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Use of Differential Scanning Calorimetry To Study Lipid Oxidation. 1. Oxidative Stability of Lecithin and Linolenic Acid

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The oxidation of linolenic acid (LNA) and soy lecithin was studied by differential scanning calorimetry (DSC) with linear programmed heating rates (non-isothermal mode). The interpretation of the shape of DSC curves is discussed, and it has been concluded that temperatures of the extrapolated start of heat release are the most reliable data for the rapid estimation of the oxidative stability of lipid materials. The Ozawa−Flynn−Wall method was used to calculate the kinetic parameters of the process: for LNA autoxidation the activation energy, E_a, and pre-exponential factor, Z, are 66 ± 4 kJ/mol and 1.5×10^7 s^{-1}, respectively, and the autoxidation of lecithin is described by $E_a = 98 \pm 6$ kJ/mol and $Z = 9.1 \times 10^{10}$ s^{-1}. Values of E_a and Z can be applied for calculation of the overall first-order rate constant of autoxidation at various temperatures, $k(T)$. For the two studied lipids the comparison of $k(T)$ values shows the inversion of their oxidative stabilities; that is, below 167 °C lecithin is more stable than LNA, $k(T)_{lecithin} < k(T)_{LNA}$, and above that temperature (termed the isokinetic temperature) $k(T)_{lecithin} > k(T)_{LNA}$. The calculated inversion of oxidative stabilities can be an explanation of similar observations for other pairs of lipids if the results of accelerated tests measured at temperatures above 100 °C are compared with the results obtained at temperatures below 100 °C.

KEYWORDS: Lipid oxidation; fatty acids; lecithin; autoxidation; DSC; thermal analysis; kinetics

INTRODUCTION

Studies on autoxidation and oxidative stability of food and food components, that is, lipids, edible oils, and fats, attract great attention due to its important economical, nutritional, and health reasons. Complex kinetics of autoxidation makes it difficult to obtain quantitative kinetic measurements for this free radical chain process; therefore, the importance of the improvement of analytical methods of examination of food is currently being stressed (*1*). Common studies are limited to accelerated tests (Rancimat, OSI) in that the qualitative measurements lead to determination of the time at which a lipid sample heated at temperature ≥100 °C reaches a desired level of rancidity, automatically detected when volatile products of oxidation are formed. The accelerated tests take usually several hours, and the results, usually induction times, cannot be simply transformed into such kinetic parameters as, for example, rate constants. Moreover, the conclusions drawn on the basis of volatile product detection may be misleading because for various classes of lipids the gaseous product formation can occur at different extents of autoxidation (*2*, *3*). Other analytical methods based on primary changes, for example, measurements of weight gain, peroxide number by titration, hydroperoxides, and conjugated dienes measurements (*4*), give the knowledge about the actual state of the sample; however, the methods are time and solvent (halocarbons) consuming, and their relevance to chemical kinetics is quite limited. Instrumental methods, such as ESR, IR, NMR, and chemiluminescence measurements, are sensitive to interferences and noises coming from autoxidation products and intermediates, and these methods, although excellent for some analytical aspects of autoxidation studies, have rather limited applicability in the fast determination of kinetic parameters.

Because autoxidation is a process in which heat is released, thermal analysis is a simple and direct analytical method used to follow the reaction course by continuous monitoring of total thermal effect of lipid oxidation occurring in the microcalorimeter vessel. Moreover, the application of non-isothermal conditions of measurements (linear heating rate, β) makes the thermal analysis methods much faster than other methods determining kinetic parameters of autoxidation. Non-isothermal differential scanning calorimetry (DSC) has been used in several studies of edible oils autoxidation (*5*−*9*). Recently, the theoretical basis of DSC and its applications in this field have been reviewed by one of us (*10*). Under sufficient oxygen pressure (>13 kPa) the three main steps of autoxidation, initiation, propagation, and termination, can be described in kinetic analysis by a rate of initiation (R_i), a rate constant of propagation (k_p, which denotes the process of hydrogen atom abstraction from lipid by peroxyl radical: $LH + ROO^{\bullet} \rightarrow L^{\bullet} + ROOH$), and a rate constant of termination (k_t, describing the square recombination process: $2ROO^{\bullet} \rightarrow$ nonradical products). Other processes, recombination of alkyl ($R^{\bullet}$) and alkoxyl radicals ($RO^{\bullet}$), can be neglected as the formation of peroxyl radicals, $R^{\bullet} + O_2$

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$\rightarrow$ ROO$^{\bullet}$, is several orders of magnitude faster than k_p. Therefore, at initial stage the rate of oxidation is described by a first-order kinetic equation:

$$v = k_p\sqrt{\frac{R_i}{2k_t}}[\mathrm{LH}] \quad (1)$$

According to this equation, determination of any parameter related to v can be used for monitoring of oxidation extent. During the initial stage of oxidation R_i is effectively constant and $k_p(R_i/2k_t)^{1/2} = k = \text{const}$; thus, k is a global (overall) rate constant (*11*). Further steps of oxidation lead to decomposition of hydroperoxides into ketones, alcohols, acids, and other products and can be described also by first-order kinetics: $v_{decomp} = k_{decomp}[\mathrm{ROOH}]$.

The kinetic parameters of these first-order (or pseudo-first-order) processes are described by simple Arrhenius equation: $k = Z\exp(-E_a/RT)$, where Z is a pre-exponential factor, E_a is activation energy, R is the gas constant, and T is absolute temperature. If temperature is increased at a programmed linear heating rate, $\beta = \mathrm{d}T/\mathrm{d}\tau$, the non-isothermal Ozawa−Flynn−Wall (OFW) method (*12*, *13*) can be used for calculation of E_a and Z parameters by using temperatures of constant conversion (T_i) determined from DSC curves for various β:

$$E_a = -2.19\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T_i)} \quad (2)$$

Temperatures of extrapolated start of the process and temperatures of peak maximum are easy to determine points of constant conversion and, hence, these temperatures are usually used in the OFW method.

In our studies on the oxidative stability of lipid analogues in bulk phase we successfully used a non-isothermal DSC method to determine Arrhenius parameters of common fatty acids and their esters (*14*−*17*) and edible oils (*18*−*20*). However, this method of analysis has not been used to study the oxidation of phospholipids. Phospholipids are constituents of all cell membranes, and they are present in food from plant and animal sources. Soy lecithin is a mixture of naturally occurring phospholipids, phosphatidylcholine (13−18%), phosphatidylethanolamine (10−15%), and phosphatidylinositol (10−15%), and is utilized in a wide variety of food and industrial applications (*21*). This excellent source of choline (essential nutrient) is also used as a nutritional supplement. Lecithin helps to smooth the texture of food and serves as an emulsifying agent in margarine, chocolate, caramels, and coatings (to control viscosity, crystallization, weepage, and sticking) and chewing gum (as a softening and plasticizing agent). Some baked goods, confections, infant formulas, cheese products, and instant products contain lecithin as emulsifier, dispersant, viscosity modifier, or wetting agent. Industrial applications of lecithin include paints, waxes, polishes, wood coating, plastic, magnetic-type media, paper and printing, and many others (*21*). Production of cosmetics is an example of another still growing field of lecithin application. Refined grade lecitin (containing up to 99.7% of phospholipids) is used for pharmaceutical applications and research. Two crucial polyunsaturated fatty components of soy lecithin are linoleic acid and linolenic acid, and their carbon chains are the most sensitive sites for autoxidation. Thus, the aim of this research was to study the oxidative stability of soy lecithin by non-isothermal DSC and to obtain kinetic parameters of its autoxidation. Comparison of the kinetics of soy lecithin autoxidation with the kinetics of linolenic acid autoxidation gives an opportunity to gain new knowledge about the differences in thermoxidative behaviors of simple and complex lipids.

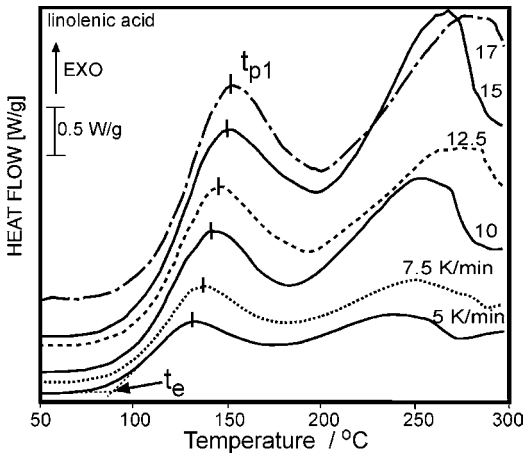


Figure 1. DSC curves of non-isothermal oxidation of linolenic acid with defined temperature of extrapolated start of oxidation, T_e, and temperature of first peak, T_p. Numbers denote heating rates in K/min.

MATERIALS AND METHODS

Linolenic acid (99%, Sigma-Aldrich) and refined soy lecithin (95%, ICN Biochemicals) were used without further purification. The compounds were stored at 0 °C in darkness.

All calorimetric measurements were carried out using a DSC apparatus DuPont 910 differential scanning calorimeter with a DuPont 9900 thermal analyzer and normal pressure cell. TA Instruments software (General V4.01) was used for collecting the data and for determination of temperatures from DSC curves. The apparatus was calibrated with high-purity indium. Unless otherwise specified, the experiments were performed under an oxygen flow of 6 dm^3/min. Samples ($\sim$5 mg) of compound were heated from 50 to 300 °C in an open pan at a linear heating rate β (5−20 K/min), and as a reference material an empty aluminum pan was used each time. Temperatures of the extrapolated start of oxidation (t_e) and temperatures of maximum of heat flow (t_p) are defined in **Figure 1**. In further considerations t means temperature in °C and T means temperature expressed in K.

Thermogravimetric measurements were carried out with a thermobalance DuPont 951 (precision, ±0.4%; minimal mass, 0.02 mg) coupled with thermal analyzer DuPont 9900.

Calculation of the activation energy of oxidation is a simple consequence of eq 2: when $\log\beta$ is plotted versus $1/T_e$ (or $1/T_p$), the straight line

$$\log\beta = AT^{-1} + B \quad (3)$$

is obtained with the slope $A = -0.4567E_a/R$ and reciprocal $B = -2.315 + \log(ZE_a/R)$ (*7*, *5*, *10*). The standard deviations of the slopes calculated for confidence level 90% have been used for estimation of activation energy errors listed as $\pm\Delta E$. The parameters E_a are the mean values calculated from two or three separate experiments, and they are given with absolute errors, that is, maximal differences between two or three values of E_a (see Results). Values E_a and Z can be used to calculate rate constants from the Arrhenius equation (see the Introduction).

RESULTS

Typical DSC curves of the non-isothermal oxidation of LNA for different heating rates are shown in **Figure 1**. Because there are three double bonds and two bis-allyl positions in the LNA carbon chain, the oxidation starts at moderately low temperatures (within the range of 85−105 °C, depending on β, see **Figure 1**). **Table 1** presents extrapolated temperatures of oxidation start,

Table 1. Temperatures t_e, T_e, and t_{p1} and T_{p1} Determined from DSC Curves of Oxidation of LNA with Various Heating Rates (β)[a]

β/ °C min^{-1}	t_e/°C	T_e/K	t_{p1}/°C	T_{p1}/K	statistical and kinetic parameters	from T_e[b]	from T_{p1}
5.0	85.5	358.7	131.5	404.7	A	–3.57	–4.34
7.5	92.09	365.3	136.8	410.0	B	10.66	11.44
10.0	95.87	369.1	141.8	415.0	R^2	0.9958	0.9919
12.5	99.53	372.7	146.3	419.5	σ	0.12	0.20
15.0	103.6	376.8	148.8	422.0	$\sigma_{90\%}$	0.22	0.38
17.0	105.9	379.1	152.7	425.9	E_a	65.0 ± 4.0	78.9 ± 6.9
					Z	2.03×10^7	9.91×10^7

[a] Parameters of eq 3 are given with standard errors (σ) and errors calculated for confidence level 90% ($\sigma_{90\%}$). Activation energy (E_a in kJ mol^{-1}) and pre-exponential factor (Z in s^{-1}) were calculated from eqs 2 and 3. [b] Parameters calculated from repeated measurements for another sample gave $E_a = 65.9 \pm 8.5$ kJ/mol and $Z = 8.9 \times 10^6$ s^{-1} (see Supporting Information).

temperatures of the first exothermal peak, and kinetic parameters calculated from both series of temperatures.

In contrast to the mild shape of the first peak of non-isothermal oxidation of LNA (see **Figure 1**), the first peak of lecithin oxidation shown in **Figure 2A** is sharp and narrow. To ensure that the observed peak is an effect of oxidation and that no endothermic process interferes with exothermic oxidation (leading to a negative peak or to a false saddle point), the lecithin has been heated with $\beta = 10$ K/min under nitrogen. The bottom flat line in **Figure 1A** demonstrates only small fluctuations and no significant exo- and endothermic effects. Therefore, melting, evaporation, and polymerization do not occur at 50−450 °C. This observation is supported by thermogravimetric measurements of weight loss during the heating of lecithin under nitrogen. Lecithin is more stable (less volatile) than LNA (see **Figure 2B**), and below 200 °C only a 4% weight loss has been recorded (7% for LNA; see Table S1 in the Supporting Information). At temperatures >250 °C the process of evaporation or other kinds of thermal degradation occur more rapidly. The results of thermogravimetric experiments demonstrate that thermal changes in lecithin between 100 and 200 °C monitored under oxygen atmosphere (**Figure 2C**,**D**) can be attributed to autoxidation. As for all non-isothermal processes the temperature of extrapolated start of exothermal effect increases with increasing heating rate as can be clearly seen in **Figures 1** and **2**.

Table 2 presents temperatures determined for three samples of soy lecithin: there are full sets of temperatures, t_e, t_{p1}, and t_{p2}, for sample 1, and kinetic parameters calculated from these temperatures (after conversion of t into T). The parameters calculated for the start of oxidation differ from the ones calculated for further oxidation stages, and, taking into account the interpretation of the DSC curve of lipid oxidation (see Discussion), peaks 1 and 2 were excluded from further considerations as not correlated directly with autoxidation. For samples 2 and 3 the values of t_e only were determined and applied for calculations. The activation energy of 98 ± 6 kJ/

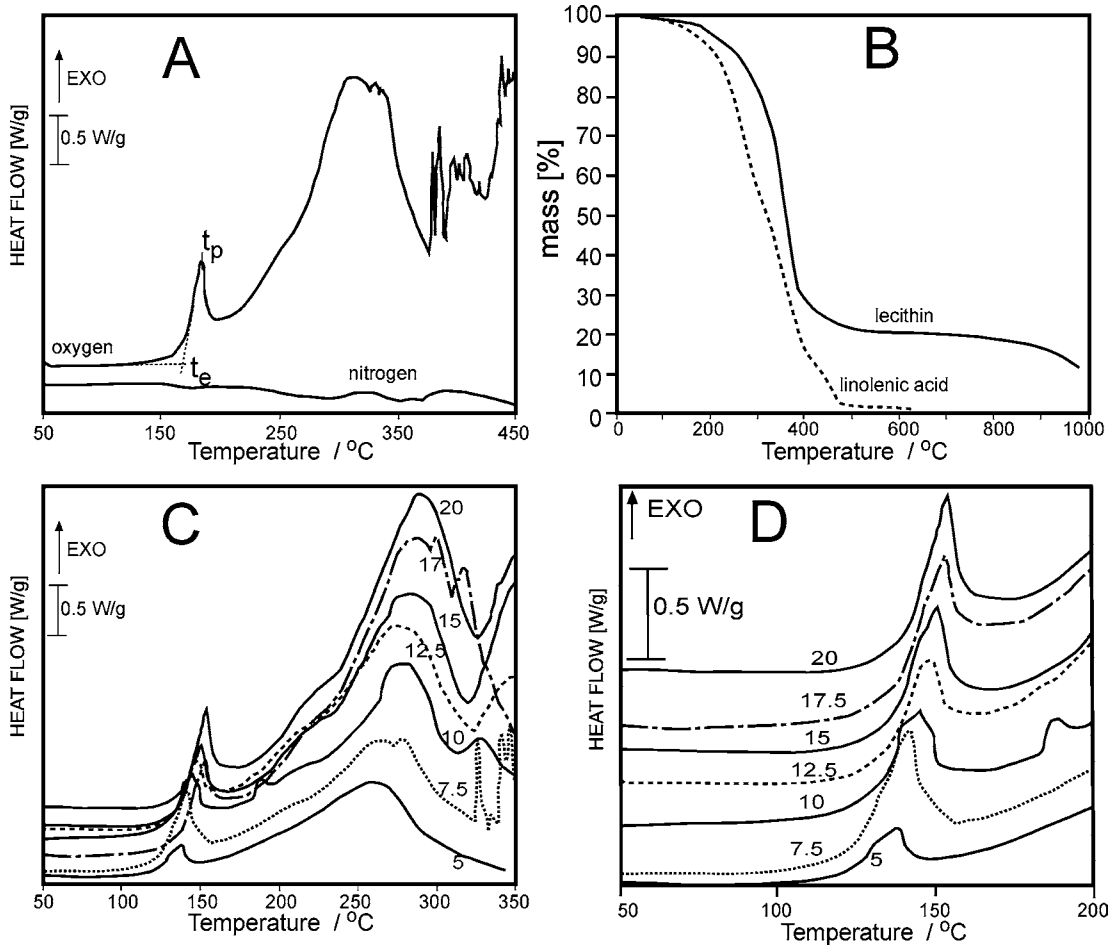


Figure 2. (**A**) Comparison of thermal effect of lecithin heated at $\beta = 5$ K/min under oxygen atmosphere (upper line) and under N_2 (bottom line). (**B**) Thermogravimetric curve of weight loss of lecithin and linolenic acid heated at $\beta = 10$ K/min under nitrogen. (**C**) Curves of non-isothermal oxidation of lecithin. Numbers denote heating rates in K/min. DSC curves have been shifted vertically (without rescaling of the plots) in order to have a clearer view. (**D**) Inset of (**C**) limited to first peak of oxidation.

Table 2. Temperatures t_e, t_{p1}, and t_{p2} Determined from DSC Curves of Oxidation of Soy Lecithin with Various Heating Rates (β)[a]

sample 1				sample 2		sample 3	
β/°C min^{-1}	t_e/°C	t_{p1}/°C	t_{p2}/°C	β/°C min^{-1}	t_e/°C	β/°C min^{-1}	t_e/°C
5	156.0	176.8	302.2	5.0	158.7	5.0	157.6
7.5	161.7	181.3	302.2	8.0	165.7	7.5	162.1
10	165.0	184.7	317.8	10.0	169.3	10.0	167.1
12.5	168.6	187.8	312.8	12.0	171.9	12.5	170.7
15	173.4	189.6	319.4	15.0	175.7	15.0	173.3
17.5	174.8	191.4	324.4	20.0	182.0	17.0	174.9
20	177.5	193.0	329.4				
Statistical Parameters							
A	–5.33	–7.74	–6.68	–5.15		–5.72	
B	13.14	17.89	12.24	12.63		14.00	
R^2	0.9909	0.9991	0.8658	0.9957		0.9958	
σ	0.23	0.1	1.16	0.17		0.18	
$\sigma_{90\%}$	0.44	0.2	2.25	0.33		0.36	
Kinetic Parameters							
E_a =	97 ± 8	141 ± 4	122 ± 42	94 ± 6		104 ± 7	
Z =	2.44×10^{11}	9.46×10^{15}	2.45×10^{10}	1.3×10^{9}		2.74×10^{10}	

[a] Parameters of eq 3 are given with standard errors (σ) and errors calculated for confidence level 90% ($\sigma_{90\%}$). Activation energies (E_a/kJ mol^{-1}) and pre-exponential factors (Z/s^{-1}) were calculated from eqs 2 and 3.

mol has been determined as the mean of all three E_a values (columns 2, 6, and 8) collected in **Table 2**. The pre-exponential factor calculated as a mean of the Z factors for three lecithin samples is 9.1×10^{10} s^{-1}.

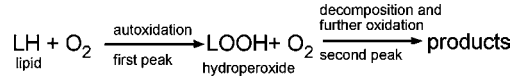
DISCUSSION

A good analytical method of determination of oxidative stability should be relatively fast. This restriction can be met for the oxidation carried out at higher temperatures. On the other hand, an excellent method should result in kinetic parameters that allow the prediction of the oxidative behavior of lipids in lower temperatures characteristic for the thermal conditions of food and fat storage and handling. A third requirement is that the analytical signal monitored by an "ideal method" must be directly connected with the chemical changes occurring in the oxidized sample. This last requirement is obvious if different products of oxidation for all varieties of lipids and foods are considered. Moreover, primary oxidation products (peroxides) can be decomposed at different rates; hence, methods based on measurements of secondary product (aldehydes, ketones, hydrocarbons, alcohols) concentration may be misleading.

Our previous research on the application of DSC to the study of the autoxidation processes included saturated (*14*, *15*) and unsaturated fatty acids (*16*, *17*) and their esters as well as edible oils (*18*−*20*). It has been demonstrated that the first peak on the DSC curve of non-isothermal oxidation can be interpreted as autoxidation (formation of peroxides) and the next peaks are the exothermal effects of decomposition and further oxidation processes (*10*, *17*, *20*).

Because the first and second exothermal peaks can overlap (and usually do), from the analytical point of view the beginning of autoxidation (temperature of extrapolated start of the process, t_e, see **Figure 2**) is the best point to calculate kinetic parameters of autoxidation. Moreover, as a point of constant conversion (which is close to zero in this particular case), the start of oxidation can be used in isoconversional methods (e.g., the OFW method) to calculate kinetic parameters of the observed process. That is, *the start of the thermal effect of autoxidation (T_e value) is the most rational point for the calculation of kinetic parameters* (see **Scheme 1**). Some authors still interpret the first

Scheme 1



peak as the oxidation of the unsaturated component of fat, on the basis of Keisersberger's hypothesis that the first peak of some edible oils oxidation "has to be related to oxidation of unsaturated fatty acids" (*22*). Such interpretation has been accepted with neither analytical nor computational evidence and despite the fact that two peaks are observed even for the thermal oxidation of pure saturated fatty acids (lauric, myristic, palmitic, and stearic acid and their esters) (*15*).

There are three main reasons to interpret the shape of the DSC curve of lipid oxidation as in **Scheme 1**: (i) The start of oxidation (T_e parameter) is the most sensitive point on the presence of hydroperoxides; the first peak is not as sensitive, and the second peak does not correlate with the peroxide number of the lipid sample (*17*). (ii) It has been shown that only a sequential reaction scheme with autocatalytic start of the process fits the computer-simulated DSC curves to experimental data; other reaction schemes, competitive, parallel, and sequential, do not fit experimental data (*20*). (iii) The kinetic parameters calculated from T_e are in good agreement with kinetic parameters obtained by means of isothermal methods (*14*, *17*). (iv) Addition of antioxidants causes retardation of autoxidation at the initial stage; hence, the T_e parameter is more sensitive for inhibition than T_{p1} and T_{p2} (*23*).

The activation energy of LNA oxidation measured in the current study is 65 ± 4 kJ/mol and $Z = 1.45 \times 10^7$ s^{-1}. These parameters are the mean of two values (see footnote *b* of **Table 1**). The obtained E_a is within the value range of 62−70 kJ/mol as was reported previously for LNA (*16*, *17*). It is also in good agreement with $E_a = 60 \pm 7$ kJ/mol obtained by using the isothermal method (*17*). Oxidizability of lipids is correlated exponentially with the number of bis-allyl $-CH_2-$ sites (*24*), and, indeed, among all saturated and unsaturated lipid analogues studied by us, LNA shows the smallest oxidative stability; this property makes it a convenient standard (matrix) for studying the antioxidant activity of added phenolic compounds (*17*).

For soy lecithin the kinetic parameters are considerably higher: $E_a = 98 \pm 6$ kJ/mol and $Z = 9.1 \times 10^{10}$ s^{-1} (see **Table 2** and Results for statistical data).

Comparison of the temperatures of the start of oxidation shows that oxidative stability is much lower for LNA than for lecithin. The same conclusion can be drawn on the basis of activation energies and calculated rate constants, $k(T)$. For example, for lecithin $k_{100°C} = 1.8 \times 10^{-3}$ s^{-1}. The same calculations for linolenic acid give 1.6×10^{-2} s^{-1} (or 5.2×10^{-3} s^{-1}, see footnote *b* in **Table 1**). However, this is not the case for higher temperatures. **Figure 3** presents the plots of the rate constants calculated for lecithin and LNA oxidation in the temperature range of 100−200 °C.

For autoxidation of these two lipids the isokinetic temperature, T_{iso}, that is, the temperature at which rate constants of two processes are equal, $k_1 = k_2$, can be calculated from their Arrhenius dependencies: $Z_1 \exp(-E_{a1}/RT) = Z_2 \exp(-E_{a2}/RT)$. Taking for lecithin $E_{a1} = 98$ kJ/mol and $Z_1 = 9.1 \times 10^{10}$ s^{-1} and for linolenic acid $E_{a2} = 66$ kJ/mol and $Z_1 = 1.45 \times 10^7$ s^{-1}, the value of $T_{iso} = 440$ K (167 °C). This means that below 167 °C the oxidative stability of lecithin is better than the oxidative stability of LNA, whereas above T_{iso} the oxidation of lecithin will occur more quickly than the oxidation of LNA. The consequence of this observation is that any accelerated test

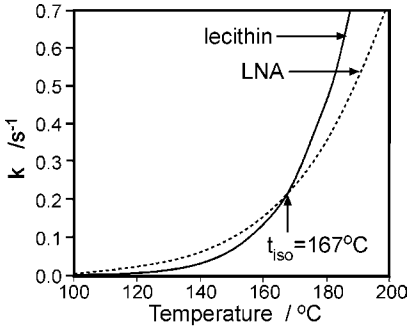


Figure 3. Plots of rate constants calculated for the oxidation process of lecithin and LNA. The rate constants are listed in Table S3 of the Supporting Information.

in which oxidation is carried out at a temperature below 150 °C will indicate that LNA is less stable. The same test conducted at 150−170 °C will indicate the same oxidative stability for both lipids. Moreover, if a hypothetical accelerated test is performed at t > 170 °C, the oxidation will be faster for the lecithin sample. In some other cases T_{iso} can be smaller than 150 °C and, therefore, mechanistic extrapolation of the oxidative stability determination from higher to lower temperatures is misleading (*10*).

In conclusion, the presented data showed that DSC can be successfully applied to the study of the autoxidation of simple (linolenic acid) and complex (lecithin) lipids. Careful interpretation of the shape of non-isothermal oxidation curves allows one to determine Arrhenius kinetic parameters, and the results can be used for calculation of the rate constant of oxidation at temperatures below and above the isokinetic temperature; hence, the results of such studies are more universal than the results of conventional accelerated tests.

Supporting Information Available: Temperatures and kinetic parameters determined for oxidation of LNA (Table S1), the weight loss for linolenic acid and lecitin heated under nitrogen (Table S2), first-order rate constants for lecithin and LNA oxidation (100−200 °C) (Table S3) and plots of log β versus 1000/T for LNA and lecithin (Figures S1−S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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