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A Differential Scanning Calorimetry Study on the Oxidation of C_{12}–C_{18} Saturated Fatty Acids and Their Esters

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ABSTRACT: The autoxidation of lauric, myristic, palmitic, and stearic acids, their ethyl esters, and palmitic and stearic triglycerides was investigated by means of the isothermal and non-isothermal differential scanning calorimetry methods under oxygen flow. The activation energies of oxidation of all investigated compounds were similar (106.0–134.3 kJ/mol) and did not depend on length of the carbon chain. Kinetic parameters of start of the oxidation were similar for each investigated fatty acid and ester. Esterification of carboxyl group did not interfere with the reaction rate. The study showed good agreement between isothermal and nonisothermal data.

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KEY WORDS: Activation energy, autoxidation, DSC, fatty acids.

There is a considerable interest in characterization of thermooxidative properties of the fatty acids, their esters, and kinetics of their oxidation. Natural fats and oils are very complicated systems of mono-, di- and triglycerides, higher lipids, phospholipids, antioxidants, and other compounds. In the basic research they should be replaced by simple lipid analogs such as free fatty acids and their esters. Although autoxidation of saturated hydrocarbons was the subject of many investigations (1–6) there are only a few papers describing autoxidation of natural saturated fatty acids and their esters. Former studies on autoxidation of saturated normal hydrocarbons suggested the applicability of the results to oxidation of saturated fatty acid esters. Moreover, it was found that autoxidation rates were increasingly proportional to the carbon chain length (1). Recent studies in which overall reactivities of n-paraffins determined by analysis of monoderivatives at the initial stage of oxidation (7) led to conclusion that the reactivity probably does not depend on length of carbon chain.

Presence of two maxima on the nonisothermal differential scanning calorimetry (DSC) oxidation curves indicates that thermoxidation can be characterized by at least two-step exothermic effect. Each reaction is characterized by different kinetic parameters. Thus, the kinetic parameters of autoxidation (start of the exothermic process) and destruction of autoxidation products (occurring at higher temperatures) can be determined

(8,9). In this study, oxidation of the natural saturated fatty acids: lauric, myristic, palmitic, and stearic, their ethyl esters, and glycerol tripalmitate and tristearate was investigated by DSC methods. The kinetics of the autoxidation of materials containing fatty acids was investigated by thermoanalytical procedures (10–13). However, no data concerning thermoxidative behavior of pure saturated fatty acids and esters have been reported as yet. This study was undertaken in order to establish the kinetics parameters of thermoxidation of these classes of compounds.

EXPERIMENTAL PROCEDURES

Materials. The following fatty acids—lauric, palmitic, stearic—and ethyl esters—laurate, myristate, palmitate and stearate (all 99%)—were purchased from Sigma-Aldrich (St. Louis, MO). Purity of glycerol tripalmitate (BDH, Poole, United Kingdom) and tristearate (Fluka AG, Buchs, Switzerland) was 98%. The acids and esters were used without further purification. All investigated compounds were stored under nitrogen at 0°C.

Methods. All calorimetric measurements were carried out using a DSC apparatus: Du Pont model 910 differential scanning calorimeter (TA Instruments, Alzenau, Germany) with a Du Pont 9900 thermal analyzer and a normal pressure cell. The apparatus was calibrated with a high-purity indium standard. Both isothermal and non-isothermal experiments were performed under an oxygen flow of about 6 dm^3/h.

In nonisothermal method samples of compounds (5–8 mg) were heated from 120 to 300°C with linear heating rate β (2–20 K/min). The apparent activation energies of oxidation were calculated by the Ozawa-Flynn-Wall method from Equation 1:

$$E_a = -2.19R \frac{d\log \beta}{dT_e^{-1}} \qquad [1]$$

where R is the gas constant and T_e is the extrapolated initial temperature of oxidation in K. Determination of T_e is presented in Figure 1. Full description of the calculation procedure was shown previously (8).

During isothermal measurements samples were heated at several fixed temperatures (155–180°C). E_a was calculated from the following equation:

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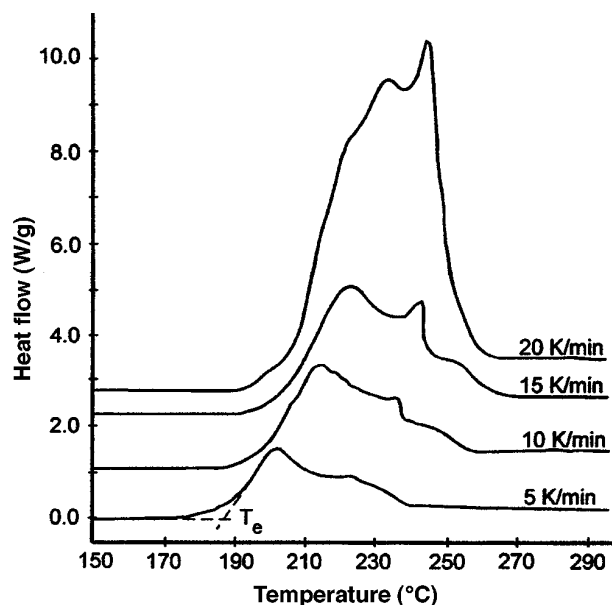E-mail: litwin@alfa.chem.uw.edu.pl

FIG. 1. Differential scanning calorimeter scans of lauric acid oxidation obtained for different heating rates. T_e, temperature of extrapolated start of oxidation.

$$E_a = 2.29R \; \frac{d\log \tau}{dT^{-1}} \qquad [2]$$

where T is experimental temperature (in K) and τ is the time of the maximum heat flow (in minutes) according to details described elsewhere (9).

Reality of E_a obtained by thermoanalytical methods was verified by the conventional method in which the progress of reaction was followed. A weighed sample (about 10 mg) of lauric acid was heated at 154°C under oxygen flow in DSC cell for 5 min. Next, samples of the acid were oxidized at the same conditions for 11, 24, and 30 min. After stopping the oxidation, each sample was removed from the apparatus, diluted with acetone, and the amount of unreacted acid was determined by gas chromatography (GC). Experiments were repeated at 171 and 183°C. Chromatographs of analyzed lauric acid after 7, 15, and 35 min of oxidation at 183°C are presented in Figure 2. Under excess of oxygen the reaction rate is defined as: $-dC/dt = kC$. Measurements of substrate concentration C (or any parameter proportional to the concentration) during the reaction course allows one to obtain the rate constant k from integrated equation: $-\ln C = kt + \text{const}$. Activation energy can be determined from the Arrhenius equation: $k = A \exp(-E_a/RT)$ where A is the Arrhenius constant. When $\ln k$ is plotted vs. the reciprocal of the absolute temperature, $-E_a/R$ represents the slope (14,15). The same method was used to determine the kinetic parameters of stearic acid oxidation. Measurements of contents of unreacted fatty acids during oxidation were performed using Hewlett-Packard 6890 gas chromatograph (Waldbronn, Germany; column HP5 30 m × 0.32 mm i.d., film thickness 0.25 μm, carrier gas: argon, flame-ionization detector 300°C, split 100:1, oven program: 1 min 50°C, then increased at 10°C/min to 200°C).
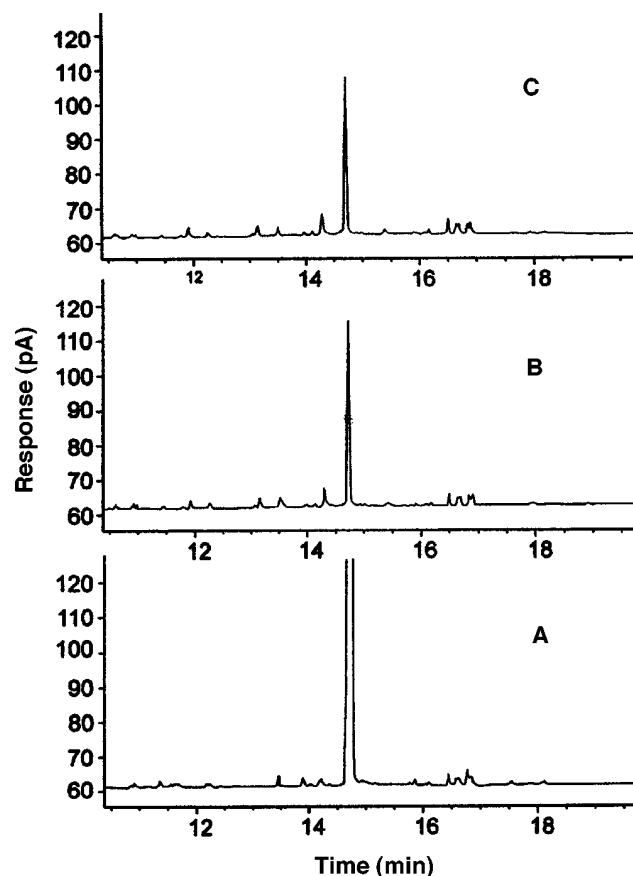

FIG. 2. Gas chromatographs of lauric acid after oxidation at 183°C during: (A) 7 min, (B) 15 min, (C) 35 min.

RESULTS AND DISCUSSION

Typical DSC curves of nonisothermal oxidation for different heating rates are shown in Figure 1. In all experiments start of the oxidation was above 170°C and was higher than for unsaturated fatty acids (86–110°C for linolenic acid) and edible oils (130–180°C) (8–12). Values of the activation energies obtained from isothermal and nonisothermal experiments are collected in Table 1.

Rate constants of lauric acid oxidation calculated from GC measurements were: 0.0083 ± 0.0027 min^{-1} (154°C), 0.0368 ± 0.0032 min^{-1} (171°C) and 0.0604 ± 0.0121 min^{-1} (183°C). Activation energy calculated from these values was 112.6 ± 19.3 kJ/mol. Similarly, rate constants obtained for stearic acid oxidation: 0.0095 ± 0.0014 min^{-1} (155°C), 0.0219 ± 0.0077 min^{-1} (166°C) and 0.0605 ± 0.0017 min^{-1} (183°C) gave $E_a = 120.1 \pm 14.9$ kJ/mol. Results from DSC experiments (Table 1) are in good agreement with values obtained by this alternative method.

Presented values of E_a do not vary substantially; the differences can be demonstrated within the experimental error of 3–16%. Our experiments demonstrate that the rate of autoxidation of saturated C_{12}–C_{18} fatty acids is not correlated with the length of the carbon chain. Lauterbach and Pritzkow (7) described similar relative reactivities of hydrocarbons but only monofunctional derivatives of oxidation were moni-

TABLE 1
Activation Energies of Isothermal and Nonisothermal Thermoxidation of Fatty Acids

	Activation energy (kJ/mol)	
	Isothermal method	Nonisothermal method
Palmitic acid	125.1 ± 11.2	125.3 ± 3.6
Ethyl palmitate	126.6 ± 5.0	124.5 ± 4.5
Glycerol tripalmitate	105.3 ± 7.7	108.0 ± 4.3
Stearic acid	134.3 ± 12.0	115.4 ± 4.8
Ethyl stearate	128.5 ± 2.6	106.0 ± 7.5
Glycerol tristearate	102.5 ± 10.9	117.8 ± 17.7
Lauric acid	97.3 ± 7.3	116.7 ± 1.7
Ethyl laurate	127.3 ± 6.4	118.7 ± 19.6
Ethyl myristate	117.1 ± 5.4	119.0 ± 12.0

tored. However, the increasing reactivity was expected and authors suggested that probably more difunctional derivatives were formed (not monitored). In our study, the start of exothermal effects and kinetic parameters of oxidation do not depend on the chain length, and observed DSC signal gives information about gross reactivity of oxidized compound.

Presented activation energies of oxidation provide that the start of the process is similar for all classes of investigated compounds: fatty acids, their ethyl esters, and triglycerides. From these results we can state that oxidation does not take place on free or esterified carboxyl groups of fatty acids. Therefore, free fatty acids or their simple esters can be used as lipid analogs to investigate the autoxidation processes.

The comparison of activation energies of nonisothermal oxidation with E_a obtained in isothermal oxidation shows that both methods are equally suitable for investigations of autoxidation kinetics.

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