

The experimental and fitted results are shown in Figure 2 by the symbols and the solid lines, respectively. The oxidation rate of β-carotene was slower at higher initial α-tocopherol concentrations and with a decrease in the temperature or in oxygen composition in the supplied gas (Fig. 2A). The fitted results for the β-carotene concentration gave sigmoidal curves, and consequently a difference between the calculated and experimental results appeared. The difference became larger as the oxidation rate slowed. These facts suggested that the consumption reaction of β-carotene concerned with α-tocopherol, which was not taken into account in the model, occurred and that the effect of the reaction became stronger with a decrease in the oxidation rate of β-carotene. Except for this point, the calculated results described well the observed results. On the other hand, under any condition, the DO concentration initially increased and then fell after a certain time (Fig. 2B). The time at which the concentration began to decrease was delayed with an increase in the initial α-tocopherol concentration and with a decrease in temperature or in the oxygen composition. The calculated lines were in good agreement with the experimental results under any conditions.

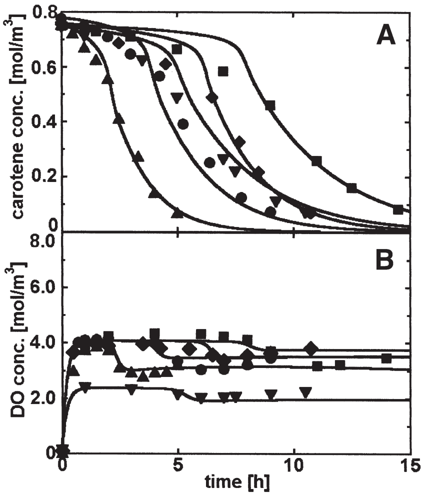

FIG. 2. Experimental and fitted results for β-carotene oxidation in oleic acid with addition of α-tocopherol. (A) β-Carotene concentration, (B) DO concentration: (●) 3.8×10^{-3} mol·m^{-3}; (◆) 7.5×10^{-3} mol·m^{-3} of initial α-tocopherol concentration at 333 K and 40 mol% of oxygen composition; (■) 323 K; (▲) 343 K at 3.8×10^{-3} mol·m^{-3} of initial α-tocopherol concentration and 40 mol% of oxygen composition; (▼), 20 mol% of oxygen composition at 333 K and 3.8×10^{-3} mol·m^{-3} of initial α-tocopherol concentration. Solid lines, fitted results. For abbreviation see Figure 1.

The estimated values of each constant are listed in Table 2. The kinetic constants, $k_{IT,EL}$, $k_{CT,LA}$, and $k_{PT,L}$, defined by Equations 36–38, corresponded to the constant for the reaction of the peroxyl radical divided by the square root of the constant for termination. The activation energy of such kinetic constants was reported to be in the range of 24 to 75 kJ·mol^{-1} (9). In this study, these values were estimated to be 23.4, 25.8, and 38.5 kJ·mol^{-1}, respectively, and were close to or within the literature value range. There was no literature value for the activation energy of the kinetic constant for the hydroperoxide decomposition, $k_{I2,LA}$. However, the estimated value of 32.0 kJ·mol^{-1} was within the range of the activation energy of the kinetic constant concerned with the oxidation, 20 to 150 kJ·mol^{-1} (10). Therefore, these estimated values in this study seemed to be reasonable.

To elucidate the sensitivity of these constants, the sum of the squares of the relative error, S, was determined by numerical calculation. The value of only one constant was changed to +50 or −50% of the estimated value at a temperature of 333 K without changing other constants. The calculated results are listed in Table 3. The values of S obtained by changing each constant were larger than the minimum values, $S_{\min}$, by at least 19.6%. Thus, the reliability of the constants obtained in this study was considered to be high.

TABLE 2
Estimated Values of Kinetic Constants in the Model

	$k_i = B_i\exp(-E_i/RT)$	
Constants	Pre-exponential factor, B_i	Activation energy, E_i (J·mol)
$k_{I2,LA}$	6.85×10^3 ($\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$)	3.20×10^4
$k_{IT,EL}$	3.08×10^5 ($\text{mol}^{-1/2}\cdot\text{m}^{3/2}\cdot\text{s}^{-1/2}$)	2.34×10^4
$k_{CT,LA}$	5.74×10^3 ($\text{mol}^{-1/2}\cdot\text{m}^{3/2}\cdot\text{s}^{-1/2}$)	2.58×10^4
$k_{PT,L}$	1.88×10^3 ($\text{mol}^{-1/2}\cdot\text{m}^{3/2}\cdot\text{s}^{-1/2}$)	3.85×10^4

TABLE 3
Sensitivity of Kinetic Constants in the Model

Constants	Value	S	Deviation $(S - S_{\min})/S_{\min}$
$k_{I2,LA}$	9.803×10^1	1.491	+54.4%
	6.535×10^1	0.965	Minimum
	4.357×10^1	1.546	+60.1%
$k_{IT,EL}$	2.700×10^3	1.155	+19.6%
	1.800×10^3	0.965	Minimum
	1.200×10^3	1.360	+40.9%
$k_{CT,LA}$	2.382×10^1	2.100	+117.4%
	1.588×10^1	0.965	Minimum
	1.059×10^1	2.208	+128.6%
$k_{PT,L}$	8.346×10^{-2}	1.433	+48.4%
	5.564×10^{-2}	0.965	Minimum
	3.709×10^{-1}	1.398	+44.7%

SIMULATION FOR PRACTICAL STORAGE CONDITIONS

Our oxidation experiments were performed in atmospheres between 323 and 343 K. When β-carotene is actually used as a food additive, the storage temperature is much lower than the experimental one and the storage term should be much longer. The proposed kinetic model is considered to permit simulation for oxidation behavior under such a practical storage condition. Thus, a similar oxidation experiment was performed at room temperature (298 K) in air (21 mol% of the oxygen composition in the supplied gas) for about 10 d, and the experimental result was compared with the simulated result shown in Figure 3. The initial concentrations of β-carotene and α-tocopherol were 0.75 and 3.8×10^{-2} mol·m^{-3}, respectively. The simulated result gave a remarkable sigmoidal curve, and the calculated β-carotene concentration decreased slower than the experimental one up to 200 h. A similar tendency was observed in Figure 2. The oxidation rate of β-carotene under these conditions was much smaller than that under the progressive conditions in Figure 2, so that the larger difference between the calculated and experimental results is considered to be reasonable. The line was in good agreement with the experimental result after 200 h and simulated well the time for which β-carotene was consumed.

The effect of the initial α-tocopherol concentration on the β-carotene oxidation was simulated under the above storage conditions. The time courses of the concentrations of β-carotene and α-tocopherol are shown in Figure 4. The β-carotene concentration (Fig. 4A) sharply decreased from the beginning of the reaction in the absence of α-tocopherol, and β-carotene was almost consumed up to 100 h. The time at which β-carotene was consumed was 150 h (about 1 wk) at 3.8×10^{-3} mol·m^{-3} of α-tocopherol and was 1500 h (about 2 mon) at 3.8×10^{-2} mol·m^{-3}. Under any condition, the α-tocopherol concentration (Fig. 4B) linearly decreased with the passage of time. After α-tocopherol was completely consumed, the β-carotene concentration was found to decrease sharply. Thus, adding α-tocopherol at a concentration of one-twentieth of the initial β-carotene concentration allowed the suppression of the β-carotene oxidation during about 2 mon of storage at room temperature in air.

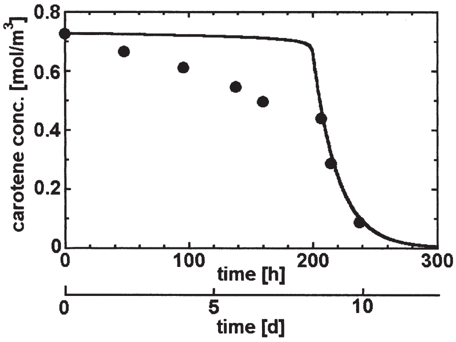

FIG. 3. Experimental and simulated results for β-carotene concentration in oleic acid with addition of 3.8×10^{-3} mol·m^{-3} α-tocopherol obtained at 298 K and 21 mol% of oxygen composition. Solid line, simulated result.

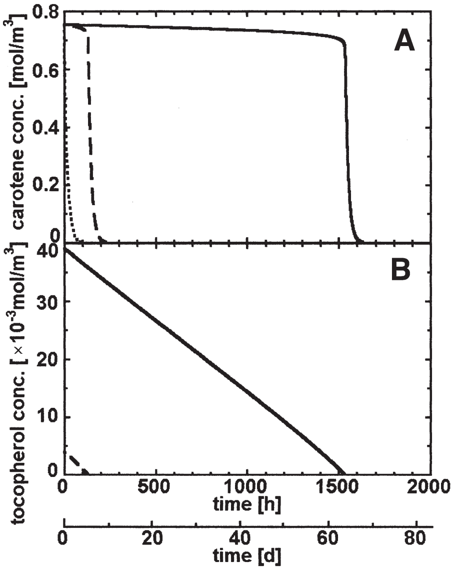

FIG. 4. Simulated results for β-carotene oxidation in oleic acid with α-tocopherol at 298 K and 21 mol% of oxygen composition. (A) β-Carotene concentration, (B) α-tocopherol concentration. Dotted line, 0; broken line, 3.8×10^{-3} mol·m^{-3}; solid line, 3.8×10^{-3} mol·m^{-3} of initial α-tocopherol concentration.

ACKNOWLEDGMENT

The study was supported by the Japan Society for the Promotion of Science Research Fellowships for Young Scientists (No. 01592).

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[Received June 16, 2003; accepted December 31, 2003]