

Study on the Autoxidation Kinetics of Fat Components by Differential Scanning Calorimetry. 2. Unsaturated Fatty Acids and Their Esters

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Natural unsaturated fatty acids oleic, erucic, linoleic, and linolenic and their ethyl esters and, additionally, glycerol trioleate and trilinoleate were oxidized with linear-programmed heating rates of 1–25 K/min at 50–300 °C. The oxidation course was monitored by differential scanning calorimetry to determine the oxidative stability of these fat components without any solvents and in the absence of free-radical initiators; i.e., in conditions of industrial processing and exploitation. The kinetic parameters of oxidation of investigated compounds were obtained by the Ozawa–Flynn–Wall method. The activation energies, preexponential factors, and rate constants of oxidation concern the gross reactivity of oxidized compounds. The start of oxidation and the overall oxidation rate constants were dependent on the number of double bonds in the carbon chain. Esters are more stable than free fatty acids.

Introduction

Unsaturated fatty acids are the major components of vegetable fats which not only are used as edible oils but frequently find application in pharmacy and industry. They are intermediates in the manufacture of fatty alcohols, alkanolamides, and amines. Technical applications of fatty acids and esters obey, for example, metal soaps, detergents, cosmetics, resins, paints, rubber, tires, and impregnating agents. The semidrying agents such as cottonseed, sesame, corn, and sunflowerseed oils are used as edible fats and also as lubricants and soaps. Drying oils—safflower, linseed oil, poppy seed oil, and tung oil—are applied for paints, varnishes, artists' paints, and soft soap production. Fatty acid derivatives are used as wetting, leveling and finishing agents, and lubricants in the textile industry.¹

Reaction of fatty materials with atmospheric oxygen is of great interest because of possible applications in oxidation processes, but on the other side, oxidation processes led to the deterioration of fats and fat-containing materials during manufacturing, transport, storage, and usage. The mechanism of autoxidation has been extensively studied over the past 50 years and reviewed by Richardson and Korycka-Dahl,² Frankel,³ and Allen and Hamilton.⁴ Recent review work including discussion about mechanisms of various reaction types of the primary steps of peroxidation was given by Porter et al.⁵ The kinetics has been reviewed by Labuza.⁶

The kinetics of the net oxidation process at early stages was discussed in part 1 concerning autoxidation of saturated hydrocarbon, and these assumptions are valid for any olefins and unsaturated lipids. At the steady state the rate of oxidation is given by equation:

$$r_{\text{RH}} = k_p(R_i/2k_t)^{1/2}[\text{RH}] \quad (1)$$

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where k_p and k_t are the rate constants of the propagation and termination steps, R_i denotes the rate of initiation, and $[\text{RH}]$ is the concentration of oxidized hydrocarbon or lipid.⁷ The parameter $k_p/(2k_t)^{1/2}$, named oxidizability, is used for comparison of oxidative stabilities of substances. At the initial autoxidation stage, R_i is constant and the global (overall) rate constant of oxidation is $k = k_p(R_i/2k_t)^{1/2}$; therefore, the complex autoxidation process is assumed to be a first-order reaction.

The total rate of hydrocarbon autoxidation is determined by the rate of hydroperoxide formation (during the initial stage, eq 1), and in the early stages, when the hydrocarbon conversion and the hydroperoxide concentration are low, the decomposition of primary products is expected to be first order:

$$r_{\text{decomp}} = (k_2 + k_3 + k_4)[\text{ROOH}] \quad (2)$$

where k_2 , k_3 , and k_4 are the rate constants of hydroperoxide decomposition to ketones, acids, and alcohols, respectively (see part 1, Introduction).

The first stages of oxidation have received great attention because of their destructive role in biological organisms. The investigations are focused on the fundamental transformations and on peroxidation in aggregates similar to natural systems. These factors can have dramatic consequences for the kinetics of autoxidation, and obtained data do not regard the industrial applications, where the reaction products often undergo further oxidation, decarboxylation, and polymerization. The studies on the oxidative stability of diluted substances at higher temperatures, i.e., at the conditions similar to those in manufacturing and in exploitation, require methods for reliable, quick, and simple assessment methods. Therefore, thermoanalytical methods such as the Ozawa–Flynn–Wall method⁸ (OFW) are useful to obtain kinetic parameters: overall activation energy E , preexponential factor Z , and rate constant of oxidation k calculated for oxidation of fats by means of differential scanning calorimetry (DSC). The OFW method and the meanings of E , Z , and k parameters

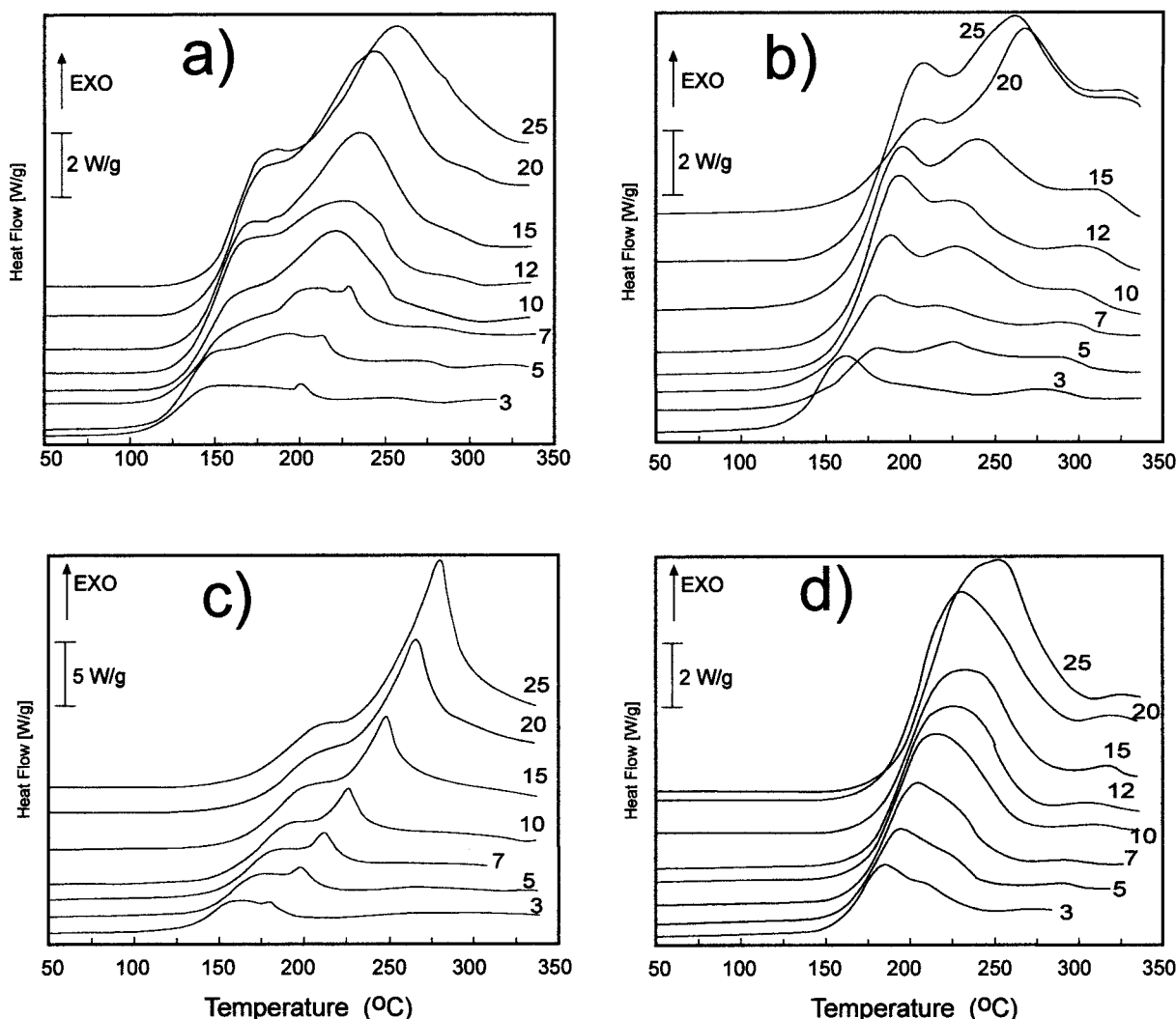


Figure 1. DSC oxidation curves of (a) linoleic acid, (b) ethyl linoleate, (c) glycerol trilinoleate, and (d) ethyl oleate. Numbers denote the heating rates in K/min.

were described in part 1 concerning autooxidation of saturated fatty compounds.

The aim of our research was to study the uncatalyzed oxidation of the unsaturated natural fatty acids *cis*-9-octadecanoic acid (oleic acid, $C_{18:1}$), *cis*-13-docosenoic acid (erucic acid, $C_{22:1}$), *cis,cis*-9,12-octadecadienoic acid (linoleic acid, $C_{18:2}$), and *all-cis*-9,12,15-octadecatrienoic acid (linolenic acid $C_{18:3}$) and their ethyl esters and, additionally, glycerol trioleate and trilinoleate at the temperature range 50–300 °C without any solvents and in the absence of free-radical initiators.

Experimental Procedures

Materials. Erucic and oleic acids (98%) were produced by BDH (Pool, U.K.). Linoleic acid and ethyl esters oleate, linoleate, linolenate, glycerol trioleate, and trilinoleate (all 99%) were purchased from Sigma-Aldrich (St. Louis, MO). The purity of linolenic acid (Carl Roth KG, Karlsruhe, Germany) 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. The study was carried out in an oxygen atmosphere. The general experimental procedures and method of determination of extrapolated

onset temperatures (T_e) and temperatures of maximum heat flow (T_{p1} and T_{p2}) have been described in part 1. The apparent activation energies of oxidation and pre-exponential factors were calculated by the OFW method.

Results and Discussion

Typical DSC curves of oxidation obtained by heating with different heating rates (β) are presented in Figure 1. The shape of the DSC plot is dependent on the heating rate and on the kind of oxidized substance. For monounsaturated oleic acid and its esters, the first maximum of the heating rate overlapped with the second maximum. It can be explained by the similarity of kinetic parameters of autooxidation and further oxidation processes at temperatures 165–250 °C for monounsaturated compounds. Because oleic and erucic acids and their esters consume less oxygen, the exothermal effect of autooxidation is not as visible as it is for polyunsaturated compounds. For compounds $C_{18:2}$ and $C_{18:3}$ the exothermal effect of autooxidation is greater at lower temperatures and the first “autooxidation” peak was separated from exothermal peaks of further oxidation processes. In each case, after the oxidation the small residue of coke was observed.

Raemy⁹ investigated the heating of methyl linolenate under nitrogen, and no exothermal effect of polymeri-

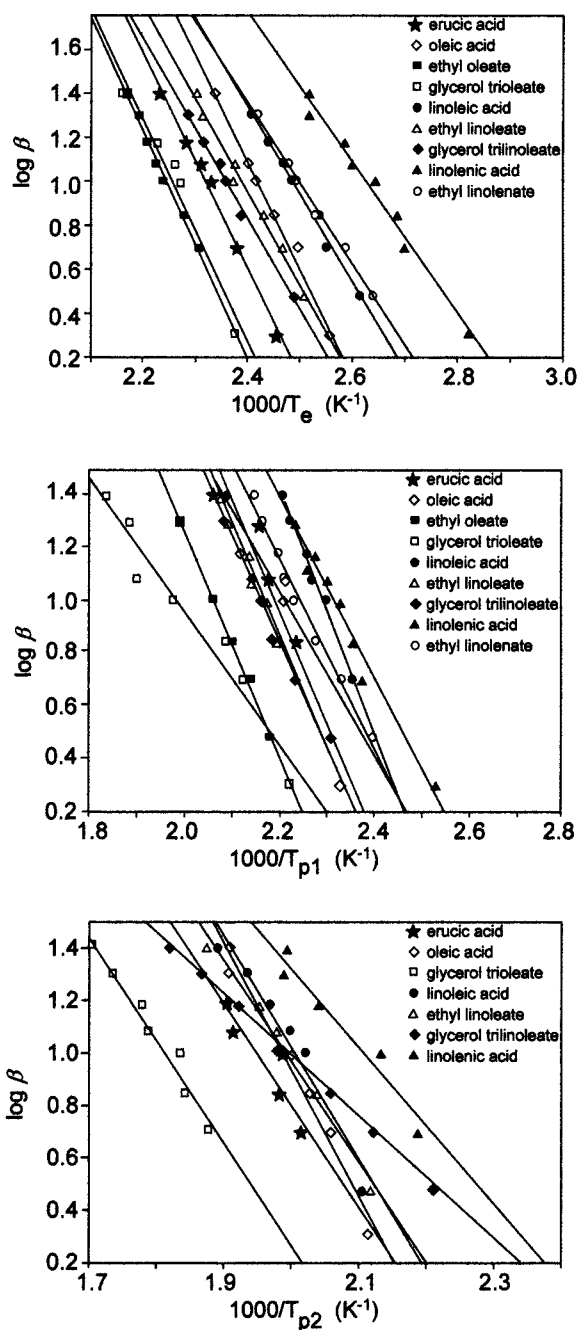


Figure 2. Plots of eq 3 obtained for temperatures of extrapolated start of oxidation (T_e), first maximum of heat flow (T_{p1}), and second maximum (T_{p2}).

zation, isomerization, and decomposition was observed. Under an oxygen atmosphere the autoxidation of investigated unsaturated compounds is the first step of the oxidative polymerization, but the effect of polymerization is expected to occur in further stages of oxidation, after the decomposition of hydroperoxides (the second maximum). Because oxidative polymerization is slower than the autoxidation process, it does not interfere with the exothermal effect of autoxidation during the first several minutes of the experiment (start and first maximum).

As observed in Figure 1, the influence of heating rate β on oxidation temperatures T_e , T_{p1} , and T_{p2} was used for calculation of the parameters of equation

$$\log \beta = aT^{-1} + b \quad (3)$$

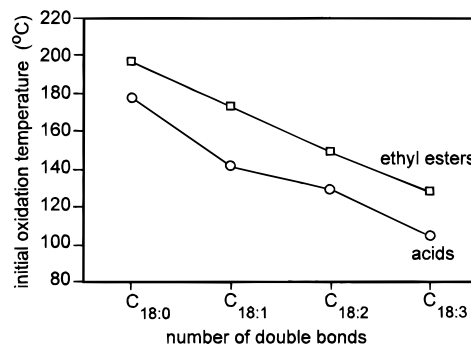


Figure 3. Values of the initial temperatures of oxidation for mono-, di-, and triunsaturated fatty acids and their esters ($\beta = 10$ K/min).

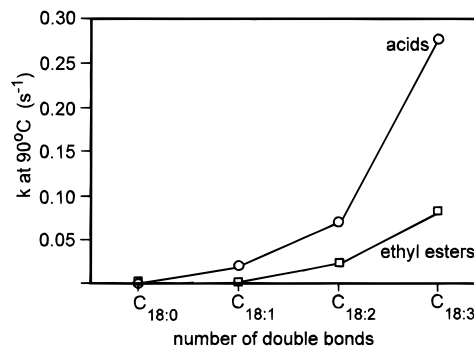


Figure 4. Rate constants of oxidation at 90 °C for mono-, di-, and triunsaturated fatty acids and their esters.

The straight line plots of eq 3 for T_e , T_{p1} , and T_{p2} are shown in Figure 2. The parameters of eq 3 with standard deviations and overall kinetic parameters calculated for individual stages of oxidation (start and first and second peaks) calculated in the way described in part 1 are listed in Table 1.

For all investigated compounds, temperatures T_e (Figure 3) for acids were about 20 °C lower than those for esters. This observation is in agreement with the overall rate constants of autoxidation presented in Figure 4. In part 1 we described the possibility of the propagation step on a polar carboxylic group, and these considerations are also valid for unsaturated fatty acids.

Figure 3 presents the decreasing oxidative stability with increasing number of double bonds. The oxidizability of polyunsaturated fatty acids and triacylglycerols in a homogeneous solution is known to be dependent on the number of bisallylic positions ($-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$) available for oxidation.^{10–13} Our data (Table 1 and Figure 4) confirm those observations. The ratio of oxidation rate constants of mono-, di-, and triunsaturated esters at 90 °C is 1:3:12 and it is smaller than that given by Howard and Ingold (1:23:44),¹⁰ but their experiments were carried out at 30 °C in chlorobenzene and the autoxidation was initiated by azo compounds.

There are very few Arrhenius parameters in the literature with which the present work may be compared. Denisov described the global activation energy of oleic acid oxidation as 22.5 kcal/mol (94.1 kJ/mol).¹⁴ Our overall activation energy calculated from T_e is equal to 88.4 ± 4.7 kJ/mol.

To compare our data for esters, we used the equation

$$E = E_p + \frac{1}{2}E_i - \frac{1}{2}E_t \quad (4)$$

where the activation energy of initiation (E_i) described

Table 1. Parameters a and b of Equation 3 with Standard Deviations (σ_a and σ_b), Square Regression Coefficients (R^2), and Calculated Kinetic Parameters: Activation Energy (E), Preexponential Factor (Z), and Rate Constant of Oxidation at 90 °C (k)

	a	σ_a	b	σ_b	R^2	$E/(\text{kJ mol}^{-1})$	Z/s^{-1}	$k(90\text{ °C})/\text{s}^{-1}$
Erucic Acid								
start	-4.92	0.24	12.41	0.04	0.9903	89.6 ± 4.4	4.93×10^{10}	6.33×10^{-3}
1st peak	-2.99	0.37	7.59	0.04	0.9698	54.5 ± 6.8	1.33×10^6	1.80×10^{-2}
2nd peak	-2.65	0.48	6.14	0.10	0.8824	48.3 ± 8.8	4.91×10^4	5.60×10^{-3}
Oleic Acid								
start	-4.86	0.26	12.75	0.04	0.9889	88.4 ± 4.7	1.08×10^{11}	2.05×10^{-2}
1st peak	-4.09	1.22	9.60	0.19	0.8490	74.5 ± 22.2	2.05×10^8	3.93×10^{-3}
2nd peak	-4.80	0.44	10.54	0.08	0.9683	87.4 ± 7.9	6.77×10^8	1.82×10^{-4}
Ethyl Oleate								
start	-5.22	0.26	12.72	0.03	0.9876	95.0 ± 4.7	9.43×10^{10}	2.02×10^{-3}
1st peak	-4.21	0.17	9.68	0.02	0.9950	76.7 ± 3.0	1.07×10^8	9.99×10^{-4}
Glycerol Trioleate								
start	-5.04	0.73	12.38	0.12	0.9409	91.8 ± 13.3	4.49×10^{10}	2.78×10^{-3}
1st peak	-2.51	0.27	5.98	0.10	0.9445	45.8 ± 5.0	3.6×10^4	9.56×10^{-3}
2nd peak	-3.89	0.38	8.06	0.06	0.9554	70.8 ± 6.8	2.78×10^6	1.79×10^{-4}
Linoleic Acid								
start	-3.96	0.16	10.84	0.03	0.9917	72.0 ± 2.9	1.63×10^9	7.00×10^{-2}
1st peak	-4.64	0.22	11.63	0.03	0.9915	84.5 ± 3.9	8.73×10^9	6.11×10^{-3}
2nd peak	-4.24	0.45	9.50	0.08	0.9571	71.1 ± 8.2	6.98×10^7	5.56×10^{-4}
Ethyl Linoleate								
start	-4.20	0.273	11.03	0.05	0.9793	76.4 ± 5.0	2.41×10^9	2.41×10^{-2}
1st peak	-4.16	0.203	10.03	0.04	0.9883	75.8 ± 3.7	2.43×10^8	2.98×10^{-3}
2nd peak	-3.85	0.21	8.66	0.04	0.9878	70.1 ± 3.9	1.14×10^7	9.28×10^{-4}
Glycerol Trilinoleate								
start	-4.08	0.17	10.62	0.03	0.9934	74.3 ± 3.0	9.66×10^8	2.00×10^{-2}
1st peak	-4.04	0.26	9.743	0.05	0.9750	73.6 ± 4.8	1.29×10^8	3.33×10^{-3}
2nd peak	-2.34	0.10	5.68	0.03	0.9900	42.6 ± 1.8	1.91×10^4	1.41×10^{-2}
Linolenic Acid								
start	-3.43	0.20	9.99	0.05	0.9790	62.4 ± 3.7	2.69×10^8	2.77×10^{-1}
1st peak	-3.66	0.35	9.52	0.08	0.9450	66.8 ± 6.2	8.53×10^7	2.19×10^{-2}
2nd peak	-3.00	0.48	7.327	0.08	0.9301	54.6 ± 8.6	6.67×10^5	9.21×10^{-3}
Ethyl Linolenate								
start	-4.09	0.45	11.27	0.08	0.9312	74.5 ± 8.2	4.29×10^9	8.25×10^{-2}
1st peak	-3.61	0.18	9.08	0.04	0.9842	65.7 ± 3.3	3.14×10^7	1.09×10^{-2}

in the literature for oxidation of methyl oleate is 142.1 ± 5.0 kJ/mol (at 70–80 °C), that for linoleate is 92.4 ± 2.9 kJ/mol (at 40–60 °C), and that for linolenate is 76.5 ± 4.2 kJ/mol (40–50 °C).¹⁴ The activation energy of propagation E_p for autooxidation of monoenes and dienes described in ref 15 is 47.7 kJ/mol. Assuming the activation energy of the termination process as $E_t = 10$ –25 kJ/mol,¹⁵ the overall E calculated from eq 4 denotes about 93–100 kJ/mol for methyl oleate, 69–76 kJ/mol for methyl linoleate, and 61–69 kJ/mol for methyl linolenate. These estimative values are within experimental errors of our data: 95.0 ± 4.7 , 76.4 ± 5.0 , and 74.5 ± 8.2 kJ/mol, respectively.

Conclusions

A nonisothermal DSC study of the noninitiated oxidation of erucic, oleic, linoleic, and linolenic acids and their esters with ethanol and glycerol at temperatures from 60 to 300 °C was described. The start of the oxidation process is detected as the exothermal effect on the DSC curve. The Arrhenius kinetic parameters of autooxidation obtained by the thermal analysis method indicate that oxidative stability of free fatty acids is decreased in comparison with their ethyl esters. The oxidative stability is dependent on the number of double bonds at the carbon chain. The activation energies, Z factors, and rate constants of oxidation in the liquid phase in the absence of other solvents and free-radical initiators concern the total effect of oxidation. They can be used

for comparison of the oxidative stability of fats and their components in conditions similar to high-temperature manufacturing and exploitation. The DSC method is simple, convenient, and fast for the determination of oxidative stability. The determination of the initial oxidation temperature from a single run allows one to assess the oxidative stability quickly and comparatively, whereas evaluation of the overall Arrhenius parameters should be made by at least five runs with different heating rates.

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