

OXIDATION OF SATURATED FATTY ACIDS ESTERS

DSC investigations

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Abstract

Oxidation of saturated fatty acids ethyl esters: laurate, myristate, palmitate and stearate was investigated by means of DSC techniques under isothermal and non-isothermal conditions. The activation energies of isothermal oxidation were similar to each other (112–123 kJ mol⁻¹) and no influence of carbon length on the rate of oxidative decomposition was observed. Results obtained from non-isothermal experiments were similar only for the first stage of oxidation.

Keywords: DSC, fatty acids esters, kinetics, oxidation

Introduction

Currently, there is a considerable interest in characterization of thermal-oxidative stability and kinetics of the fatty acids esters oxidation, since these esters are analogues of the triacylglycerides which play key roles in many chemical (e.g. autoxidation) and biochemical (lipid peroxidation) processes. In this communication we present results of thermoanalytical investigations of isothermal and non-isothermal oxidation of some natural fatty acids ethyl esters: ethyl dodecanoate (laurate), ethyl tetradecanoate (myristate), ethyl hexadecanoate (palmitate) and octadecanoate (stearate). In previous experiments [1–3], concerning autoxidation of edible oils, we observed discrepancies between kinetic data obtained using different thermoanalytical methods. The edible oils containing saturated, mono- and polyunsaturated fatty acids triacylglycerides and some natural antioxidants are too complicated to evaluate comprehensive conclusions.

Therefore, this work was undertaken to investigate the influence of the carbon chain length on the rate of thermoxidation and on the activation energy of the process of the oxidation. The second reason was to answer the question: which peak observed during non-isothermal oxidation is related to peak observed in isothermal experiment. Moreover, the aim of the performed experiments was de-

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scription of the relationship between thermal behaviour of fatty acids under isothermal and non-isothermal oxidation.

These investigations were the part of the research concerning applications of thermal analysis in investigation of the autoxidation of fats, edible oils and lipids.

Experimental

Following fatty acids: lauric, palmitic, stearic and ethyl esters: laurate, myristate, palmitate and stearate (all 99%) purchased from Sigma-Aldrich were used without further purification. All investigated compounds were stored under nitrogen at a temperature about 0°C.

The DSC apparatus: A DuPont model 910 Differential Scanning Calorimeter with a DuPont 9900 Thermal Analyser and a normal pressure cell were used in measurements. The apparatus was calibrated with a high-purity indium standard. The study was carried out in an oxygen atmosphere. Both isothermal and non-isothermal experiments were performed under oxygen flow about 6 dm³ h⁻¹.

Non-isothermal measurements

Samples of 3–5 mg were heated from 120 to 300°C with linear heating rate β (2–20 K min⁻¹). The DSC curves of oxidation of palmitic acid ethyl ester vs. temperature is shown in Fig. 1. The extrapolated initial temperatures of oxidation (T_{on}) and temperatures of maximum heat flow (T_{max}) listed in Table 1 showed linear dependency:

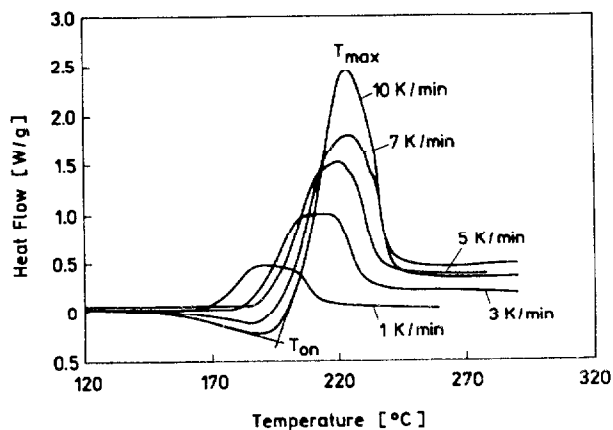


Fig. 1 The DSC curves of oxidation of palmitic acid ethyl ester vs. temperature

$$\log\beta = AT^{-1} + a \quad (1)$$

where A and a are coefficients calculated by least squares method. The obtained data were used to calculate the apparent activation energy by the Ozawa-Flynn-Wall method [4] from equation:

$$E = -2.19R \frac{d\log\beta}{dT^{-1}} \quad (2)$$

where R is the gas constant and T is T_{on} or T_{max} in K. The calculated activation energies and errors of estimation are presented in Table 2.

Table 1 Temperatures of the extrapolated start oxidation and temperatures of the maximum heat flow obtained for different heating rates

Ester	$\beta/\text{K min}^{-1}$	T/K		
		onset	maximum 1	maximum 2
Ethyl laurate	3	457.0	475.3	—
	5	461.4	489.0	—
	7	468.8	502.2	—
	10	478.0	506.7	—
Ethyl myristate	1	449.9	464.8	482.6
	3	463.9	482.1	507.5
	5	470	491.9	517.7
	7	473.2	496.0	529.3
	10	484.7	504.6	547.7
Ethyl palmitate	1	443.8	461.1	473.0
	3	459.1	477.8	489.7
	5	464.1	483.6	493.8
	7	470.3	486.9	497.6
	10	474.6	493.0	507.7
Ethyl stearate	2	450.4	466.0	481.5
	5	460.9	485.9	501.0
	10	471.1	496.8	518.7
	12	477.5	501.4	525.1
	15	479.8	503.3	—
	17	481.4	505.8	—
	20	488.8	511.6	539.5

Isothermal measurements

Each investigated sample was heated under isothermal conditions at several temperatures. Typical DSC curves obtained in isothermal conditions are shown

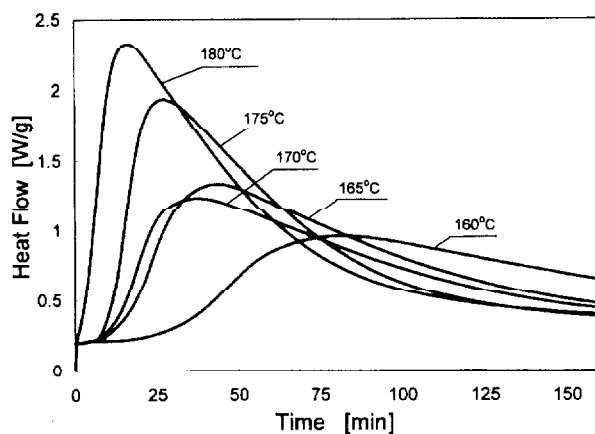
Table 2 Data obtained from DSC curves by non-isothermal method. A and a -coefficients of Eq. (1) with standard deviations

Ester		A	δ_A	a	σ_a	R^2	$E/\text{kJ mol}^{-1}$
Ethyl laurate	onset	-6.52	1.08	14.78	0.05	0.9483	118.7±19.6
	max1	-4.40	0.36	9.98	0.04	0.9867	80.2±6.6
Ethyl myristate	onset	-6.54	0.66	14.57	0.08	0.9705	119.0±12.0
	max1	-5.91	0.17	12.73	0.02	0.9974	107.6±3.1
	max2	-4.17	0.36	8.694	0.07	0.9779	75.9±6.6
Ethyl palmitate	onset	-6.84	0.25	15.41	0.03	0.9960	124.5±4.5
	max1	-7.21	0.35	15.62	0.04	0.9929	131.3±6.4
	max2	-7.23	0.66	15.31	0.079	0.9756	131.1±12.0
Ethyl stearate	onset	-5.82	0.41	13.29	0.06	0.9757	106.0±7.5
	max1	-5.44	0.23	11.96	0.04	0.9909	99.1±4.2
	max2	-4.46	0.12	9.58	0.02	0.9979	81.2±2.1

in Figs 2 and 3. Times of the maximum heat flow (τ) can be described by linear dependency:

$$\log \tau = BT^{-1} + b \quad (3)$$

where T is the temperature in K and B and b are coefficients calculated by means of least squares method [5]. Plots of these dependencies are presented on Fig. 4.

**Fig. 2** DSC plots of oxidation of ethyl palmitate under isothermal conditions

The activation energy was calculated from the following equation:

$$E = 2.29R \frac{d \log \tau}{dT} \quad (4)$$

Parameters of the Eq. (4) and the values of the activation energy of oxidation under isothermal conditions are listed in Table 3.

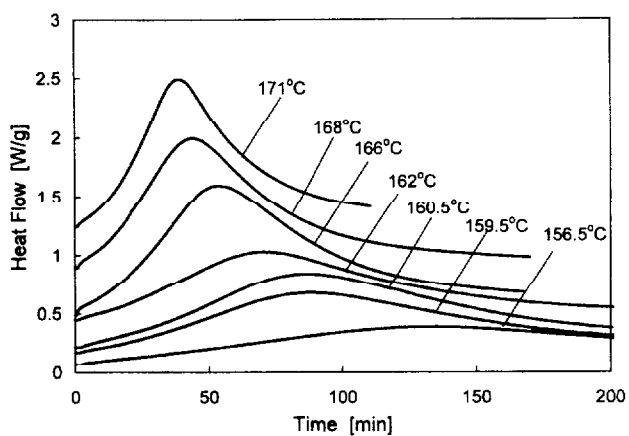


Fig. 3 Thermal effect of oxidation of ethyl myristate at constant temperatures

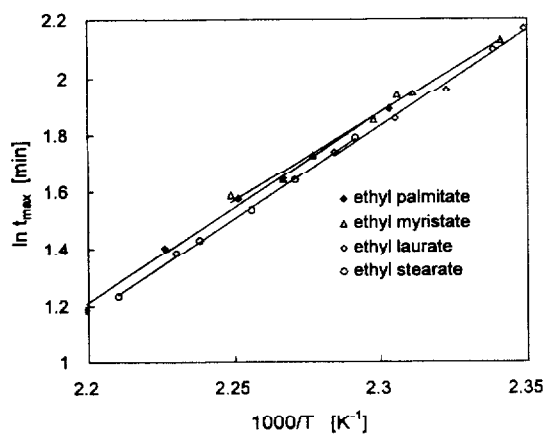


Fig. 4 Plots of Eq. (3) for investigated esters

Results and discussion

Comparing results of calculations performed for non-isothermal oxidation it is clear that start of the process is similar for each investigated ester and the values of activation energy do not vary substantially and the differences can be dem-

Table 3 Data obtained from isothermal experiments, coefficients of Eq. (3) with standard deviations and calculated values of activation energy

Ester	T/K	τ/min	B	δ_b	b	σ_b	R^2	$E/\text{kJ mol}^{-1}$
Ethyl myristate	427.2	134.5	6.15	0.28	-12.26	0.02	0.9894	117.1±5.4
	432.7	88.1						
	433.7	86.9						
	435.3	71.2						
	439.0	53.6						
	441.3	44						
	444.7	38.7						
Ethyl laurate	425.7	147	6.69	0.34	-13.55	0.02	0.9923	121.7±6.2
	427.7	125						
	430.6	91						
	433.8	72						
	437.8	55						
Ethyl palmitate	434.0	77.5	6.65	0.26	-13.43	0.02	0.9953	126.6±5.0
	441.0	44.3						
	444.4	37.6						
	449.4	25.3						
	454.7	15.4						
Ethyl stearate	436.4	61.7	6.75	0.14	-13.78	0.01	0.9983	128.5±2.6
	440.4	43.8						
	443.3	34.3						
	446.8	26.9						
	448.4	24.2						
	452.4	17.1						

onstrated within the experimental error of 3–16%. The error of estimated activation energy was greater for ethyl laurate and ethyl myristate, what can be caused by greater volatility of these compounds than of stearate and palmitate. Therefore, the temperatures of the start of oxidation were extrapolated with lower precision than the ones for longer chain fatty esters. The shape of all non-isothermal DSC curves indicates that at least two processes giving two overlapping maxima of heat flow proceeded. The kinetic parameters estimated using temperatures of these peaks differed significantly when we used for calculation T_{on} and in this case data were scattered over a wide range. The most probable interpretation of the above observation is that destruction of the carbon chains at higher temperatures occurs and that the thermal effect of this process interferes with autoxidation taking place at the start of the oxidation course. In order to confirm this hypothesis we compared activation energies from non-isothermal experiments with isothermal ones. The data obtained for studied esters during isothermal oxidation are collected in Table 3. The results of calculations are in good agreement

with one another, the activation energies range from 117 to 128.5 kJ mol⁻¹ with maximal errors of 5% and the results are consistent with kinetic parameters obtained from the onset point of non-isothermal curves.

Conclusions

The calculated activation energies of oxidation were similar and not depended on length of the carbon chain. At the start of the oxidation the thermal effect observed during linear programmed increase of temperature is caused by the same process as during the isothermal oxidation.

The shape of the DSC exotherms can be utilised to calculate the activation energy from the point at constant conversion. Oxidation of lipids is a complex process and the calculations of the E_a from the usually utilised points of constant conversion (temperatures of the maximum heat flow) is erroneous. We postulate the utility of the start point of the process as the best one to obtain the kinetic information about autoxidation of fats and fatty acids.

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