Thermochimica Acta, 177 (1991) 9–14
Elsevier Science Publishers B.V., Amsterdam

EVALUATION OF THE STABILITY OF SOME ANTIOXIDANTS FOR FAT-BASED FOODS

BOLESŁAW KOWALSKI

Department of Food Technology, Agricultural University, 26/30 Rakowiecka Str., 02-528 Warsaw (Poland)

(Received 14 May 1990)

ABSTRACT

This paper discusses the evaluation of the stabilities of 2-*t*-butyl-4-methoxyphenol, 2,6-di-*t*-butyl-4-methylphenol and propyl gallate, which are frequently incorporated as antioxidants in fat-based foods. The stability of an antioxidant depends upon its volatilization, thermal decomposition and oxidation. The results of investigations performed by differential scanning calorimetry, pressure differential scanning calorimetry and thermogravimetry have shown that the stabilities of the materials studied increase in the above-mentioned order of antioxidants.

INTRODUCTION

Deterioration of fat-based foods by autoxidation is a well-known phenomenon. As the autoxidation of food lipids is a radical-promoted chain reaction it is frequently inhibited by the incorporation of certain organic additives into fat-based foods [1,2]. Besides tocopherols, the most frequently used are phenols hindered by *t*-butyl substituents at the 2 and 6 positions and methyl, methoxyl or ester groups in position 4. Such additives are known as antioxidants. As the addition of antioxidants to fat-based foods raises health and nutritional issues the fate of antioxidant molecules during the autoxidation of inhibited oils and fats has been extensively studied [3–5]. A good antioxidant, if it passes health tests, should protect oil or fat from autoxidation at low levels of treatment. Accordingly the activity of antioxidants is also an important factor in their assessment. Two types of antioxidant activity are considered. The first is concerned with the storage of fat-based food at ambient temperature and atmosphere, while the second is related to prolonged high temperature applications of oils and fats, such as deep frying or other forms of cooking. Several methods for the assessment of antioxidants have been developed. Generally they are based on a comparison of the oxidative stabilities of samples with and without antioxidants. As

0040-6031/91/$03.50

the tests are usually accelerated by a rise in temperature and oxygen concentration, the thermal and oxidative stabilities of antioxidants are of paramount importance.

In the work described in this paper the thermal and oxidative stabilities of some phenolic antioxidants were studied using differential scanning calorimetry (DSC) under ambient and oxygen atmospheres, pressure differential scanning calorimetry (PDSC) under elevated pressure of oxygen and thermogravimetry (TG) under argon.

EXPERIMENTAL

Materials

The antioxidants used were: 2-*t*-butyl-4-methoxyphenol (BHA), 2,6-di-*t*-butyl-4-methylphenol (BHT) and propyl gallate (PG) (all from Koch-Light). The BHT and PG were declared 99% pure so they were used as supplied. As the BHA was yellow–brown in colour and showed a double DSC peak in its melting region it was recrystalized from *n*-pentane before use. The purified BHA showed a single spot on thin layer chromatography (TLC) plates and a single DSC melting peak.

Apparatus and experiments

A Du Pont system (910 differential scanning calorimeter, 1090 B thermal analyzer and 1091 disc memory) was used for the DSC measurements. In experiments performed at elevated pressure the normal-pressure DSC cell was replaced by a high-pressure DSC cell (PDSC, model No. 900830-902). The instrument was calibrated using high-purity cyclohexane, indium and tin as standards. The measuring conditions were as follows: DSC dynamic measurements—sample masses 3–7 mg, static air or oxygen flow (100 cm^3 min^{-1}), aluminium open pans, reference pan empty, heating rate 10 °C min^{-1}; PDSC dynamic measurements—1800 kPa pressure of oxygen, other conditions as in DSC experiments; PDSC isothermal measurements—159 °C, 1800 kPa pressure of oxygen. All DSC/PDSC experiments were recorded on 8-in. floppy discs and then analyzed using the Du Pont Oxidative Stability V 2.0 and Interactive DSC V 3.0 programs.

The TG measurements were carried out by means of the Derivatograph (OD-102 type, MOM Budapest). Samples (330–480 mg) were placed in a ceramic crucible (α-Al_2O_3 was used as a reference material) and were heated at a rate of 10 °C min^{-1} under argon gas flowing at 400 cm^3 min^{-1}.

RESULTS AND DISCUSSION

The dynamic DSC and PDSC traces for the antioxidants studied are shown in Figs. 1–3. The sharp major endothermic peaks are typical features in all the DSC/PDSC traces of these antioxidants and they correspond to the temperature regions of their fusion transitions. From these peaks the temperatures and heats of melting were determined as shown on the DSC/PDSC curves and listed in Table 1. As can be seen from the DSC/PDSC traces for PG this antioxidant was not as pure as declared. Besides a small endothermic peak (melting) at $62 \pm 2°C$, recorded irrespective of the cell type and atmosphere used, another was recorded at about $146 \pm 1°C$ which overlaps with the main melting peak of the PG.

For the stabilities of the antioxidants studied three points have to be considered: volatilization, thermal decomposition and susceptibility to oxidation. All of them can be estimated by DSC/PDSC and TG techniques. The DSC traces in air show that both BHA and BHT are volatile; they show DSC endothermic peaks between 100 °C and 240 °C and between 100 °C and 190 °C respectively. This has been confirmed by TG measurements (listed in Table 1, where percentage weight losses are reported). The temperature diferences between DSC and TG measurements were caused by different measuring conditions (i.e. atmospheric composition, DSC pan- and TG crucibles-type, and sample mass). The DSC endothermic transitions for PG obtained in the ranges 180 °C–280 °C (oxygen) and 200 °C–320 °C (air)

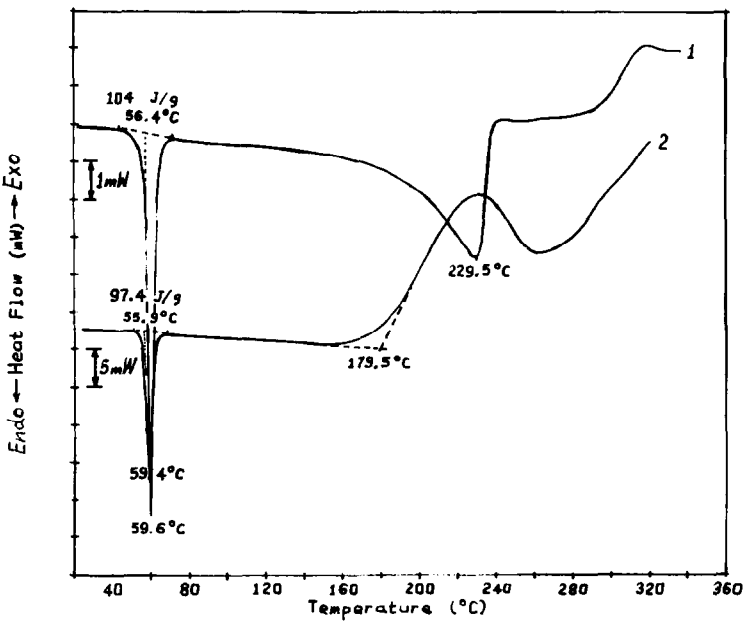

Fig. 1. DSC scan in air (1) and PDSC scan (2) at 1800 kPa of oxygen for BHA.

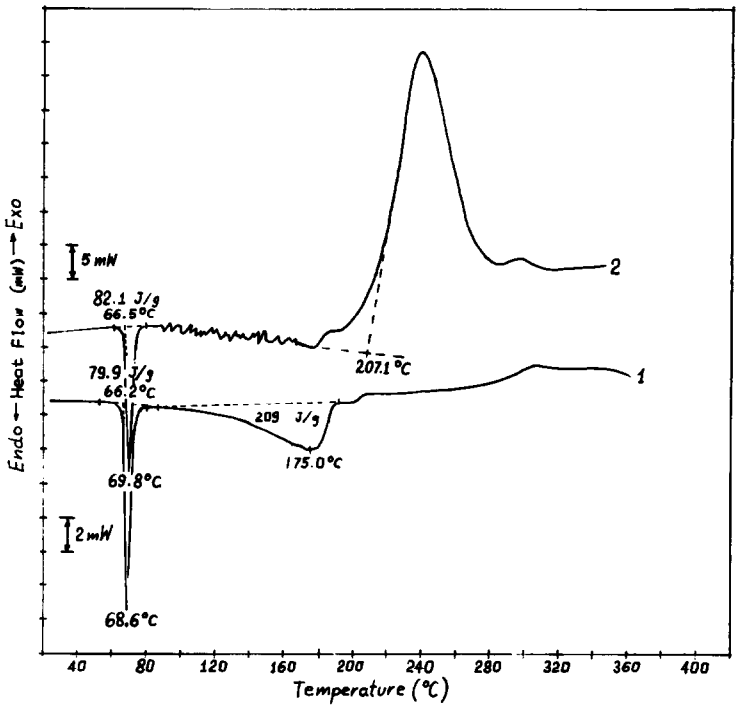

Fig. 2. Plot for BHT, as Fig. 1.

correspond to specific heat changes and to thermal decomposition of this antioxidant.

As the susceptibility of BHA and BHT to oxidation could not be evaluated in open pans at normal pressure, the experiments at elevated pressure (1800 kPa) were performed in both dynamic and isothermal modes. The pressure (1800 kPa) of oxygen effectively suppressed the evaporation of BHA and BHT and at such a concentration of oxygen the oxidation of samples was accelerated. The scans obtained at a heating rate of 10 °C min^{-1} and at 1800 kPa oxygen pressure show that the onset temperatures

TABLE 1

Thermal properties of antioxidants studied

Anti-oxidant	MP (°C)		Heat of melting J g^{-1}	Percentage weight loss at					
	t_{ON} [a]	t_M [a]		100 °C	150 °C	200 °C	250 °C	300 °C	350 °C
BHA	56.2±0.2	59.5±0.1	101±3	1	3	10	53	100	–
BHT	66.3±0.2	69.2±0.6	81±3	0.5	1.6	9	47	86	–
PG	147.3±0.6	149.5±0.3	121±2	0.5	0.5	0.8	1.5	6.8	41.7

[a] t_{ON} and t_M are melting temperatures determined by DSC/PDSC as the extrapolated onset and the minimum of the melting peak, respectively.

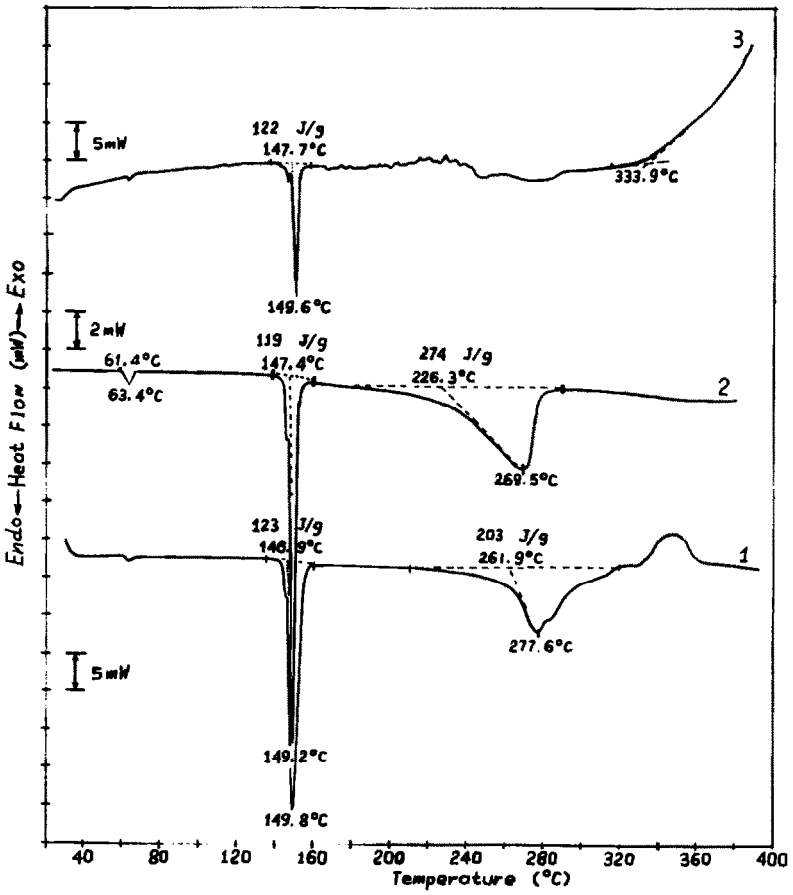

Fig. 3. DSC scans in air (1) and in oxygen (2) and PDSC scan (3) at 1800 kPa of oxygen for PG.

for PDSC exotherms of oxidation are 179.5 °C, 207.1 °C and 333.9 °C for BHA, BHT and PG respectively. Such onset temperatures of oxidation are often referred to as a measure of oxidative stability. More direct information on oxidative stability can be obtained from PDSC measurements performed in the isothermal mode. The times required to reach a maximum in the PDSC exothermic curve (τ_{max}) obtained at constant temperature can be used to rank oxidative stabilities of the samples [6]. Accordingly, the higher the τ_{max} value the more resistant is the substance to oxidation, and vice versa. From the PDSC exotherms obtained at 159 °C (Fig. 4) it is clear that under the experimental conditions PG undergoes practically no oxidation. The PDSC experiments at 159 °C for BHA and BHT show that their τ_{max} values are 16.5 and 32.5 min, respectively.

Considering the volatilization, thermal decomposition and susceptibility to oxidation of the antioxidants studied they can be ranked in the order BHA < BHT < PG, with PG the most and BHA the least stable of the three.

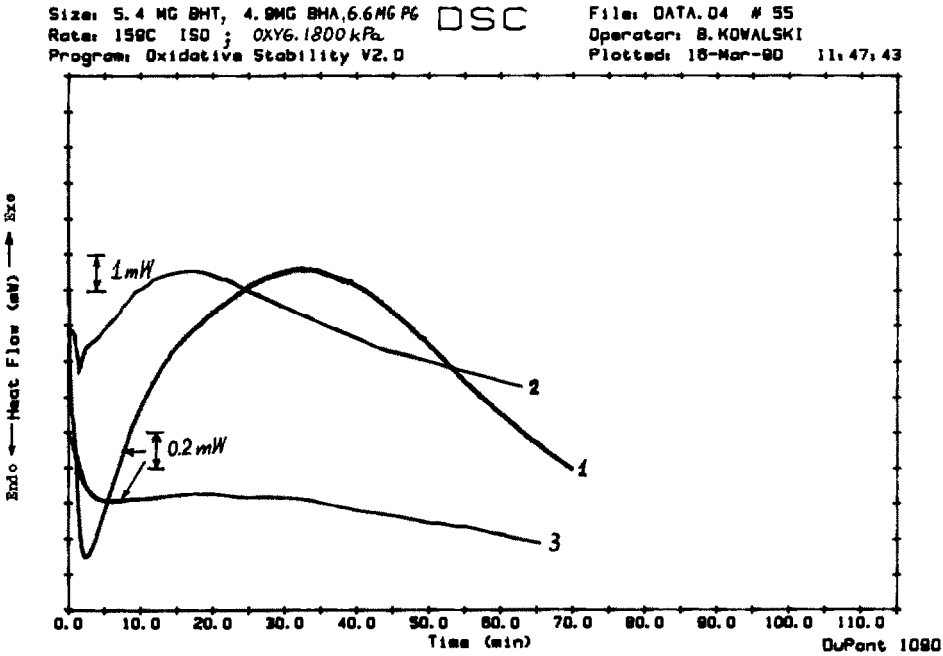

Fig. 4. PDSC exotherms at 159 °C and at 1800 kPa of oxygen for (1) BHT, (2) BHA, (3) PG.

The efficiency of antioxidants in a fat or oil matrix can be different from their stabilities determined by thermal analysis, as the protection of fats from autoxidation depends on many factors. DSC/PDSC studies on the efficiency of antioxidants in edible oils and fats are in progress and the results will be reported.

REFERENCES

1 N. Uri, Mechanism of Antioxidation, in W.O. Lundberg (Ed.), Autoxidation and Antioxidants, Vol. 1, Interscience, New York, 1961, Chapter 4, pp. 133–169.
2 T. Richardson and M. Korycka-Dahl, Lipid Oxidation, in P.F. Fox (Ed.), Developments in Dairy Chemistry, Elsevier Applied Science, London, 1983, Chapter 7A, pp. 241–342.
3 T. Kurechi and T. Yamaguchi, J. Am. Oil Chem. Soc., 57 (1980) 216.
4 T. Kurechi and T. Kato, J. Am. Oil Chem. Soc., 57 (1980) 220.
5 T. Kurechi and A. Kunugi, J. Am. Oil Chem. Soc., 60 (1983) 33.
6 B. Kowalski, Thermochim. Acta, 156 (1989) 347.