Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 639–646

AUTOOXIDATION OF UNSATURATED FATTY ACIDS AND THEIR ESTERS

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Abstract

The shape of DSC curves of non-isothermal oxidation of fats was explained. Two main exothermic effects overlapped partially are caused by hydroperoxide formation (first peak) and by further oxidation of peroxides (second peak). The oxidation of oils and lipid analogues of various peroxide concentration showed that only the start of the oxidation process is affected by initial concentration of peroxides, other temperatures determined from DSC curves are not connected with this parameter. The computer simulations gave the best agreement of theoretical and experimental data for kinetic scheme of a two-step consecutive reaction with autocatalytic start. The comparison of activation energies calculated for isothermal and non-isothermal autooxidation of unsaturated fatty acids and their esters also confirmed this interpretation.

Keywords: autooxidation, DSC, fatty acids, lipids, oxidative stability

Introduction

There is a considerable interest in the characterisation of thermoxidative properties of the unsaturated fatty acids, their esters and kinetics of their autooxidation. Unsaturated fatty acids are the major components of vegetable fats which are not only used as edible oils but frequently find application in pharmacy and industry (soaps, detergents, cosmetics, resins, paints, rubber, impregnating agents, lubricants and many other products). Standard tests used for the assessment of oxidative stability are Shaal test, oxygen bomb test, active oxygen method (AOM), oxidative stability index (OSI) and Rancimat method. These methods, called accelerated tests are based on high temperature oxidation (80–120°C) of fatty material and periodic analysis of peroxide contents or detection of low molecular volatile products of oxidation. The disadvantages of accelerated tests are their length (several hours or days) and the induction time determined by these methods is a non-kinetic parameter. Therefore, new methods for accurate, quick and simple assessment of oxidative stability of undiluted substances at higher temperatures are in demand. Since autooxidation is accompanied by heat changes, the aim of our research was to evaluate a method in which the oxidation

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

as thermal process is monitored by non-isothermal differential scanning calorimetry (DSC).

Kinetic parameters: overall activation energy E, pre-exponential factor Z and rate constant k can be calculated by means of Ozawa–Flynn–Wall (OFW) method [1] from equations:

$$\log\beta = a/T_\alpha + b \tag{1}$$

$$a = -0.4567\,E/R \tag{2}$$

$$b = -2.315 + \log(ZE/R) \tag{3}$$

where: β – heating rate, R – gas constant, T_α – temperature (in K) of constant degree of conversion α, and the rate constant is obtained from Arrhenius equation: $k=Z\exp(-E/RT)$.

The shape of typical DSC curves of non-isothermal oxidation for linseed oil is shown in Fig. 1a. Since autooxidation is complicated, multistep chain process and OFW method is an isoconversion method, the basic problem is: what point of DSC curves (what values of T_α) should be taken for calculations? In our previous papers [2–4] we reported studies on non-isothermal autooxidation of fatty acids and their esters and also the

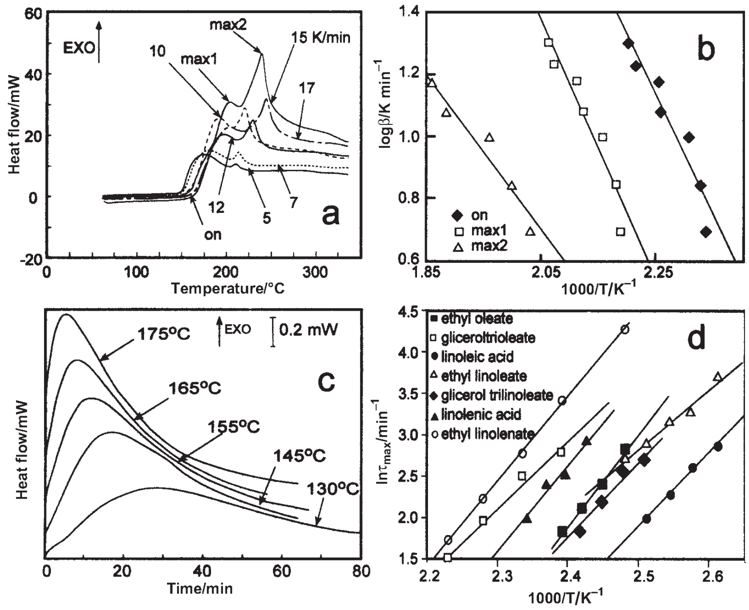

Fig. 1 Examples of typical DSC curves of lipid oxidation and dependencies used for calculation of kinetic parameters.
a – DSC curves of non-isothermal oxidation of linseed oil for various heating rates: 7, 5, 10, 12, 15 and 17 K min^{-1}, b – Plots of Eq. (1): logarithm from heating rate ($\log\beta$) *vs.* reciprocal of absolute temperature ($1/T$) of onset, first and second maximum of DSC curves for linseed oil, c – Heat effect of isothermal oxidation of ethyl linoleate, d – Plots of $\log\tau_{max}$ *vs.* reciprocal of oxidation temperature ($1/T$) for investigated lipids

studies on inhibited autooxidation [5]. In thermal analysis the kinetic parameters can be calculated from any point of α=*const.* on DSC curve when the observed reaction is simple. In autooxidation studies, the observed thermal effect is complicated due to complex mechanism of reaction. Therefore, in order to interpret the DSC curve of oxidation the influence of prooxidants concentration on temperatures of start of oxidation and temperatures of first and second maximum should be studied in detail. Moreover, in this paper the kinetic parameters of non-isothermal autooxidation of lipid analogues were compared with parameters of oxidation under isothermal conditions. Although isothermal calorimetry was used to study the autooxidation of fats and oils [6–8], the single experiment is about 60 min long and several experiments are needed to determine the kinetic parameters of the oxidation. The use of non-isothermal DSC measurements would shorten a single run to 15–30 min.

Materials and apparatus

Unsaturated fatty acids and their ethyl esters: *cis*-9-octadecanoic acid (oleic, $C_{18:1}$), *cis*-13-docosenoic acid (erucic acid, $C_{22:1}$), *cis,cis*-9,12-octadecadienoic acid (linoleic, $C_{18:2}$), *all-cis*-9,12,15-tridecanoic acid (linolenic, $C_{18:3}$) and glycerol trioleate and trilinoleate of (all of purity 98–99%) were purchased from Sigma Aldrich.

Commercial edible corn oil (10% of saturated fatty acids, 27% of $C_{18:1}$, 62% of $C_{18:2}$ and <1% $C_{18:3}$) and pharmaceutical grade linseed oil (9% of saturated fatty acids, 17% of $C_{18:1}$, 17% of $C_{18:2}$ and 53% of $C_{18:3}$) were from local markets. Fatty acid composition of oils was determined by GLC.

Corn oil, linseed oil, oleic acid and glycerol trioleate with different peroxide number (PN) were obtained by heating 100 g samples of each substance under air at 80°C. Samples weighing 4 g samples were taken periodically to DSC experiments and to analyse the peroxide number according to the Polish standard [9].

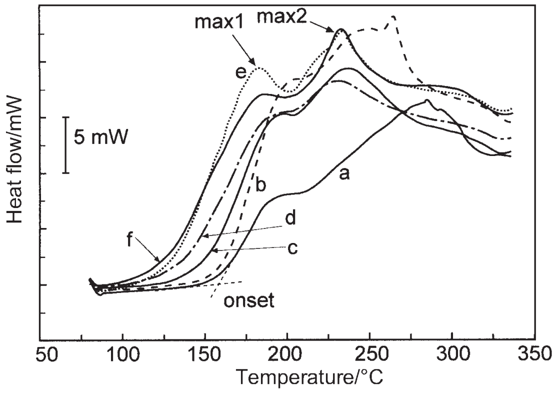

Fig. 2 DSC curves of non-isothermal oxidation of corn oil. Initial concentration of peroxides: a – 0.8; b – 47.6; c – 93.8; d – 136.6; e – 145.8; f – 158.2 mmol O_2/kg. Heating rate β=10 K min^{-1}

All calorimetric measurements were carried out using a DSC apparatus: DuPont model 910 differential scanning calorimeter with a DuPont 9900 thermal analyzer and a normal pressure cell. The apparatus was calibrated with a high-purity indium standard. The study was carried out in an oxygen atmosphere. Experiments were performed under oxygen flow about 6 $dm^3 h^{-1}$. 5 mg samples of compounds were heated from 50 to 300°C in open aluminum pan with linear heating rate β=10 K min^{-1}. The extrapolated onset temperatures (t_{on}) and temperatures of maximum heat flow (t_{max_1}, t_{max_2}) are defined in Figs 1a and 2 and they were determined from each DSC scan by using program GENERAL V4.01 (TA Instruments). All values are averages of at least three determinations.

The apparent activation energies for oxidation of pure fatty acids and esters were calculated by the Ozawa–Flynn–Wall method [1] from Eqs (1)–(3). A full description of the calculation procedure was shown in previous papers [4, 10, 11]. The kinetic parameters calculated for corn and linseed oil oxidation are presented in Table 1.

Table 1 Parameters of Eq (1) and kinetic parameters of oxidation for corn and linseed oil

Substance	a	σ_a	b	σ_b	R^2	E/k mol^{-1}	Z/min^{-1}
Corn oil							
onset	–3.82	0.53	9.70	0.07	0.9274	69.5±9.7	$1.25\cdot10^{8}$
max1	–4.14	0.55	9.87	0.07	0.9187	75.4±10.0	$1.70\cdot10^{8}$
max2	–2.33	0.18	5.47	0.04	0.9711	42.5±3.2	$1.22\cdot10^{4}$
Linseed oil							
onset	–7.29	0.48	17.95	0.03	0.9786	132.7±8.8	$1.15\cdot10^{16}$
max1	–4.01	0.35	9.70	0.05	0.9631	73.1±6.4	$1.10\cdot10^{8}$
max2	–4.16	0.42	9.33	0.05	0.9604	75.7±7.7	$4.85\cdot10^{7}$

Fatty acids and their esters were oxidized also in isothermal conditions in order to compare isothermal and non-isothermal data. The typical plot of isothermal oxidation is shown in Fig. 1c. Values of time of maximal heat effect (τ_{max}, Fig. 1c) gave linear dependencies: $\log\tau=AT^{-1}+B$ (Fig. 1d) and the slope A=0.4367 E/R was used for the calculation of activation energy of isothermal oxidation [6–8, 12–14].

Results and discussion

At first stage of our research the starting temperatures of the non-isothermal oxidation and temperatures of maximum heat flow were measured for oxidation of fats of known peroxide concentration. The investigated systems were corn oil, linseed oil, oleic acid and glycerol trioleate with different peroxide number (PN). Typical DSC curves of oxidation of corn oil at heating rate 10 K min^{-1} are shown in Fig. 2. The increase of PN caused a decrease in the starting temperature of the oxidation (onset point) but the temperatures of first and second maximum of heat flow were not connected with value of PN. The temperatures t_{on}, t_{max_1} and t_{max_2} for all four systems are presented in Fig. 3. The lack of influence of peroxide number on temperatures of second maximum proves that only the first observed exothermal process is autooxidation, in which the hydroperoxides are formed and the second exothermal process shown by DSC curves is caused by further oxidation of peroxides. In order to explain the shape of DSC oxidation curves the thermoanalytical signal was calculated by using the kinetic scheme of two-step reaction with autocatalytic start:

$$a \xrightarrow{\text{cat. } b} b \longrightarrow \text{oxidation products} \tag{4}$$

where: a – substrate (lipid), b – peroxides.

Autocatalytic effect of the first process was introduced by Šesták–Berggren function [15] of degree of conversion: $f(\alpha)=\alpha(1-\alpha)$. In this case the influence of b on the rate of substrate a uptake ($-\mathrm{d}a/\mathrm{d}T$) and rate of peroxide formation ($\mathrm{d}b/\mathrm{d}T$) can be calculated from equations:

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\left(\frac{Z_\mathrm{a}}{b}\right)a\exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{5}$$

$$\frac{\mathrm{d}b}{\mathrm{d}T}=\left(\frac{Z_\mathrm{a}}{\beta}\right)ab\exp\left(\frac{-E_\mathrm{a}}{RT}\right)-\left(\frac{Z_\mathrm{b}}{\beta}\right)b\exp\left(\frac{-E_\mathrm{b}}{RT}\right) \tag{6}$$

where: E_a, E_b, Z_a, Z_b are activation energies and pre-exponential factors of processes from Scheme (4). Kinetic parameters used for calculations for linseed oil and corn oil are listed in Table 1.

The overall rate of process is given as temperature derivative $\mathrm{d}\alpha/\mathrm{d}T=-\mathrm{d}a/\mathrm{d}T+\mathrm{d}b/\mathrm{d}T$. Predicted temperatures determined from the simulated plots of $\mathrm{d}\alpha/\mathrm{d}T$ *vs.* temperature are in good agreement with experimental temperatures, determined from DSC curves (Table 2). This comparison confirms the validity of kinetic scheme of non-isothermal oxidation of fats with autocatalytic start. Similar calculations undertaken for mustard oil oxidation described in previous paper [11] for several simple kinetic schemes resulted in about 20% differences between experimental and simulated temperatures and the best results ($\delta<3\%$) were obtained for two-step consecutive reaction with autocatalytic start. Such interpretation of DSC curves of non-isothermal oxidation of fats led to the conclusion, that only the starting temperature of the oxidation process can be used to calculate the E, Z and k parameters (from Eqs (1)–(3)) for quantitative assessment of oxidative stability. To confirm this hypothesis additionally, the activation energies of non-isothermal oxidation of pure fatty acids and their esters were compared with kinetic parameters of isothermal oxidation. Figure 1c presents typical DSC curves of isothermal oxidation of ethyl linoleate. At constant temperature only one autooxidation peak is visible and further oxidation (second peak in non-isothermal DSC curve – at higher temperature) does not occur. Comparison of activation energies calculated for isothermal oxidation (details in Experimental section) with activation energies calculated from onset temperatures in non-isothermal oxidation given in Table 3 showed, that this was the same process.

Table 2 Calculated (T_{calc}) and experimental (T_{exp}) values of temperatures, errors $\Delta T=T_{calc}-T_{exp}$ and relative errors $\delta=\Delta T^{*}100\%/\ T_{exp}$ for onset and first maximum temperatures (onset and max1) for oxidation of corn oil and linseed oil with different initial peroxide number (PN)

Peroxide number/ mmol O_2/kg	Onset				Max1			
	T_{calc}/K	T_{exp}/K	ΔT/K	δ/%	T_{calc}/K	T_{exp}/K	ΔT/K	δ/%
Linseed oil								
31.30	420.3	419.2	1.1	–0.3	442.8	458.6	–15.8	–3.4
119.80	406.7	407.0	–0.3	0.1	439.3	453.5	–14.2	–3.1
180.30	400.0	404.7	–4.7	1.2	437.9	451.4	–13.5	–3.0
252.70	393.9	400.7	–6.8	1.7	436.8	453.3	–16.5	–3.6
349.90	392.7	397.2	–4.5	1.1	435.5	459.0	–23.5	–5.1
383.60	390.3	396.7	–6.4	1.6	434.6	466.4	–31.8	–6.8
Corn oil								
47.55	432.6	421.4	11.2	–8.8	455.0	469.1	–14.1	–3.0
70.90	429.1	417.2	11.9	–9.3	453.3	466.2	–12.9	–2.8
93.82	419.0	412.6	6.4	–5.0	451.4	462.3	–10.9	–2.4
136.60	411.3	412.6	–1.3	1.0	449.4	459.6	–10.2	–2.2
145.80	401.3	403.9	–2.6	2.0	449.5	453.0	–3.5	–0.8
158.20	398.8	402.5	–3.7	2.9	449.1	451.7	–2.6	–0.6

Table 3 Values of activation energy of isothermal (calculated from τ_{max}) and non-isothermal (calculated from t_{on}, from [3]) autooxidation of unsaturated fatty acids and esters

Substance	E/kJ mol^{-1}	
	Isothermal	Non-isothermal
Oleic acid	90.6±5.2	89.6±4.4
Ethyl oleate	85.5±1.1	88.4±4.7
Glycerol trioleate	85.1±13.0	95.0±4.7
Erucic acid	79.6±11.5	91.8±13.3
Linolic acid	72.9±8.5	72.0±2.9
Ethyl linoleate	67.6±6.5	76.4±5.0
Glycerol trilinoleate	52.1±7.1	74.3±3.0
Linolenic acid	59.9±6.5	62.4±3.7
Ethyl linolenate	73.5±2.5	74.5±8.2

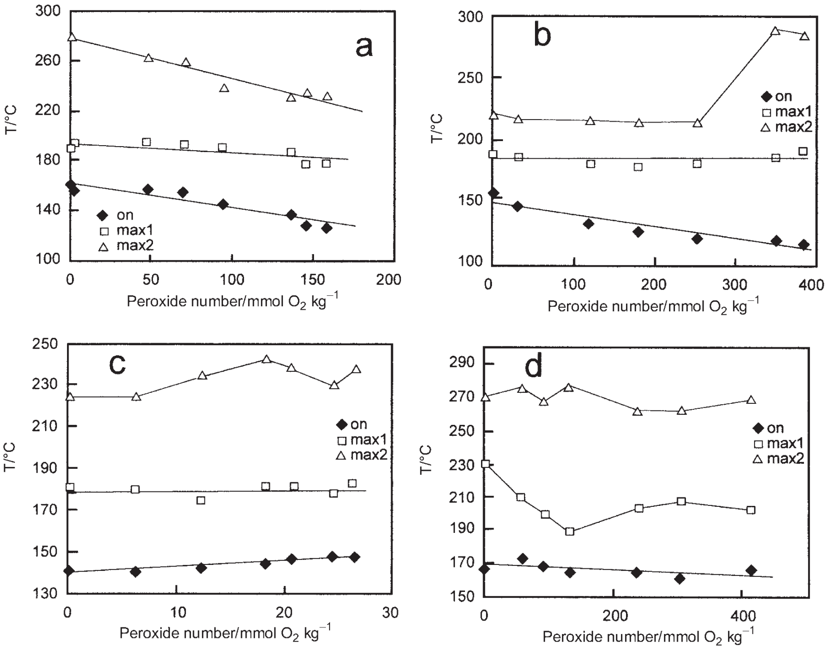

Fig. 3 Temperatures of onset point, maximum 1 and maximum 2 for substances of different initial peroxide number. a – corn oil, b – linseed oil, c – oleic acid, d – glycerol trioleate

Conclusions

On the basis of undertaken experiments and calculations the non-isothermal autooxidation can be described by a simple kinetic model of consecutive two-step reaction with autocatalytic start:

$$\text{lipid} \longrightarrow \text{hydroperoxides} \longrightarrow \text{oxidation products}$$

Practical conclusion of this work is that non-isothermal DSC measurements can be well used for assessment of oxidative stability of fats and the starting temperatures of oxidation are useful for accurate calculations of kinetic parameters of autooxidation.

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This work was supported by grant 120-501/68-BW-1483/20/2000.

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