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Oxidative Degradation Kinetics of Tocopherols during Heating

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Abstract

Tocopherols are important lipid-phase antioxidants that are subject to heat degradation. Therefore, kinetic analyses for oxidative degradation of tocopherols as a function of temperatures and times were performed. Alpha-, gamma- and delta-tocopherols dissolved in glycerol were heated at 100~250°C for 5~60 min. Oxidized tocopherols were analyzed by HPLC using a reversed phase μ-Bondapak C_{18}-column with two kinds of elution solvent systems in a gradient mode. The degradation kinetics for tocopherols followed a first-order kinetic model. The rate of tocopherol degradation was dependent on heating temperatures. The degradation rate constants for γ- and δ-tocopherols were higher than those for α-tocopherol. The experimental activation energies of α-, γ- and δ-tocopherols were 2.51, 6.05 and 5.34 kcal/mole, respectively. The experimental activation energies for the oxidative degradation of γ- and δ-tocopherols were higher than that of α-tocopherol.

Key words: tocopherols, oxidative degradation, heating, kinetics

INTRODUCTION

The oxidative degradation pattern of tocopherols in a model food system during heating was previously studied (1-3). The oxidative degradation pattern of tocopherols could be useful for understanding the effects of food processing such as cooking and frying.

Tocopherols have been mainly used as antioxidants to prevent the oxidation of oils or food products during the frying process of manufacturing snacks and ramens (4). Their ability to take up oxygen gives them important antioxidant properties (5-13). Frying is one of the manufacturing processes that utilizes high temperature heating. Thus, the kinetics of tocopherol degradation could be used as the first criteria for maximizing the shelf-life of tocopherols during heating.

Previous kinetic analyses of tocopherols have been focused on the degradation of tocopherols mainly at room temperature during storage (14-17). Livingston et al. (15) reported that α-tocopherol degraded during the storage of dry alfalfa, and the loss rate of α-tocopherol increased as a function of moisture content of the alfalfa. Widicus et al. (16) reported that the degradation of α-tocopherol was enhanced by increasing the water activity (0.10 to 0.65), storage temperature (20 to 37°C), or oxygen availability (15 to 1,450 moles O_2/mole α-tocopherol).

In this study, the kinetics of tocopherol degradation as affected by heating time and heating temperatures was investigated. Kinetic parameters such as reaction rate constants, activation energies and thermodynamic properties were determined to define the oxidative degradation reaction of tocopherols during heating.

MATERIALS AND METHODS

Materials

Tocopherols were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Glycerol was purchased from Junsei Chemical Co. (Tokyo, Japan) and membrane filter from Acrodisc Gelman (Gelman LC13, 0.45 μm, Ann Arbor, MI, USA) was used. All other chemicals were the same as in the previous studies (1-3), unless otherwise specified.

Experimental methods

A mixture of 50 mg α-tocopherol and 10 mL glycerol in a crucible was placed in a temperature-controlled muffle furnace (Thermolyne 6000, Dubuque, IA, USA) and heated at 100, 150, 200 and 250°C for 5, 15, 30 and 60 min. The stability of temperature was within ±2%. After heating, the crucible containing α-tocopherol, glycerol and the nonvolatile oxidative degradation product was removed from the furnace. After cooling the mixture for 30 min at room temperature, the oxidative degradation products of α-tocopherol were extracted from the glycerol with hexane. The hexane layer containing the oxidative degradation products of α-tocopherol was filtered through a membrane filter (Gelman LC13, 0.45 μm, Ann Arbor, MI, USA) to analyze the components.

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The same method was applied for 2 mg of γ-tocopherol and 4 mg of δ-tocopherol.

Chromatographic instrumentation

Tocopherols and their oxidative degradation products which were extracted with hexane were simultaneously separated by HPLC with the same analytical conditions as previously described (1-3). The HPLC system consisted of a Waters 501 and 510 HPLC pumps, and a Waters 745B Data Module integrator (Millipore, Milford, MA, USA). The peaks of tocopherols and their oxidative degradation products were observed at 295 nm using a Waters 484 UV detector. A reversed phase HPLC chromatography was performed on a μ-Bondapak C_{18}-column, using elution solvents with A, acetonitrile : methanol (3:2); B, acetonitrile : methanol : 2-propanol : chloroform : methylene chloride (3:2:5:0.5:0.5) in a linear gradient mode according to the previous studies (1-3). The injection volume was 3 μL.

Kinetic data analysis

The oxidative degradation kinetics of each tocopherol was analyzed by determining the rate constants of degradation of tocopherols during heating. In the preliminary study, it was determined whether the thermal degradation kinetics of tocopherols obeyed zero- or first-order kinetics by calculating the regression coefficient. The regression coefficients were 0.70~0.78 for the zero-order kinetics, and 0.87~0.98 for the first-order kinetics, respectively. Thus, the first-order kinetic equations were employed in this study (Table 1).

$$v = \frac{d[P]}{dt} = -\frac{d[C]}{dt} \quad (1)$$

$$-\frac{d[C]}{dt} = kd[C] \quad (2)$$

$$\frac{d[C]}{[C]} = -k_d dt \quad (3)$$

Table 1. Reaction rate constants and correlation coefficients for tocopherol degradation[1)]

Tocopherols	Temperature (°C)	Rate constant ($M^{-1}min^{-1}$)	R^2
α-tocopherol	100	0.0035	0.737
	150	0.0054	0.832
	200	0.0071	0.841
γ-tocopherol	100	0.0086	0.979
	150	0.0150	0.989
	200	0.0504	0.988
δ-tocopherol	100	0.0136	0.994
	150	0.0281	0.998
	200	0.0636	0.995

[1)]Values obtained from linear regression data of ln plot of residual tocopherol content.

$$\ln\frac{[C]}{[C_0]} = -k_d t \quad (4)$$

$$\ln[C] = [C_0] - k_d t \quad (5)$$

where, v and $[P]$ are the initial velocity and product concentration, $[C]$ = residual tocopherol content during heating, $[C_0]$ = tocopherol content at the beginning of heating (t = 0), t = heating time, k_d = rate constant of the first-order kinetics.

The activation energy (E_a) and frequency factor (ln A) were determined from the Arrhenius model (18):

$$\ln A = \ln k + E_a/RT \quad (6)$$

where R is the gas constant and T is absolute temperature (K).

The enthalpy of activation (ΔH) was obtained by plotting ln (k/T) vs. $1/T$, and the entropy of activation (ΔS) was obtained from the expression of rate constants based on the transition state theory:

$$\ln(k/T) = \ln(k_b/h) + \Delta S/R - \Delta H/RT \quad (7)$$

where k_b is Boltzmann's constant and h is Planck's constant.

RESULTS AND DISCUSSION

Degradation kinetics of tocopherols

The kinetics for the degradation of tocopherols was studied with respect to time and temperature. The parameters are: times of 5, 15, 30 and 60 min; temperatures of 100, 150 and 200°C. At 250°C, which is above the decomposition temperature of tocopherols, the results were not suitable to determine the kinetics of reaction because the content of tocopherols decreased too steeply. For all temperature conditions except 250°C, the rate constant of tocopherol degradation was described by the first-order kinetic model, i.e., ln $[C] = [C_0] - k_d t$. The rate of the degradation of tocopherols in the model food system depended on temperature. The activation energies were obtained from the Arrhenius equations by using the experimental data describing the temperatures dependence of tocopherols degradation.

Jensen (14) showed that the rate of α-tocopherol degradation in seaweed meal was accelerated by increasing the storage temperature or the moisture content. Labuza and Tannenbaum (19) evaluated the data published by Jensen (14) and analyzed the results by a first-order reaction. Widicus et al. (16) reported that the degradation of α-tocopherol in a model food system containing no fat could be modeled by first-order kinetics. On the other

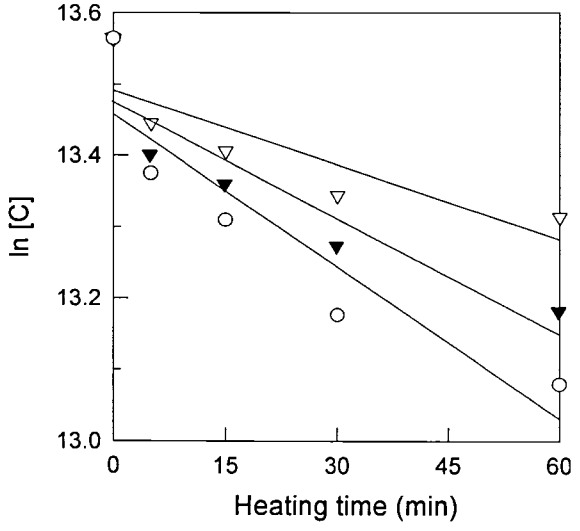

Fig. 1. ln plot of residual α-tocopherol content during heating at various temperatures.
▽: 100°C, ▼: 150°C, ○: 200°C.

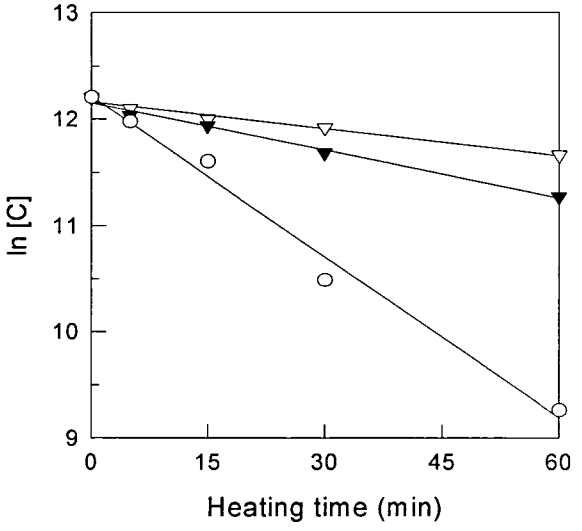

Fig. 2. ln plot of residual γ-tocopherol content during heating at various temperatures.
▽: 100°C, ▼: 150°C, ○: 200°C.

hand, Widicus and Kirk (17) reported the loss of α-tocopherol in a model food system containing methyl linoleate was described by zero-order kinetics.

Fig. 1 shows the plot of α-tocopherol content vs. heating time. The degradation rate constants of α-tocopherol, estimated from the linear regression data, were 0.0035, 0.0054 and 0.0071 $M^{-1}min^{-1}$ at 100, 150 and 200°C, respectively (Table 1). The experimental activation energy calculated for the oxidative degradation of α-tocopherol was 2.51 kcal/mole (Table 2). Labuza and Tannenbaum (19) reported that the activation energies of α-tocopherol for the data published by Jensen (14) ranged from 9.81~10.5 kcal/mole. Widicus et al. (16) reported that the experimental activation energies calculated for the degradation of α-tocopherol ranged from 8.85~13.05 kcal/mole. Their experimental conditions, however, were different from the model food system using glycerol in this study.

Fig. 2 also shows the plot of γ-tocopherol content vs. heating time. The degradation rate constants ranged from 0.0086 to 0.0504 $M^{-1}min^{-1}$ for γ-tocopherol (Table 1). The experimental activation energy for the oxidative degradation of γ-tocopherol was 6.05 kcal/mole (Table 2). From the plot of δ-tocopherol content vs. heating time (Fig. 3), the degradation rate constants ranged from

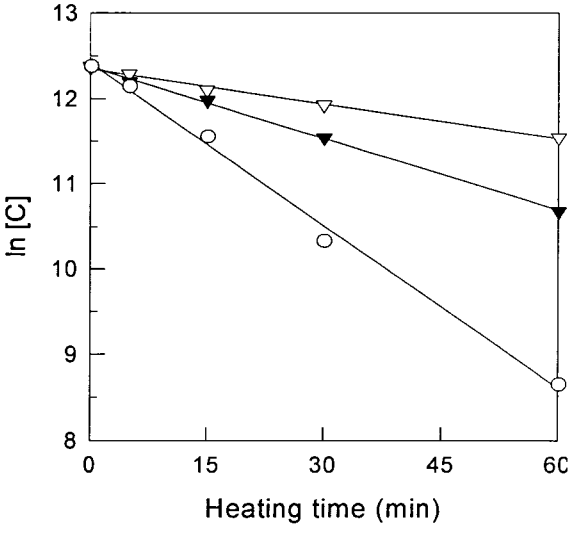

Fig. 3. ln plot of residual δ-tocopherol content during heating at various temperatures.
▽: 100°C, ▼: 150°C, ○: 200°C.

0.0136 to 0.0636 $M^{-1}min^{-1}$ (Table 1). The experimental activation energy for the oxidative degradation of δ-tocopherol was 5.34 kcal/mole (Table 2). Higher temperatures and longer heating times increased the oxidative degradation of tocopherols (Figs. 1~3). It was reported

Table 2. Activation energies and thermodynamic properties for tocopherol degradation

Tocopherols	Activation energy (kcal/mole)[1)]	Intercept ln A[1)]	R^2	Enthalpy of activation (kcal/mole)[2)]	Entropy of activation (kcal/mole·K)[2)]	R^2
α-tocopherol	2.51	2.27	0.994	1.69	-28.73	0.983
γ-tocopherol	6.05	3.27	0.923	5.23	-39.74	0.903
δ-tocopherol	5.34	2.86	0.989	4.51	-38.93	0.986

[1)]Values obtained from slope, intercept and linear regression of Arrhenius plot.
[2)]Values obtained from slope, intercept and linear regression of transition state theory equations.

that, in general, the decrease of tocopherols during heating could be explained by either combination with radical compounds or reduction by hydrogen-donating reducing agents during oxidation to stop the chain mechanism of oxidation (20).

Kinetic parameters

Table 1 and 2 summarize the kinetic analysis for the degradation of α-, γ- and δ-tocopherols. The rate of degradation of tocopherols depends on heating temperatures. The rate of degradation of tocopherols increases with increasing temperature. These results indicate that heating temperature affects the degradation rate of tocopherols. Therefore, heat degradation needs to be considered when attempting to maximize the stability of tocopherols.

The similar rate constants and activation energies indicate that the degradation mechanisms for γ- and δ-tocopherols are similar. The degradation rate constants for γ- and δ-tocopherols are higher than those for α-tocopherol; suggesting that the thermal degradation of α-tocopherol is less than γ- and δ-tocopherols.

The Arrhenius model and transition state theory were used to determine the influence of temperature on the reaction rates. The activation energy (E_a) and frequency factor (ln A) were determined from the Arrhenius model, and enthalpy (ΔH) and entropy (ΔS) were obtained from transition state theory. The activation energy and enthalpy for the oxidative degradation of γ- and δ-tocopherols were higher than those for α-tocopherol, and little difference could be seen between the activation energies of γ- and δ-tocopherols. These results suggest that the degradation of γ- and δ-tocopherols was more affected by the change of heating temperatures than that of α-tocopherol.

In conclusion, tocopherol degradation follows the first-order kinetics. The rate of tocopherol degradation depends on the heating temperatures and heating times. As heating temperature and heating time increased, the oxidative degradation of tocopherols increased accordingly. The activation energy and enthalpy for the oxidative degradation of α-tocopherol was different from those of γ- and δ-tocopherols, and those of γ- and δ-tocopherols were similar.

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