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Decomposition kinetics of monoacyl glycerol and fatty acid in subcritical water under temperature-programmed heating conditions

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Abstract

The decompositions of monocaprylin, monocaprin, monolaurin and their corresponding fatty acids in subcritical water were measured under temperature-programmed heating conditions where the reaction temperature was linearly increased from room temperature to 350 °C at specified rates to estimate the activation energies E_i and the frequency factors k_{i0} for the decompositions. The decompositions of both monoacyl glycerol and fatty acid obeyed first-order kinetics, and the decomposition of a monoacyl glycerol proceeded consecutively to form its constituent fatty acid and then further decomposition compounds. There was a tendency for both the E_i and k_{i0} values for a monoacyl glycerol or fatty acid with a longer acyl chain to be smaller, and it was shown that the enthalpy–entropy compensation held for the decompositions of monoacyl glycerols and fatty acids as well as for those of fatty acid esters with various acyl and alkyl chains in subcritical water.

Keywords: Activation energy; Kinetics; Monoacyl glycerol; Subcritical water; Temperature-programmed decomposition

1. Introduction

Water that maintains its liquid state in a temperature range from 100 to 374 °C is called subcritical water. Subcritical water has characteristics different from those of ambient water: one is a much lower relative dielectric constant for subcritical water. For example, the relative dielectric constant of water at 200 °C is about 35, which is approximately equal to that of ambient ethanol (Miller & Hawthorne, 1998). Another is that the ion product of subcritical water is in the order of 10^{-11} which is larger by three orders of magnitude than that of ambient water (Clifford, 1998). The former characteristic suggests that subcritical water can be used as a solvent for extraction of hydrophobic compounds, such as essential oils (Ayalal & Luque de Castro, 2001; Basile, Jimenes-Carmona, & Clifford, 1989; Gámiz-Cracia & Luque de Castro, 2000; Kubátová, Miller, & Hawthorne, 2001). However, if the subcritical water extraction is applied to oils or fats, their hydrolysis would occur (Holliday, King, & List, 1997; Møller, 1997; Patil, Butala, Raghunathan, & Shankar, 1988) due to the latter characteristic; that is, concentrations of hydrogen and hydroxide ions, which act as acid and base catalysts, of subcritical water are high. The decomposition of fatty acids, which are produced through the hydrolysis of oils or fats, would also occur in subcritical water (Bell, Palmer, Barnes, & Drummond, 1994; Maiella & Brill, 1998; Yu & Savage, 1998).

The kinetics of the decomposition or hydrolysis of oils and of the decomposition of fatty acids in subcritial water do not seem to be fully established. We reported

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the kinetics of the hydrolysis of fatty acid esters with various acyl and alkyl chains (Khuwijitjaru, Fujii, Adachi, Kimura, & Matsuno, 2004). Although practical oils or fats are mixtures of various triacyl glycerols, the kinetics for their hydrolysis would not be simple because their solubility is low, even in subcritical water, and the reaction occurs in a heterogeneous system.

In this content, we measured the decomposition kinetics of monoacyl glycerols and fatty acids in subcritical water in which the initial concentrations of the substrates were below their solubility in water at room temperature. At these concentrations, the decompositions proceeded in a homogeneous reaction system, and the kinetic analysis was much easier than that in a heterogeneous reaction system. The temperature-programmed heating conditions were also adopted to estimate the activation energy and the frequency factor for the rate constant of the decomposition of monoacyl glycerol or fatty acid from a few sets of experiments.

2. Materials and methods

2.1. Materials

Monocaprylin (purity; >95%), monolaurin (>98%), and caprylic acid (>98%) were purchased from Tokyo Kasei Kogyo, Tokyo, Japan. Monocaprin (>99%) was a product of Sigma, St. Louis, MO, USA. Capric and lauric acids (both; >99%) were purchased from Wako Pure Chemical Industries, Osaka, Japan.

2.2. Decomposition of monolaurin under isothermal conditions

In order to examine the type of kinetic equation applicable to the decomposition of monoacyl glycerol in subcritical water and the appropriateness of the activation energy and frequency factor evaluated from the analysis of the temperature-programmed decomposition of the monoacyl glycerol, the isothermal decomposition of monolaurin was observed at various temperatures according to our previous procedures for the hydrolysis of fatty acid esters with alkyl chains (Khuwijitjaru et al., 2004).

Monolaurin was dissolved in ethanol at a concentration of 1 g/l. A 100 μl portion of the solution was pipetted into a pressure-resistant vessel (Taiatsu Garasu Kogyo, Tokyo), which was made of SUS316 stainless steel and the inner volume of which was 10.2 ml. The ethanol as evaporated under reduced pressure, and 9.0 ml of distilled water were introduced to the vessel. The vessel was tightly closed and placed in an oven held at the desired temperature. The temperature of the solution in the vessel was monitored, and the reaction time was set to zero at the moment when the temperature reached the desired value. After a specific reaction time had elapsed, the vessel was removed from the oven and rapidly quenched in an ice water bath to stop the reaction.

The reaction mixture was removed and placed in a test tube, and ca. 0.3 g of anhydrous sodium sulfate was added to the mixture for deposition of the unreacted monolaurin (Holliday et al., 1997). One hundred microlitres of 6.94×10^{-2} M octanoic acid dissolved in methanol were added to the mixture as an internal standard, and 10 ml of chloroform were also added to the mixture. The mixture was vortex-mixed and allowed to stand at room temperature for phase separation. The chloroform–methanol phase was removed and placed in a vial, and the solvent was removed under reduced pressure. The remainder was dissolved with 100 μl of methanol, and the unreacted monolaurin was determined using an LC-10AT HPLC (Shimadzu, Kyoto) with an ODS AP-302 (YMC, Kyoto; 4.6 mm i.d. × 150 mm) and an SPD-10AV/VP UV detector (Shimadzu; 210 nm). The eluent used was a mixture of methanol and water (80/20 (v/v)) at 1.0 ml/min.

2.3. Temperature-programmed decomposition of monoacyl glycerol or fatty acid

An aqueous solution of monoacyl glycerol was degassed by sonication. The concentrations of monocaprylin, monocaprin and monolaurin were 1.0×10^{-4}, 1.0×10^{-4} and 1.0×10^{-5} mol/l, which were below the solubilities of the corresponding fatty acids at room temperature (Bell, 1973). The solution (6 ml) was placed in the pressure-resistant vessel, which was the same vessel as that used for the isothermal decomposition, and its headspace was filled with helium gas. The vessel was tightly closed and then placed in the oven. The temperature of the reaction mixture was increased at a rate of 5.97, 9.92 or 13.6 °C/min. The temperature programmes for the oven that gave the rates of temperature increase were determined by preliminary experiments. After a prescribed time, the vessel was removed from the oven and immediately quenched by immersing it in ice water to stop the decomposition reaction. The concentrations of the remaining monoacyl glycerol and formed fatty acid were determined.

The decompositions of caprylic, capric and lauric acids were also measured in the same manner. The initial concentrations of caprylic and capric acids were 1.0×10^{-4} M, and that of lauric acid was 1.0×10^{-5} M.

In these experiments, the remaining monoacyl glycerol was determined by gas chromatography because GC analysis was greater in sensitivity than HPLC analysis. One millilitre of the reaction mixture was placed in a test tube, and about 20 mg of NaCl were added to the solution for possible demulsification (Ayalal & Luque de Castro, 2001). A 100 μl portion of an internal standard for the GC analysis, which was dissolved in a mixture of chloroform and methanol (2/1 (v/v)), was added to the tube, and 2.0 ml of the chloroform–methanol mixture were further added to the tube. The solution in the tube was vortex-mixed and then allowed to stand at room temperature for phase separation. Methyl laurate (>98%, Wako) at 1.0×10^{-3} mol/l was used as the internal standard for quantifying monocaprylin and monocaprin, and propyl caprate (>95%, Wako) at 1.0×10^{-4} mol/l was used for the determination of monolaurin. Myristic acid (>98%, Wako), dissolved in the chloroform–methanol mixture at a concentration of 1.0×10^{-3} or 1.0×10^{-4} mol/l was used as the internal standard for the determination of caprylic and capric acids or lauric acid. The lower phase (1.4 ml) was pipetted into a vial and evaporated under reduced pressure.

The concentration of the remaining monoacyl glycerol was determined as follows: the residue was dissolved with 1.0 ml of methanol, and 0.1 ml of sodium methoxide dissolved in methanol at 0.5 g/l was then added. The solution was vortex-mixed and allowed to stand at 70 °C for 40 min to convert monoacyl glycerol to the methyl ester of the corresponding fatty acid. After acetic acid (10 μl) was added to stop the reaction, the solvent was removed under reduced pressure. The residue was again dissolved with 100 μl of hexane, and the methyl esters were determined using a Shimadzu GC-14B gas chromatograph with a hydrogen flame-ionization detector (Kyoto, Japan). The column used was a glass column (3.2 mm i.d. × 3.1 m length) packed with 5% Thermon-3000 on Shincarbon 60–80. Both the injector and detector temperatures were 230 °C, and the column temperature was 110 °C for methyl caprylate, 115 °C for methyl caprate, and 120 °C for methyl laurate. The carrier gas was nitrogen gas at 50 ml/min, and the hydrogen and air pressures were 0.6 and 0.5 kg f/cm^2, respectively.

Fatty acid, which was formed during the decomposition of the monoacyl glycerol or remained after its decomposition, was determined using an HPLC. The residue, after the evaporation of the lower phase, was dissolved with 0.5 ml of acetonitrile; 3.8 mM, 3-bromomethyl-6,7-dimethoxy-1-memyl-2(1*H*)-quinoxaline-2-one (0.25 ml; >96%, Wako) and 0.8 mM 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) (0.25 ml; >98%, Wako) were then added to the solution, and 50 mg of potassium carbonate was also added.

After the mixture was vortex-mixed, it was allowed to stand at 80 °C for 40 min in the dark for fluorescence derivatization (Yamaguchi, Hara, Matsunaga, Nakamura, & Ohkura, 1985). The solution was cooled with running tap-water and used for determination. The LC-10AT HPLC system (Shimadzu) with the YMC-Pack ODS-AP 302 and RF-535 fluorescence detector (Shimadzu) was used. The excitation and fluorescent wavelengths were 370 and 455 nm, respectively. The volume of the injected sample was 20 μl. The eluent used was a mixture of acetonitrile and water (70/30 (v/v) for caprylic acid; 80/20 for capric and lauric acids) at 1.0 ml/min.

2.4. Kinetic analysis of the temperature-programmed decomposition

As shown later, the decomposition of monocaprylin in subcritical water under isothermal conditions obeyed first-order kinetics. Because it was reported that the decomposition of formic and acetic acids in subcritical water also obeyed first-order kinetics (Bell et al., 1994; Maiella & Brill, 1998; Yu & Savage, 1998), the decompositions of caprylic, capric and lauric acids in subcritical water were assumed to be expressed by the same kinetics.

The temperature-dependence of the rate constant, k_i, for the decomposition of monoacyl glycerol or fatty acid (species *i*) is assumed to be expressed by the Arrhenius equation

$$k_i = k_{i0} \exp(-E_i/RT), \tag{1}$$

where k_{i0} is the frequency factor, E_i is the activation energy, and R is the gas constant. Species *i* is expressed by MG and FA for monoacyl and fatty acid, respectively. The temperature, T, was changed linearly with time, t, at a constant rate, α, in the temperature-programmed decomposition. For the decomposition under these conditions, the following relationship can be obtained (Kanbe, 1975):

$$\ln\left(-\frac{\alpha}{RT^2}\ln Y_i\right) = -\frac{E_i}{RT} + \ln\left(\frac{k_{i0}}{E_i}\right), \tag{2}$$

where Y_{i0} is the ratio of the concentration of the remaining *i* at any time to its initial concentration. Therefore, the plots of the left-hand term of Eq. (2) versus $1/T$ should give a straight line, irrespective of the α values, and the E_i and and k_{i0} values can be evaluated from the slope and the intercept, respectively, of the line.

As shown and verified later, the decomposition of monoacyl glycerol proceeds through the following consecutive reactions; that is, monoacyl glycerol was decomposed to fatty acid and the fatty acid was further decomposed.

Because each step obeyed first-order kinetics, the changes in the concentrations of monoacyl glycerol and fatty acid, which were normalized by the initial concentration of monoacyl glycerol and are represented by Y_{MG} and Y_{FA} with time are expressed by Eq. (3) (Kanbe, 1975) and Eq. (4) (Levenspiel, 1972), respectively

$$Y_{\mathrm{MG}} = \exp\left[-\frac{k_{\mathrm{MG}0}R(T_0+\alpha t)^2}{\alpha E_{\mathrm{MG}}}\exp\left(-\frac{E_{\mathrm{MG}}}{R(T_0+\alpha t)}\right)\right], \tag{3}$$

$$Y_{\mathrm{FA}} = \frac{1}{1-\kappa}\left(Y_{\mathrm{MG}}^{\kappa} - Y_{\mathrm{MG}}\right), \tag{4}$$

where T_0 is the initial temperature, and κ is the ratio of k_{FA} to k_{MG} ($K_{\mathrm{MG}} \neq K_{\mathrm{FA}}$) and is a function of time, t as given by Eq. (5) under the temperature-programmed heating condition

$$\kappa = \frac{k_{\mathrm{FA0}}}{k_{\mathrm{MG0}}} \exp\left(\frac{E_{\mathrm{MG}} - E_{\mathrm{FA}}}{R(T_0 + \alpha t)}\right). \tag{5}$$

3. Results and discussion

3.1. Isothermal decomposition of monolaurin

The isothermal decomposition of monolaurin was observed at different temperatures. Fig. 1 shows the relationships between the concentration of the remaining monolaurin normalized by its initial concentration and the reaction time on a semi-logarithmic scale. The plots for each temperature gave a straight line passing through unity at time $t = 0$, indicating that the decomposition obeyed first-order kinetics at every temperature. The rate constant k_{MG} was evaluated from the slope of the line. According to Eq. (1), the k_{MG} values are plotted versus the reciprocal of the absolute temperature, T, in the inset of Fig. 1. The plots also gave a straight line, and the activation energy E_{MG} and the frequency factor K_{MG0} for monolaurin decomposition were determined to be 77.5 kJ/mol and $1.01 \times 10^5\ \mathrm{s}^{-1}$, respectively.

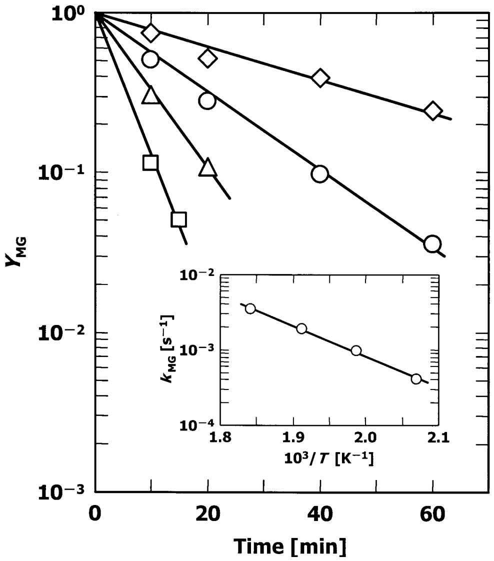

Fig. 1. Decomposition of monolaurin in subcritical water under isothermal conditions. Temperatures were (◇) 210 °C, (○) 230 °C, (△) 250 °C and (□) 270 °C. The ordinate indicates the ratio Y_{MG} of the concentration of remaining monolaurin to its initial concentration. Inset shows the Arrhenius plots for the rate constant, k_{MG}, for the decomposition of monolaurin in subcritical water. T represents the absolute temperature.

3.2. Temperature-programmed decomposition of monoacyl glycerols

The decomposition processes of monocaprylin, monocaprin and monolaurin under the temperature-programmed heating conditions are shown in Fig. 2(a)–(c), respectively. As shown by the solid lines in the figures, the rates of temperature increase were 5.97, 9.92 and 13.6 °C/min. The figures also show the changes in the concentrations of free fatty acids normalized by the initial concentrations of the corresponding monoacyl glycerols on a molar basis. Every monoacyl glycerol began to decompose (hydrolyze) at ca. 200 °C to produce its constituent fatty acid at any rate of temperature increase. The concentration of fatty acid increased with time, reached a maximum, the temperature at which was about 300 °C, and then declined at higher temperatures due to the thermal decomposition of the fatty acid. These results indicate that the decomposition of a monoacyl glycerol in subcritical water proceeds by consecutive reactions; that is, the monoacyl glycerol is first hydrolyzed to its constituent fatty acid and glycerol, and the produced fatty acid is further decomposed or converted to other molecules.

The decomposition processes of each monoacyl glycerol under the temperature-programmed heating condi-

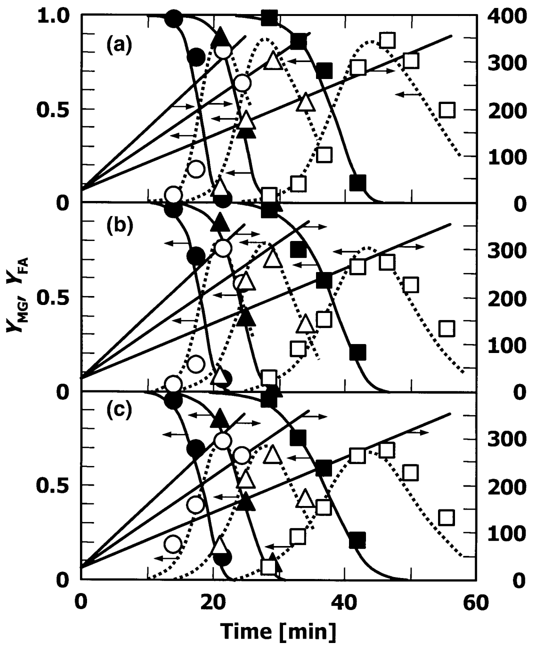

Fig. 2. Changes in (closed symbols) the ratio Y_{MG} of the concentration of remaining monoacyl glycerol to its initial concentration, (open symbols) the ratio Y_{FA} of the concentration of produced fatty acid to the initial concentration of the corresponding monoacyl glycerol, and (solid line) the temperature during the decomposition of a monoacyl glycerol under the temperature-programmed heating conditions. Figs. (a)–(c) show the decompositions of monocaprylin, monocaprin and monolaurin at the rates of temperature increase of (■, □) 5.97, (▲, △) 9.92 and (●, ○) 13.6 °C/min.

tions were analyzed according to Eq. (2), as shown by the closed symbols in Fig. 3. The plots for the different rates of temperature increase gave a straight line for every monoacyl glycerol, and the E_{MG} and k_{MG0} values were estimated from that line. The E_{MG} and k_{MG0} values for monocaprylin, monocaprin and monolaurin are shown in Fig. 4. The values obtained for the temperature-programmed decomposition of monolaurin (73.9 kJ/mol and $5.65 \times 10^4\ s^{-1}$) were consistent with the values obtained for its isothermal decomposition. There would be a tendency for both the E_{MG} and k_{MG} values to be smaller for a monoacyl glycerol with a longer acyl chain. This dependence on the acyl-chain length is opposite to that observed for the decomposition of methyl esters of fatty acids in subcritical water (Khuwijitjaru et al., 2004), although the reason for the reverse dependence is unclear.

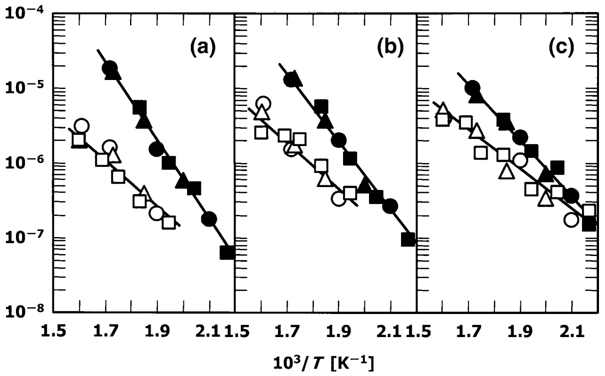

Fig. 3. Estimation of the activation energy and the frequency factor for the temperature-programmed decompositions in subcritical water of: (a) monocaprylin and caprylic acid, (b) monocaprin and capric acid and (c) monolaurin and lauric acid, based on Eq. (1). The keys are the same as in Fig. 2.

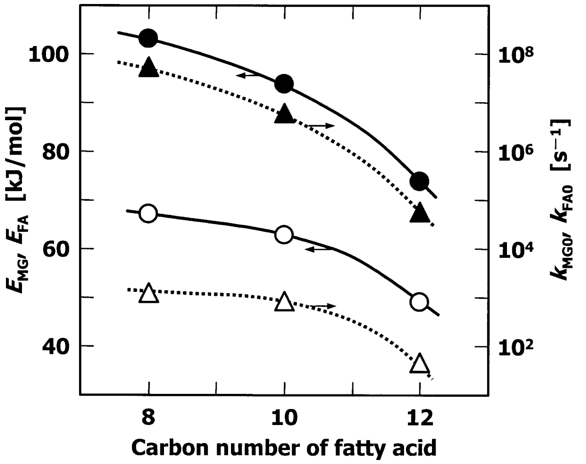

Fig. 4. Effects of the carbon number of the acyl chain of monoacyl glycerol or fatty acid on the activation energies, (●) E_{MG} and (○) E_{FA}, and the frequency factors, (▲) k_{MG0} and (△) k_{FA0} for their decomposition in subcritical water. The subscripts, MG and FA, represent the decompositions of monoacyl glycerol and fatty acid, respectively.

The changes in the Y_{MG} with time t were calculated by substituting the operating conditions, T_0 and α, and the estimated E_{MG} and k_{MG0} values into Eq. (3) and are represented by the solid curve in Fig. 2. The calculated results well express the experimental ones.

3.3. Temperature-programmed decomposition of fatty acids

The decomposition processes of caprylic, capric and lauric acids, under the temperature-programmed heating conditions, were also observed at different rates of temperature increase, and the decreases in the concentrations of the fatty acids with time are shown in Fig. 5(a)–(c). The concentration began to decrease at ca. 200 °C for every fatty acid at any rate of temperature increase. During the decomposition of monoacyl glycerol, a decline in the fatty acid concentration was observed at ca. 300 °C. This high temperature would be ascribed to the fact that the decomposition of fatty acid during the decomposition of monoacyl glycerol is the second step in the consecutive reactions.

The decomposition processes of the fatty acids were also analyzed according to Eq. (2), as shown by the open symbols in Fig. 3. The plots at different rates of temperature increase gave a straight line for every fatty acid, indicating that the decomposition of the fatty acid also obeyed first-order kinetics. The activation energy, E_{FA},

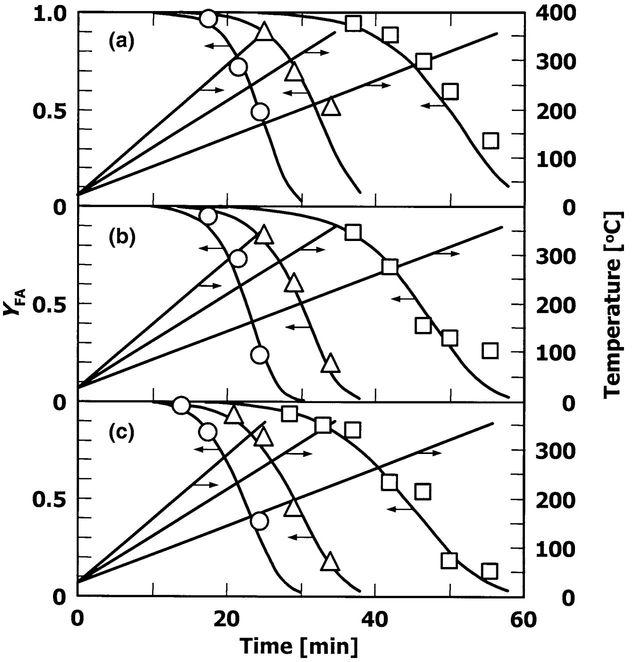

Fig. 5. Decomposition of (a) caprylic, (b) capric and (c) lauric acids in subcritical water under the temperature-programmed heating conditions. The ordinate indicates the ratio Y_{FA} of the concentration of remaining fatty acid to its initial concentration. The rates of temperature increase were (□) 5.97, (△) 9.92 and (○) 13.6 °C/min. The solid lines indicate the temperature changes.

and frequency factor, k_{FA0}, for the fatty acid decomposition were estimated from that line. The E_{FA} and k_{FA0} values for caprylic, capric and lauric acids are shown in Fig. 4. Both the E_{FA} and k_{FA0} values were generally smaller than the E_{MG} and k_{MG0} values, although there was a tendency for the E_{FA} and k_{FA0} values for a fatty acid with a longer acyl chain to be smaller.

The changes in the fatty acid concentrations during the decomposition under the temperature-programmed heating conditions were calculated using the estimated E_{FA} and k_{FA0} values, as shown by the solid curves in Fig. 5.

3.4. Change in the concentration of fatty acid during the decomposition of monoacyl glycerol

Because the E_{MG}, k_{MG0}, E_{FA} and k_{FA0} values have been estimated, we can calculate the change in the concentration of the fatty acid during the decomposition of a monoacyl glycerol under the temperature-programmed heating conditions using Eqs. (3)–(5). The calculated results are shown by the dotted curves in Fig. 2, and they express the experimental results well. This fact confirmed the appropriateness of the assumption that acyl glycerol was decomposed by consecutive reactions.

3.5. Enthalpy–entropy compensation in the decomposition

We reported that the enthalpy–entropy compensation held for the hydrolysis of various alkyl esters of fatty acids in subcritical water (Khuwijitjaru et al., 2004). Because Eq. (6) is one of the expressions of the compensation,

$$E_i = RT_\beta \ln k_{i0} + \gamma \tag{6}$$

the activation energy E_i is plotted versus the logarithms of the frequency factor, k_{i0}, in Fig. 6 in order to determine whether the compensation also holds for the decompositions of acyl glycerols and fatty acids in subcritical water. The E_i and k_{i0} values for the hydrolysis of alkyl esters of fatty acids are also shown in the figure. All of the plots gave a straight line, and the isokinetic temperature T_β was determined to be 435 K (=162 °C). This fact indicates that the hydrolysis of monoacyl glycerols and alkyl esters of fatty acids, and the decomposition of fatty acids, proceed essentially by the same reaction mechanism, and that the rate constant is common for all the reactions at the isokinetic temperature.

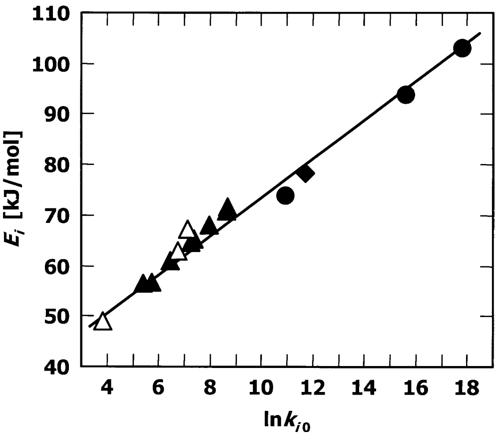

Fig. 6. Enthalpy–entropy compensation for the hydrolysis or decomposition of monoacyl glycerols (MG), fatty acids (FA) and alkyl esters of fatty acids (AF). E_i, and k_{i0} represent the activation energy and the frequency factor, respectively, for the decomposition or hydrolysis of species i (i = MG, FA or AF). The symbols ● and △ represent the values estimated for the decomposition of monoacyl glycerols and fatty acids, respectively, under the temperature-programmed heating conditions. The symbol ◆ indicates the value obtained for monolaurin under isothermal condition. The values represented by the symbol ▲ for the hydrolysis of alkyl esters of fatty acids are cited from our previous work (Khuwijitjaru et al., 2004).

4. Conclusion

The decompositions of monoacyl glycerols and their corresponding fatty acids in subcritical water were observed under heating conditions of linear increase in the reaction temperature. Evidently decomposition of a monoacyl glycerol proceeded consecutively; that is, the monoacyl glycerol was hydrolyzed to the corresponding fatty acid and glycerol, and the fatty acid was further decomposed. Each step was expressed by first-order kinetics, and the activation energy and the frequency factor were evaluated. Both the activation energy and frequency factor for a monoacyl glycerol or fatty acid with a longer acyl chain were smaller. The enthalpy–entropy compensation held for the hydrolysis or decomposition of monoacyl glycerols, alkyl esters of fatty acids and fatty acids themselves in subcritical water, indicating that the hydrolysis and decomposition proceeded essentially by the same reaction mechanism.

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