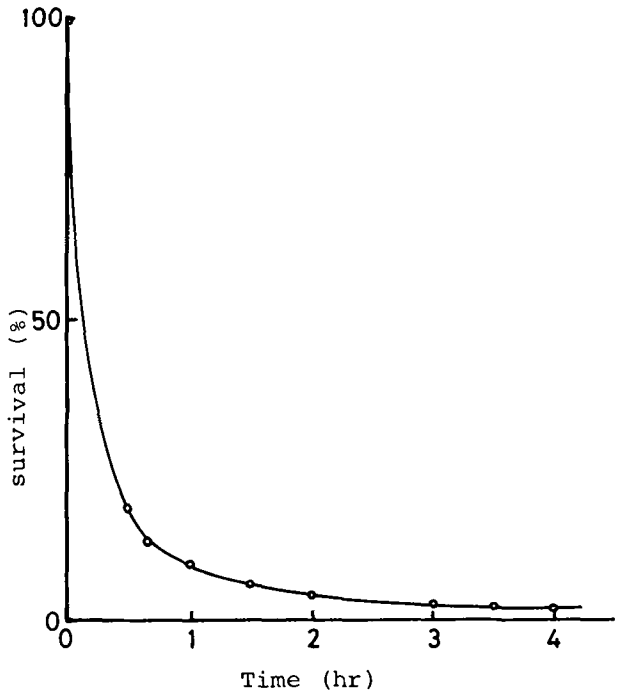


FIG. 4. Change of residual 2-*tert*-butyl-*p*-benzoquinone with time under AOM in methyl oleate.

from the relative ratio of the induction period on oil of TBHQ to that of its oxidation products.

ARE has antioxidative activity on methyl oleate and lard. It was observed particularly that its antioxidative activity on methyl oleate was remarkably stronger than that of the base compound TBHQ. In contrast to this, on soybean oil, it was shown to have some effect to promote oxidation.

Measurement of Residual TQ Quantity

TQ showed little antioxidative activity on any of the basic oils used, so further experiment was carried out to determine the reason. The evaporated quantity of TQ during the AOM test on methyl oleate was measured by HPLC. As shown in Figure 4, a large quantity of TQ was evaporated during the AOM test: its residual rate was ca. 10% after 1 hr and 5% after 2 hr. It seems that this result is closely related to the lack of the antioxidative activity of TQ on basic oils.

REFERENCES

1. Kurechi, T., Eisei Kagaku 13:191 (1967).
2. Kurechi, T., Ibid. 15:301 (1969).
3. Kurechi, T., and T. Taki, Yakugaku Zasshi 97:1174 (1977).
4. Kurechi, T., and A. Kunugi, JAOCS 60:109 (1983).
5. Kurechi, T., K. Kikugawa and S. Aoshima, Chem. Pharm Bull. 29:2351 (1981).
6. Kurechi, T., and T. Yamaguchi, JAOCS 57:216 (1980).
7. Wheeler, D.H., Oil Soap (Chicago) 9:89 (1932).
8. Orlando, C.M., Jr, H. Mark, A.K. Bose and M.S. Manhas, J. Am. Chem. Soc. 89:6526 (1967).

[Received June 21, 1982]

⁂ Studies on the Antioxidants XIX: Photooxidation Products of Tertiary Butyl Hydroquinone (TBHQ) (II)

T. KURECHI and **A. KUNUGI**, Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo, 192-03, Japan

ABSTRACT

A series of studies have been made with a view to pursuing the fate of antioxidant molecules during the antioxidation processes. In this study following that reported in the preceding paper, tertiary butyl hydroquinone (TBHQ) in benzene solution was irradiated with ultraviolet rays and the chemical structure and antioxidative activities of the resulting photooxidation products were examined. They were identified as the following three compounds: 2-(2-[3'-*tert*-butyl-4'-hydroxyphenoxy]-2-methyl-1-propyl)hydroquinone, which was a dimer of the intermediate generated by photorearrangement of the *tert*-butyl group and the substrate TBHQ, 2-(2-hydroxy-2-methyl-1-propyl)hydroquinone, which was formed by interaction of the rearranged *tert*-butyl group with water, and 2-*tert*-butyl-4-ethoxy-phenol, which was formed from a secondary decomposition of the dimer. All of the resulting oxidation products showed antioxidative activity on methyl oleate, soybean oil and lard in the stability test by the active oxygen method (AOM).

INTRODUCTION

In the course of the investigation with the view to pursuing the fate of antioxidant molecules during the antioxidation processes, Kurechi et al. have studied the chemical structures of various oxidation products obtained from butylated hydroxyanisole (BHA) (1-3), ethyl protocatechuate (EP) (4), propyl gallate (PG) (5) and their mixtures (6,7). The fact that their oxidation products were formed corresponding to the positions of dehydrogenation of antioxidants has been clarified through structural analysis of the resulting products.

In the present study, the chemical structures and the antioxidative activity of photooxidation products of tertiary butyl hydroquinone (TBHQ) were examined.

When benzene solution of TBHQ was irradiated with ultraviolet (UV) rays for oxidation, some oxidation products were formed. Besides 2-*tert*-butyl-*p*-benzoquinone and 2,2-dimethyl-2,3-dihydro-5-hydroxybenzo (b) furan, 2-(2-[3'-*tert*-butyl-4'-hydroxyphenoxy]-2-methyl-1-propyl) hydroquinone, 2-(2-hydroxy-2-methyl-1-propyl)hydroquinone and 2-*tert*-butyl-4-ethoxy-phenol were newly identified. Moreover, when the antioxidative activity of these products was examined in various base oils, it was proved that they still retained their antioxidative activity.

EXPERIMENTAL PROCEDURES

Materials

Commercially available reagent grade tertiary butyl hydroquinone (mp 127 C) (Wako Junyaku Co., Tokyo) was repeatedly recrystallized from hexane.

Butylated hydroxyanisole (mp 64 C) was obtained as the commercial product "Sustane" (Nikki Universal Co., Tokyo) and was repeatedly recrystallized from petroleum ether. BHA was 2-*tert*-butyl-4-methoxyphenol (2-BHA).

Soybean oil, lard and methyl oleate were the same products used in our previous paper (5).

The coloration test was carried out with 2,6-dichloroquinone-4-chloroimide ethanol solution.

Assay Methods

Thin layer chromatographic (TLC) examination of the products was made on 0.25 mm silica gel coated plates. These were, in most cases, developed in the solvent system of chloroform/methanol (19:1, v/v).

Column chromatography was carried out using a column with 3 cm id and packed with 50-100 g of 100-mesh silica gel (Kanto Kagaku Co., Tokyo). The column was eluted with chloroform and chloroform/methanol (97:3, v/v).

Nuclear magnetic resonance (NMR) spectrum was measured by a Nihondenshi Model PS-100, 100 Mc. The solvents used were DMSO-d_6 and $CDCl_3$. The chemical shift was expressed as ppm using tetramethylsilane (Me_4Si) as internal standard.

Mass spectrum (MS) was measured by a Hitachi mass spectrometer Model RMU-7L.

Procedure

UV irradiation and isolation of oxidation products. One gram of TBHQ was dissolved in 100 mL benzene in a glass dish 12 cm diameter and 3 cm deep. The solution was placed in a UV irradiation box and irradiated continuously for 72 hr. The distance between the light source and the sample was set at 30 cm. The amount of benzene corresponding to the decrease by evaporation was supplemented intermittently. The reaction products after the completion of UV irradiation were identified by TLC.

TBHQ/benzene photooxidized solution was distilled under reduced pressure to remove benzene, and the residue was extracted with three portions of 50 mL hexane. The combined extracts were filtered, hexane was removed under reduced pressure, and the residue was dissolved in a trace amount of chloroform. The chloroform solution was placed on the top of the column and the column was developed with chloroform. Each fraction was identified by TLC, and the fractions which contained the same oxidation products were put together. The solvent was removed from each fraction under reduced pressure to isolate three reaction products, which were purified by repeated column chromatography. Then, the refined oxidation products were recrystallized from hexane, and yellow needle crystals (**I**, 2-*tert*-butyl-*p*-benzoquinone), white needle crystals (**III**, benzofuran derivative) and white needle crystals (**II**) were obtained.

The above residue of hexane extraction was subsequently extracted twice with 50 mL benzene. The extract was filtered, benzene was removed under reduced pressure, and the residue was dissolved in a trace amount of chloroform. The chloroform solution was placed on the top of the column, and the column was developed with chloroform and chloroform/methanol (97:3, v/v) in this order. Each fraction was identified by TLC and the fractions which contained the same oxidation products were put together. The solvent was removed from each fraction under reduced pressure to isolate two reaction products, which were purified by repeated column chromatography, and were recrystallized from benzene until white needle crystals (**IV** and **V**) were obtained.

Peroxide value (POV). The POV was determined according to the Wheeler method (8).

Antioxidative activity. The antioxidative activity of these products was determined by the active oxygen method (AOM) reported in our previous paper (2). Each of oxidation products **I**, **II**, **III**, **IV**, **V**, TBHQ and BHA was added to 20 mL of methyl oleate, soybean oil or lard, each at 0.01%, and was placed in an AOM oxidation tube. As the control, 20 mL of each of the base oils was placed in an AOM oxidation tube. These tubes were set in the AOM apparatus and oxidized by bubbling air with heating. The POV was measured for the samples taken at certain intervals, and the antioxidative activity was determined by comparison with the standard POV curve. The stability of these sample oils was expressed by the time it took the POV to reach 100 meq/kg.

RESULTS AND DISCUSSION

Formation of Oxidation Products

The benzene solution of TBHQ was UV-irradiated. The progress of the reaction was examined by TLC. Figure 1 shows the thin layer chromatogram for the sample irradiated for 24 hr. Six spots with Rf values of 0.79, 0.63, 0.58, 0.52, 0.12 and 0.03 were observed in addition to the known spots for the starting compound TBHQ (Rf 0.22), oxidation product **I** (Rf 0.70) and oxidation product **III** (Rf 0.41). The color of these compounds was developed with 2,6-dichloroquinone-4-chloroimide, and they were assumed to have a phenolic hydroxide group.

Isolation and Purification of Oxidation Products

To obtain the reaction products **I-V**, which seem to be the main oxidation products among the eight products, benzene solution of TBHQ was irradiated with UV rays for 72 hr. Benzene in the solution was removed by distillation under reduced pressure, and the residue was extracted repeatedly with hexane. The extract was applied to silica gel column chromatography as already described. Fractions of **I**, **II** and **III** were eluted in this order by chloroform. These three fractions were repeatedly purified by column chromatography to collect the portions with Rf values of 0.70, 0.52 and 0.41 only. Each of these portions was repeatedly recrystallized from hexane to obtain yellow needle crystals **I**, white needle crystals **II** and **III**, respectively. As these compounds show the single spot on the TLC plate with Rf values of 0.70, 0.52 and 0.41, respectively, they are assumed to be the oxidation products in Figure 1.

The residue of hexane extraction was extracted repeatedly with benzene. The extract was eluted on silica gel column chromatography as already described. This product of TBHQ was eluted with chloroform (this fraction previously showed Rf value of 0.22 on the TLC plate). The fractions with TLC-Rf values 0.12 and 0.03 were eluted with chloroform/methanol (97:3, v/v). These two fractions were repeatedly purified by column chromatography to collect the portions with Rf values of 0.12 and 0.03 only. Each of these portions were repeatedly recrystallized from benzene to obtain white needle crystals **IV** and **V**, which showed the single spot on the TLC plate with Rf values of 0.12 and 0.03, respectively.

Chemical Structures of Oxidation Products

Compound **II** is a white needle crystal with mp 98.5 C. It is soluble in ethanol, chloroform, benzene and other solvents, but insoluble in water. The mass spectrometry (Fig. 2) showed the molecular ion peak at 194 m/e. The molecular formula was agreed on as $C_{12}H_{18}O_2$ derived from the elemental analysis. Figure 3a shows the NMR spectrum of **II**. The presence of an ethoxy group was recognized by the triplet at 1.38 ppm (3H, J = 7.2 Hz) and the quartet at

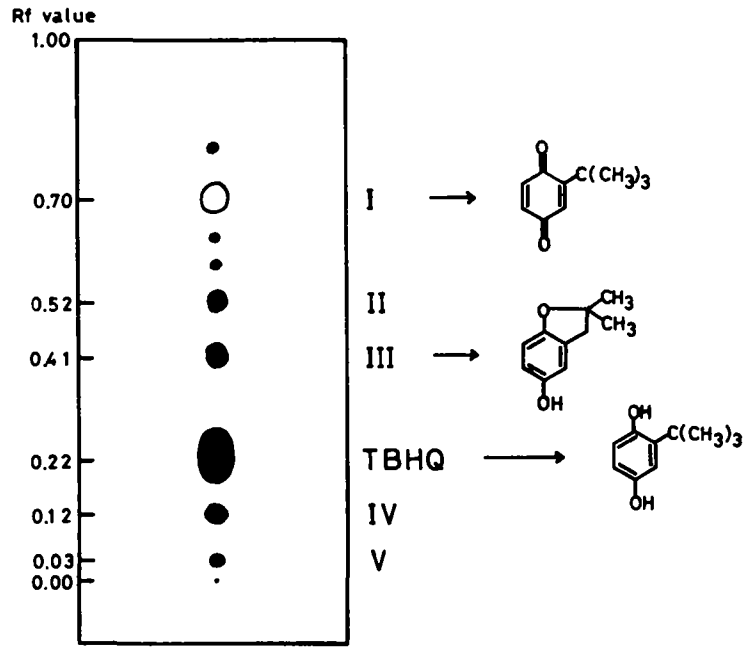


FIG. 1. Thin layer chromatogram of oxidation products of TBHQ in benzene under irradiation of UV light.

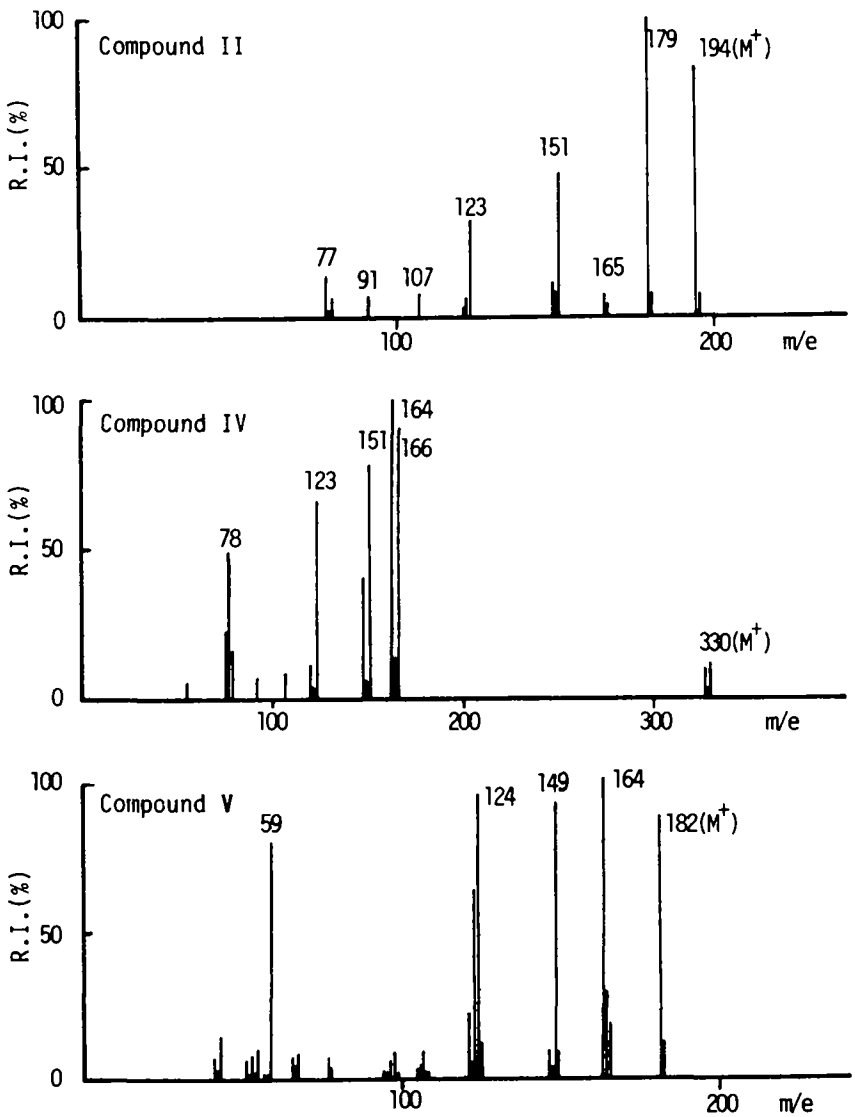


FIG. 2. Mass spectra of compounds II, IV and V.

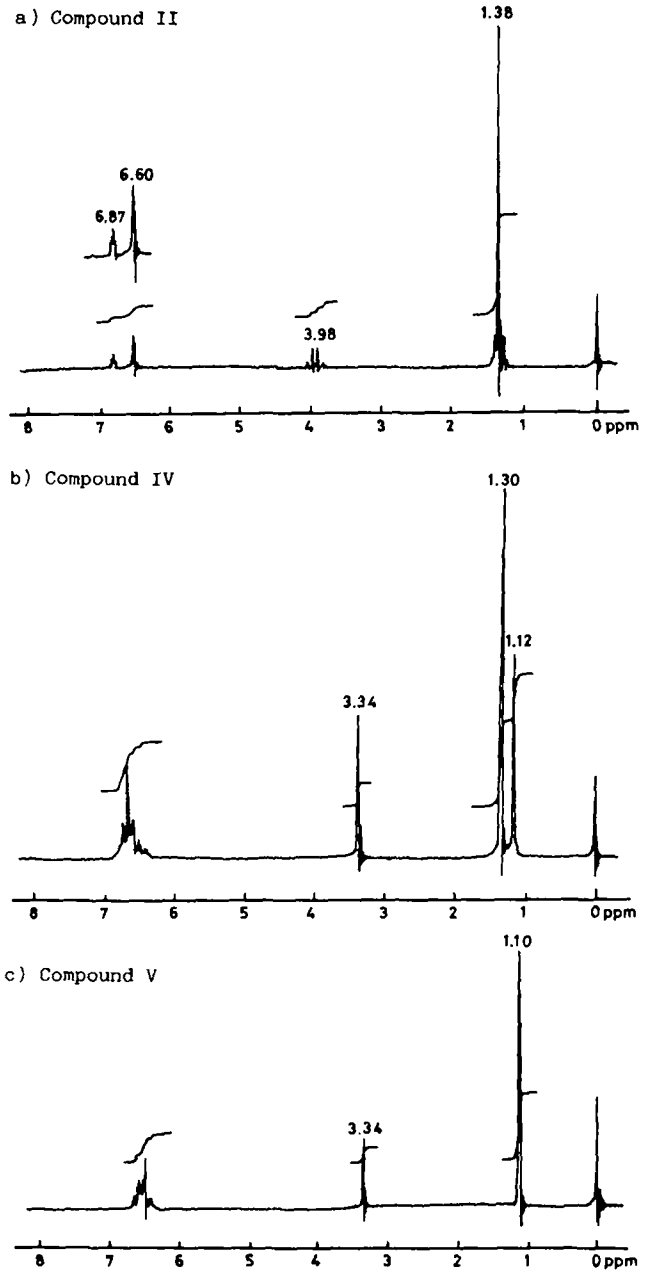


FIG. 3. NMR spectra of compounds II, IV and V.

3.98 ppm (2H, J = 7.2 Hz), and a *tert*-butyl group appeared at 1.38 ppm (9H) as a singlet; however, this peak overlapped with that of the methyl signal. In the nuclear proton field, two broad singlets were observed at 6.60 ppm (2H) and 6.68 ppm (1H). These are derived from the hydrogens at positions 5 and 6 and the hydrogen at position 3, respectively. Their signals suggest that the substitution form in the benzene ring was not altered from that in substrate TBHQ. On the basis of these spectral data, the oxidation product **II** was identified as 2-*tert*-butyl-4-ethoxy-phenol with the chemical structure shown in Scheme 1. In addition, the structure of this product was confirmed by direct comparison with the authentic sample, which was prepared by ethylation of TBHQ with diethyl sulfate.

Compound **IV** is a white needle crystal with mp 179.5 C. It is soluble in benzene and chloroform, but insoluble in water. The mass spectrometry (Fig. 2) showed the molecular ion peak at 330 m/e. The molecular formula was agreed on as $C_{20}H_{26}O_4$ derived from the elemental analysis. The NMR spectrum of **IV** (Fig. 3b) showed two singlets at 1.12 ppm (6H) and 3.34 ppm (2H). The presence of two of the methyl groups and an Ar-CH_2 group was therefore recognized and that of a *tert*-butyl group was recognized by the singlet at 1.30 ppm (9H). The signal of aromatic protons appeared at 6.40-6.72 ppm as a multiplet (6H). In view of the above data, the oxidation product **IV** was assumed to be 2-(2-[3′-*tert*-butyl-4′-hydroxyphenoxy]-2-methyl-1-propyl)hydroquinone with the chemical structure shown in Scheme 1.

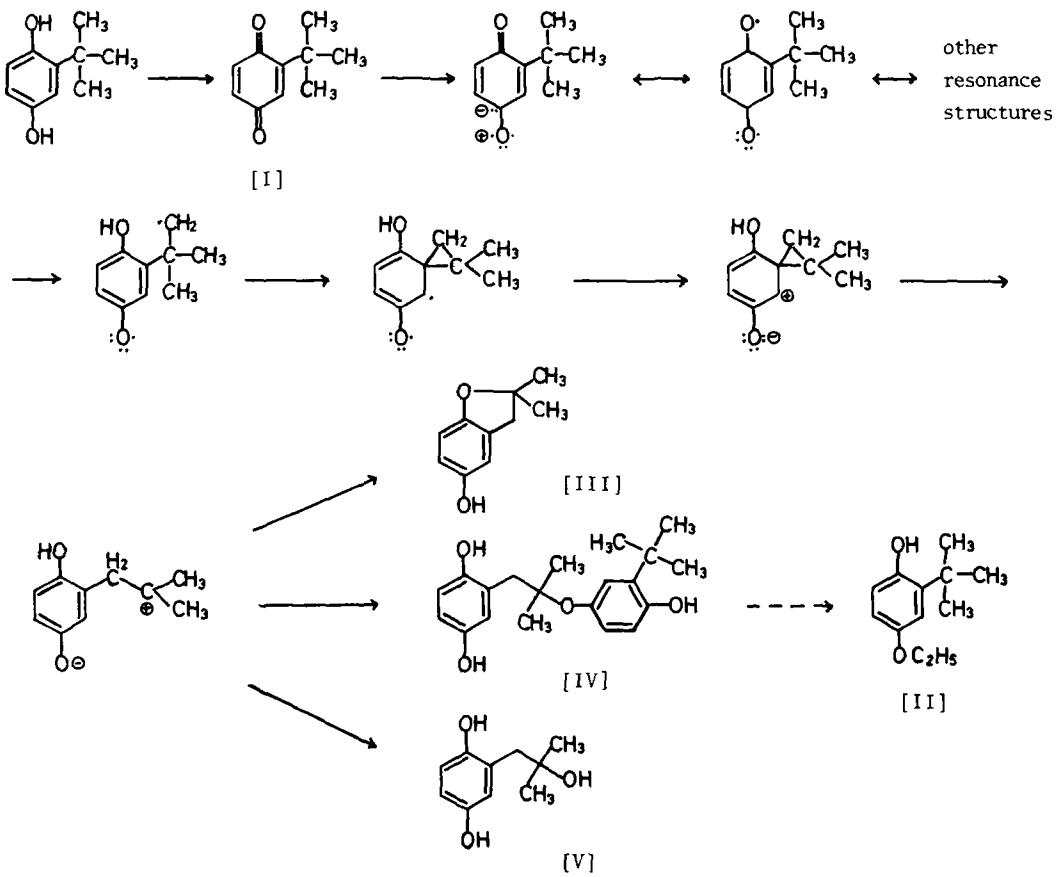
Compound **V** is a white needle crystal with mp 145 C. It is soluble in ethanol, slightly soluble in benzene and chloroform, but insoluble in water. The mass spectrometry (Fig. 2) showed the molecular ion peak at 182 m/e. The molecular formula was agreed on as $C_{10}H_{14}O_3$ derived from the elemental analysis. The NMR spectrum of **V** (Fig. 3c) showed two singlets at 1.10 ppm (6H) and 3.34 ppm (2H). Two methyl groups and an Ar-CH_2 group were therefore recognized. The signal of aromatic protons appeared at 6.42-6.64 ppm as a multiplet (3H). In view of the above data, the oxidation product **V** was assumed to be 2-(2-hydroxy-2-methyl-1-propyl)-hydroquinone with the chemical structure shown in Scheme 1.

In view of the structures of oxidation products **I-V** obtained from TBHQ, it is considered that, as shown in Scheme 1, 2-*tert*-butyl-*p*-benzoquinone (**I**) was at first formed by oxidation of TBHQ, followed by the oxidation products **III**, **IV** and **V** which were formed by the photolysis of **I**. Furthermore, it was recognized that the oxidation product **II** was formed by a secondary decomposition of **IV**. In addition, when 2-*tert*-butyl-*p*-benzoquinone (**I**) was used as a starting material, the above compounds **II**, **III**, **IV** and **V** were also obtained as photooxidation products. However, in the absence of oxygen, namely under the conditions of no formation of 2-*tert*-butyl-*p*-benzoquinone from TBHQ, the bond isomerization eventually yielded rearranged hydroquinones **IV** and **V**. Furthermore, it was recognized that the oxidation product **II** was formed by a secondary decomposition of **IV**. In addition, when 2-*tert*-butyl-*p*-benzoquinone I was used as a starting material, the above compounds **II**, **III**, **IV** and **V** were also obtained as photooxidation products. However, in the absence of oxygen, namely under the conditions of no formation of 2-*tert*-butyl-*p*-benzoquinone from TBHQ, all oxidation products were scarcely obtained by photooxidation of TBHQ. On the basis of these data, it seems most reasonable to conclude that the pathway for the formation of oxidation products of TBHQ by photooxidation is analogous to that postulated by Orlando Jr. et al. (9,10) for photoreaction. This reaction mechanism for the formation of these oxidation products is not observed in photooxidation of BHA, although its chemical structure is analogous to that of TBHQ. It is chemically interesting that the oxidation products with unusual chemical structures were formed during photooxidation processes, and these results give a new suggestion for the fate of antioxidant molecules.

Antioxidative Activity of Oxidation Products

The antioxidative activity of oxidation products I-V measured by the active oxygen method (AOM) in various base oils is as follows.

Antioxidative activity on methyl oleate. Figure 4a shows the change in POV after adding oxidation products **I-V**, TBHQ and BHA, each at 0.01%, to methyl oleate. As is obvious from the POV curves, all of these oxidation products were confirmed to have antioxidative activity on methyl oleate. The order of the antioxidative activity on methyl oleate was: **II** > BHA > **III** > **IV** = **V** > TBHQ > **I**.



SCHEME 1. Formation of oxidation products of TBHQ.

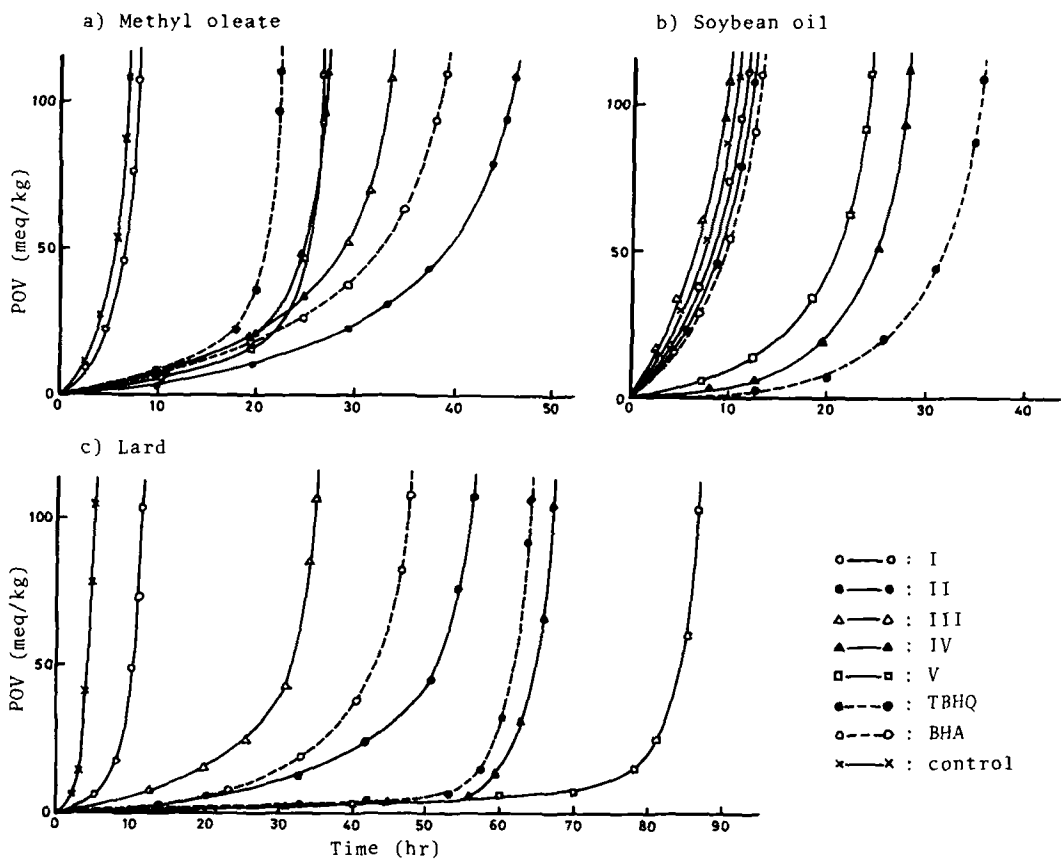


FIG. 4. Antioxidative effect of oxidation products of TBHQ on methyl oleate, soybean oil and lard.

Antioxidative activity on soybean oil. By the POV changes (Fig. 4b) after oxidation products I-V, TBHQ and BHA were added, each at 0.01%, to soybean oil, all of these oxidation products, except III, were confirmed to have antioxidative activity on soybean oil, too. The order of the antioxidative activity was: TBHQ > IV > V > BHA > II > I > III.

Antioxidative activity on lard. By the changes in POV (Fig. 4c) after adding oxidation products I-V, TBHQ and BHA, each at 0.01%, to lard, all of these oxidation products were confirmed to have antioxidative activity on lard, too. The order of antioxidative activity was: V > IV > TBHQ > II > BHA > III > I.

From the results mentioned above, it was confirmed that these oxidation products increased the stability of three base oils over AOM, and that all of these five had antioxidative activity. However, this activity depended on the kinds of base oils. Table I shows the induction periods and the antioxidation ratios calculated from the relative ratios of the induction periods over that of TBHQ. It is notable that these oxidation products, except I, developed significant antioxidative activity stronger than that of the base compound TBHQ when methyl oleate was used as the base oil. Both IV and V developed remarkable antioxidative activity on soybean oil, whereas the activities of I, II and III were almost the same as that of BHA and comparatively low. The antioxidative activity of both IV and V on lard were the highest.

TABLE I

Antioxidative Activity of Oxidation Products of TBHQ on Methyl Oleate, Soybean Oil and Lard

	Methyl oleate		Soybean oil		Lard	
Compound[a]	IP[b]	AR[c]	IP	AR	IP	AR
None	7.0 hr		10.3 hr		5.1 hr	
I	8.0	0.05	10.8	0.02	10.8	0.10
II	45.8	2.53	11.8	0.06	56.5	0.87
III	33.5	1.73	9.6	−0.03	35.1	0.51
IV	27.1	1.31	27.3	0.68	67.0	1.05
V	27.0	1.31	24.3	0.56	86.8	1.39
TBHQ	22.3	1.00	35.1	1.00	64.0	1.00
BHA	38.8	2.08	12.5	0.09	47.8	0.72

[a]Concentration : 0.01%.

[b]IP : induction period.

[c]AR : antioxidation ratio = $\frac{IP_{sample} - IP_{control}}{IP_{TBHQ} - IP_{control}}$.

Antioxidative activity

Methyl oleate: II > BHA > III > IV = V > TBHQ > I
Soybean oil: TBHQ > IV > V > BHA > II > I > III
Lard: V > IV > TBHQ > II > BHA > III > I

From the results mentioned above, it was confirmed that these oxidation products increased the stability of three base oils over AOM, and that all of these five had antioxidative activity. However, this activity depended on the kinds of base oils. Table I shows the induction periods and the antioxidation ratios calculated from the relative ratios of the induction periods over that of TBHQ. It is notable that these oxidation products, except I, developed significant antioxidative activity stronger than that of the base compound TBHQ when methyl oleate was used as the base oil. Both IV and V developed remarkable antioxidative activity on soybean oil, whereas the activities of I, II and III were almost the same as that of BHA and comparatively low. The antioxidative activity of both IV and V on lard were the highest.

REFERENCES

1. Kurechi, T., Eisei Kagaku 13:191 (1967).
2. Kurechi, T., Ibid. 15:301 (1969).
3. Kurechi, T., and H. Senda, Ibid. 23:267 (1977).
4. Kurechi, T., and T. Taki, Yakugaku Zasshi 97:1174 (1977).
5. Kurechi, T., and A. Kunugi, JAOCS 60:109 (1983).
6. Kurechi, T., and T. Yamaguchi, JAOCS 57:216 (1980).
7. Kurechi, T., and T. Kato, JAOCS 57:220 (1980).
8. Wheeler, D.H., Oil Soap (Chicago) 9:89 (1932).
9. Orlando, C.M., Jr., H. Mark, A.K. Bose and M.S. Manhas, J. Am. Chem. Soc. 89:6527 (1967).
10. Orlando, C.M., Jr., H. Mark, A.K. Bose and M.S. Manhas, J. Org. Chem. 33:2512 (1968).

Interpenetrating Polymer Networks from Triglyceride Oils Containing Special Functional Groups: A Brief Review[1]

L.H. SPERLING and **J.A. MANSON**, Materials Research Center, Lehigh University, Coxe Laboratory 32, Bethlehem, PA 18015

ABSTRACT

Although most triglyceride oils contain only double bond functionality, a few oils such as castor oil, vernonia oil, lesquerella oil, etc., contain other functional groups. These functional groups include hydroxy and epoxy groups, permitting the easy formation of polyesters and/or polyurethanes. In addition to the natural formation of epoxy-bearing oils, the double bond functionality in ordinary triglyceride oils can be epoxidized. When these oils are polymerized to form polyesters or polyurethanes in the presence of polystyrene to synthesize interpenetrating polymer networks (IPN), a new class of tough plastics is formed.

INTRODUCTION

Although most triglyceride oils contain only double bonds as functional groups in the fatty acid hydrocarbon chains, a few of these oils are endowed with special functionalities (1,2). Some of these functionalities include hydroxyl groups and epoxy (or oxirane) groups. These oils can react with many chemical reagents yielding polyurethane or polyester polymer networks. When such polymer networks are combined with a second polymer in network form, an interpenetrating polymer network (IPN) is produced. Such IPN form impact-resistant plastics or reinforced elastomers depending on overall composition and phase continuity.

The present research program began in 1974 as an international program with Colombia, South America. The original intent was to develop castor oil-based interpenetrating polymer networks as castor beans now grow wild in Colombia. It was intended to develop a domestic crop at a suitable time. This research resulted in several publications (3-16) and a patent (17).

Beginning in 1978, the program was broadened to include polymers containing oxirane groups. Two types of materials were examined: (a) vernonia oil, which is a triglyceride oil that naturally contains 80% epoxy groups on an acid residue basis, and (b) ordinary triglyceride oils, such as linseed oil, whose double bonds were deliberately epoxidized. These oxirane groups can be polymerized with materials such as sebacic acid, which itself is derived from castor oil, to produce polyester networks. In addition, the hydroxyl groups on lesquerella oil have been esterified with sebacic acid, leading to new elastomers and IPN.

This paper will review the research to date, and also describe new oils now under examination.

[1]Presented at the symposium on Nonfood Applications for Whole Plant Oils, 72nd annual AOCS meeting, 1982.