Journal of Thermal Analysis 37 (1991) 411-426

SYNTHESIS OF THE MONOMERIC ANTIOXIDANT 3,5-di-tert-butyl-4-hydroxy-styrene by the thermal decomposition of *trans*-3,5-di-tert-butyl-4-hydroxycinnamic acid

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(Received August 2, 1990)

The thermal decomposition of *trans*-3,5-di-tert-butyl-4-hydroxy-cinnamic acid (BHC) in the solid state, in aqueous solution and in solutions in organic solvents was studied in order to develop a preparative method for the synthesis of the monomeric antioxidant 3,5-di-tert-butyl-4-hydroxystyrene (BHS). Thermal methods of analysis showed that, during the solid-state decomposition of BHC, its decarboxylation was accompanied by desalkylation and polymerization of the styrenic decomposition products. BHC decarboxylation is aqueous solution was also accompanied by polymerization. A kinetic study of BHC decomposition in organic solvents by ^{1}H-NMR spectrometry revealed that only the decomposition of BHC in aprotic dipolar solvents such as dimethylsulphoxide and dimethylformamide, at temperatures lower than 150°C, could be used as a preparative method for the synthesis of BHS. The decarboxylation of BHC took place by zero-order kinetics through a mechanism involving the ionization of BHC in the aprotic dipolar solvent. The reaction rate increased drastically with increasing solvent polarity and in the presence of trace amounts of BHC sodium salt. Both monomeric antioxidants, i.e. BHS and BHC, may be used to obtain polymer-bound antioxidants, e.g. by melt-grafting onto polyethylene.

Improved polymer stabilization continues to be an area of much intense effort in both industrial and academic laboratories. Two factors are responsible for the effectiveness of stabilizers: the intrinsic stabilizer behaviour and the permanence of the stabilizer in the polymer. The effectiveness of antioxidants may be increased by improvement of the antioxidant permanence

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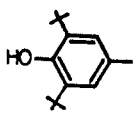
in the polymer, and by minimizing physical losses due to incompatibility, volatility and extractability of the antioxidants during processing and use. Basically, there are two approaches to attain an increase of the persistance of an antioxidant. One is to produce antioxidants of high molecular weight and therefore of low volatility or extractability. The other is to bind the antioxidant to the polymer chemically, thereby guarenteeing its permanence in the polymer matrix. Many attempts have been made to do this and routes to obtain such permanent antioxidants have been reviewed [1-8].

Some routes to obtain high molecular weight or polymer-bound antioxidants make use of monomeric antioxidants, i.e. dual functional compounds bearing an antioxidant function and a polymerizable group. The monomeric antioxidants are capable of homopolymerization, random copolymerization with different monomers, and graft copolymerization onto polymer chains. General methods for the synthesis of monomeric antioxidants have been reported [1, 4]. However, many of the are sophisticated and expensive methods which require unusual reactants.

It was the objective of our work to prepare the monomeric antioxidant 3,5-di-tert-butyl-4-hydroxystyrene (BHS) by a simple method, i.e. the thermal decomposition of *trans*-3,5-di-tert-butyl-4-hydroxy-cinnamic acid (BHC), and to study the mechanism of the decarboxylation reaction

$$R\text{-}CH=CH\text{-}COOH \rightarrow R\text{-}CH=CH_2 + CO_2$$



R- CH = CH_2 (BHS)

R- CH = COOH (BHC)

Experimental

Synthesis of 3,5-di-tert-butyl-4-hydroxycinnamic acid (BHC)

The first step in the synthesis of BHC was the synthesis of 3,5-di-tert-butylbenzaldehyde (BHA) by a new approach, i.e. the Duff synthesis. A solution of glycoboric acid, i.e. the catalyst, in ethylene glycol, i.e. the solvent, was first obtained by heating a mixture of ethylene glycol and boric acid at 150°. Then, 2,6-di-tert-butyl-phenol and hexamethylenetetramine

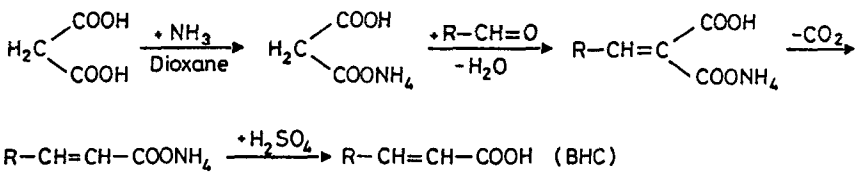
were added to this reaction mixture. Formylation of the phenol occurred by cations $^{+}CH=NH$ resulting from the decomposition of hexamethylenetetramine in the acid medium. The resulting imine was hydrolyzed in the presence of sulphuric acid:

$$R-H + {}^{+}CH=NH \xrightarrow{-H^{+}} R-CH=NH \xrightarrow[H_2SO_4\,30\%]{H_2O} \underset{(BHA)}{R-CH=O} + NH_3$$

BHC was synthesized by the condensation of BHA with malonic acid in dioxane, i.e. a new Knoevenagel condensation method. First, gaseous ammonia was bubbled into a dioxane solution of malonic acid, forming monoammonium malonate. Then, BHA was added and the reaction mixture was refluxed for 2-3 hours. The reaction product was converted to the acid form and the resulting BHC was purified by recrystallization:

Thermal analysis

Methods of thermal analysis (DTA, TG, DTG, EGA) were used to investigate the solid-state decomposition of BHC and some related compounds.



All measurements were made in a dynamic atmosphere of nitrogen (5 l/h), at constant heating rates, using the Derivatograph 1500 T (MOM, Budapest). A gas-titrimeter (MOM, Budapest) was coupled with the derivatograph in order to determine the amount of CO_2 evolved during the thermal decomposition of BHC.

Decomposition in organic solvents

The decomposition of BHC in organic solvents at different temperatures was followed by ^{1}H–NMR spectrometry, using the characteristic resonance lines of the BHC and BHS protons. Solutions of 0.3-0.7 mol.BHC/kg deuterated solvent were maintained at constant temperature under gentle nitrogen bubbling. At different time intervals, with the aid of a microsyringe, 0.1 ml solution was drawn out from the reaction flask and injected directly into the measuring cell of the spectrometer. The cell was rapidly cooled to room temperature in an ice-bath. The NMR spectra were recorded on a

TESLA BS 487 C spectrometer at 80 MHz and room temperature. The chosen analytical signals of BHC and BHS protons were integrated and the corresponding heights were measured. For each sample, five integrations were performed and the mean values of the integrated heights were used to calculate the BHC conversion to BHS.

Results and discussion

The thermal decarboxylation of BHC may be performed as a solid-state decomposition, in aqueous solution or in organic solvents. Therefore, we studied these approaches in order to developed a preparative method for the synthesis of BHS antioxidant.

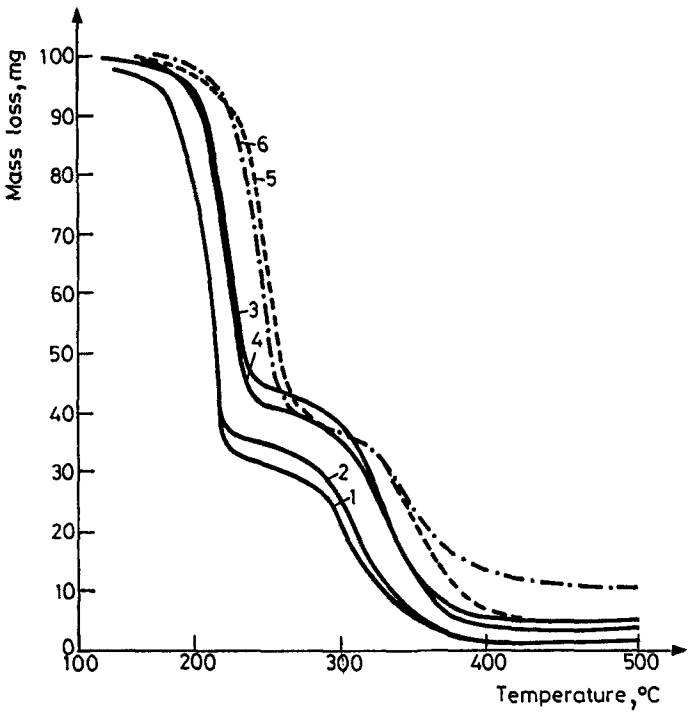


Fig. 1 Decomposition of the BHC at different heating rates: 1 - 0.8 deg/min, 2 - 1.6 deg/min, 3 - 3.2 deg/min, 4 - 5.2 deg/min, 5 - 12.0 deg/min, 6 - 23.3 deg/min (100 mg sample weight, 5 l/h nitrogen stream)

Solid-state decomposition of BHC

Braun and Meyer [9] reported a solid-state decomposition of BHC at 210° and 12 mm Hg, obtaining 69-84% BHS yields. This seems to be a surprising result, because under such conditions the resulting BHS may polymerize. Therefore, we studied the solid-state decomposition of BHC by thermal methods of analysis, i.e. differential thermal analysis (DTA), thermogravimetry (TG) derivative thermogravimetry (DTG) and evolved gas analysis (EGA).

The thermal decomposition of BHC, investigated by TG at different heating rates (0.8-23.3 deg/min), occurred in two steps (Fig. 1). The first weight losses appeared at 170-180°. Depending on the heating rate, the first decomposition step ended at 220-280°, where 45-65% weight loss occurred. The DTG curve also emphasized the two-step decomposition of BHC, showing the temperatures where the maximum decomposition rate for each interval occurred, i.e. T_{m1} and T_{m2} (Fig. 2). The DTA curve revealed three endothermic peaks for the first decomposition range (T_1-T_3) and a single

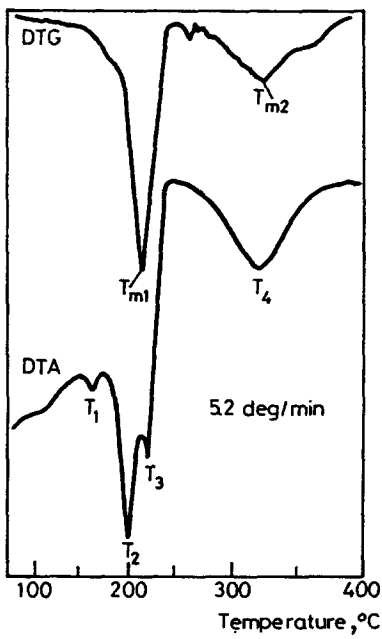


Fig. 2 DTA and DTG curves for BHC decomposition (5.2 deg/min heating rate)

one for the second decomposition range (T_4) (Fig. 2). These characteristic temperatures depended on the heating rate (Table 1).

The weight loss at the end of the first range of decomposition BHC was higher than the theoretical one for the decarboxylation (BHC→ BSH + CO_2; 16% CO_2 loss) and approached the theoretical weight loss for the elimination of CO_2 and two molecules of isobutene (56.5%). A model compound without tert-butyl groups, i.e. *p*-hydroxy-cinnamic acid (HCA), also displayed two-step thermal decomposition (Fig. 3).

Table 1 Characteristic temperatures in DTA and DTG curves for the decomposition of BHC at different heating rates

Heating rate, deg/min		0.8	1.6	3.2	5.2	12.0	23.3
DTA curve	T_1, °C	172	165	178	172	178	168
	T_2, °C	203	198	208	202	215	210
	T_3, °C	212	212	223	223	255	255
DTG curve	T_{m1}, °C	212	212	225	225	255	255
	T_{m2}, °C	–	310	330	330	350	347

However, the weight loss at the end of the first decomposition range was about 28%, because only the decarboxylation reaction took place (the theoretical weight loss is 26.8%). The DTA curve for HCA exhibited a single endothermic peak instead of the three peaks for BHC.

The weight loss due to decarboxylation alone was measured by EGA, i.e. the continuous potentiometric titration of CO_2 evolved during BHC heating. Both TGT and DTGT curves showed the initial temperature (T_i) where CO_2 evolution began, and the DTGT curve revealed the temperature where the maximum decarboxylation rate occurred (T_m) (Fig. 4). Simultaneous TG and EGA of BHC demonstrated that the first weight losses appeared before the evolution of CO_2, and the total CO_2 loss (9%) was lower than the theoretical value of 16% corresponding to the decarboxylation reaction. In contrast, for HCA decomposition the TG and TGT curves practically overlapped and the total CO_2 loss (28%) approached the theoretical value of 26.8% due to the decarboxylation.

During the solid-state decomposition of BHC, the polymerization of the styrenic decomposition products also occurred. The ^{1}H–NMR spectrum of the decomposition product obtained by maintaining BHC for 3 minutes above its melting point, i.e. at 225°, showed resonance lines for both BHC and BHS monomers, and the resonance line at δ = 7.12 ppm (CH_{Ar}) for the BHS polymer.

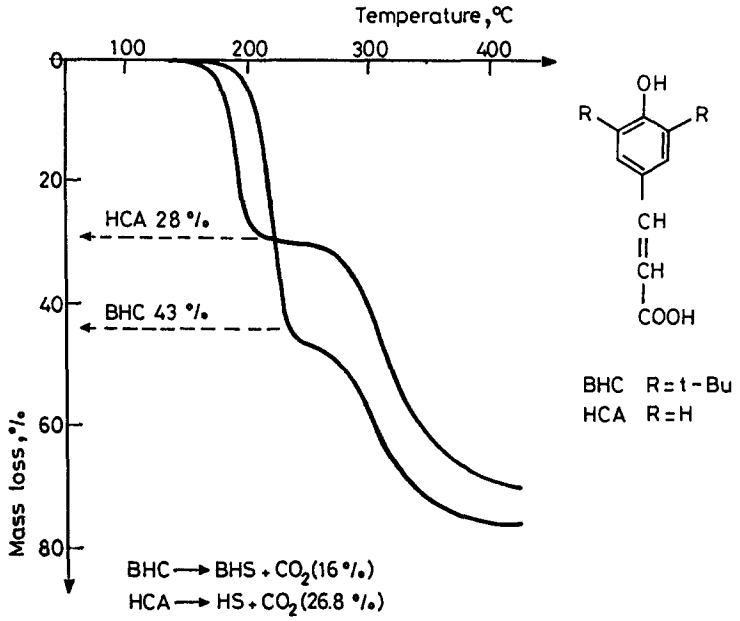


Fig. 3 Thermoanalytical curves for BHC and HCA decomposition (5.2 deg/min heating rate)

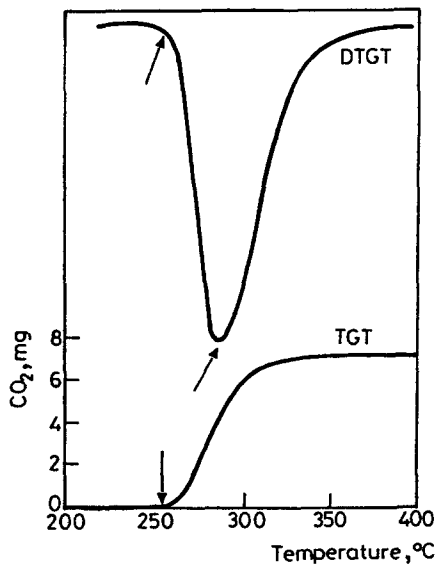
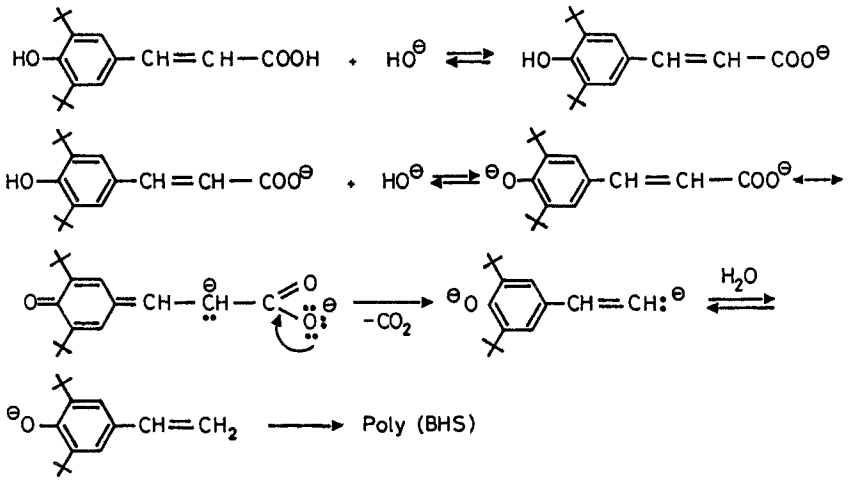


Fig. 4 Evolved gas (CO_2) analysis of BHC (26.4 deg/min heating rate)



Consequently, the solid-state decomposition of BHC may not be used to obtain the BHS antioxidant, because decarboxylation was accompanied by desalkylation and polymerization.

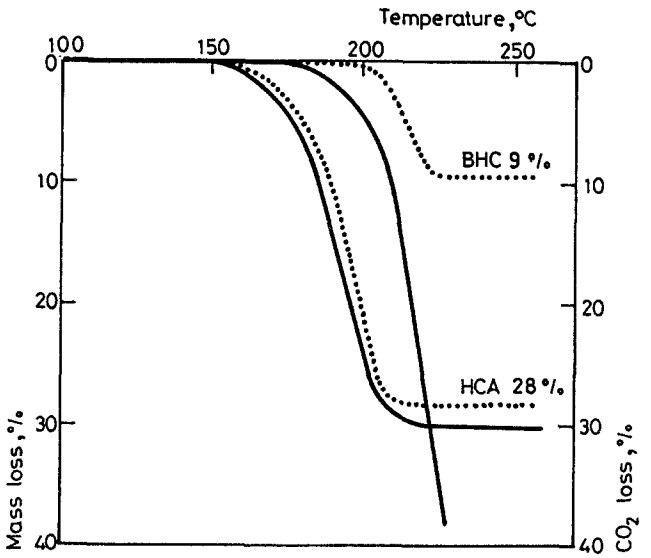


Fig. 5 TG coupled with EGA of BHC and HCA (5.2 deg/min heating rate)

Decomposition of BHC in aqueous solution

It has been reported, [10, 11] that both HCA and BHC may decompose in aqueous solution at different *pH* values. However, although decarboxylation did take place, only the corresponding polymers could be isolated, because decarboxylation was accompanied by homopolymerization of the decomposition products. The decomposition of BHC was faster in a basic medium than in an acidic one, and this suggested an anionic reaction mechanism involving formation of the BHC anion or dianion , which underwent further decarboxylation. Due to the steric hindrance of the tert-butyl groups, it was assumed that the dianion underwent a faster decomposition. Indeed, kinetic studies showed that at $pH = 8.5$ the decomposition of BHC was 2.5 times faster than that of HCA [11]. Because the attempts to obtain BHS by decarboxylation of aqueous solutions of BHC failed too, we studied BHC decomposition in organic solvents.

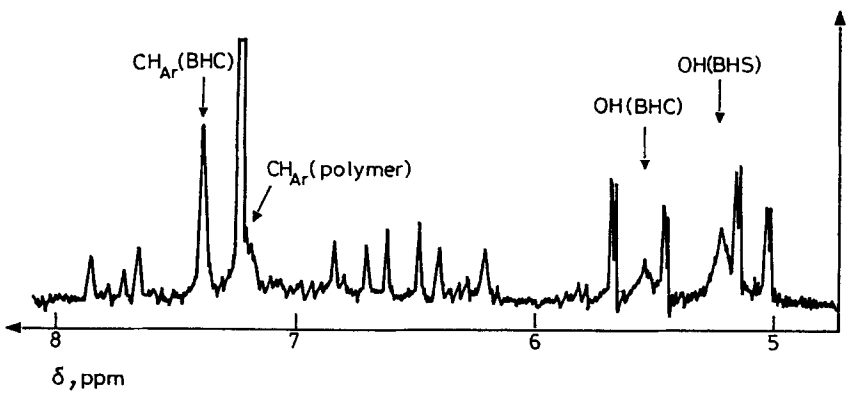


Fig. 6 ^{1}H–NMR spectrum of the BHC decomposition product (following heating for 3 min at 225°C)

Decomposition of BHC in organic solvents

The first attempts to decompose BHC in organic solvents were performed by refluxing solutions of 0.3-0.7 mol BHC/kg solvent. The BHC decomposition was followed by ^{1}H–NMR spectrometry by measuring the disappearance of the –CH=CH– bonds of BHS (δ =6.31 and 7.74 ppm) and the appearance of the –CH=CH$_2$ bonds of BHS (δ =5.07 and 5.54 ppm). First, we used nitrobenzene, because its boiling point (209°) is near the decomposition temperature of BHC in the solid-state (about 225°,

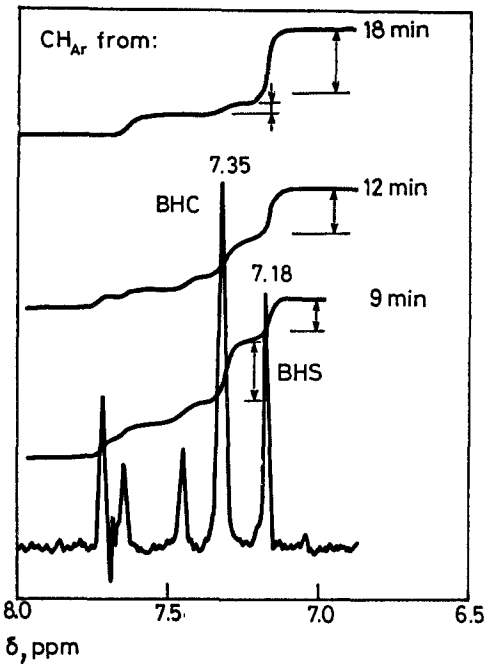


Fig. 7 ^{1}H-NMR spectra for the decomposition of BHC in d_6-DMSO solution at 121°C

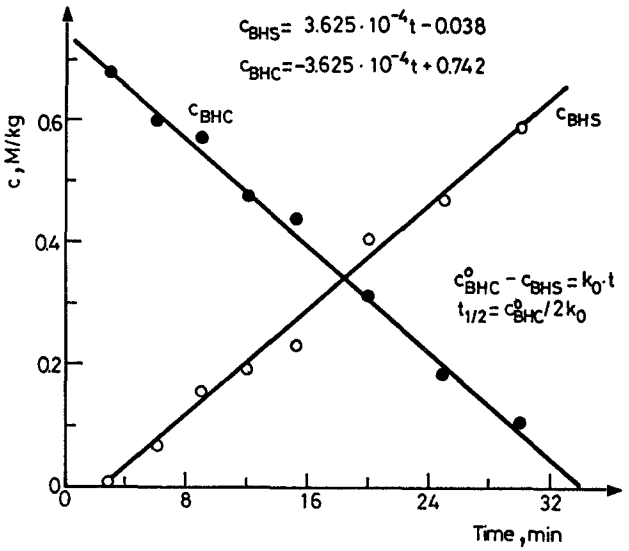


Fig. 8 Dependence of BHC and BHS concentrations on reaction time during the decomposition of BHC in d_6-DMSO solution at 109°C

with decomposition). A complete conversion of BHC was achieved in 5 minutes, but the decomposition was accompanied by polymerization, and after a 40-min, refluxing no more BHS monomer was found in the reaction mixture. This very fast decomposition is most probably an ionic one, because nitrobenzene is an aprotic dipolar solvent. Indeed, no decomposition occurred in a less polar solvent such as *o*-xylene (*o*-X), even following refluxing for one hour, i.e. at about 145°. Consequently, BHC decomposition has to be performed in a relatively polar solvent such as dimethylsulphoxide (DMSO) or dimethylformamide (DMF), but at temperature lower than 200° in order to avoid BHC desalkylation and the polymerization of BHS. The spectrum of a BHC solution in a 34:66 DMSO:*o*-X mixture demonstrated 100% BHC conversion to BHS and no polymerization of BHS following heating of the solution at 120° for 10 min.

A kinetic study of BHC thermal decomposition in various solvents and at different temperature was performed in order to establish the optimum reaction conditions. The rate of BHC decomposition in solution was measured by ^{1}H–NMR spectrometry, using the characteristic resonance lines of the aromatic protons from BHC, i.e. at $\delta = 7.35$ ppm, and from BHS, i.e. at $\delta = 7.18$ ppm (see, for example, Fig. 7). The concentrations of BHC and BHS in the reaction mixture were measured by using N,N-diethyl-o-methylcarbamate as internal standard, i.e. the resonance line of the $-OCH_3$ protons at $\delta = 3.47$ ppm (Fig. 7). Plots of both BHC and BHS concentrations *vs.* reaction time yielded linear relationships (Fig. 8). This behaviour corresponded to a zero-order reaction, i.e. $c^{\circ}_{BHC} - c_{BHC} = k_o \cdot t$, where c°_{BHC} and c_{BHC} are the initial concentration and the concentration of BHC after reaction time of t seconds, and k_o is the rate constant. For such a reaction, the half-time ($t_{1/2}$), i.e. the time required to decompose 50% of the BHC, is given by $t_{1/2} = c^{\circ}_{BHC}/2 \cdot k_o$.

The decomposition of BHC took place only in dipolar organic solvents such as DMSO and DMF, or in their mixtures with low polar solvents such as *o*-X (Table 2). The reaction rate decreased drastically with decreasing solvent polarity. Thus, at the same temperature, i.e. 130°, the decomposition rate was lower in DMF than in DMSO, because DMF is a less polar solvent than DMSO, and the decomposition was 27 times slower in the *o*-X:DMSO mixture than in DMSO. An Arrhenius type plot, i.e. $\log k_o = 7.806 - 4.71 \cdot 10^3/T$, was obtained by using the data for the decomposition of BHC in d_6–DMSO at different temperatures (Table 2). The high values found for the activation enthalpy ($\Delta H^{\#} = 87.5$ kJ/mol and entropy ($\Delta S^{\#} = -27.2$ J/mol·deg)

are typical for a thermal decomposition reaction involving the breaking of covalent bonds.

Table 2 Rate constant (k_o) and decomposition half-time ($t_{1/2}$) for the zero-order decarboxylation reaction of BHC

Temp., °C	Solvent	c^0_{BHC}, mol/kg	$k_o \cdot 10^3$, mol/kg·s	$t_{1/2}$, min.
97.5	d_6-DMSO	0.608	0.141	35.93
98	d_6-DMSO	0.587	0.152	32.13
109	d_6-DMSO	0.602	0.343	14.61
109	d_6-DMSO	0.721	0.362	16.58
120.5	d_6-DMSO	0.660	0.833	6.60
121	d_6-DMSO	0.614	0.866	5.91
122	d_6-DMSO	0.556	0.917	5.06
130	d_6-DMSO	0.651	1.585	3.42
130	d_6-DMSO	0.571	1.622	2.93
130	d_7-DMF	0.590	0.956	5.14
130	d_7-DMF	0.621	0.948	5.46
130.5	d_{10}-o-X:d_6-DMSO mixture (1:1)	0.645	0.059	90.86

For the above kinetic study, was used only BHC recrystallized from o-X. With BHC recrystallized from dioxane, the decomposition in solution was faster and a different solid-state decomposition was observed. The initial decomposition temperature decreased and the shape of the chromatogram changed. The experimental weight loss in the first decomposition interval approached theoretical value of 16% corresponding to the decarboxylation of BHC (Fig. 9).

We assumed a catalytic effect of BHC sodium salt (BHC^-) present as traces in the synthesized BHC. This salt is soluble in dioxane, but not in o-xylene. Organic bases such as pyridine, dimethylaniline and carbazole have no catalytic effect, but small amounts of alkali metal hydroxides and carbonates drastically increased the rate of decomposition of BHC. We therefore studied the decomposition of BHC in organic solvents and in the presence of its sodium salt (Table 3).

A linear relationship between the rate constant of the zero-order reaction and the salt concentration was obtained, i.e.

$$k_{exp} = k_o + k_1 \cdot [BHC^-],$$

where: k_{exp} and k_o are the rate constants in the presence and in the absence of the salt, respectively,
k_1 is the rate constant of the unimolecular reaction, and [BHC$^-$] is the concentration of the sodium salt.

For BHC decomposition in the 1:1 *o*-X:DMSO mixture at 130° (Table 3), we found $k_{exp} = 0.061 + 0.166$ [BHC$^-$].

Table 3 Rate constant (k_o) and decomposition half-time ($t_{1/2}$) for the zero-order decarboxylation reaction of BHC in the presence of its sodium salt (BHC$^-$) at 130°C in an 1:1 o-xylene:dimethylsulphoxide mixture

c^0_{BHC}, mol/kg	$c^0_{BHC} \cdot 10^3$, mol/kg	$k_o \cdot 10^3$, mol/kg·s	$t_{1/2}$, min.
0.645	–	0.059	90.86
0.302	1.65	0.326	7.72
0.270	3.70	0.669	3.36
0.340	4.52	0.820	3.39
0.274	5.35	0.942	2.42

Organic compounds rarely react by zero-order kinetics. However, the obtained experimental results may lead to the conclusion that the thermal decarboxylation of BHC in aprotic dipolar solvents took place by such a zero-order kinetic reaction. A reaction mechanism involving the following steps is proposed:

$$HO\text{–}X\text{–}CH=CH\text{–}COOH + S^- \rightleftarrows HO\text{–}X\text{–}CH=CH\text{–}COO^- + SH^+ \quad (1)$$

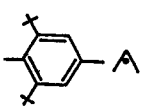
$$HO\text{–}X\text{–}CH=CH\text{–}COO^- \rightarrow HO\text{–}X\text{–}CH=CH: + CO_2 \quad (2)$$

$$HO\text{–}X\text{–}CH=CH^- \rightleftarrows {}^-O\text{–}X\text{–}CH=CH_2 \quad (3)$$

$$HO\text{–}X\text{–}CH=CH\text{–}COOH + {}^-O\text{–}X\text{–}CH=CH_2 \rightarrow$$

$$HO\text{–}X\text{–}CH=CH\text{–}COO^- + HO\text{–}X\text{–}CH=CH_2 \quad (4)$$

where S is an aprotic dipolar solvent such as DMSO and DMF, and X is



The mechanism assumes the ionization of BHC in the aprotic dipolar solvent (reaction 1). The resulting BHC anion decomposes slowly by decarboxylation, forming the BHC carbanion (reaction 2), which undergoes fast tautomerization to the BHS anion (reaction 3). The BHS anion is a stronger base than the solvent *S*, and therefore abstracts a proton from BHC during the fast reaction step (reaction 4). The proposed mechanism is supported by the following experimental results: the thermal decarboxylation reaction took place by zero-order kinetics, but only in aprotic dipolar solvents; the dependence on the sodium salt concentration; the values of the activating parameters.

The results obtained led to the following preparative method for the synthesis of BHS. A solution of 10 g BHC in 10 ml DMF was heated at 135-140° until no CO_2 was evolved, i.e. about 30 min. The reaction mixture was then poured into an ice-bath. Following separation from the aqueous solution, the upper, organic layer was treated again with cold water and maintained in

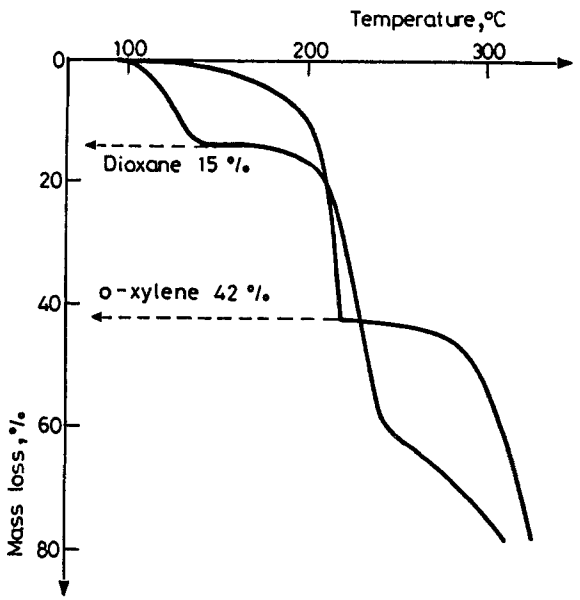


Fig. 9 Weight losses during the solid-state decomposition of BHC recrystallized from dioxane and o-xylene (thermoanalytical curves at 5 deg/min heating rate, 100 mg·sample weight, 5 l/h nitrogen stream)

refrigerator at about 4° for 24 hours. Following filtration and drying, 8 g BHS was obtained (95% yield).

Conclusions

Attemps were made to synthesize the BHS monomeric antioxidant by the thermal decarboxylation of BHC in the solid-state, in aqueous solution and in solutions in organic solvents. Only BHC decomposition in aprotic dipolar solvents such as DMSO and DMF, at temperatures lower than 150°, could be used as a preparative method for the synthesis of BHS. The decarboxylation of BHC took place by zero-order kinetics through a mechanism involving the ionization of BHC in the aprotic dipolar solvent. Therefore, the reaction rate increased drastically with increasing solvent polarity and in the presence of trace amounts of BHC sodium salt.

Both monomeric antioxidants (BHS and BHC) were used to obtain polymer-bound antioxidants, e.g. grafted polyethylenes. Thus, BHS was melt-grafted onto PE chains in the presence of organic peroxides. The solid-state decomposition of BHC was used for the "in situ" formation and grafting of BHS onto PE. In the presence of trace amounts of its sodium salt, BHC decomposed in the PE melt at about 150° and the resulting BHS was grafted onto PE chains [12, 13].

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Zusammenfassung — Für die Ausarbeitung eines Verfahrens zur Herstellung des monomeren Antioxidans 3,5-Di-terc-butyl-4-hydroxystyrol (BHS) wurde die thermische Zersetzung von *trans*-3,5-Di-terc-butyl-4-hydroxyzimtsäure (BHC) im festen Zustand, in wäßriger Lösung und in Lösungen mit organischen Lösungsmitteln untersucht. Thermoanalytische Verfahren zeigten, daß bei der Feststoffzersetzung von BHC ihre Decarboxylierung durch Desalkylierung und durch Polymerisierung der Styrol-Zersetzungsprodukte begleitet wird. Auch die BHC-Decarboxylierung in wäßriger Lösung wurde durch Polymerisierung begleitet. Mittels ^{1}H-NMR Spektroskopie angefertigte kinetische Studien der Zersetzung von BHC in organischen Lösungsmitteln zeigten, daß die Zersetzung von BHC nur in aprotischen dipolaren Lösungsmitteln, wie z.B. in Dimethylsulfoxid und Dimethylformamid und nur bei Temperaturen unterhalb von 150C als präparatives Verfahren zur Synthese von BHS geeignet ist. Die Decarboxylierung von BHC verlief nach einer Reaktionsordnung 0-ter Ordnung, am Mechanismus ist die Ionisierung von BHC im aprotischen dipolaren Lösungsmittel beteiligt. Die Reaktionsgeschwindigkeit wird mit steigender Lösungsmittelpolarität und in Gegenwart von Spuren von BHC-Natriumsalz drastisch angehoben. Beide monomeren Antioxidationsmittel, d.h. BHS und BHC, können verwendet werden, um Polymerbindungs-Antioxidationsmittel herzustellen, z.B. durch Schmelz-Aufpolymerisieren auf Polyethylen.