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Note

Thermokinetic properties of inhibited vegetable oils

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Abstract

Castor, corn and linseed oils with the addition of inhibitors were investigated using a DSC equipped with a pressure DSC cell. The inhibitors used in the experiments were 2,6-di-*t*-butyl-4-methylphenol and propyl gallate. The measurements were carried out under isothermal conditions in an atmosphere of oxygen. Thermal curves from DSC runs permitted the determination of onset and maximum points of the peak which were then compared to those of the pure oils. The apparent activation energies of oxidation of the oils were calculated using the model of the autocatalytic reaction and the Arrhenius equation.

INTRODUCTION

The thermal-oxidative decomposition of edible oils and fat-based food is a very important problem in food science. To minimize the influence of autoxidation on the quality of fat-based products, some phenyl-based compounds can be used as inhibitors [1–3].

Because the autoxidation of vegetable oils is a radical-promoted chain reaction, it can be inhibited by the introduction of free radical acceptors [3] such as 2,6-di-*t*-butyl-4-methylphenol (BHT) and propyl gallate (PG).

The most common inhibition reaction mechanism is

$$\text{InH (inhibitor)} + n\text{RO}_2^{\cdot} \rightarrow \text{Inactive products} \quad (1)$$

According to this mechanism the hydrogen atom from the inhibitor molecule is removed by the lipid radical $\text{RO}_2^{\cdot}$, which leads to formation of hydroperoxide molecules and an inactive inhibitor radical. It should be borne in mind, however, that under some experimental conditions, dimerization of the free radicals $\text{RO}_2^{\cdot}$ occurs as an alternative mechanism of antioxidation.

The kinetic parameters of the autoxidative reaction can be calculated using the general autocatalytic model

$$dC/dt = kC^m(1 - C)^n \quad (2)$$

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For calculations, the logarithmic form of this equation is more usable [4]

$$\log(dC/dt) = \log k + n \log[(1 - C)C^{m/n}] \quad (3)$$

where dC/dt is the reaction rate, k the rate constant, and n and m are parameters.

In DSC measurements

$$C = \frac{\Delta h}{\Delta H} \quad (4)$$

In this ratio, Δh is the heat evolved at a given point of time and ΔH the total heat evolved in the process.

EXPERIMENTAL

Materials

Castor, corn and linseed oils were purchased from the Institute of Industrial Chemistry in Warsaw. Their composition was tested by means of high performance liquid chromatography (Table 1).

To avoid uncontrolled autoxidation of the oils, they were kept in darkness under nitrogen.

The inhibitors, BHT and PG, were purchased from Merck.

Apparatus and experiments

All the measurements were carried out using a Du Pont Instruments 910 differential scanning calorimeter with a 9900 computer/thermal analyzer and a pressure cell calibrated with the use of high-purity indium.

Thoroughly homogenized samples of the oils (7–8 mg) were placed in empty aluminum pans and heated to a constant temperature, in an oxygen atmosphere (an empty aluminum pan was the reference, with oxygen pressure 2 atm, and flow 6 l h^{-1}).

TABLE 1

Fatty acid composition (in %) of the investigated edible oils

Oil	Saturated fatty acids C_{16}–C_{22}	Fatty acids with double bonds			Other acids
		Oleic	Linoleic	Linolenic	
Castor	5	9	2	–	84
Corn	11	42	47	–	–
Linseed	8	25	10	57	–

The thermal stability of the antioxidants at high temperatures has no influence on the inhibition process. The weight loss of the investigated inhibitors was minimal at the experimental temperatures [5].

RESULTS AND DISCUSSION

The heat evolved during the autoxidation process was observed as an exothermic peak (Fig. 1). Two points that are particularily important for a description of the autoxidation can be distinguished, i.e. the onset point t_{on} (determined by the intersection of the baseline with a line tangential to the rising part of the oxidation exotherm) and the maximum point t_{max} (determined by the intersection of two tangents to the peak), see Table 2.

Pure oils exhibit smaller values of t_{on} and t_{max} than oils with added BHT or PG. This is evidence of the inhibiting properties of the investigated compounds. The addition of BHT and PG delays the propagation step of the oxidation of oils.

The activation energies calculated by means of the Arrhenius equation and eqn. (3) for both inhibited and uninhibited oils were approximately equal, see Table 3. According to the literature [6, 7], an increased concentration of some phenolic-type antioxidants does not have to result in a longer induction time of the autoxidation reaction. On the contrary, too high a concentration of such an inhibitor may cause an acceleration of oxidation. In the present work, this phenomenon was not observed. Only a lowering of the antioxidant efficiency of the studied inhibitors was found; this is illustrated in Fig. 2.

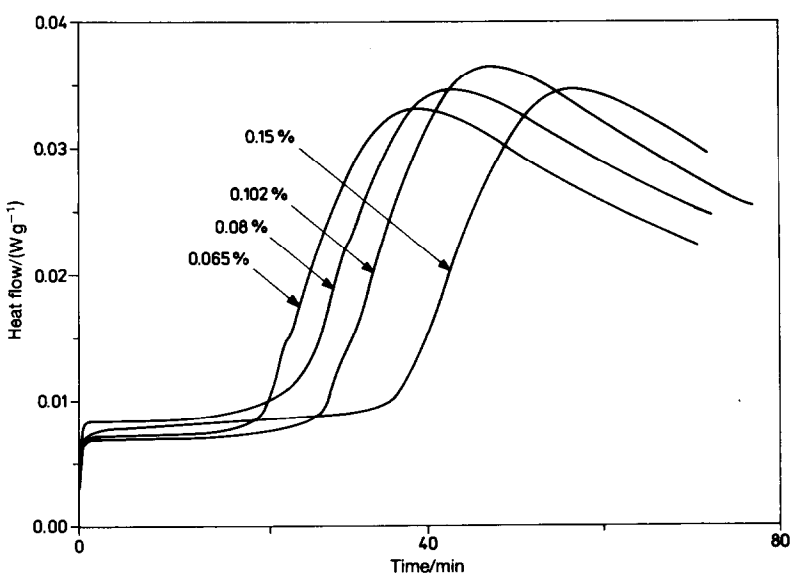

Fig. 1. Thermograms of corn oil with different amounts of BHT.

TABLE 2

DSC onset and maximal points for different concentrations of inhibitors and different temperatures

Oil	Concentration/%	142°C		147°C		152°C		157°C	
		t_{on}	t_{max}	t_{on}	t_{max}	t_{on}	t_{max}	t_{on}	t_{max}
Corn	0.00	21.71	34.35	16.52	29.25	11.34	20.54	3.61	16.80
oil	0.065	24.78	40.00	20.90	32.34	14.52	21.82	11.04	18.21
+	0.080	27.46	44.61	23.43	37.87	15.97	26.02	13.01	23.77
BHT	0.102	30.77	49.58	26.59	43.06	18.57	31.96	15.56	28.82
	0.150	37.56	59.32	31.25	49.36	22.01	37.85	18.00	32.09
	0.194	45.84	67.82	34.50	54.67	24.25	41.42	19.12	36.10
	0.302	51.31	69.02	35.74	55.12	25.03	42.63	19.77	38.87
	0.330	52.00	70.01	36.14	56.02	25.26	43.05	20.13	39.10
Corn	0.065	37.71	52.21	31.54	45.45	22.36	34.25	11.56	20.32
oil	0.081	40.05	55.36	35.32	50.04	24.54	37.95	14.56	24.05
+	0.125	44.61	59.02	39.24	55.47	28.56	40.21	18.24	28.36
PG	0.160	46.71	64.25	42.36	57.34	31.25	43.21	20.03	30.52
	0.203	48.25	67.84	43.21	58.78	33.65	45.67	21.45	31.25
	0.211	50.01	69.03	43.89	59.47	34.05	46.24	22.36	32.07
	0.280	50.54	70.12	44.15	60.52	34.98	46.92	22.98	32.58
	0.310	50.56	70.57	44.52	61.02	35.07	47.12	23.33	32.87
	0.330	51.02	70.97	44.85	61.32	35.52	47.32	23.45	33.04
Linseed	0.00	6.47	14.50	4.25	11.97	2.15	10.21	0.95	7.31
oil	0.065	9.58	18.37	6.03	13.65	3.22	11.65	1.98	8.21
+	0.090	11.57	20.57	7.36	14.98	4.57	12.34	2.36	8.95
BHT	0.104	13.78	22.21	8.59	17.64	5.78	15.05	4.01	10.07
	0.160	15.26	26.74	11.25	20.06	7.34	16.31	6.32	12.37
	0.203	17.86	28.68	13.65	22.95	8.12	16.91	7.39	13.05
	0.280	18.24	30.01	14.57	23.77	8.55	17.03	8.25	13.64
	0.330	18.25	30.32	14.65	23.98	8.65	17.04	8.21	13.78
Linseed	0.064	14.32	25.87	10.37	16.34	6.81	12.54	4.65	9.47
oil	0.090	19.34	27.54	13.01	18.71	8.97	14.02	5.87	10.01
+	0.105	23.85	31.19	15.19	20.88	10.32	15.15	7.04	13.80
	0.160	25.41	34.78	17.87	22.97	13.02	17.98	10.63	15.46
	0.200	27.41	37.01	18.31	24.01	14.87	20.10	12.34	16.04
	0.280	28.03	38.10	18.57	24.95	15.12	20.71	12.94	16.37
	0.330	28.25	38.25	18.64	25.07	15.32	21.08	13.00	16.41
Castor	0.00	27.05	34.25	17.14	24.64	15.04	23.67	10.47	19.21
oil	0.065	34.51	43.78	25.54	32.54	22.13	30.21	16.54	25.64
+	0.090	37.84	47.64	28.04	36.41	25.41	34.74	18.00	27.14
	0.105	39.07	48.21	29.07	38.24	27.41	35.01	19.12	28.57
	0.160	40.31	49.24	29.88	39.12	27.88	35.98	19.97	29.01
	0.204	41.00	49.54	30.05	39.87	28.12	36.31	20.12	29.54
	0.280	41.52	50.01	30.74	40.12	28.34	36.78	20.31	29.87
	0.330	40.71	50.31	31.00	40.57	28.37	37.00	20.57	30.07
Castor	0.065	38.14	48.23	28.98	37.14	25.99	34.78	20.34	29.42
oil	0.092	43.47	55.64	35.41	44.78	32.15	41.58	25.31	35.34
+	0.106	46.28	57.34	36.42	46.97	34.31	43.27	28.01	38.97
PG	0.160	48.00	58.71	37.35	48.12	35.14	45.64	28.56	39.45
	0.205	48.57	59.13	38.01	48.75	35.87	45.97	29.53	40.05
	0.280	49.01	59.74	38.36	49.02	36.12	46.20	30.07	40.65
	0.330	49.12	59.97	38.47	49.12	36.27	46.24	30.14	40.72

TABLE 3

Activation energy E of the autoxidation reaction of the investigated oils

Concenitration of BHT/ %	E/kJ mol^{-1}		
	Corn oil	Castor oil	Linseed oil
0.000	86.2 ± 5.2	85.7 ± 3.4	56.8 ± 3.5
0.065	85.6 ± 4.2	87.2 ± 4.5	55.3 ± 4.3
0.090	86.3 ± 3.7	81.3 ± 5.6	49.6 ± 5.7
0.160	84.2 ± 5.4	79.8 ± 6.4	57.3 ± 8.2
0.280	89.4 ± 3.7	84.5 ± 2.3	55.4 ± 4.2
0.330	81.3 ± 5.0	84.7 ± 5.1	52.1 ± 2.4

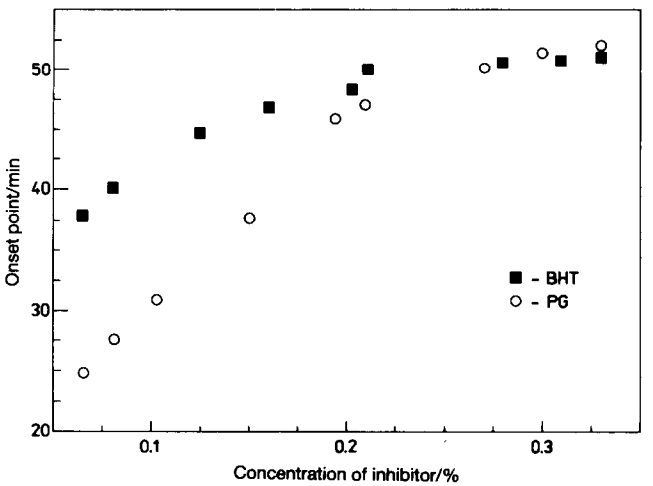

Fig. 2. Onset points of corn oil inhibited by different amounts of BHT and PG at 415 K.

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