Thermal Decomposition of Some Phenolic Antioxidants

Anwar A. Hamama† and Wassef W. Nawar*

Department of Food Science, University of Massachusetts, Amherst, Massachusetts 01003

The loss of antioxidants at elevated temperatures occurs as a result of both evaporation and decomposition. The stability of four phenolic antioxidants at 185 °C was examined by TLC and gas chromatography and found to be in the order BHT > PG > BHA > TBHQ. Several products arising from thermal oxidation of the antioxidants were separated and identified by gas chromatography/mass spectrometry and mechanisms for their formation suggested.

INTRODUCTION

Antioxidants play an important role in manufacturing, packaging, and storage of fats and fatty foods. Numerous compounds have been evaluated as antioxidants in fats, oils, and fatty foods by various investigators (Stuckey, 1962; Uri, 1961, Chipault, 1962; Thompson and Sherwin, 1966; Sherwin and Thompson, 1967).

The phenolic compounds, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and *tert*-butylhydroquinone (TBHQ), originally developed for petroleum protection, were authorized in the United States as antioxidants for use in food (Marino and Mitchell, 1972; Pascal; 1974, Astill et al., 1975; Branen, 1975; Saheb and Saheb, 1977; Hansen and Meyer, 1978; Porter, 1987). The addition of these compounds is subject to government regulations and varies with type of food. In general, the total amount of antioxidants that may be used, alone or in combination, is limited to 0.02% or less by weight of the fat content of the food.

Although both the effectiveness and the biological impact of phenolic antioxidants have been evaluated (Marino and Mitchell, 1972; Pascal, 1974; Astil et al., 1975; Branen, 1975; Saheb and Saheb, 1977; Hansen and Meyer, 1978; Buck, 1981; Sherwin, 1985), the effects of their interaction with food components during food processing have not been thoroughly studied.

Recently attention has been focused on the amount of phenolic antioxidants remaining unchanged or retained by the oil after deep-fat frying. This varied widely, i.e., 1–85% of the original substrate, depending on the stability of the antioxidant, techniques employed, and frying conditions (Furia and Bellanca, 1977; Lin et al., 1981; Fritsch, 1981; Stevenson et al., 1984; Warner et al., 1986; Kim and Pratt, 1988).

There have been only a few papers concerning the detection, isolation, and identification of the decomposition products of antioxidants in food matrices. Mihara et al. (1974) identified diphenylethane and diphenyl ether derivatives of BHA in soybean oil after prolonged exposure to sunlight. Leventhal et al. (1976) reported the formation of a stilbenylquinone derivative of BHT in vegetable oils heated at 190 °C for 11 days. Lin et al. (1981) reported the decomposition of BHA and BHT in partially hydrogenated vegetable oil heated at 190 °C for 4.5 h. Moreover, the photochemically induced oxidations of BHA and BHT (Kurechi and Kato, 1980), BHA and PG (Kurechi and Kunugi, 1983a), and TBHQ (Kurechi et al., 1983; Kurechi and Kunugi, 1983b) have been reported. The structure and antioxidant activity of some photolytic oxidation products isolated from phenolic antioxidants were examined (Kurechi, 1967, 1969; Taki and Kurechi, 1977; Kurechi et al., 1981; Kurechi and Kunugi, 1983a,b).

Studies with ^{14}C ring-labeled BHA, BHT, and TBHQ were also carried out to investigate the fate of these antioxidants and the associated decomposition products in deep-fat frying and cookie packing (Warner et al., 1986). The results indicated that all three antioxidants underwent extensive decomposition in deep-fat frying. 2,6-Di-*tert*-butylbenzoquinone was found to be a major degradation

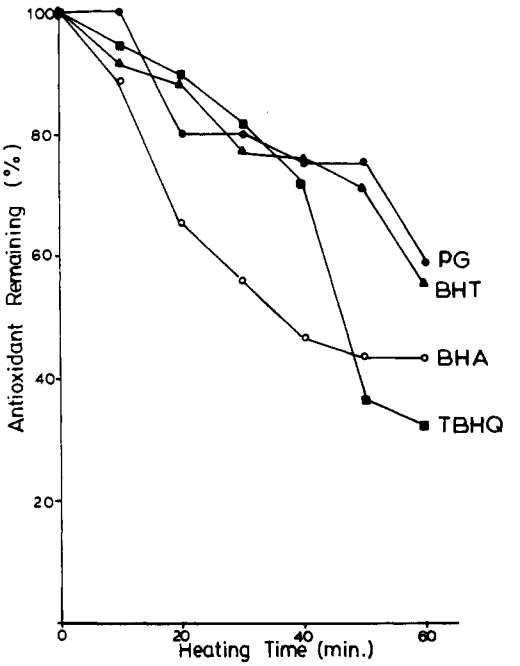

Figure 1. Loss of antioxidants (from TLC analysis) as a function of heating time at 185 °C. PG, propyl gallate; BHT, butylated hydroxytoluene; BHA, butylated hydroxyanisole; TBHQ, *tert*-butylhydroquinone.

Table I. Fate of Antioxidants[a] after Heating for 1 h at 185 °C

antioxidant	unaltered, % nonvolatile[a]	volatile	total	altered,[b] %
BHA	43.9	13.3	57.2	42.8
BHT	55.2	24.4	79.6	20.4
PG	59.8	3.1	62.9	37.1
TBHQ	32.1	20.2	52.3	47.7

[a] From TLC analysis. [b] Calculated by difference.

* To whom correspondence should be addressed.
† Permanent address: Department of Biochemistry, Faculty of Agriculture, University of Cairo, Giza, Egypt.

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Table II. Characteristic MS Fragment Ions of Some Volatile Compounds from Heated BHA

peak no.	Rt	fragment ions, m/z (rel abundance, %)	tentative ID
1	43.61	121 (100), 164 (90.2), 93 (85.4), 149 (78), 54 (68.3), 77 (48.8), 108 (34.1)	3-methyl-2,3-dihydro-5-methoxybenzo[*b*]furan
2	107.06	287 (100), 358 (74.6), 302 (52.6), 57 (49.5), 246 (40.5), 272 (22.0), 255 (17.6)	2,4′-di-*tert*-butyl-5′-hydroxy-2′,4-dimethoxydiphenyl ether
3	117.4	149 (100), 164 (55.1), 358 (42.6), 57 (24.8), 302 (18.3), 179 (13.0)	2,3′-di-*tert*-butyl-2′-hydroxy-4,5′-dimethoxydiphenyl ether
4	121.73	287 (100), 358 (89.9), 57 (72.9), 302 (65.1), 246 (40.4), 272 (22.0), 325 (22.0), 255 (19.0), 340 (18.8), 41 (18.3), 136 (17.6)	2,2′-dihydroxy-5,5′-dimethoxy-3,3′-di-*tert*-butylbiphenyl (DHDP)
5	125.50	358 (100), 343 (63.8), 287 (51.5), 325 (40.3), 57 (40.1), 340 (32.6), 302 (22.7), 136 (21.6), 150 (18.4), 272 (15.0), 246 (13.3)	2,3′-dimethoxy-2′,5-dihydroxy-3′,4-di-*tert*-butylbiphenyl
6	127.97	358 (100), 343 (64.3), 325 (59.4), 340 (52.6), 287 (47.0), 57 (37.1), 302 (24.1), 272 (12.5), 246 (12.0)	5,5′-dihydroxy-2,2′-dimethoxy-4,4′-di-*tert*-butyldiphenyl

Table III. Characteristic MS Fragment Ions of Some Volatile Compounds from Heated BHT

peak no.	Rt	fragment ions, m/z (rel abundance, %)	tentative ID
1	54.91	149 (100), 121 (80.1), 164 (35.8), 91 (19.6), 77 (16.6), 51 (4.4)	2-*tert*-butyl-4-methylphenol
2	64.60	161 (100), 203 (61.0), 218 (43.9), 175 (36.6), 91 (22.0), 189 (17.1), 128 (14.6), 77 (12.2)	5-methyl-7-*tert*-butyl-2,2-dimethyl-2,3-dihydrobenzo[*b*]furan
3	81.21	219 (100), 191 (31.3), 234 (25.6), 57 (10.6)	2,6-bis(1,1-dimethylethyl)-4-methyl-1-methoxybenzene
4	121.00	177 (100), 191 (59.3), 161 (54.1), 382 (28.1), 57 (27.6), 176 (23.2), 148 (21.6), 206 (21.2), 367 (17.4), 326 (15.8), 91 (14.4)	3,5,3′-tri-*tert*-butyl-4,4′-dihydroxydiphenyl)ethane
5	149.06	219 (100), 57 (9.1), 203 (5.5), 438 (3.7), 161 (3.1)	1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane

product of BHA and TBHQ, while BHT formed an alkylperoxyl derivative (Kim and Pratt, 1988).

The purpose of the present work was to investigate the loss of phenolic antioxidants at elevated temperature in some detail.

MATERIALS AND METHODS

Reagents. BHA, BHT, PG, TBHQ, and *p*-hydroxybenzoic acid *n*-butyl ester were purchased from Sigma Chemical Co. and used without further purification.

Heat Treatment. *Nonvolatile Fraction.* Samples of BHA, BHT, PG, and TBHQ (100 mg each) were individually placed in 10-mL test tubes and heated in air at 185 °C for 0, 10, 20, 30, 40, 50, and 60 min. The tubes were then cooled to room temperature and their contents dissolved in 1 mL of ethyl acetate.

Volatile Fraction. Samples of BHA, BHT, PG, and TBHQ (100 mg each) were placed in 250-mL round-bottom flasks, which were then securely capped and heated in a silicon oil bath at 185 °C for the same lengths of time as above. After heating, the flasks were allowed to cool and the volatiles collected by high-vacuum cold finger distillation as described previously (Nawar et al., 1969). The volatiles were then dissolved in 10 mL of ethyl acetate containing 5 mg of *p*-hydroxybenzoic acid *n*-butyl ester as an internal standard for quantitation and concentrated to 1 mL under a low stream of N_2.

A separate sample was placed in a 150-mL round-bottom flask connected with an ethyl acetate double trap. The latter system was used for the determination of unaltered antioxidant in both the volatile and nonvolatile fractions.

An aliquot, 1–5 μL each, of the volatile and nonvolatile concentrates was subjected to TLC, GC, and GC/MS analyses as described below. The combined value of the volatile and nonvolatile intact antioxidant was expressed as total unaltered substrate. The amount of antioxidant altered by heating was calculated by difference.

Thin-Layer Chromatography (TLC). Separation was carried out on 0.25 mm (20 cm × 20 cm) silica gel coated plates. The following solvent systems were used: chloroform/methanol (19:1 v/v) for TBHQ (Kurechi and Kunugi, 1983b); hexane/toluene (1:1 v/v) for BHT (Kurechi and Kato, 1980); and chloroform/methanol/acetic acid (90:4:4 v/v) for BHA and PG (Kurechi and Kunugi, 1983a). A solution of 3% $Cu(CH_3COO)_2$ in 8.5% $HClO_4$ was used as a color developing agent. For quantitation, a Kontes densitometer was used.

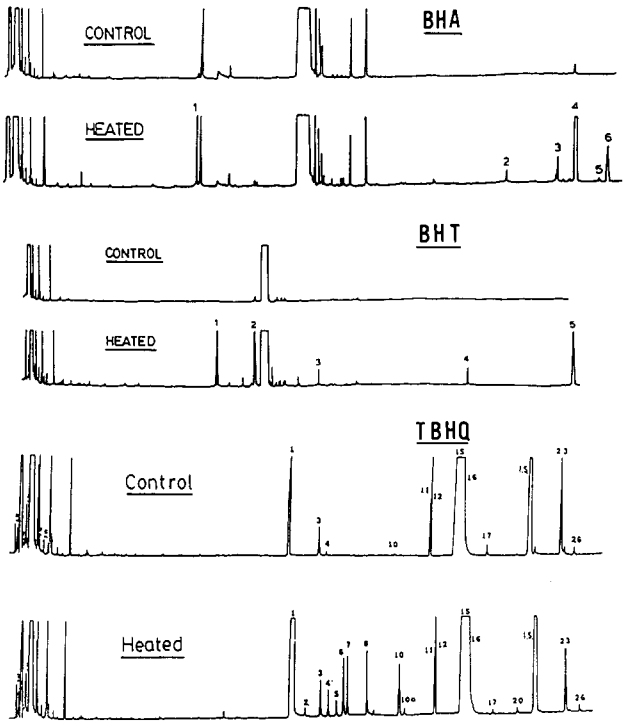


Figure 2. Gas chromatographic analysis of the volatile decomposition products of BHA, BHT, and TBHQ after heating at 185 °C for 1 h. Peak numbers correspond to those in Tables II–IV. Peaks listed in the tables but not seen in the figure represent trace compounds requiring further concentration and separate GC analysis.

Gas Chromatography/Mass Specrometry. One-microliter samples of the volatile fraction were analyzed in a Perkin-Elmer Model 3920 B gas chromatograph on a 40 m × 0.32 mm (i.d.) HP-1 fused silica capillary column. Stationary phase film thickness was 1.05 μm (Hewlett-Packard Co., Avondale, PA). Helium was used as a carrier gas at a flow rate of 1.85 mL/min.

Table IV. Characteristic MS Fragment Ions of Some Volatile Compounds from Heated TBHQ

peak no.	Rt	fragment ions, m/z (rel abundance, %)	tentative ID
1	45.32	121 (100), 149 (90.2), 93 (56.1), 164 (48.8), 77 (46.3), 108 (24.4), 54 (24.8)	2-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (2-*tert*-butyl-*p*-benzoquinone or TBBQ)
2	46.70	57 (100), 124 (73.7), 96 (42.9), 41 (32.7), 149 (16.1), 109 (11.1), 164 (8.8)	2,2-dimethyl-2,3-dihydro-5-hydroxybenzo[*b*]furan
3	48.73	110 (100), 81 (25.7), 54 (15.2)	1,4-benzenediol (hydroquinone)
4	49.90	123 (100), 109 (100), 59 (52.8), 67 (50.3), 166 (49.5), 151 (24.9), 82 (22), 55 (21.5), 41 (19.8)	2-(1-methylethyl)-5-methyl-1,4-benzenediol
5	51.03	109 (100), 67 (99.2), 137 (95.4), 95 (75), 79 (50.8), 41 (45.7), 55 (26.5), 152 (21.5), 161 (16.5), 180 (2.2)	2-(2-methylpropyl)-6-methyl-1,4-benzenediol
6	51.99	137 (100), 180 (98.3), 165 (89.4), 82 (57.7), 91 (47.4), 55 (45.9), 69 (40.9), 119 (38.7), 109 (38.0), 39 (21.6)	2-(2-methylpropyl)-5-methyl-1,4-benzenediol
7	52.53	69 (100), 138 (91.3), 165 (53.3), 180 (45.7), 123 (35.9), 53 (32.6), 98 (30.4), 109 (27.2), 152 (23.9)	2-(2-methylpropyl)-3-methyl-1,4-benzenediol
8	55.29	165 (100), 137 (69.9), 69 (66.5), 180 (65.3), 109 (44.2), 67 (39.9), 79 (32.7), 53 (30.9), 91 (29.8), 41 (27.7), 123 (22.0), 147 (16.5)	2-(2-methyl-2-hydroxypropyl)-*p*-benzoquinone
9	56.22	124 (100), 57 (38.7), 96 (34.6), 69 (18.3), 152 (14.6), 41 (13.2), 137 (3.7), 165 (2.0), 180 (2.0)	3-(2-methylpropyl)-4-methoxyphenol
10	59.81	164 (100), 149 (94.5), 121 (43.3), 77 (17.6), 91 (14.4), 107 (10.9), 65 (10.6), 55 (9.7), 135 (5.9)	2-(2-methyl-1-propenyl)-1,4-benzenediol
10A	60.59	149 (100), 121 (79.0), 164 (68.8), 103 (22.0), 77 (17.2), 91 (16.7), 53 (14.5)	2-(2-methyl-2-propenyl)-1,4-benzenediol
10B	61.89	123 (100), 151 (97.1), 166 (53.4), 94 (19.4), 77 (17.5), 136 (12.6)	2-(1-methylethyl)-6-methyl-1,4-benzenediol
11	65.0	151 (100), 123 (96.9), 166 (57.6), 77 (16.1), 107 (11.5), 55 (9.9), 93 (9.7)	2-(2-methylpropyl)-1,4-benzenediol
12	65.16	205 (100), 163 (92.7), 220 (90.5), 177 (78.8), 135 (52.3), 67 (50.1), 91 (44.7), 41 (38.8), 149 (37.9), 77 (33.9), 121 (31.2), 107 (26.8), 53 (25.0), 191 (7.4)	2,6-bis(1,1-dimethylethyl)-*p*-benzoquinone (DBBQ)
12A	71.61	205 (100), 51 (43.9), 91 (26.8), 105 (22.0), 145 (22.0), 220 (20.0), 177 (19.5), 41 (17.1)	2,5-bis(1,1-dimethylethyl)-*p*-benzoquinone
20	77.34	124 (100), 149 (82.9), 164 (53.7), 182 (35.0), 95 (17.1), 77 (14.6), 43 (14.6), 107 (12.2), 135 (4.9)	2-(2-methyl-2-hydroxypropyl)-1,4-benzenediol
22	83.40	188 (100), 205 (8.4), 160 (8.4), 41 (8.4), 178 (7.2), 94 (7.2), 56 (6.0), 220 (1.2)	2,2-dimethyl-2,3-dihydro-5-hydroxy-7-(1,1-dimethylethyl)benzo[*b*]furan
23	84.37	207 (100), 220 (28.5), 151 (7.2), 123 (5.7), 91 (5.7), 77 (4.3), 57 (2.9), 41 (2.9)	2,6-bis(1,1-dimethylethyl)-1,4-benzenediol
24	84.90	205 (100), 222 (39.0), 177 (19.5), 91 (14.6), 149 (12.2), 123 (12.2), 163 (9.8), 77 (7.3), 55 (4.9)	2-(2-methyl-1-propenyl)-6-(1,1-dimethylethyl)-1,4-benzenediol
25	85.40	149 (100), 205 (77.8), 123 (72.2), 101 (61.1), 173 (50.0), 164 (44.4), 59 (44.4), 220 (36.6), 43 (27.8), 91 (22.2), 77 (16.7), 191 (5.6)	2-(2-methyl-2-propenyl)-6-(1,1-dimethylethyl)-1,4-benzenediol
26	86.41	151 (100), 123 (38.9), 222 (16.6), 191 (8.3), 77 (8.3), 57 (8.3), 164 (5.6), 41 (5.6), 207 (2.8)	2,5-bis(1,1-dimethylethyl)-1,4-benzenediol
30	90.26	205 (100), 165 (83.3), 238 (55.6), 220 (44.4), 100 (38.9), 149 (33.3), 123 (33.3), 137 (27.8), 180 (27.8), 91 (22.2), 77 (22.2), 55 (22.2), 191 (5.6), 212 (2.8)	2-(2-methyl-2-hydroxypropyl)-6-(1,1-dimethylethyl)-1,4-benzenediol

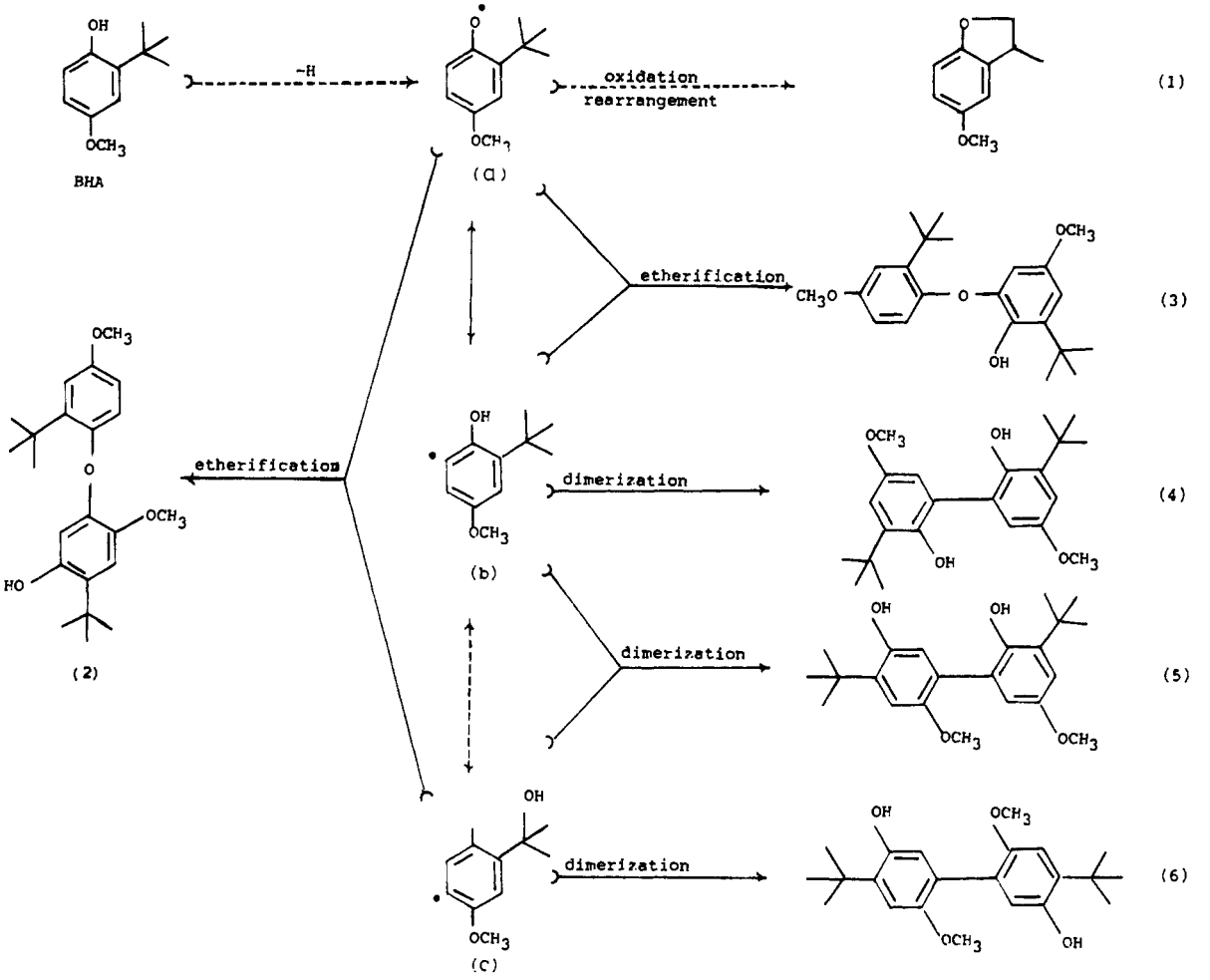
Split ratio (with a custom-made splitter attachment) was 1:50. The oven temperature was programmed from 50 to 270 °C at 2 °C/min. For identification, a Hewlett-Packard Model 5985 B gas chromatography/mass spectrometry (GC/MS) system was used. A constant head pressure of 5 psi was maintained on the column, and sample injection was made by using a Grob-type split/splitless injector operated in the splitless mode.

RESULTS AND DISCUSSION

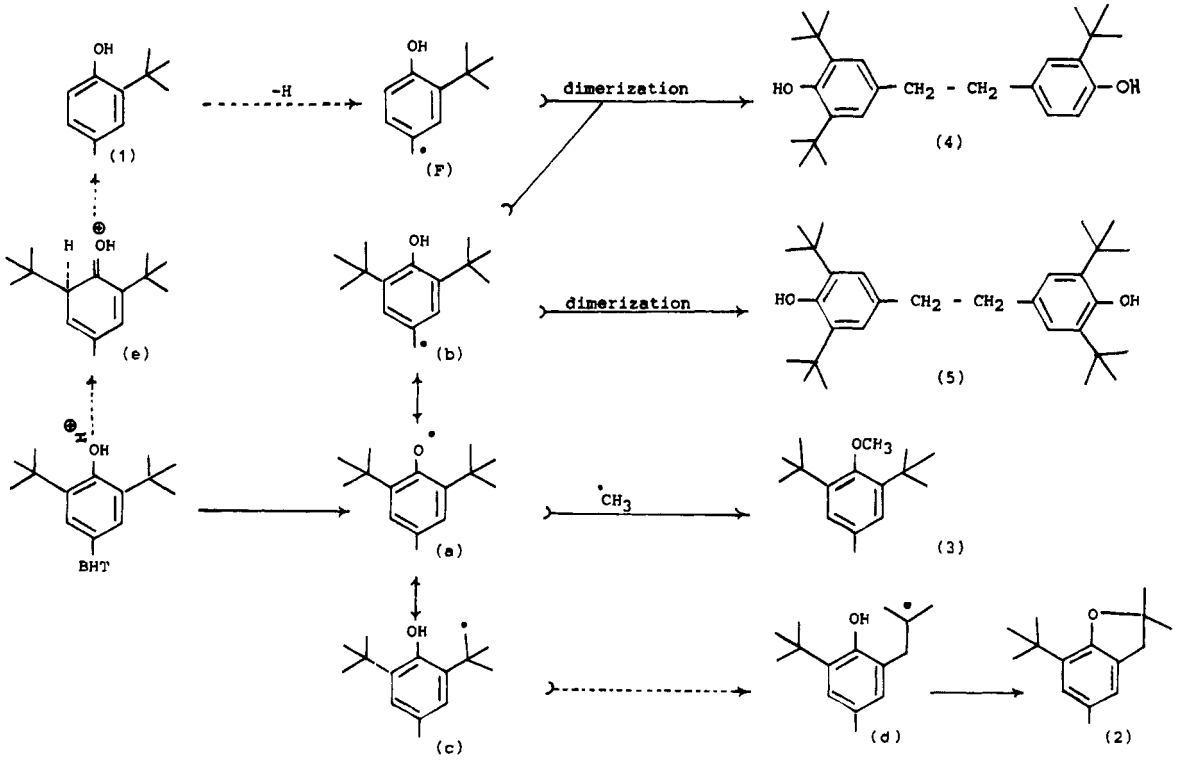
Loss of Antioxidants by Heat. Of the four antioxidants heated at 185 °C, BHA exhibited the highest rate of loss, with approximately half remaining after 45 min (Figure 1). BHT and PG exhibited a similar rate of loss, while the curve for TBHQ became relatively steep after 40 min. Beyond this point, its loss appeared to surpass that of BHA.

It should be pointed out that these antioxidants possess varying degrees of volatility. Obviously, the loss of a given antioxidant at such elevated temperatures results from evaporation as well as chemical decomposition. To determine the nature of this loss in each case, the unaltered antioxidant after 1 h of heating was quantitated in both the volatile and nonvolatile phases (Table I). While PG showed relatively low volatility, approximately one-fifth and one-fourth of the original amounts of TBHQ and BHT, respectively, were lost by evaporation. BHA displayed

Scheme I. Reaction Mechanisms Proposed for Thermal Decomposition of BHA



Scheme II. Reaction Mechanisms Proposed for Thermal Decomposition of BHT



medium volatility. The stability of these antioxidants against thermal oxidation was in the order BHT > PG > BHA > TBHQ. This was confirmed by thin-layer chromatography (TLC data not shown). BHT and PG gave rise to very few decomposition products as compared to BHA and TBHQ. Obviously the decomposition products

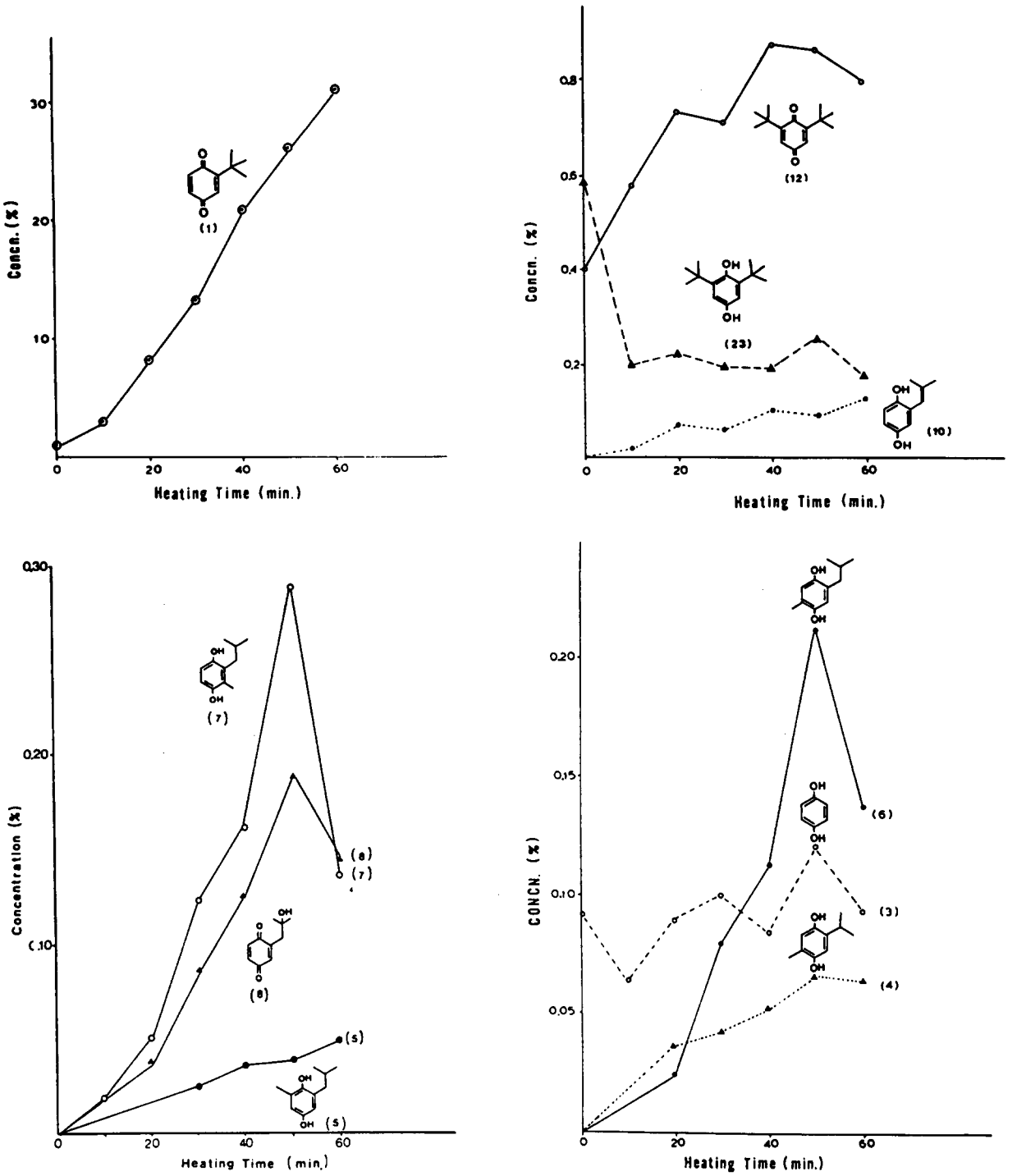


Figure 3. Effect of heating time at 185 °C on the amounts of some decomposition products of TBHQ.

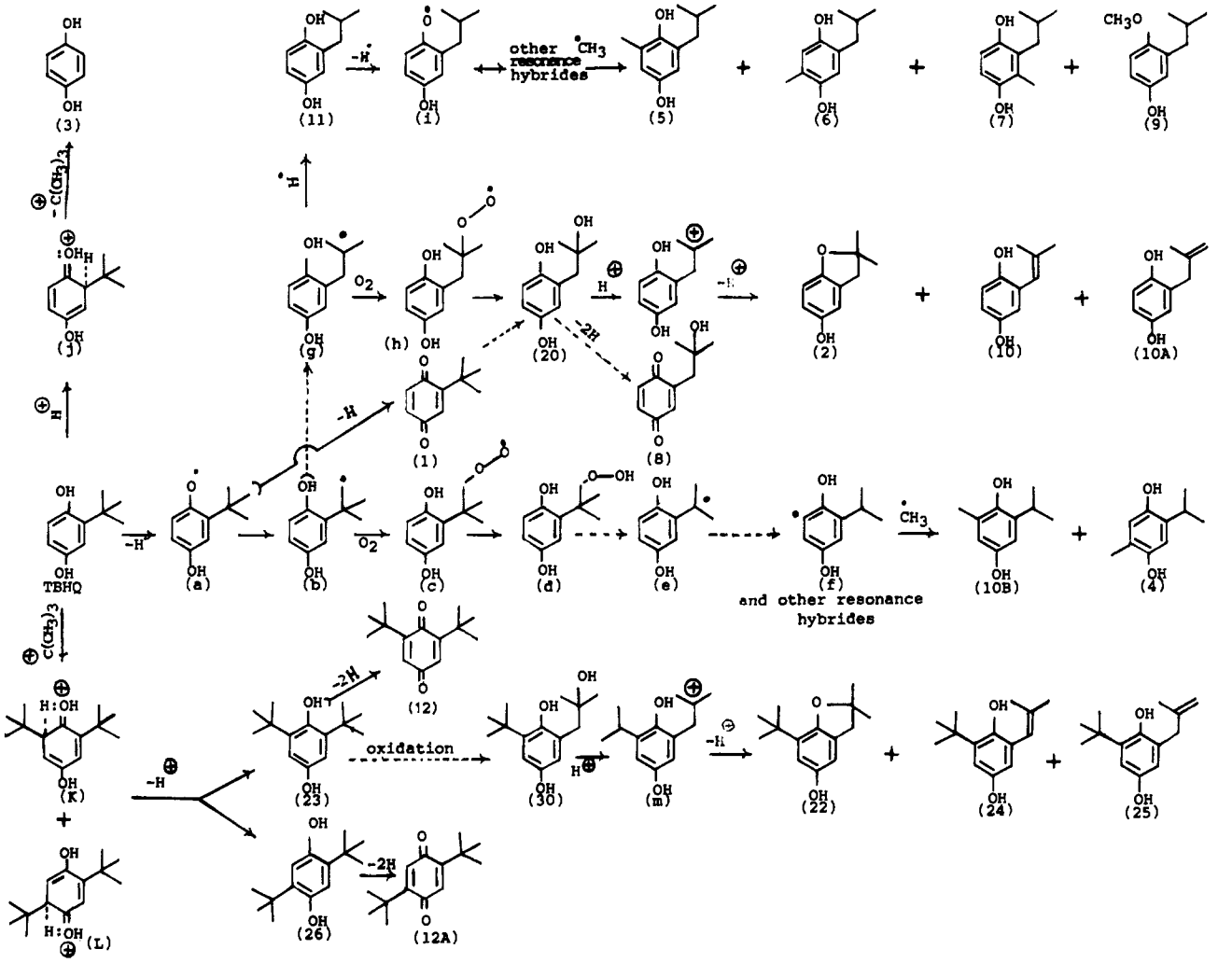
include both volatile (Figure 2) and nonvolatile compounds.

Identification and Mechanisms. Gas chromatographic analysis of the volatiles from BHA, BHT, and TBHQ after 1 h of heating is shown in Figure 2. Mass spectral data are given in Tables II–IV. The major peak in each gas chromatogram is that of the substrate. Since the volatile fraction of PG contained very few peaks at low intensity (data not shown here), no effort was made to identify them. While most of the decomposition products of BHA and BHT had retention times longer than those of their substrates, those from TBHQ eluted prior to the substrate.

BHA. Of the compounds produced from BHA by heat only six were formed in quantities sufficient for tentative identification (Figure 2). Two compounds, 2,3′-di-*tert*-butyl, 2′-hydroxy, 4,5′-dimethoxydiphenyl ether (**3**), and 2,2′-dihydroxy-5,5′-dimethoxy-3,3′-di-*tert*-butylbiphenyl (**4**), were identified previously by other workers (Kurechi and Kato, 1980). A mechanism for the thermal decomposition of BHA is given in Scheme I. The antioxidant loses a hydrogen atom, giving rise to the free-radical species a–c. Oxidation of radical a produces compound 1, while various recombinations of the resonant hybrid result in the formation of the dimeric products.

BHT. Abstraction of a hydrogen atom from the antioxidant generates free-radical resonant species a–d (Scheme II). Free-radical combinations yield products **3–5**. Compound **5** was previously identified (Leventhal et al., 1976; Kim and Pratt, 1988). Compound **2** may result by rearrangement of free radical d. Formation of com-

Scheme III. Reaction Mechanisms Proposed for Thermal Decomposition of TBHQ



pound 1 could be attributed to the action of H^+ catalyzing the elimination of the *tert*-butyl group.

TBHQ. Although several compounds could be detected in the unheated control, it is clear that this antioxidant underwent extensive degradation and gave rise to numerous decomposition products (Figure 2). Most of these compounds significantly increased with heating time (Figure 3). Compound **23**, however, was present in the control, but its concentration declined with heating. This compound may be a heat-labile TBHQ decomposition product which was formed before heating. Its decomposition upon heating may lead to the generation of compound **12** as suggested by the curves in Figure 3 (upper right). Proposed reaction mechanisms are given in Scheme III. Oxidation of TBHQ produces compound 1. Kurechi and Kunugi (1983b) suggested that compound 1 can transform via a complex mechanism to compound **20**. It can be theorized that compound **20** can undergo further oxidation leading to the formation of products **2**, **10**, **10A**, and **8**.

Various free-radical species from TBHQ recombine to produce higher molecular weight products, e.g., compounds **5–7** and **9**. Compounds **10B** and **4** may result via peroxidation of free-radical species b.

In the presence of H^+, TBHQ may decompose to form compound **3** and a carbonium ion $^+C(CH_3)_3$ which may attack another molecule of TBHQ to form products **23** and **26**. These may in turn be further oxidized to give compounds **12** and **12A**. Furthermore, compound **23** may undergo a series of rearrangement and oxidation reactions leading to the formation of products **30**, **22**, **24**, and **25**.

Figure 3 shows the change in concentration of some TBHQ decomposition products with heating time. Most of the volatile compounds reached their maximum levels after 40–50 min of heating at 185 °C, and then their amounts declined, reflecting the decomposition of such intermediates to generate other oxidation products. Indeed, both the formation and the destruction of the decomposition products may be occurring simultaneously but at different rates (Figure 3). Hence, the level of any given decomposition product will vary significantly with heating time. This is consistent with the reaction schemes discussed above.

Mechanisms similar to those proposed here were postulated by Orlando et al. (1967, 1968), Kurechi and Kato (1980), and Kurechi and Kunagi (1983a,b) in their work with photooxidation.

It is clear from this study that phenolic antioxidants exhibit significant decomposition at elevated temperatures and give rise to a number of breakdown products which in turn can further decompose. Since the levels of antioxidants allowed in food are relatively low, the amounts of decomposition products formed would be expected to be extremely small. Further studies are needed to evaluate the antioxidant and biological properties of these compounds.

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Registry No. BHA, 25013-16-5; BHT, 128-37-0; PG, 121-79-9; TBHQ, 1948-33-0; 3-methyl-2,3-dihydro-5-methoxybenzo[*b*]furan, 133447-17-3; 2,4-di-*tert*-butyl-5′-hydroxy-2,4′-dimethoxydiphenyl ether, 133447-18-4; 2,3′-di-*tert*-butyl-2′-hydroxy-4,5′-dimethoxydiphenyl ether, 20236-47-9; 2,2′-dihydroxy-5,5′-dimethoxy-3,3′-di-*tert*-butylbiphenyl, 14078-41-2; 2,3′-dimethoxy-2,5′-dihydroxy-3′,4-di-*tert*-butylbiphenyl, 133447-19-5; 5,5′-dihydroxy-2,2′-dimethoxy-4,4′-di-*tert*-butylbiphenyl, 133447-20-8; 2-*tert*-butyl-4-methylphenol, 2409-55-4; 5-methyl-7-*tert*-butyl-2,2-dimethyl-2,3-dihydrobenzo[*b*]furan, 133447-21-9; 2,6-bis(1,1-dimethylethyl)-4-methyl-1-methoxybenzene, 1518-53-2; 3,5,3′-tri-*tert*-butyl-4,4′-dihydroxydiphenylethane, 133447-22-0; 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane, 1516-94-5; 2-(1-methylethyl)-6-methyl-1,4-benzenediol, 133447-23-1; 2-(2-methylpropyl)-1,4-benzenediol, 4197-78-8; 2,6-bis(1,1-dimethylethyl)-*p*-benzoquinone, 719-22-2; 2,5-bis(1,1-dimethylethyl)-*p*-benzoquinone, 2460-77-7; 2-(2-methyl-2-hydroxypropyl)-1,4-benzenediol, 35205-16-4; 2,2-dimethyl-2,3-dihydro-5-hydroxy-7-(1,1-dimethylethyl)benzo[*b*]furan, 17075-82-0; 2,6-bis(1,1-dimethylethyl)-1,4-benzenediol, 2444-28-2; 2-(2-methyl-1-propenyl)-6-(1,1-dimethylethyl)-1,4-benzenediol, 133447-24-2; 2-(2-methyl-2-propenyl)-6-(1,1-dimethylethyl)-1,4-benzenediol, 133447-25-3; 2,5-bis(1,1-dimethylethyl)-1,4-benzenediol, 2444-28-2; 2-(2-methyl-2-hydroxypropyl)-6-(1,1-dimethylethyl)-1,4-benzenediol, 133447-26-4; 2-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione, 3602-55-9; 2,2-dimethyl-2,3-dihydro-5-hydroxybenzo[*b*]furan, 6956-76-9; 1,4-benzenediol, 123-31-9; 2-(1-methylethyl)-5-methyl-1,4-benzenediol, 2217-60-9; 2-(2-methylpropyl)-6-methyl-1,4-benzenediol, 133447-27-5; 2-(2-methylpropyl)-5-methyl-1,4-benzenediol, 133447-28-6; 2-(2-methylpropyl)-3-methyl-1,4-benzenediol, 133447-29-7; 2-(2-methyl-2-hydroxypropyl)-*p*-benzoquinone, 35205-34-6; 3-(2,2-dimethylethyl)-4-methoxyphenol, 78805-56-8; 2-(2-methyl-1-propenyl)-1,4-benzenediol, 133447-30-0; 2-(2-methyl-2-propenyl)-1,4-benzenediol, 38149-52-9.