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THE INFLUENCE OF SOME CHAIN-BREAKING ANTIOXIDANTS ON THERMAL-OXIDATIVE DECOMPOSITION OF LINOLENIC ACID

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Abstract

Thermoxidation of linolenic acid inhibited by addition of 2,6-di-*t*-butyl-4-methylphenol and 2,4,6-trimethylphenol at various concentrations was investigated. The measurements were carried out under non-isothermal conditions in an atmosphere of oxygen. DSC curves permitted the determination of onset point and maximum points of the peaks. The influence of inhibitor concentration on temperature of the start of oxidation was noticed. However, no significant changes in temperatures of the maximum heat flow was observed. Measurements and calculations described in this report prove that the assessment of the antioxidant activity of chain-breaking inhibitors can be performed only from the onset temperatures. Calculations of the activation energy of inhibited linolenic acid thermoxidation were performed in order to elucidate the antioxidant activity of the phenolic compounds.

Keywords: antioxidants, DSC, thermoxidation

Introduction

The most common reaction of inhibition is the chain-breaking action of phenolic compounds:

$$\mathrm{PhOH} + n\mathrm{RO}_2^{\cdot} \rightarrow \text{inactive products} \qquad (1)$$

According to this reaction the hydrogen atom from the phenolic hydroxyl group is abstracted by the lipid peroxy radical and inhibitor radical is not able to propagate of the autoxidation kinetic chain. As long as the reaction (1) occurs, the oxidised system is at the state known as induction period.

The dynamic DSC studies carried out under normal pressure of oxygen were used to determine the kinetic parameters of thermal oxidative decomposition of the most popular edible oils and fats [1, 2]. Although interpretation of the results from the non-isothermal measurements is more complicated than those from isothermal experiments, several advantages as: short time of single run and sharp

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shape of the DSC signal make these methods more accessible for fast assessment of thermal stability and to determine the kinetics parameters of oxidation of oils and fats. However, the antioxidant activity of phenyl based compounds used as inhibitors has been the subject of thermoanalytical investigations under isothermal conditions exclusively [3–5].

This report concerns the influence of measurement conditions on shape of the DSC curves and interpretation of data obtained from characteristic points of DSC curves: temperatures of the extrapolated start of the exothermic oxidation process and temperatures of the maximum heat flow. Series of these temperatures, obtained for various fixed linear heating rates (β), can be described by:

$$\log\beta = AT^{-1} + a \tag{2}$$

where T is temperature in K, β-heating rate in K min^{-1}, A and a are coefficients. The approximate values of activation energy can be calculated as follows:

$$E = -2.19R\left(\log\beta / \mathrm{d}T^{-1}\right) \tag{3}$$

where R is the gas constant.

The present study was undertaken to investigate the linolenic acid oxidation inhibited by two simple phenolic derivatives. Linolenic acid was selected as the lipid analogue most convenient for thermoanalytical investigation on autoxidation of lipids. Due to the presence of three double bonds in the long carbon chain, this non-volatile fatty acid is more easily oxidised than mono- and di-unsaturated fatty acids and the oxidation process manifests in clear shape of DSC heat flow curve.

Experimental

Materials

Linolenic acid (LNA) was obtained from Carl Roth, Germany. The acid was stored in sealed vials (under nitrogen) under reduced temperature. The purity grade determined by GLC was >99%. Phenolic derivatives were purchased from Fluka. 2,4,6-trimethylphenol (TMP) (purity grade of 98–99%) was purified by vacuum distillation; commercial 2,6-di-*t*-butyl-4-methylphenol (BHT) was used without further purification. These compounds were stored under nitrogen at temperature about 0°C. Chloroform was dried by calcium chloride and distilled in atmosphere of nitrogen.

Apparatus and methods

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 study was carried out in an oxygen atmosphere. The oxygen flow rate was 15 l h^{-1}. The apparatus was calibrated with a high-purity indium standard.

In order to prepare the inhibited linolenic acid (concentration ranges from 0.26 to 20 mmol of phenolic compound per mol of LNA) the appropriate amounts (2–200 μl) of the chloroform solution of compound were added by variable volume pipette to a weighted amount (~1 ml) of pure LNA. The mixture was gently stirred with 0.5 ml of chloroform and excess of solvent was removed under reduced pressure on a rotary vacuum evaporator. Prepared mixtures were immediately used in DSC experiments.

Determination of the kinetic parameters for the thermoxidation of LNA was described in previous papers concerned with thermoxidation of edible oils [2]. A 3–5 mg sample placed on an aluminium pan was heated at linear heating rates (β) of 5, 10, 20, 40 and 80 K min^{-1} in oxygen flow. Oxidation of the inhibited LNA was followed in the same way.

Results and discussion

Figures 1 and 2 show the typical plots of heat flow *vs.* temperature for various β obtained during oxidation of pure linolenic acid and during oxidation of LNA in the presence of 2,4,6-trimethylphenol. The shapes of the curves were similar for each investigated system and at any concentration of phenolic derivatives. The low heating rates (β =5 and 10 K min^{-1}) only the one maximum of the heat flow was clearly observed. When the higher heating rate was used, the second maximum appeared and, for β = 40 and 80 K min^{-1} – the second peak was evidently predominating. All experiments were carried out under such extremely different heating rates (5–80 K min^{-1}) in order to obtain the data from all three

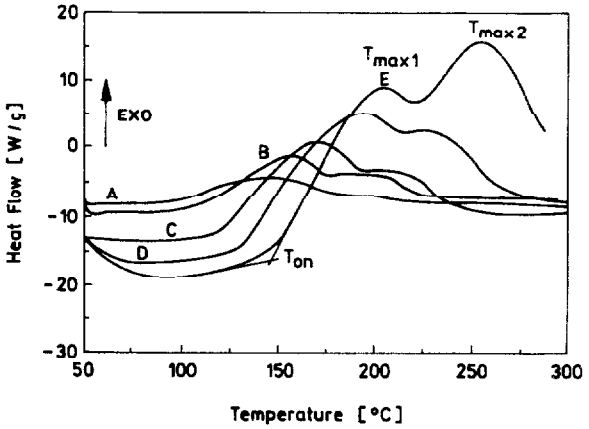

Fig. 1 DSC curves of linolenic acid thermoxidation. Heating rates: A – 5 K min^{-1}, B – 10 K min^{-1}, C – 20 K min^{-1}, D – 40 K min^{-1}, E – 80 K min^{-1}

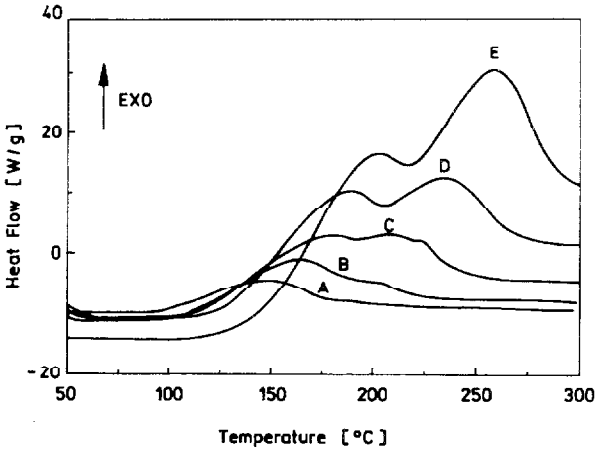

Fig. 2 DSC curves of linolenic acid thermoxidation inhibited by addition of TMP at concentration of 3.10 mmol per mol of LNA. Heating rates: A, B, C, D, and E the same as in Fig. 1

characteristic points: onset point and first and second peak. The kinetic activation energy of uninhibited linolenic acid was 70.40±0.5 when onset point temperatures were used in Eq. (2), 80.1±4.8 when calculations were based on T_{max1} data and for the second peak E_a was equal 89.8±7.6.

The influence of concentration of 2,6-di-*t*-butyl-4-methylphenol on obtained values of temperatures of the start of the oxidation (T_{on}) and on the temperatures of both peaks (T_{max1}, T_{max2}) is shown in Fig. 3. Comparing these plots it should be noticed that only T_{on} was shifted with increasing concentration of phenolic compounds. The temperatures of the first peak were less affected by increase of phenolic compound concentration while no correlation between values of T_{max2} and concentration of inhibitor was observed. Above phenomenon was typical for both investigated compounds. Temperatures of extrapolated start of oxidation process increased with increasing heating rate and plots of those tendencies are shown in Fig. 4. For each heating rate the large shifts of T_{on} were observed in low concentration range. Above 2 mmol of inhibitor per mol of LNA the changes are rather insignificant. The calculated parameters of Arrhenius plot described by Eq. (2) and values of activation energy of inhibited thermoxidation are shown in Table 1 (for 2,6-di-*t*-butyl-4-methylphenol) and in Table 2 (2,4,6-trimethylphenol). The standard errors of coefficient A were used for calculation of errors of estimated activation energy (ΔE_a).

A considerable dispersion of activation energy values and large errors of estimation (higher than 10%) for calculations based on temperatures of maximum heat flow make these points inappropriate for calculations. On the other hand, E_a values computed from the onset temperatures of the oxidation were charac-

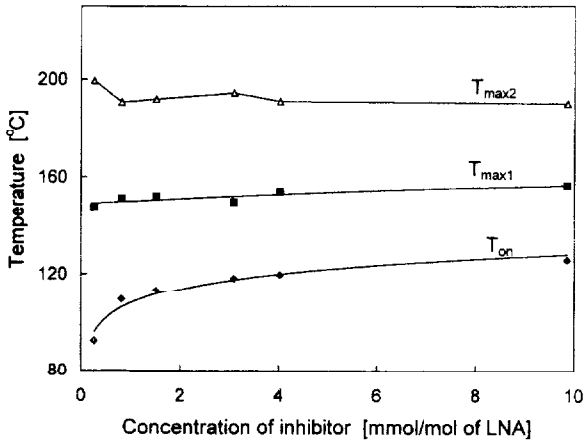

Fig. 3 Influence of BHT concentration (in mmol of compound per mol of LNA) on temperatures obtained from DSC curves of thermoxidation of LNA

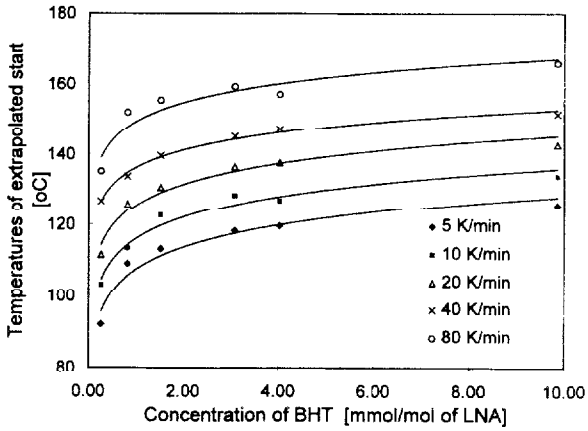

Fig. 4 Temperatures of extrapolated starts of the oxidation *vs.* concentration of BHT for different heating rates

terized by small errors of measurement (apart from one, these errors are about 2.6–6.3%) and an increase of E_a is observed with increasing concentration of BHT or TMP. Therefore, temperatures of the onset points of non-isothermal DSC curves are the most suitable data for assessment of antioxidant activity of inhibitor. Although the first peak and onset point are caused by the same process, the maximum rate of this process overlaps with second peak, which is probably caused by further oxidation of peroxides. Second peak appears at temperature range about 160–270°C and according to works [6, 7] this peak is thermal effect

Table 1 Parameters of Eq. (2), calculated activation energies (E) of thermoxidation of linolenic acid inhibited by addition of 2,6-di-*t*-butyl-4-methylphenol and errors of estimation for various concentration in mmol mol^{-1} of LNA

Concentration/ mmol mol^{-1}	a*	Error**a	R^2	A	Error***A	E/ kJ mol^{-1}	ΔE/ %
onset							
0.27	11.8223	0.0489	0.9922	–4.0642	0.2087	73.0±3.7	5.1
0.82	12.396	0.0989	0.9676	–4.4316	0.4682	79.6±8.4	10.6
1.52	13.274	0.0600	0.9881	–4.8477	0.3071	87.1±5.5	6.3
3.08	13.775	0.0467	0.9928	–5.116	0.2578	91.9±4.5	4.9
4.02	14.299	0.0243	0.9981	–5.334	0.1362	95.8±2.4	2.6
9.86	14.1116	0.0506	0.9915	–5.3365	0.2846	95.8±5.1	5.3
maximum 1							
0.27	10.71	0.06	0.9895	–4.23	0.25	76.9±4.6	5.9
0.82	9.64	0.18	0.8941	–3.73	0.74	67.9±13.5	19.9
1.52	11.10	0.16	0.9124	–4.41	0.79	80.3±14.4	17.9
3.08	11.39	0.12	0.9562	–4.56	0.56	83.0±10.3	10.3
4.02	11.83	0.25	0.7956	–4.74	1.39	86.4±25.3	29.3
9.86	12.45	0.05	0.9930	–5.07	0.25	92.2±4.5	4.8
maximum 2							
0.27	10.64	0.14	0.9342	–4.66	0.71	84.8±13.0	15.3
0.82	9.38	0.17	0.9076	–4.02	0.74	73.1±13.5	18.4
1.52	10.97	0.23	0.8249	–4.74	1.26	86.4±23.0	26.6
3.08	9.18	0.13	0.9438	–3.90	0.55	71.0±10.0	14.1
4.02	8.10	0.16	0.9140	–3.34	0.59	60.8±10.8	17.7
9.86	10.34	0.12	0.9496	–4.45	0.59	81.0±10.8	13.3

* a – constant; ** standard error of a; ***standard error of A

of oxidative decomposition of the peroxides formed previously (at temp. below 160°C). The decomposition of peroxides can occur in different ways and exothermic effects of these processes are too complicated to obtain reproducible data, so temperatures of the second peak are imprecise and high errors of estimation are observed.

The iso-conversional methods (in our calculations the Ozawa-Flynn-Wall method) are based on points at constant conversion state. These points are used for estimation of activation energy. The start of the exothermic process of oxidation is the end of induction period and at this time the consumption of all inhibi-

Table 2 Parameters of Eq. (2), calculated activation energies (E) of thermoxidation of linolenic acid inhibited by addition of 2,4,6-trimethylphenol and errors of estimation

Concentration/ mmol mol^{-1}	R^2	A	Error* A	E/ kJ mol^{-1}	ΔE/ %
onset					
0.47	0.9886	–3.8818	0.30	70.7±5.3	7.6
3.10	0.9948	–4.8153	0.20	87.7±3.7	4.2
5.89	0.9815	–4.5855	0.45	83.5±8.1	9.7
7.60	0.9993	–4.8535	0.07	88.4±1.3	1.5
11.75	0.9995	–4.9915	0.08	90.9±1.5	1.6
maximum 1					
0.47	0.9906	–6.61	0.37	120.4±6.8	5.6
3.10	0.9809	–4.74	0.38	86.3±6.9	8.0
5.89	0.8352	–3.24	0.83	59.1±15.1	25.7
7.60	0.7551	–5.22	1.71	95.0±31.2	32.9
11.75	0.6157	–5.53	2.52	100.7±45.9	45.6
maximum 2					
0.47	0.9741	–4.20	0.40	76.4±7.2	9.4
3.10	0.9476	–4.06	0.55	73.9±10.0	13.6
5.89	0.9818	–3.90	0.31	71.1±5.6	7.9
7.60	0.9825	4.41	0.34	80.2±6.2	7.7
11.75	0.9846	–4.40	0.32	80.1±5.8	7.2

* Standard error of A

tor molecules is assumed. Therefore, the end of induction period can be treated as 100% conversion of inhibitor and can be used in iso-conversional methods. Although the antioxidant action is not exothermic enough to be manifested by DSC signal, the immediate acceleration of autoxidation process of lipid after total conversion of inhibitor is easily detected by thermoanalytical equipment.

Concluding, the extrapolated onset temperatures obtained from DSC plots are the most suitable data to calculate the kinetic parameters of inhibited autoxidation of unsaturated fatty acids and for assessment the antioxidant activity. Results calculated from these data gave smaller errors while calculations based on other characteristic points of DSC curve do not denote the inhibitory effect of investigated compounds.

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References

1 G. Litwinienko, T. Kasprzycka-Guttman and M. Jarosz-Jarszewska, J. Thermal Anal. 45 (1995) 741.
2 T. Kasprzycka-Guttman and D. Odzeniak, Thermochim. Acta, 204 (1992) 303.
3 T. Kasprzycka-Guttman, D. Odzeniak and M. Supera, Thermochim. Acta, 237 (1994) 207.
4 T. Kasprzycka-Guttman and D. Odzeniak, Thermochim. Acta, 231 (1994) 161.
5 B. Kowalski, Thermochim. Acta, 213 (1993) 135.
6 G. Hess and A. O'Hare, Ind. Eng. Chem., 42 (1950) 1424.
7 J. Fugger, J. A. Cannon, K. T. Zilch and H. J. Dutton, J. Am. Oil Chem. Soc., 28 (1951) 285.