Kinetic Model for Autoxidation of β-Carotene in Organic Solutions

Atsushi Takahashi, Naomi Shibasaki-Kitakawa, and Toshikuni Yonemoto*

Department of Chemical Engineering, Tohoku University, Sendai 980-8579, Japan

ABSTRACT: Autoxidation of β-carotene was studied experimentally using *n*-decane as a solvent under various reaction conditions of temperature and dissolved oxygen concentration. A novel kinetic model was proposed on the basis of an autocatalytic free-radical chain reaction mechanism. A secondary initiation reaction by decomposition of hydroperoxide and reactions concerned with a β-carotene-derived C-centered radical in propagation and termination processes were taken into consideration in the model. There were four unknown kinetic constants, and the constants were estimated by fitting the model with the experimental data. The fitted results are in good agreement with the experimental data in all stages of the kinetics of autoxidation and over a wide range of oxygen concentrations. The model described not only the appearance of the induction stage but also the effect of the oxygen concentration on the autoxidation rate. In addition, the model predicted the behavior of autoxidation in another solvent at low temperature that had been reported by other researchers.

Paper no. J8856 in *JAOCS 76*, 897–903 (August 1999).

KEY WORDS: Autoxidation, β-carotene, free radicals, hydroperoxides, kinetic model.

β-Carotene, found in most plants, is widely used as a pigment and a provitamin (1). Recently, β-carotene has been reported to serve as an active oxygen quencher and as an antioxidant to prevent free-radical formation (2,3). Because the accumulation of active oxygen species and free radicals *in vivo* is suggested to be a contributory factor in human diseases such as cancer (4), much attention has been given to the utilization of β-carotene as a food additive. β-carotene is very susceptible to oxidation in the air owing to its highly unsaturated chemical structure (5). Such oxidation before incorporation into the human body leads to a loss of its biological activity. Therefore, preventing the oxidation of β-carotene during processing and long-term storage is key to its utilization in food systems. Understanding the kinetics of β-carotene oxidation is basic for its use in foods.

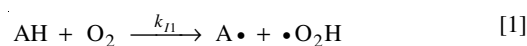Although a large number of studies have been made on the kinetics of β-carotene oxidation, many researchers have used a simple first-order kinetic model to describe the reaction behavior (6–10). This is because most of the oxidation experiments have been performed under special conditions such as high reaction temperatures, short reaction times, and the presence of initiators. The oxidation of β-carotene is generally considered to be an autocatalytic free-radical chain reaction that involves induction, propagation, and termination stages (11). Thus, the consumption curve of β-carotene is mostly sigmoidal. Kasaikina *et al.* (12,13) studied the kinetics of β-carotene oxidation in organic solutions and constructed a simplified free-radical reaction model. Their model can describe the propagation and termination stages of the oxidation but cannot describe the induction stage. Ozhogina *et al.* (14) modified the model in order to describe the induction stage. In their model, the rate of initiation was assumed to increase proportionally to the amount of β-carotene consumed. The model can describe the induction stage, but cannot describe the effect of the oxygen concentration on the oxidation rate, which is considered to be an important factor in the oxidation process.
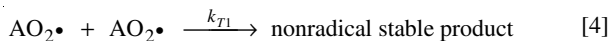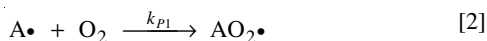
In this study, a novel kinetic model, which can describe not only all stages of the kinetics of autoxidation quantitatively but also the effect of oxygen concentration on the kinetics, was constructed by modification of the models proposed by Kasaikina *et al.* (12,13) and Ozhogina *et al.* (14). The autoxidation experiments were carried out using *n*-decane as a solvent under various conditions of reaction temperature and dissolved oxygen concentration. The validity of the kinetic model was demonstrated by simulating the concentration of one of the primary oxidation products, β-carotene hydroperoxide. Furthermore, the universality of the model was also explored by simulating the previous experimental results obtained in *n*-hexane.

CONSTRUCTION OF KINETIC MODEL

The autoxidation of β-carotene is generally considered to be an autocatalytic free-radical chain reaction that involves chain initiation (I), propagation (P), and termination (T), similar to the autoxidation of hydrocarbon (15). Kasaikina *et al.* (12,13) constructed a simplified model on the basis of the free-radical reaction as follows:

$$AH + O_2 \xrightarrow{k_{I1}} A\bullet + \bullet O_2H \qquad [1]$$

$$A\bullet \ + \ O_2 \ \xrightarrow{\ k_{P1}\ } \ AO_2\bullet \qquad [2]$$

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

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

Here, AH is β-carotene, A• and AO_2• are β-carotene-derived C-centered and peroxyl radicals, and AOOH is hydroperoxide. By assuming the pseudo-steady-state for the formation rates of respective radicals in the system, the consumption rate of β-carotene is

$$-\frac{dC_{AH}}{dt} \ = \ w_i \ + \ a\,C_{AH}\,w_i^{1/2} \qquad [5]$$

$$\text{initial conditions:} \ \ t \ = \ 0; \ C_{AH} \ = \ C_{AH}\,(0) \qquad [6]$$

where w_i and a in Equation 5 are given as follows:

$$w_i \ = \ k_{I1}\,C_{AH}\,C_{O_2} \qquad [7]$$

$$a \ = \ k_{P2}\,(2k_{T1})^{-1/2} \qquad [8]$$

where C_{AH} and C_{O_2} are the concentrations of the residual β-carotene and the dissolved oxygen (DO) in the solution, respectively.

At the beginning of the autoxidation the induction stage, in which the reaction rate is extremely small, is generally observed. The period of the induction stage is known to be closely associated with the storage life of β-carotene (16). However, the model of Kasaikina *et al.* (12,13) cannot represent the induction stage because the consumption rate of β-carotene, Equation 5, has a maximum at the beginning of the reaction.

Ozhogina *et al.* (14) modified the model in order to describe the induction stage of the autocatalytic reaction. In their model, the rate of initiation, w_i, was assumed to increase proportionally to the amount of β-carotene consumed as follows:

$$w_i \ = \ k_{I1}\,C_{AH}\,C_{O_2} \ + \ b\,C_{AH}(0) \ - \ C_{AH} \qquad [9]$$

Here, b is the kinetic parameter representing the activities of oxidized β-carotene in initiation.

The autoxidation rate of β-carotene is known to increase with oxygen concentration, and the magnitude of the increase becomes smaller with increasing oxygen concentration. However, the model of Ozhagina *et al.* (14) cannot describe the effect of the oxygen concentration on the oxidation rate.

The hydroperoxide generated by the autoxidation is considered to decompose to free radicals (17). The radicals are certain to take part in the initiation reaction (16,18). Thus, the rate of initiation increases proportionally to the amount of hydroperoxide generated by the oxidation. These phenomena contribute to the appearance of the induction stage in the autoxidation.

We have considered a secondary initiation reaction by the decomposition of the hydroperoxide as follows:

$$AOOH \ + \ O_2 \ \xrightarrow{\ k_{I2}\ } \ AO_2\bullet \ + \ \bullet O_2H \qquad [10]$$
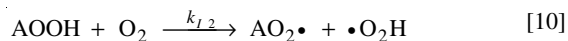
The autoxidation of β-carotene proceeds by the mechanism of the reactions as shown in Equations 1–4 and 10. This is a first modification of the model proposed by Kasaikina *et al.* (12,13).

It has been reported that the secondary oxidation products such as epoxide or alcohol are generated by the further reaction of the hydroperoxide (19). These secondary products are detected in much smaller amounts than β-carotene (5), and, their effect on the oxidation behavior of β-carotene is considered to be extremely small. The reactions of the secondary products formation were not taken into account in our model.

In assuming the pseudo-steady-state for the formation rates of the respective radicals in the system similar to the model proposed by Kasaikina *et al.* (12,13), the consumption rate of β-carotene is

$$-\frac{dC_{AH}}{dt} \ = \ w_i \ + \ a\,C_{AH}\,(w_i \ + \ k_{I2}\,C_{AOOH}\,C_{O_2})^{1/2} \qquad [11]$$

$$\text{initial conditions:} \ \ t \ = \ 0; \ C_{AH} \ = \ C_{AH}(0) \qquad [12]$$

where w_i and a in Equation 11 are given as follows:

$$w_i \ = \ k_{I1}\,C_{AH}\,C_{O_2} \qquad [13]$$

$$a \ = \ k_{P2}\,(2k_{T1})^{-1/2} \qquad [14]$$

where C_{AOOH} is the concentration of hydroperoxide.

Furthermore, the β-carotene-derived C-centered radical is considered to be much more stable than the hydrocarbon-derived one. The propagation reaction concerned with the radical should be reversible (20) rather than irreversible as proposed by Kasaikina *et al.* (12,13). The reaction concerned with the radical should also be taken into consideration in the termination process (20). These reactions contribute to the change in autoxidation rate with the oxygen concentration. The reversible reaction of Equation 2 is given as

$$AO_2\bullet \ \xrightarrow{\ k_{-P1}\ } \ A\bullet \ + \ O_2 \qquad [15]$$
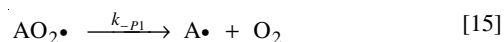
Here, the minus symbol of k_{-P1} represents a kinetic constant of the reversible reaction. The termination reaction with the radical is also expressed as

$$A\bullet \; + \; AO_2\bullet \; \xrightarrow{k_{T2}} \; \text{nonradical stable product} \qquad [16]$$

The autoxidation of β-carotene proceeds by the mechanism of the reactions shown in Equations 15 and 16 and the equations of the first modification. This is our Novel Model.

In assuming the pseudo-steady-state for the formation rates of the respective radicals in the system, the consumption rate of β-carotene is

$$-\frac{dC_{AH}}{dt} \; = \; w_i \; + \; a\left(1 + \frac{k'}{C_{O_2}}\right)^{-1/2} C_{AH}\left(w_i \; + \; k_{l2}\,C_{AOOH}\,C_{O_2}\right)^{1/2} \qquad [17]$$

$$\text{initial conditions}: \; t \; = \; 0; \; C_{AH} \; = \; C_{AH}(0) \qquad [18]$$

where w_i, a, and k' in Equation 17 are given as follows:
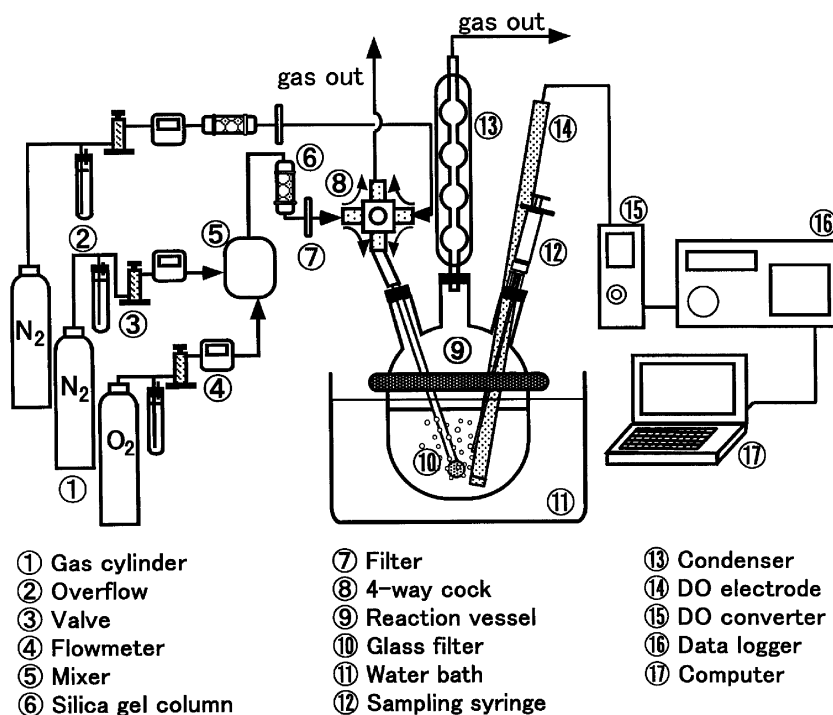
$$a \; = \; k_{P2}\,(2k_{T1})^{-1/2} \qquad [19]$$

$$w_i \; = \; k_{I1}\,C_{AH}\,C_{O_2} \qquad [20]$$

$$k' \; = \; \frac{k_{T2}\,k_{-P1}}{k_{T1}\,k_{P1}} \qquad [21]$$

where C_{AOOH} is the concentration of hydroperoxide.

EXPERIMENTAL PROCEDURES

β-Carotene and *n*-decane were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All chemicals were of reagent grade and used without further purification. The schematic diagram of the experimental apparatus is shown in Scheme 1. The reaction vessel was made of stainless steel and its volume was 500 cm^3. Aeration gas, a mixture of O_2 and N_2, was supplied through a glass filter at the rate of 100 cm^3 $\times$ min^{-1} at atmospheric pressure. A condenser was set at the outlet for the gas in order to condense the evaporated solvent. β-Carotene was added to 300 cm^3 of *n*-decane at a concentration of 7.5×10^{-4} mol $\cdot$ dm^{-3}. After the solution was sufficiently aerated by inert N_2 gas, the reaction was started by switching to the reaction gas mixture. The reaction temperature and the oxygen concentration were regulated from 50 to 70°C and from 10 to 100 mol%, respectively. The DO concentration in the reaction solution was monitored with a DO electrode (TOA Electronics Ltd., Tokyo, Japan). Sample solutions were taken out at specific time intervals. The concentration of residual β-carotene in the sample was measured spectroscopically at 450 nm in hexane. The peroxide concentration was determined by standard titration (21). The standard titration method is generally used for analysis of lipid hydroperoxides. In this method, the concentration of lipid hydroperoxide is indirectly determined by measuring the amount of iodine (I_2) formed by the reaction of perhydroxy group (–OOH) of lipid hydroperoxide with potassium iodide (KI). The perhydroxy group of carotenoid hydroperoxide is

① Gas cylinder   ⑦ Filter   ⑬ Condenser
② Overflow   ⑧ 4–way cock   ⑭ DO electrode
③ Valve   ⑨ Reaction vessel   ⑮ DO converter
④ Flowmeter   ⑩ Glass filter   ⑯ Data logger
⑤ Mixer   ⑪ Water bath   ⑰ Computer
⑥ Silica gel column   ⑫ Sampling syringe

SCHEME 1

considered to react with potassium iodide to give iodine similarly to lipid hydroperoxide, so this method is considered to be applicable for determining the concentration of β-carotene hydroperoxide.

RESULTS AND DISCUSSION

Measurement of DO concentration. An example of the time course of the DO concentration is shown in Figure 1. The concentration increased rapidly during the first 15 min and then remained constant during course of reaction. This tendency was observed under all the reaction conditions tested. The period in which the concentration increased (15 min) was negligibly short compared with the whole reaction time (15 h). Therefore, the DO concentration was assumed to be constant all through the reaction period. The constant values of the DO concentration measured under various conditions are listed in Table 1. The values increased with the oxygen concentration in the supplied gas and hardly depended on the reaction temperature.
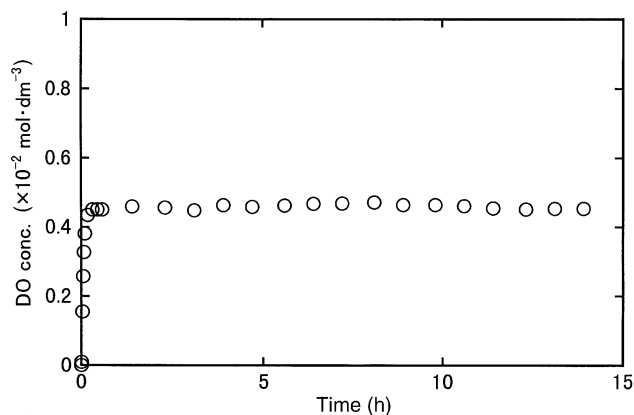
Application of the model. The First Modified Model was applied to the experimental results. There are three unknown kinetic constants, k_{I1}, a and k_{I2}, in the model. Furthermore, by considering the temperature dependence of the Arrhenius type to describe the effect of reaction temperature, the constants are defined as follows:

$$k_{I1} = B_1 \exp(-E_{a,1}/RT) \qquad [22]$$

$$a = B_2 \exp(-E_{a,2}/RT) \qquad [23]$$

$$k_{I2} = B_3 \exp(-E_{a,3}/RT) \qquad [24]$$

Thus, there are six constants, B_1, B_2, B_3, $E_{a,1}$, $E_{a,2}$, and $E_{a,3}$. These constants were estimated using the Simplex parameter-fitting method (22) to minimize S, which is the sum of the squares of the relative errors between the calculated values of the β-carotene concentration and eight sets of experimental data obtained under different reaction conditions defined as follows:

$$S = \sum \left[\frac{C_{AH,calc.} - C_{AH,exp.}}{(C_{AH,calc.} + C_{AH,exp.})/2} \right]^2 \qquad [25]$$

To obtain the calculated values under a certain set of parameters, the differential equation, Equation 11, was solved numerically using the Runge-Kutta method. The time step for the numerical calculation was set at 60 s. The experimental values obtained at the start of the reaction were used for the initial values of the β-carotene, $C_{AH}(0)$, and the measured values listed in Table 1 were used for the DO concentrations, C_{O2}, under each reaction condition.

The experimental and fitted results are shown in Figure 2. This figure describes the effect of the oxygen concentration on the oxidation rate. The plots represent the experimental data and the solid lines represent the fitted results by the First Modified Model. For reference, the fitted results by the model proposed by Kasaikina *et al.* (12,13) are also shown in the figure by broken lines. The estimated values of each constant in the two models are listed in Tables 2 and 3, respectively. The model proposed by Ozhogina *et al.* (14) was also applied to the experimental results. However, the results by Kasaikina *et al.* (12,13) and by Ozhogina *et al.* (14) almost overlapped each other. Equation 9 proposed by Ozhogina *et al.* consists of two reaction terms. The first is identical to that proposed by Kasaikina *et al.* (12,13) and the second was originated by Ozhogina *et al.* (14) to express the appearance of the induction stage. The kinetic constant in the second term obtained by fitting Equation 9 with all the experimental results was so small that the induction stage actually did not appear. Therefore, the calculation results show the same behavior as those by Kasaikina *et al.* (12, 13).

Under any reaction conditions, the residual concentration of β-carotene obtained experimentally decreased sigmoidally, and the concentration was hardly changed at the beginning of the reaction. The period is considered to correspond to the induction stage. However, the curve calculated by the model proposed by Kasaikina *et al.* (12,13) shows a marked decrease

FIG. 1. Time course of dissolved oxygen (DO) concentration measured at a temperature of 60°C and an oxygen concentration in the supplied gas of 40 mol%.

TABLE 1
Dissolved Oxygen Concentration Measured under Various Conditions

Temperature (°C)	Oxygen conc. in supplied gas (mol%)	Dissolved oxygen conc. ($\times 10^{-3}$ mol·dm^{-3})
50	40	4.81
60		4.58
70		4.89
60	10	1.02
	20	2.14
	30	3.19
	40	4.58
	70	8.12
	100	11.10
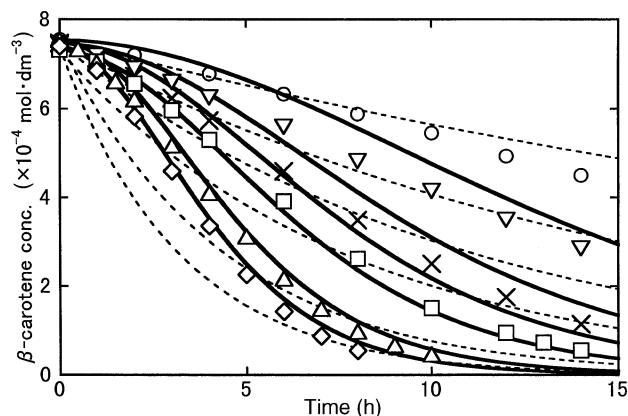
FIG. 2. Experimental data obtained at a temperature of 60°C and results fitted by the models: ○,10; ▽, 20; ×,30; □,40; △,70; ◇, 100 mol% of oxygen concentrations; broken lines, the model proposed by Kasaikina *et al.* (12,13); solid lines, the First Modified Model.

from the start of the reaction and does not describe the induction stage. On the other hand, the curves calculated by the Modified Model can describe the induction stage and were in agreement with the experimental data. A difference in the residual concentration of β-carotene still exists, however, between the calculated results by the Modified Model and the experimental data for the oxygen concentration of less than 20 mol%. Thus, the First Modified Model cannot completely describe the effect of oxygen concentration on the autoxidation rate.

Next, the Novel Model was applied to the experimental results. There are four unknown kinetic constants, k_{I1}, a, k_{I2} and k', in the model. Furthermore, by considering the temperature dependence of the Arrhenius type similarly to the First Modified Model, the constants are defined as follows:

$$k_{I1} = B_1 \exp(-E_{a,1} / RT) \qquad [26]$$

$$a = B_2 \exp(-E_{a,2} / RT) \qquad [27]$$

$$k_{I2} = B_3 \exp(-E_{a,3} / RT) \qquad [28]$$

$$k' = B_4 \exp(-E_{a,4} / RT) \qquad [29]$$

There are eight constants, B_1, B_2, B_3, B_4, $E_{a,1}$, $E_{a,2}$, $E_{a,3}$, and $E_{a,4}$. These constants were estimated using the Simplex parameter-fitting method (22) similarly to the First Modified Model.

The experimental and fitted results are shown in Figures 3

TABLE 2
Estimated Values of Constants in First Modified Model

	Preexponential factor B	Activation energy E_a (J · mol^{-1})
k_{I1}	4.25×10^{12} (mol^{-1} · dm^3 · s^{-1})	1.39×10^5
a	5.21×10^5 (mol$^{-1/2}$ · dm$^{3/2}$ · s$^{-1/2}$)	2.74×10^4
k_{I2}	1.12×10^2 (mol^{-1} · dm^3 · s^{-1})	4.85×10^4

TABLE 3
Estimated Values of Constants in Model Proposed by Kasaikina *et al.* (12,13)

	Preexponential factor B	Activation energy E_a (J · mol^{-1})
k_{I1}	3.04×10^{10} (mol^{-1} · dm^3 · s^{-1})	8.03×10^4
a	5.03×10^5 (mol$^{-1/2}$ · dm$^{3/2}$ · s$^{-1/2}$)	5.40×10^4

and 4. The former describes the effect of the oxygen concentration on the oxidation rate and the latter describes the effect of the reaction temperature. The solid lines represent the fitted results by the Novel Model and the broken lines represent the fitted results by the First Modified Model. The estimated values of each constant in the Novel Model are listed in Table 4.

Under any reaction conditions, the curves calculated by the Novel Model were in much better agreement with the experimental data than those by the First Modified Model. The differences between the calculated results by the Novel Model and the experimental data are found to decrease significantly. Therefore, the Novel Model can describe both the appearance of the induction stage and the effect of oxygen concentration on the autoxidation rate. Taking into consideration not only the secondary initiation reaction but also the reactions concerned with the β-carotene-derived C-centered radical is considered to be important.

In recent years there has been interest in prooxidant action of β-carotene in biological systems (23). According to our results, β-carotene concentration decreases significantly with the increase in the DO concentration. Thus, at high oxygen concentration, a large amount of free radical with high reactivity is formed by the oxidation. If there exists another substrate in this system, those radicals are considered to attack this substrate and to initiate the oxidation of this substrate. However, there was no other substrate than β-carotene in our reaction system. The results of our research are considered to be insufficient for revealing the prooxidant effect of β-carotene quantitatively. Thus, the prooxidant effect of β-carotene is not discussed in detail in this report.
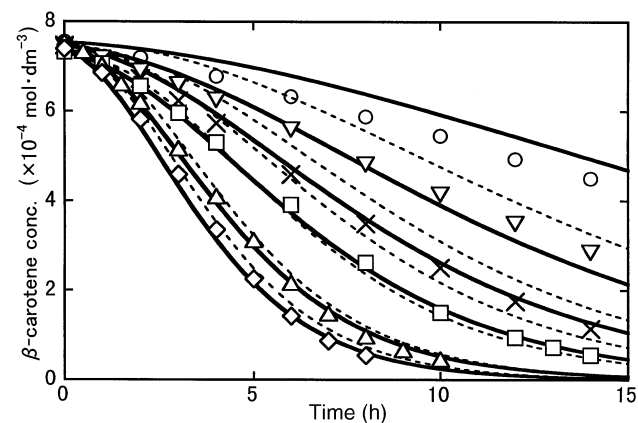

FIG. 3. Experimental data obtained at a temperature of 60°C and results fitted by the first modified model (broken lines); the novel model (solid lines). For symbols see Figure 2.
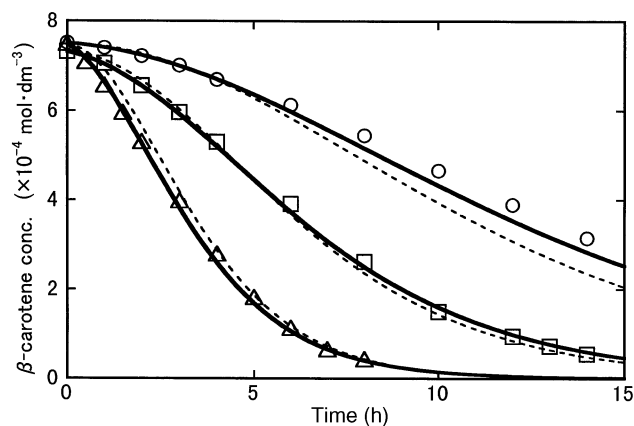
FIG. 4. Experimental data obtained at an oxygen concentration in the supplied gas of 40 mol% and results fitted by the models: temperatures ○, 50; □, 60; △, 70°C, broken lines, the First Modified Model; solid lines, the Novel Model.

TABLE 5
Sensitivity of Constants in Novel Model

Constants	Value	S	Deviation $(S - S_{min})/S_{min}$
k_{I1}	7.558×10^{-9}	0.218	+0.626%
	8.398×10^{-9}	0.217	Minimum
	9.238×10^{-9}	0.217	+0.215%
a	2.908×10^{1}	1.851	+753.7%
	3.231×10^{1}	0.217	Minimum
	3.554×10^{1}	1.914	+783.3%
k_{I2}	2.237×10^{-6}	0.624	+188.1%
	2.485×10^{-6}	0.217	Minimum
	2.734×10^{-6}	0.582	+168.7%
k'	2.237×10^{-3}	0.261	+20.47%
	2.608×10^{-3}	0.217	Minimum
	2.869×10^{-3}	0.265	+22.37%

To elucidate the sensitivity of the constants k_{I1}, a, k_{I2} and k' in the Novel Model, the sum of the squares of the relative errors, S, was calculated by numerical simulation. Only the value of one constant was changed in the range of the estimated value ± 10% at a temperature of 60°C without changing the other constants. The results are shown in Table 5. Differences in the values of S obtained by changing the rate constant of initiation, k_{I1} are slight because the initiation rate makes a small contribution to the overall autoxidation rate. The values of S obtained by changing the other constants are larger than the minimum values, S_{min}, by at least 22%. Therefore, the reliability of the model constants obtained in this research is considered to be high.

Simulation for peroxide concentration. The kinetic model can also describe the peroxide concentration formed by the autoxidation of β-carotene. In the Novel Model, the rate of change in the peroxide concentration is given as

$$\frac{dC_{AOOH}}{dt} = a\left(1 + \frac{k'}{C_{O_2}}\right)^{-1/2} C_{AH}(w_i + k_{I2} C_{AOOH} C_{O_2})^{1/2} - k_{I2} C_{AOOH} C_{O_2} \quad [30]$$

where w_i, a, and k' in Equation 30 are given as follows:

$$w_i = k_{I1} C_{AH} C_{O_2} \quad [31]$$

$$a = k_{P2}(2k_{T1})^{-1/2} \quad [32]$$

TABLE 4
Estimated Values of Constants in Novel Model

	Preexponential factor B	Activation energy E_a (J · mol^{-1})
k_{I1}	5.82×10^{13} (mol^{-1} · dm^3 · s^{-1})	1.38×10^{5}
a	7.27×10^{5} (mol$^{-1/2}$ · dm$^{3/2}$ · s$^{-1/2}$)	2.78×10^{4}
k_{I2}	5.30×10^{4} (mol^{-1} · dm^3 · s^{-1})	6.60×10^{4}
k'	2.02 (mol · dm^{-3})	1.87×10^{4}

$$k' = \frac{k_{T2}\, k_{-P1}}{k_{T1}\, k_{P1}} \quad [33]$$

In the model proposed by Kasaikina *et al.* (12,13), it is also given as

$$\frac{dC_{AOOH}}{dt} = a\, C_{AH}\, w_i^{1/2} \quad [34]$$

These equations were solved numerically using the estimated values of constants shown in Tables 3 and 4, respectively.

The experimental and simulated results obtained at a reaction temperature of 60°C and an oxygen concentration of 40 mol% are shown in Figure 5. The plots represent the experimental data. The solid and broken lines represent the simulated results by our Novel Model and those of the model proposed by Kasaikina *et al.* (12,13), respectively. As shown by the broken line, the peroxide concentration calculated by the previous model was almost zero all through the reaction. This means that peroxide is hardly formed. On the other hand, the solid line is in much better agreement with the experimental
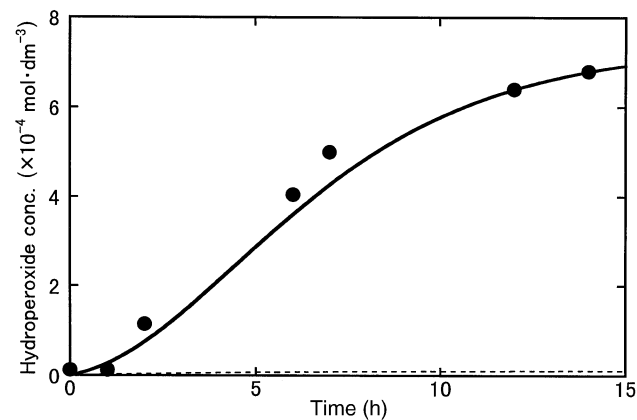

FIG. 5. Experimental data obtained at a temperature of 60°C and an oxygen concentration in the supplied gas of 40 mol%, and results simulated by the models for peroxide concentration: broken line, the model proposed by Kasaikina *et al.* (12,13); solid line, the Novel Model.
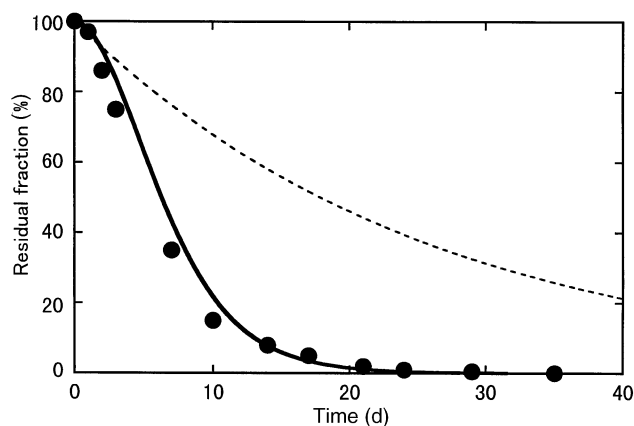
FIG. 6. Experimental data reported by Tanaka (24), and results simulated by the models: broken line, the model proposed by *Kasaikina et al.* (12,13); solid line, the Novel Model.

data. Therefore, our model could be considered to be superior to the previous models.

Application of kinetic model to other experiments. Tanaka (24) studied the autoxidation of β-carotene in *n*-hexane at low temperature. *n*-Hexane is a straight-chain hydrocarbon, as is *n*-decane used as a solvent in our experiments. It seems reasonable to suppose that the rate constants in the two solvents are identical.

The kinetic model was applied to their experimental results (24). The estimated values of the rate constants in *n*-decane were used in the numerical calculation. There is a difference in the DO concentration between the two solvents, so that the literature values of the DO concentration in *n*-hexane (25) were used in the calculation.

The results are shown in Figure 6. The reaction temperature and the oxygen concentration are 20°C and 20 mol%, respectively. The plots represent the experimental data reported by Tanaka (24). The solid and broken lines represent the simulated results by our Novel Model and those of the model proposed by Kasaikina *et al.* (12,13), respectively.

The difference between the experimental data and the broken lines calculated by the previous model is significant. On the other hand, the solid line is in much better agreement with the experimental data. Therefore, in the case of using a straight-chain hydrocarbon compound as a solvent, this model is considered to be able to predict the behavior of autoxidation of β-carotene by taking into account only the difference in the DO concentration in the solvent.

REFERENCES

1. Lachance, P., Dietary Intake of Carotenes and the Carotene Gap, *Clin. Nutr. 7*:118–122 (1988).
2. Foote, C.S., and R.W. Denny, Chemistry of Singlet Oxygen VIII. Quenching by β-Carotene, *J. Am. Chem. Soc. 90*:6233–6235 (1968).
3. Sies, H., and W. Stahl, Vitamin E and C, β-Carotene, and Carotenoids as Antioxidants, *Am. J. Clin. Nutr. 62*(suppl.): 1315S–1321S (1995).
4. Mayne, S.T., Beta-Carotene, Carotenoids, and Disease Prevention in Humans, *FASEB J. 10*:690–701 (1996).
5. Britton, G., Structure and Properties of Carotenoids in Relation to Function, *Ibid. 9*:1551–1558 (1995).
6. Henry, L.K., G.L. Catignani, and S.J. Schwartz, Oxidative Degradation Kinetics of Lycopene, Lutein, and 9-*cis* and All-*trans* β-Carotene, *J. Am. Oil Chem. Soc. 75*:823–829 (1998).
7. Arya, S.S., V. Natesan, D.B. Parihar, and P.K. Vijayaraghavan, Stability of β-Carotene in Isolated Systems, *J. Food Technol. 14*:571–578 (1979).
8. Chou, H., and W. Breene, Oxidative Decoloration of β-Carotene in Low-Moisture Model System, *J. Food Sci. 37*:66–68 (1972).
9. Ramakrishnan, T.V., and F.J. Francis, Stability of Carotenoids in Model Aqueous Systems, *J. Food Quality 2*:177–189 (1979).
10. Stefanovich, A.F., and M. Karel, Kinetics of β-Carotene Degradation at Temperatures Typical of Air Drying of Foods, *J. Food Process. Preserv. 6*:227–242 (1982).
11. Papadopoulou, K., and J.M. Ames, Kinetics of All-*trans* β-Carotene Degradation on Heating With and Without Phenylalanine, *J. Am. Oil Chem. Soc. 71*:893–896 (1994).
12. Kasaikina, O.T., A.B. Gagarina, and N.M. Emanuel, Reactivity of β-Carotene in the Interaction with Free Radicals, *Izv. Akad. Nauk USSR, Ser. Khim.*:2243–2246 (1975).
13. Kasaikina, O.T., Z.S. Kartasheva, and A.B. Gagarina, Polyene Compounds as Free-Radical Acceptors, *Ibid.*:536–540 (1981).
14. Ozhogina, O.A., and O.T. Kasaikina, β-Carotene as an Interceptor of Free Radicals, *Free Radicals Biol. Med. 19*:575–581 (1995).
15. Alekseev, E.V., A.B. Gagarina, N.M. Etveeva, L.A. Vakulova, G.I. Samokhvalov, and N.M. Emanuel, Kinetic Principles of the Oxidation of Polyenic Hydrocarbons. Communication 1. Decomposition of β-Carotene in the Presence of Free Radical Initiators, *Izv. Akad. Nauk USSR, Ser. Khim.*:2474–2480 (1968).
16. Toro-Vazquez, J.F., A.A. Castillo-M., and R. Hernandez-C., A Multiple Variable Approach to Study Corn Oil Oxidation, *J. Am. Oil Chem. Soc. 70*:261–267 (1993).
17. Encinar, J.M., F.J. Beltran, and J.M. Frades, Liquid Phase Oxidation of α-Pinene Initiated by Ozone. 1. Conversion of α-Pinene and Formation of its Hydroperoxide, *Chem. Eng. Technol. 16*:68–74 (1993).
18. Encinar, J.M., F.J. Beltran, and J.M. Frades, Liquid Phase Oxidation of α-Pinene Initiated by Ozone. 2. Formation of Verbenol, Verbenone and Acid Products, *Ibid. 17*:187–194 (1994).
19. Ito, Y., Knowledge for β-Carotene, *New Food Industry 29*: 22–29 (1987).
20. Burton, G.W., and K.U. Ingold, β-Carotene: An Unusual Type of Lipid Antioxidant, *Science 224*: 569–573 (1984).
21. Lea, C.H., The Effect of Light on the Oxidation of Fats, *Proc. R. Soc. London Ser. B. 108*:175–189 (1931).
22. Nelder, J.A., and R. Mead, A Simplex Method for Function Minimization, *Computer J. 7*:308–313 (1964).
23. Palozza, P., Prooxidant Actions of Carotenoids in Biologic Systems, *Nutr. Rev. 56*: 257–265 (1998).
24. Tanaka, Y., Physical Property and Function of Palm Carotene, *New Food Industry 37*:59–70 (1995).
25. Battino, R., Oxygen and Ozone. Hydrocarbons, *Solubility Data Ser. 7*:219 (1981).