# A Rigorous Kinetic Model for β-Carotene Oxidation in the Presence of an Antioxidant, α-Tocopherol

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**ABSTRACT:** Oxidation of β-carotene in an inert solvent, *n*-decane, in the presence of various concentrations of the antioxidant α-tocopherol was studied. The progress of carotene oxidation was suppressed as long as the tocopherol remained in the system. A rigorous kinetic model for carotene oxidation in the presence of an antioxidant was proposed based on a reaction mechanism in which not only the antioxidation but also the co-oxidation and radical-exchange reaction of tocopherol with carotene were incorporated. The model quantitatively described the oxidation behavior of carotene over a wide range of temperatures, oxygen compositions, and initial antioxidant concentrations.

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

β-Carotene, having biological activity as an active oxygen quencher, is easily oxidized in the air, thereby losing its activity. To prevent carotene oxidation in food systems during processing and long-term storage, an antioxidant such as α-tocopherol is usually added to the system; the amount of antioxidant required is determined by trial and error. To determine an appropriate amount of antioxidant, it is important to understand the oxidation mechanism of carotene in the presence of an antioxidant and to construct a kinetic model based on the oxidation mechanism.

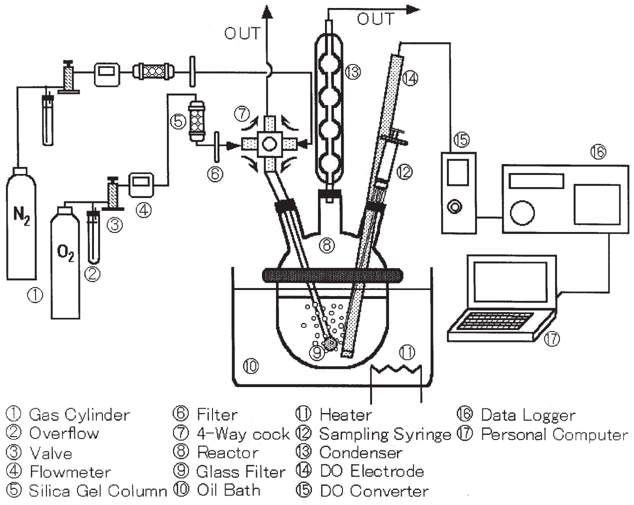
Many researchers have investigated the effect of antioxidant addition on lipid oxidation (1–5). Lipid oxidation was reported to be suppressed or accelerated by adding an antioxidant according to reaction conditions such as temperature and antioxidant concentration (1,2).

Previously, the oxidation rate was obtained from the slope of experimental data for the induction period in which lipid oxidation was suppressed by adding an antioxidant (3–5). The oxidation rate and the length of the induction period were used to evaluate the activities of various antioxidants. However, the oxidation mechanism of lipids in the presence of an antioxidant has not been elucidated. No kinetic model based on the reaction mechanism has yet been constructed.

In this study, β-carotene oxidation in *n*-decane as an inert solvent was studied experimentally under various conditions in which α-tocopherol was added as an antioxidant. A rigorous kinetic model describing oxidation behavior in the presence of an antioxidant was proposed. Validity of the proposed kinetic model was verified by comparing experimental and calculated results.

## EXPERIMENTAL PROCEDURES

β-Carotene, *n*-decane, and α-tocopherol were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All chemicals were of reagent grade and were used without purification. A diagram of the experimental apparatus (6–8) is shown in Scheme 1 (where DO is dissolved oxygen). The reaction vessel was made of stainless steel, and its volume was $5.0 \times 10^{-4}$ m$^3$. The working volume was $3.0 \times 10^{-4}$ m$^3$, and the initial β-carotene concentration was 0.75 mol·m$^{-3}$. 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 $1.7 \times 10^{-6}$ m$^3$·s$^{-1}$ at atmospheric pressure. A condenser was installed at the gas outlet to reduce the loss of solvent due to evaporation. Prior to the beginning of 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 reached a given constant value, the reaction was started by supplying the reaction gas mixture



**SCHEME 1**

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*To whom correspondence should be addressed at Department of Chemical Engineering, Tohoku University, Aoba-yama 07, Sendai 980-8579, Japan. E-mail: toshiy@rpel.che.tohoku.ac.jp in place of $N_2$ gas. An initiator was not used in this study. The reaction was stopped when carotene conversion reached 90%. The initial α-tocopherol concentration, temperature, and oxygen composition in the supplied gas were regulated between 3.8 and $7.5 \times 10^{-3}$ mol·m$^{-3}$, 323 and 343 K, and 20 and 40 mol%, respectively. The DO concentration was measured *in situ* using a monitoring system with a DO electrode (OET-8350; TOA Electronics, Ltd., Tokyo, Japan). Sample solutions were withdrawn at specific time intervals. The carotene concentration in the sample was measured spectroscopically at 450 nm. The tocopherol concentration was measured with an HPLC system (L-7100; Hitachi, Tokyo, Japan) equipped with an Inertsil ODS column (particle size $5 \times 10^{-6}$ m, i.d. 4.6 $\times 10^{-3}$ m, length 0.25 m; GL Science Inc., Tokyo, Japan) and a UV detector (L-7400; Hitachi) at 295 nm. The mobile phase was methanol and the flow rate was $0.5 \times 10^{-8}$ m$^3$·s$^{-1}$. To estimate the kinetic constant for tocopherol oxidation, experiments were performed in the same way without carotene. The temperature was regulated between 323 and 343 K. Relative errors from replicated experiments were less than 6%, and the reproducibility of the data was confirmed to be good.

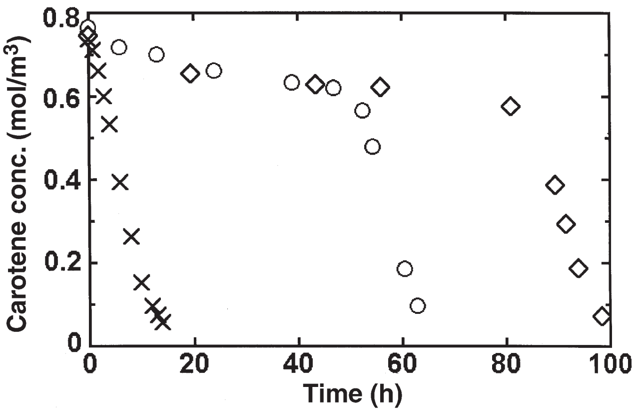

**FIG. 1.** Experimental data for β-carotene concentration obtained at an oxygen composition of 40 mol% and a temperature of 333 K: (X), 0; (○), 3.8, (◇), $7.5 \times 10^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration.

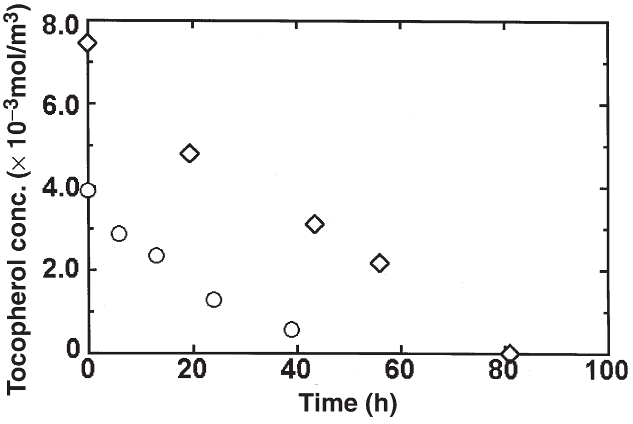

**FIG. 2.** Experimental data for α-tocopherol concentration obtained at an oxygen composition of 40 mol% and a temperature of 333 K: (○) , 3.8 and (◇), $7.5 \times 10^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration.

## RESULTS AND DISCUSSION

Figure 1 shows the time course of the β-carotene concentration obtained in the presence of tocopherol. The temperature and oxygen composition of the supplied gas were kept constant at 333 K and 40 mol%, respectively, and the initial tocopherol concentration was regulated at 3.8 or $7.5 \times 10^{-3}$ mol·m$^{-3}$. For comparison, previously reported results for oxidation experiments without tocopherol (6) are also shown in this figure. In the absence of tocopherol, the carotene concentration decreased sharply from the beginning of the reaction, and the carotene was almost consumed after 20 h. At the initial tocopherol concentration of $3.8 \times 10^{-3}$ mol·m$^{-3}$, the carotene concentration decreased slightly for about 50 h, and then decreased sharply, as was the case without tocopherol addition. The period in which the carotene concentration decreased slightly was defined as the induction period. The induction period became longer with an increase in the initial tocopherol concentration.

Figure 2 shows the time course of the α-tocopherol concentration obtained from the same experiments. The tocopherol concentration decreased linearly with the passage of time under all conditions. When taking these results into consideration together with those shown in Figure 1, we found that the carotene concentration decreased sharply after the tocopherol was completely consumed. Therefore, the progress of carotene oxidation was suppressed as long as tocopherol remained in the system.

*Construction of a kinetic model.* In this system, it is natural to take into account not only carotene oxidation but also the antioxidation reaction by tocopherol. As previously reported (6), carotene oxidation proceeds by a multistep autocatalytic free-radical chain reaction mechanism as follows:

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

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

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

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

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

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

Here, AH is β-carotene, A• and $AO_2$• are the C-centered and peroxyl radicals derived from carotene, respectively, and AOOH is hydroperoxide. Equation 1 is the chain initiation (I1), Equations 2 and 3 are the propagation ($P1_A$, $P2_A$), Equations 4 and 5 are the termination ($T1_A$, $T2_A$), and Equation 6 is the secondary initiation ($I2_A$).

α-Tocopherol, EH, is known to react with a peroxyl radical having a high reactivity and to change itself to the stable tocopheroxyl radical, E• (9). The peroxyl radical concerned with chain propagation, $AO_2$•, decreases by this reaction so that the chain oxidation of β-carotene is considered to be uppressed. Thus, the antioxidation reaction by tocopherol ($Inh_{EA}$) is taken into consideration as

$$\mathrm{EH} + \mathrm{AO_2}\bullet \xrightarrow{k_{\mathrm{Inh,EA}}} \mathrm{E}\bullet + \mathrm{AOOH} \quad [7]$$

However, the simple kinetic model based on Equations 1–7 (See Appendix) fails to describe not only the rate of change in the carotene concentration after the induction period but also the linear decrease in the tocopherol concentration, as described later. Therefore, it is necessary to take into account other reactions involving carotene and tocopherol in the kinetic model.

Tocopherol is reported to react with oxygen by itself (9), so it is reasonable to consider that tocopherol oxidation proceeds by a multistep autocatalytic free-radical chain reaction mechanism similar to carotene:

$$\mathrm{EH} + \mathrm{O_2} \xrightarrow{k_{\mathrm{I1,E}}} \mathrm{E}\bullet + \mathrm{HO_2}\bullet \quad [8]$$

$$\mathrm{E}\bullet + \mathrm{O_2} \underset{k_{-\mathrm{P1,E}}}{\overset{k_{\mathrm{P1,E}}}{\rightleftarrows}} \mathrm{EO_2}\bullet \quad [9]$$

$$\mathrm{EO_2}\bullet + \mathrm{EH} \xrightarrow{k_{\mathrm{P2,E}}} \mathrm{EOOH} + \mathrm{E}\bullet \quad [10]$$

$$\mathrm{EO_2}\bullet + \mathrm{E}\bullet \xrightarrow{k_{\mathrm{T1,E}}} \text{nonradical stable product} \quad [11]$$

$$\mathrm{EO_2}\bullet + \mathrm{EO_2}\bullet \xrightarrow{k_{\mathrm{T2,E}}} \text{nonradical stable product} \quad [12]$$

Here, $EO_2$• is the tocopherol peroxyl radical and EOOH is hydroperoxide. Equation 8 accounts for the chain initiation ($I1_E$), Equations 9 and 10 for the propagation ($P1_E$, $P2_E$), and Equations 11 and 12 for the termination ($T1_E$, $T2_E$).

In our system, the concentration of carotene was much higher than that of tocopherol; hence, the tocopherol peroxyl radical generated by Equation 9 preferentially reacts with carotene rather than with tocopherol itself. Thus, instead of Equation 10, the propagation reaction of the tocopherol peroxyl radical with carotene ($P2_{EA}$) is taken into consideration as

$$\mathrm{EO_2}\bullet + \mathrm{AH} \xrightarrow{k_{\mathrm{P2,EA}}} \mathrm{EOOH} + \mathrm{A}\bullet \quad [13]$$

Similarly, instead of Equation 11, the termination reaction of the tocopherol peroxyl radical with the carotene peroxyl radical ($T1_{EA}$) is taken into account as

$$\mathrm{EO_2}\bullet + \mathrm{AO_2}\bullet \xrightarrow{k_{\mathrm{T1,EA}}} \text{nonradical stable product} \quad [14]$$

The tocopherol hydroperoxide generated by Equation 13 is considered to decompose, as is the case for carotene. Furthermore, by taking into consideration the slight decrease in carotene concentration during the induction period, it is reasonable to consider that the tocopherol hydroperoxide reacts with carotene and carotene hydroperoxide to generate free radicals taking part in the initiation reaction of the carotene oxidation. Therefore, the secondary initiation reactions ($Hp1_{EA}$, $Hp2_{EA}$) are as follows:

$$\mathrm{EOOH} + \mathrm{AH} \xrightarrow{k_{\mathrm{Hp1,EA}}} \mathrm{EO}\bullet + \mathrm{A}\bullet + \mathrm{H_2O} \quad [15]$$

$$\mathrm{EOOH} + \mathrm{AOOH} \xrightarrow{k_{\mathrm{Hp2,EA}}} \mathrm{EO_2}\bullet + \mathrm{AO}\bullet + \mathrm{H_2O} \quad [16]$$

The alkoxyl radicals, EO• and AO•, are newly generated by Equations 15 and 16. The termination reactions concerned with these radicals generated ($T3_{EA}$, $T4_{EA}$) are also included.

$$\mathrm{EO}\bullet + \mathrm{A}\bullet \xrightarrow{k_{\mathrm{T3,EA}}} \text{nonradical stable product} \quad [17]$$

$$\mathrm{AO}\bullet + \mathrm{A}\bullet \xrightarrow{k_{\mathrm{T4,EA}}} \text{nonradical stable product} \quad [18]$$

In addition, when two resonance-stabilized radicals are present, an exchange reaction between the radicals is known to occur (10). Two resonance-stabilized radicals, E• and A•, exist in this system, so the reversible exchange reaction ($EX_{EA}$) is taken into account as

$$\mathrm{E}\bullet + \mathrm{AH} \underset{k_{-\mathrm{EX,EA}}}{\overset{k_{\mathrm{EX,EA}}}{\rightleftarrows}} \mathrm{EH} + \mathrm{A}\bullet \quad [19]$$

β-Carotene oxidation in the presence of α-tocopherol proceeds by a series of mechanisms, as shown in Equations 1–9 and 12–19. This is our rigorous model considering not only the antioxidation but also the co-oxidation and radical-exchange reaction of carotene with tocopherol.

Assuming a steady state for the concentrations of the respective radicals in the system, the rates of change in the concentrations of carotene and tocopherol are as follows:

$$\frac{dC_{\mathrm{AH}}}{dt} = -k_{\mathrm{I1,A}}C_{\mathrm{AH}}C_{\mathrm{O_2}} - k_{\mathrm{PT,A}}C_{\mathrm{AH}}r_{\mathrm{I}}^{1/2} - k_{\mathrm{Hp1,EA}}C_{\mathrm{EOOH}}C_{\mathrm{AH}} - r_{\mathrm{I1}} \quad [20]$$

$$\frac{dC_{\mathrm{EH}}}{dt} = -k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} - k_{\mathrm{IT,EA}}C_{\mathrm{EH}}r_{\mathrm{I}}^{1/2} \quad [21]$$

$$i.c. \quad t = 0; C_{\mathrm{AH}} = C_{\mathrm{AH}}(0) \quad [22]$$

$$; C_{\mathrm{EH}} = C_{\mathrm{EH}}(0) \quad [23]$$

Here, $C_i$ is the concentration of component $i$. The initiation rates, $r_{\mathrm{I}}$ and $r_{\mathrm{I1}}$, and the kinetic constants, $k_{\mathrm{PT,A}}$ and $k_{\mathrm{IT,EA}}$, in Equations 20 and 21 are given as

$$r_{\mathrm{I}} = \frac{k_{\mathrm{I1,A}}C_{\mathrm{AH}}C_{\mathrm{O_2}} + k_{\mathrm{I2,A}}C_{\mathrm{AOOH}}C_{\mathrm{O_2}} + k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}}}{1 + k_{\mathrm{R1,A}}/C_{\mathrm{O_2}} + C_{\mathrm{EH}}/(k_{\mathrm{R2,EA}}C_{\mathrm{AH}}) + C_{\mathrm{EH}}^2/(k_{\mathrm{R3,EA}}C_{\mathrm{AH}}^2)} \quad [24]$$

$$r_{\mathrm{I1}} = k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} + k_{\mathrm{Hp2,EA}}C_{\mathrm{EOOH}}C_{\mathrm{AOOH}} + k_{\mathrm{IT,EA}}C_{\mathrm{EH}}r_{\mathrm{I}}^{1/2} - \left(\frac{C_{\mathrm{EH}}}{2k_{\mathrm{R2,EA}}C_{\mathrm{AH}}} + \frac{C_{\mathrm{EH}}^2}{k_{\mathrm{R3,EA}}C_{\mathrm{AH}}^2}\right)r_{\mathrm{I}} \quad [25]$$

$$k_{\mathrm{PT,A}} = \frac{k_{\mathrm{P2,A}}}{(2k_{\mathrm{T2,A}})^{1/2}} \quad [26]$$

$$k_{\mathrm{IT,EA}} = \frac{k_{\mathrm{Inh,EA}}}{(2k_{\mathrm{T2,A}})^{1/2}} \quad [27]$$

The kinetic constants, $k_{\mathrm{R1,A}}$, $k_{\mathrm{R2,EA}}$, and $k_{\mathrm{R3,EA}}$, in Equations 24 and 25 are given as

$$k_{\mathrm{R1},A} = \frac{k_{\mathrm{T1,A}}k_{\mathrm{-P1,A}}}{k_{\mathrm{T2,A}}k_{\mathrm{P1,A}}} \quad [28]$$

$$k_{\mathrm{R2,EA}} = \frac{k_{\mathrm{T2,A}}k_{\mathrm{P1,A}}k_{\mathrm{-P1,E}}k_{\mathrm{EX,EA}}}{k_{\mathrm{T2,E}}k_{\mathrm{-P1,A}}k_{\mathrm{P1,E}}k_{\mathrm{-EX,EA}}} \quad [29]$$

$$k_{\mathrm{R3,EA}} = \frac{k_{\mathrm{T2,A}}k_{\mathrm{P1,A}}^2k_{\mathrm{-P1,E}}^2k_{\mathrm{EX,EA}}^2}{k_{\mathrm{T2,E}}k_{\mathrm{-P1,A}}k_{\mathrm{P1,}E}^2k_{\mathrm{-EX,EA}}^2} \quad [30]$$

*Application of the kinetic model.* In our experiments, the DO concentration increased rapidly during the first 15 min and then asymptotically approached a constant value under all conditions (data not shown). The period in which the concentration increased was negligibly short compared to the entire reaction time. This kind of behavior and the asymptotical constant values of the DO concentration were identical with those of carotene oxidation in *n*-decane without tocopherol (6). Therefore, the DO concentration was assumed to be constant throughout the entire reaction period, and the constant values measured in the previous study (6) were used in the calculation. These values are listed in Table 1.

There are 10 unknown constants in the model, including the kinetic constants for carotene oxidation, $k_{\mathrm{I1,A}}$, $k_{\mathrm{PT,A}}$, $k_{\mathrm{I2,A}}$, and $k_{\mathrm{R1,A}}$; the kinetic constant for tocopherol oxidation, $k_{\mathrm{I1,E}}$, and the kinetic constants for the reactions of carotene with tocopherol, $k_{\mathrm{Hp1,EA}}$, $k_{\mathrm{Hp2,EA}}$, $k_{\mathrm{IT,EA}}$, $k_{\mathrm{R2,EA}}$, and $k_{\mathrm{R3,EA}}$. The kinetic constants for carotene oxidation were hardly affected by the existence of tocopherol; hence, the previously reported values without tocopherol (6) were used (Table 2).

**TABLE 1**
**Dissolved Oxygen (DO) Concentration Measured Under Various Conditions for β-Carotene Oxidation in *n*-Decane**[a]

| Temperature (K) | Oxygen conc. in supplied gas (mol%) | DO conc. ($\mathrm{mol \cdot m^{-3}}$) |
|---|---|---|
| 323 | 40 | 4.81 |
| 333 | | 4.58 |
| 343 | | 4.89 |
| 333 | 20 | 2.14 |

[a] From Reference 6.

**TABLE 2**
**Estimated Values of Constants for β-Carotene Oxidation in *n*-Decane**[a]

| Constant | Pre-exponential factor, *B* | Activation energy, $E_a$ ($\mathrm{J \cdot mol^{-1}}$) |
|---|---|---|
| $k_{\mathrm{I1,A}}$ | $5.82 \times 10^{10}$ ($\mathrm{mol^{-1} m^3 \cdot s^{-1}}$) | $1.38 \times 10^5$ |
| $k_{\mathrm{PT,A}}$ | $2.30 \times 10^4$ ($\mathrm{mol^{-1/2} \cdot m^{3/2} \cdot s^{-1/2}}$) | $2.78 \times 10^4$ |
| $k_{\mathrm{I2,A}}$ | $5.30 \times 10$ ($\mathrm{mol^{-1} \cdot m^3 \cdot s^{-1}}$) | $6.60 \times 10^4$ |
| $k_{\mathrm{R1,A}}$ | $2.02 \times 10^3$ ($\mathrm{mol \cdot m^{-3}}$) | $1.87 \times 10^4$ |

[a] From Reference 6. See the Results and Discussion section for definitions of Constants.

*(i) Estimation of the kinetic constant for tocopherol oxidation.* The experimental results for the sole tocopherol oxidation are shown in Figure 3 by symbols. The tocopherol concentration decreased faster with increasing temperature. However, the amount of tocopherol consumption throughout the experiment was not particularly large (less than 10%). This suggests that the independent oxidation of tocopherol remained in the initial stage of the chain reaction. Therefore, it is sufficient to take into account only Equations 8 and 9. The rate of change in the tocopherol concentration is as follows:

$$\frac{dC_{\mathrm{EH}}}{dt} = -k_{\mathrm{I1,E}}C_{\mathrm{EH}}C_{\mathrm{O_2}} \quad [31]$$

To estimate the kinetic constant, $k_{\mathrm{I1,E}}$, a temperature dependence of the Arrhenius type is introduced. The constant is expressed using the pre-exponential factor, *B*, and the activation energy, $E_{\mathrm{a}}$, as

$$k_{\mathrm{I1,E}} = B\exp(-E_{\mathrm{a}}/RT) \quad [32]$$

Here, *R* is the gas constant and *T* is the reaction temperature. These constants, *B* and $E_{\mathrm{a}}$, were estimated by fitting Equation

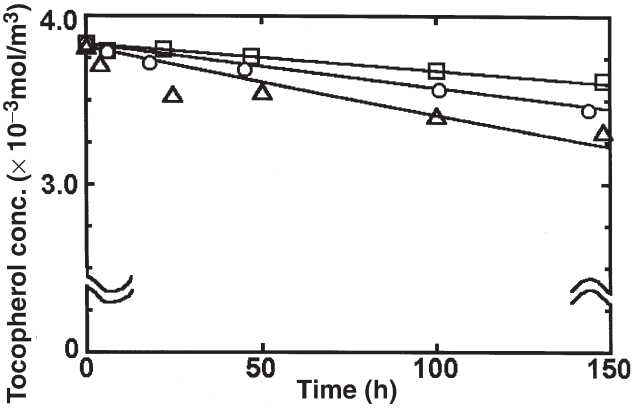

**FIG. 3.** Experimental and fitted results for α-tocopherol oxidation: (□), 323, (○) 333 and (△), 343 K at $3.8 \times 10^{-3}$ $\mathrm{mol \cdot m^{-3}}$ of initial tocopherol concentration and 40 mol% of oxygen composition; solid lines, fitted results.

31 with three sets of experimental results for the tocopherol oxidation. The fitting procedure was similar to that reported previously (6–8).

The results are also shown in Figure 3 by the solid lines. Under all conditions, the calculated lines were in agreement with the experimental results. The estimated value of $k_{\mathrm{I1,E}}$ is given as

$$k_{\mathrm{I1,E}}(\mathrm{mol}^{-1} \cdot \mathrm{m}^3 \cdot \mathrm{s}^{-1}) = 4.96 \times 10^{-1} \exp(-4.48 \times 10^4/RT) \qquad [33]$$

The activation energy of the kinetic constant concerned with oxidation is generally known to be in the range of 20 to 150 kJ·mol$^{-1}$ (11). Therefore, the estimated value, 44.8 kJ·mol$^{-1}$, was considered to be reasonable.

*(ii) Estimation of the other kinetic constants.* To estimate the kinetic constants for the reactions of carotene with tocopherol, a temperature dependence of the Arrhenius type was also introduced. The constants are expressed as

$$k_{\mathrm{Hp1,EA}} = B_1 \exp(-E_{\mathrm{a,1}}/RT) \qquad [34]$$

$$k_{\mathrm{Hp2,EA}} = B_2 \exp(-E_{\mathrm{a,2}}/RT) \qquad [35]$$

$$k_{\mathrm{IT,EA}} = B_3 \exp(-E_{\mathrm{a,3}}/RT) \qquad [36]$$

$$k_{\mathrm{R2,EA}} = B_4 \exp(-E_{\mathrm{a,4}}/RT) \qquad [37]$$

$$k_{\mathrm{R3,EA}} = B_5 \exp(-E_{\mathrm{a,5}}/RT) \qquad [38]$$

Equations 20 and 21, with five sets of experimental results for carotene oxidation in the presence of tocopherol, were used for estimations. The fitting procedure was similar to that reported previously (6–8).

The fitted and experimental results are shown in Figures 4 and 5. For reference, the fitted results for the simple kinetic model based on Equations 1–7 are shown by dotted lines. The dotted lines describe neither the length of the induction period nor the rate of change in the carotene concentration after the induction period (Fig. 4). In addition, the lines cannot describe the linear decrease in the tocopherol concentration (Fig. 5). As can be understood from Equation A1 in the simple model (see Appendix), the tocopherol concentration remained at a high value to satisfy the slow decrease in the carotene concentration in the presence of tocopherol. On the other hand, the fitted results for the rigorous model, represented by solid lines, were in much better agreement with the experimental results for the concentrations of carotene and tocopherol. Some differences between the calculated and experimental results for the carotene concentration during the induction period seemed to exist. However, the rigorous model described the length of the induction period and the sharp decrease in carotene concentration after the total consumption of tocopherol.

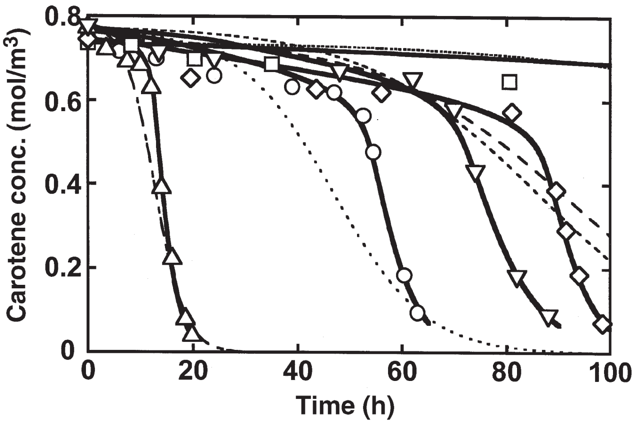

**FIG. 4.** Experimental and fitted results for β-carotene concentration: (○, ····) 3.8 and (◇, --), 7.5 × 10$^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration at 333 K and 40 mol% of oxygen composition; (□, ·····) 323 and (△, -·-) 343 K at 40 mol% of oxygen composition and 3.8 × 10$^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration; (▽, ----) 20 mol% of oxygen composition at 333 K and 3.8 × 10$^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration solid lines, results fitted by a novel model based on Equations 1–9 and 12–19; dotted lines, results fitted by a simple model based on Equations 1–7.

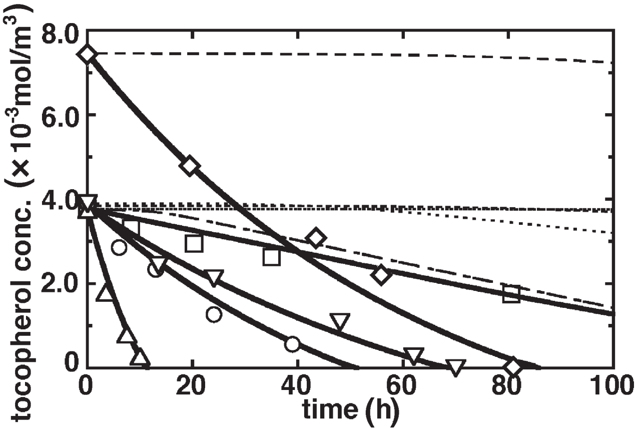

**FIG. 5.** Experimental and fitted results for α-tocopherol concentration: (○, ····) 3.8, (◇, —) 7.5 × 10$^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration at 333 K and 40 mol% of oxygen composition; (□, ·······) 323 and (△, –·–) 343 K at 40 mol% of oxygen composition and 3.8 × 10$^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration; (▽, ----) 20 mol% of oxygen composition at 333 K and 3.8 × 10$^{-3}$ mol·m$^{-3}$ of initial tocopherol concentration. Solid lines, results fitted by a novel model based on Equations 1–9 and 12–19; dotted lines, results fitted by a simple model based on Equations 1–7.

The estimated values of each constant are listed in Table 3. The kinetic constants, $k_{\mathrm{R2,EA}}$ and $k_{\mathrm{R3,EA}}$ defined by Equations 29 and 30, were combined with the constants for various reactions; hence, the values cannot be compared with those from the literature. On the other hand, the activation energy of the kinetic constant of bimolecular hydroperoxide decomposition, $k_{\mathrm{Hp2,EA}}$, and the constant $k_{\mathrm{IT,EA}}$, defined by Equation 27 were reported to be in the ranges of 95 to 135 kJ·mol$^{-1}$ (12) and 24 to 75 kJ·mol$^{-1}$ (11), respectively. In

**TABLE 3**
**Estimated Values of Constants in a Rigorous Model Based on Equations 1–9 and 12–19**[a]

| Constant | Pre-exponential factor, $B$ | Activation energy, $E_a$ ($\mathrm{J{\cdot}mol^{-1}}$) |
|---|---|---|
| $k_{\mathrm{Hp1,E}}$ | $7.83 \times 10^2$ ($\mathrm{mol^{-1}{\cdot}m^3{\cdot}s^{-1}}$) | $2.61 \times 10^4$ |
| $k_{\mathrm{Hp2,E}}$ | $7.77 \times 10^{21}$ ($\mathrm{mol^{-1}{\cdot}m^3{\cdot}s^{-1}}$) | $1.29 \times 10^5$ |
| $k_{\mathrm{IT}}$ | $8.91 \times 10^6$ ($\mathrm{mol^{-1/2}{\cdot}m^{3/2}{\cdot}s^{-1/2}}$) | $3.57 \times 10^4$ |
| $k_{\mathrm{R2}}$ | 4.27 (–) | $3.63 \times 10^4$ |
| $k_{\mathrm{R3}}$ | $7.04 \times 10^{12}$ (–) | $1.35 \times 10^5$ |

[a] See the Results and Discussion section for Equations 1–9 and 12–19 and definitions of constants.

**TABLE 4**
**Sensitivity of Constants in a Rigorous Model Based on Equations 1–9 and 12–19**[a]

| Constant | Value | S | Deviation<br>$[(S - S_{\mathrm{min}})/S_{\mathrm{min}})]$ |
|---|---|---|---|
| $k_{\mathrm{Hp1,EA}}$ | $9.381 \times 10^{-2}$ | 3.973 | +284.3% |
| | $6.254 \times 10^{-2}$ | 1.033 | Minimum |
| | $4.169 \times 10^{-2}$ | 3.929 | +279.2% |
| $k_{\mathrm{Hp2,EA}}$ | $7.967 \times 10^2$ | 3.925 | +279.7% |
| | $5.311 \times 10^2$ | 1.033 | Minimum |
| | $3.541 \times 10^2$ | 3.964 | +283.5% |
| $k_{\mathrm{IT,EA}}$ | $3.347 \times 10^1$ | 67.87 | +6466% |
| | $2.231 \times 10^1$ | 1.033 | Minimum |
| | $1.487 \times 10^1$ | 16.28 | +1474% |
| $k_{\mathrm{R2,EA}}$ | $1.302 \times 10^{-5}$ | 3.098 | +199.7% |
| | $8.680 \times 10^{-6}$ | 1.033 | Minimum |
| | $5.787 \times 10^{-6}$ | 4.855 | +369.6% |
| $k_{\mathrm{R3,EA}}$ | $7.097 \times 10^{-9}$ | 26.49 | +2463% |
| | $4.731 \times 10^{-9}$ | 1.033 | Minimum |
| | $3.154 \times 10^{-9}$ | 12.35 | +1094% |

[a] *S*, Sum of squares of the relative error; $S_{\mathrm{min}}$, minimum *S* values; see the Result and Discussion section for Equations 1–9 and 12–19 and definitions of constants.

this study, these values were estimated to be 129 and 35·7 $\mathrm{kJ{\cdot}mol^{-1}}$, respectively, and were within the range of each literature value. No literature values were available for the activation energy of the kinetic constant $k_{\mathrm{Hp1,EA}}$. However, the estimated value of 26.1 $\mathrm{kJ{\cdot}mol^{-1}}$ was within the range of the activation energy of the kinetic constant concerned with oxidation, 20 to 150 $\mathrm{kJ{\cdot}mol^{-1}}$ (11). Therefore, the estimated values in this study seemed to be reasonable.

To elucidate the sensitivity of these constants, the sum of squares of the relative error, *S*, was calculated by numerical simulation. The value of only one constant was changed to ±50% of the estimated value at a temperature of 333 K without changing other constants. The simulated results are listed in Table 4. The values of *S* obtained by changing each constant were larger than the minimum values, $S_{\mathrm{min}}$, by at least 199%. Thus, the reliability of the constants obtained in this study was considered to be high.

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## APPENDIX

*Simple kinetic model based on Equations 1–7*. The β-carotene oxidation in the presence of a-tocopherol proceeds by a series of mechanisms as shown in Equations 1–7. Assuming a steady state for the concentrations of the respective radicals in the system, the rates of change in the concentrations of carotene and tocopherol are as follows:

$$\frac{dC_{\mathrm{AH}}}{dt} = -k_{\mathrm{I1,A}}C_{\mathrm{AH}}C_{\mathrm{O_2}} - \frac{k_{\mathrm{PI,EA}}C_{\mathrm{AH}}{r_{\mathrm{I,S}}}^{1/2}}{C_{\mathrm{EH}}} \qquad \text{[A1]}$$

$$\frac{dC_{\mathrm{EH}}}{dt} = -r_{\mathrm{I,S}} \qquad \text{[A2]}$$

$$i.c. \quad t = 0; \quad C_{AH} = C_{AH}(0) \qquad \text{[A3]}$$

$$; \quad C_{EH} = C_{EH}(0) \qquad \text{[A4]}$$

The initiation rates, $r_I$, and the kinetic constant, $k_{PI,EA}$, in Equation A1 are given as

$$r_{I,S} = k_{I1,A}C_{AH}C_{O_2} + k_{I2,A}C_{AOOH}C_{O_2} \quad [A5]$$

$$k_{PI,EA} = \frac{k_{P2,A}}{k_{Inh,EA}} \quad [A6]$$

The model constant, $k_{PI,EA}$, was estimated by the model equations, Equations A1 and A2, with five sets of experimental results for carotene oxidation in the presence of tocopherol, as was the case for the rigorous model based on Equations 1–9 and 12–19. The estimated value is given as

$$k_{PI,EA}(-) = 1.06 \times 10^7 \exp(-3.71 \times 10^4 / RT) \quad [A7]$$