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Kinetics on the hydrolysis of fatty acid esters in subcritical water

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Abstract

Hydrolysis of fatty acid esters with different acyl and alkyl chains in subcritical water was examined over a temperature range of 483–543 K in a batch reactor. The concentrations of fatty acid esters were sufficiently low to assume a homogeneous reaction at every temperature. The hydrolysis of every fatty acid ester at any temperature obeyed first-order kinetics. The rate constant was observed at various temperatures, and the apparent activation energy and frequency factor were evaluated according to the Arrhenius equation for each fatty acid ester. Steric hindrance of the acyl and alkyl chains was found to increase the activation energy of the hydrolysis. The enthalpy–entropy compensation held in the hydrolysis of the fatty acid esters tested.

Keywords: Fatty acids; Esters; Hydrolysis; Kinetics; Subcritical water

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1. Introduction

Hydrolysis of food-related substances in sub- and supercritical water has been widely explored in the past decade. The most extensively studied topic is the hydrolysis of cellulose and other sugars [1–3]. Hydrolysis of proteins and degradation of amino acids were also studied [4,5]. Many types of hydrolysis processes of fats and oils have been investigated, and some of them have been commercialized. Patil et al. [6] have reported the kinetics of hydrolysis of vegetable oils and fats at 453–553 K, although their process would be steam hydrolysis rather than hydrolysis in subcritical water because the weight ratio of water to oil was 0.0067–2.0. Møller has patented a method for splitting of fats by hydrolysis at near-critical temperature [7]. More recently, Holliday et al. [8] have also reported the use of subcritical water for hydrolyzing vegetable oils to free fatty acids. However, the two latter literature sources [7,8] have not dealt with the kinetics.

In this study, fatty acid esters with various acyl and alkyl chains were hydrolyzed in a homogeneous aqueous solution using a batch reactor at 483–543 K. The kinetics of the hydrolysis was analyzed, and the effects of the acyl and alkyl chain lengths of the esters on their hydrolysis were studied.

2. Experimental

2.1. Materials

Methyl octanoate (purity >98%), methyl decanoate (>95%), methyl laurate (>98%), methyl myristate (>95%), and methyl palmitate (>95%) were purchased from Wako Pure Chemical Industries, Osaka, Japan. Ethyl laurate (>99%) was purchased from Nacalai Tesque, Kyoto, Japan. Propyl laurate (>99%) was obtained from Sigma, St. Louis, MO, USA. Butyl laurate (>99%) was purchased from Tokyo Kasei Kogyo, Tokyo, Japan. All the esters were used as received.

2.2. Apparatus

A batch reactor resistant to high pressure and temperature was fabricated by Taiatsu Techno Corporation, Osaka, Japan (Fig. 1). The reactor was made from SUS316 stainless steel with a volume of 10.2 ml (15 mm i.d.; 32 mm o.d.; 75 mm outside height). The temperature of the solution in the reactor was indirectly measured by a thermocouple inserted into a tube which was installed at about the middle of reactor. The reactor was placed in a temperature-controlled oven.

2.3. Procedure

Stock solutions of fatty acid esters were prepared by dissolving the esters in hexane at concentrations of

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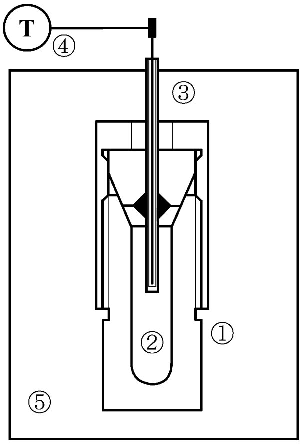

Fig. 1. Schematic diagram of experimental apparatus. ① Batch reactor resistant to high pressure and temperature, ② interior of the reactor, ③ stainless tube for inserting a thermocouple, ④ thermocouple, ⑤ oven.

6.32×10^{-2} mol/l, 5.37×10^{-3} mol/l, 4.67×10^{-3} mol/l, 2.06×10^{-3} mol/l and 5.55×10^{-4} mol/l for methyl octanoate, decanoate, laurate, myristate and palmitate, and 1.53×10^{-5} mol/l, 5.20×10^{-6} mol/l and 1.56×10^{-6} mol/l for ethyl, propyl and butyl laurates. The concentration of each ester in the stock solution was determined based on the solubility at room temperature [9] or that of the corresponding of fatty acid at high temperatures [10], so that the ester was completely dissolved under reaction conditions. In the determination of the concentration, the solubility of an ester at high temperatures was assumed to be one-tenth of that of the corresponding fatty acid. Nine hundred microliters of a stock solution was pipetted into the reactor, and the hexane was removed by evaporation. Nine milliliters of degassed water was added to the reactor. To prevent possible oxidation of an ester by dissolved oxygen, the distilled water had been purged with helium gas before use.

The reactor was tightly closed and placed in an oven which was preheated at 723 K. Prior to the hydrolysis experiments, we conducted preliminary experiments to determine a temperature program for achieving a desired value as quickly as possible. The temperature of the solution in the reactor was monitored, and the temperature of the oven was regulated according to the program determined above. The pressures at 483 and 543 K were estimated to be 35 and 134 MPa, respectively, based on the IAPWS formulation [11]. The reaction time was set to zero at the moment when the temperature reached the desired value. After a specific reaction time elapsed, the reactor was removed from the oven and rapidly quenched in an iced water bath to stop the reaction.

2.4. Analysis

The solution in the reactor was poured into a test tube (30 mm × 200 mm), and ca. 0.3 g of sodium sulfate was added to the solution [8]. An internal standard dissolved in hexane (0.9 ml) and 8.1 ml of hexane were added into the tube. Methyl laurate dissolved in hexane at a concentration of 2.33×10^{-3} mol/l or 2.33×10^{-5} mol/l was used as the internal standard for the determination of methyl octanoate, decanoate, myristate and palmitate or of ethyl, propyl and butyl laurates. Methyl decanoate (2.68×10^{-3} mol/l) dissolved in hexane was used as the internal standard for the determination of methyl laurate. The solution was vortex-mixed and allowed to stand to phase-separate. After phase-separation, 3 ml of the hexane phase was transferred into a vial, and the hexane was removed under reduced pressure. The remainder was dissolved with 100 μl of hexane for use in GC analysis. The amount of remaining ester was determined by a GC-7A gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and a glass column (3.2 mm i.d., 3.1 m length) packed with 5% Thermon-3000 on Shincarbon A packing material (60–80 mesh, Shinwa Kako, Kyoto). The analytical conditions were a column temperature of 453 K except for methyl octanoate (423 K for methyl octanoate), an injection temperature of 503 K, a detector temperature of 503 K, a sample-injection volume of 5 μl, and N_2 as the carrier gas at a flow rate of 50 ml/min.

3. Results and discussion

3.1. Hydrolysis of fatty acid esters

Methyl esters of fatty acids with different acyl chain lengths from 8 to 16 were subjected to hydrolysis in water over a temperature range of 483–543 K in the batch reactor. Fig. 2(a) shows the fraction of the concentration of a remaining ester at any reaction time relative to the concentration at zero reaction time, C/C_0, as a function of the reaction time, t, on a semi-logarithmic scale for methyl octanoate and palmitate. At every temperature, the plots for each ester gave a straight line, indicating that the hydrolysis obeyed first-order kinetics:

$$\frac{dC}{dt} = -kC \qquad (1)$$

where k is the rate constant. The hydrolysis of methyl palmitate was slower than that of methyl octanoate at every temperature. The first-order kinetics was also applied to the hydrolysis of methyl *tert*-butyl ether [12] and the decomposition of glycine [5] in subcritical water, while the rate expression of autocatalytic type was proposed for the hydrolysis of ethyl acetate [13].

The hydrolysis of ethyl, propyl and butyl laurates was also measured at those temperatures. Fig. 2(b) shows the hydrolysis of methyl and butyl laurates at various temperatures on a semi-logarithmic scale. The hydrolysis of both the laurates obeyed first-order kinetics. Butyl laurate was more slowly hydrolyzed than methyl laurate at every temperature.

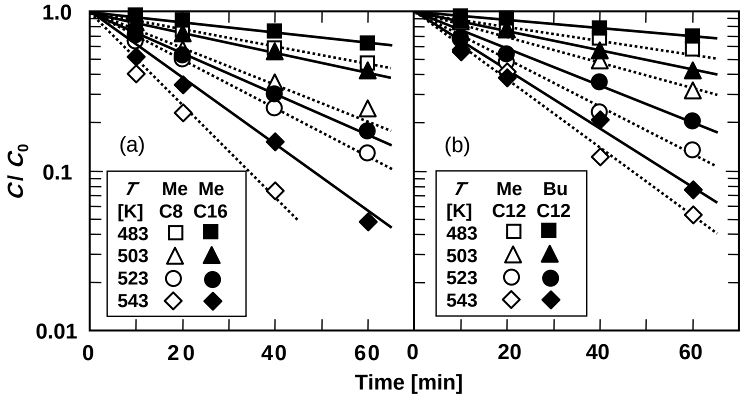

Fig. 2. Hydrolysis of (a) methyl octanoate (MeC8), methyl palmitate (MeC16), (b) methyl laurate (MeC12) and butyl laurate (BuC12) by subcritical water at various temperatures. C is the concentration of unhydrolyzed ester at any reaction time, and C_0 is the concentration at zero reaction time.

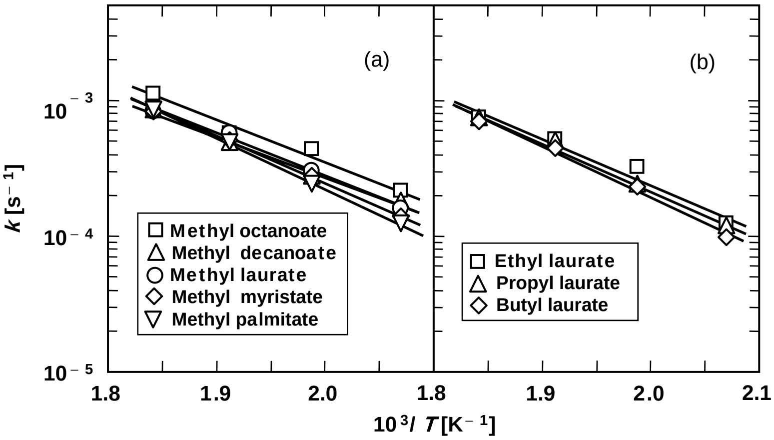

Fig. 3. Arrhenius plots of the rate constant, k, for (a) methyl esters of fatty acids and (b) laurates with different alkyl chains.

3.2. Effect of acyl or alkyl chain length of ester on the rate constant

The hydrolysis of various esters was measured at different temperatures. In all the cases, the hydrolysis of each ester obeyed the first-order kinetics, and the rate constant, k, was estimated in the same manner as in Fig. 2. Fig. 3(a) and (b), respectively, show the Arrhenius plots for methyl esters with different acyl chains and for the laurates with different alkyl chains. The plots for each ester gave a straight line, and the apparent activation energy, E, and the frequency factor, k_0, were evaluated from the line.

The E and k_0 values for the methyl esters with various acyl chains are plotted versus their acyl chain length in Fig. 4. Both the E and k_0 values were greater for the esters with a longer acyl chain. The E and k_0 values for the laurates with different alkyl chains are also plotted versus the alkyl chain length in the figure. Both the E and k_0 values were also greater for the laurate with a longer alkyl chain.

The greater E value of the ester with a longer acyl or alkyl chain would indicate the steric hindrance of the acyl or alkyl chain to the hydrolysis of fatty acid esters in subcritical water because nucleophilic attack by water becomes more difficult [14]. Bröll et al. [15] reported that the hydrolytic rate of some acetates in subcritical water rose in the sequence methyl > ethyl > n-butyl, with which the present results coincided.

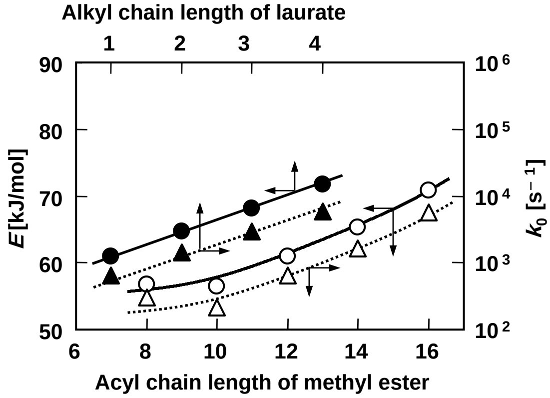

Fig. 4. Dependencies of the apparent activation energy, E, and the frequency factor, k_0, on the acyl chain length of methyl esters or alkyl chain length of laurates.

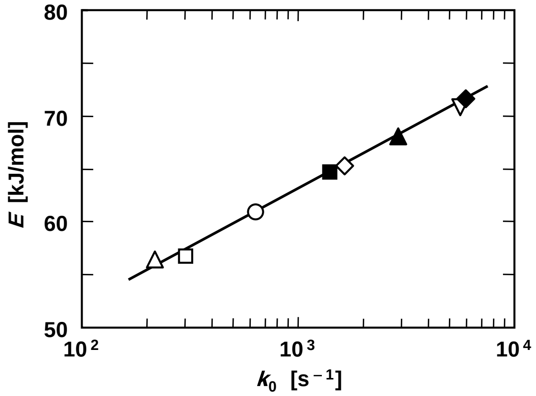

Fig. 5. Enthalpy–entropy compensation for the hydrolysis of fatty acid esters by subcritical water. E and k_0 are the apparent activation energy and the frequency factor, respectively. The open symbols (□), (△), (○), (◇) and (▽) are the same as in Fig. 3, and the closed symbols (■), (▲) and (◆) represent ethyl, propyl and butyl laurates.

3.3. Enthalpy–entropy compensation

For all the esters tested, the E values are plotted versus the logarithms of k_0 in Fig. 5. The plots lie on a straight line. This indicates that the enthalpy–entropy compensation holds in the hydrolysis of the esters in subcritical water and that the esters are hydrolyzed through essentially the same mechanism. Eq. (2) is one of the expressions of the compensation:

$$E = 2.30RT_\beta \log k_0 + \gamma \tag{2}$$

where T_β is a parameter with a dimension of temperature and is called an isokinetic temperature. The T_β value was estimated from the line to be 567 K for the hydrolysis of the esters.

4. Conclusions

Fatty acid esters with various acyl or alkyl chains were hydrolyzed in subcritical water over a temperature range of 483–543 K using a batch reactor. The hydrolysis of each ester obeyed first-order kinetics at every temperature, and the apparent activation energy, E, and frequency factor, k_0, were estimated from the temperature dependence of the rate constant of the kinetics. The E value of the ester with a longer acyl or alkyl chain was greater. This indicated a steric hindrance of the acyl or alkyl chain to the hydrolysis of the ester bond. It was also shown that the enthalpy–entropy compensation held for the hydrolysis of the esters tested.

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