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Reactions of Stabilizer Compounds. II. Formation and Thermal Decomposition of Peroxycyclohexa-2,5-dienones from Some Phenolic Antioxidants and Light Stabilizers

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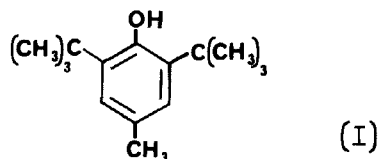
ABSTRACT

In this paper a preliminary report is presented on studies of the reaction of several commercially important hydroxyphenylbenzotriazole light stabilizers during AIBN initiated oxidation of cumene in chlorobenzene at 65°C. Each of the compounds studied reacted readily, the rate of reaction depending on the substitution pattern of the phenolic ring. In the case of 5-chloro-2-(3'-tert-butyl-2'-hydroxy-5'-methyl)phenylbenzotriazole, the major product was characterized as the corresponding cumylperoxycyclohexa-2,5-dienone. Thermal decomposition of tert-butylperoxycyclohexa-2,5-dienones derived from 2,6-di-tert-butyl-4-methylphenol, 2,4,6-tri-tert-butylphenol, and several hydroxyphenylbenzotriazole light stabilizers is reported. Decomposition by both O-O and C-O bond scission is observed, the C-O bond scission mechanism being the major pathway for thermal decomposition of the benzotriazolyl substituted tert-butylperoxycyclohexa-2,5-dienones.

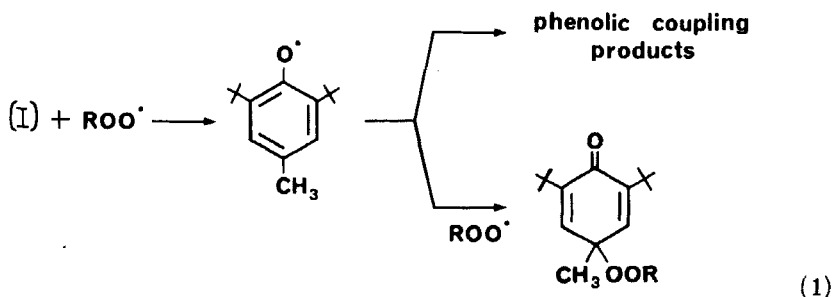
INTRODUCTION

The ageing of commercial polymeric materials consists of a complex sequence of thermal and photochemical reactions involving the entire system of polymer and additives. These reactions, which result in chain breakage, crosslinking, etc., lead to a deterioration of the properties of the polymer with eventual mechanical failure. A detailed study of the early stages of polymer ageing must necessarily involve a study of the participation of the additives in the deterioration process.

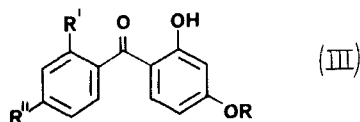
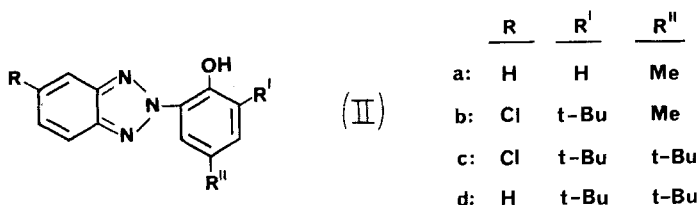
Phenolic compounds are widely used in polymeric systems as both antioxidants and light stabilizers, although the structural requirements of the two classes of stabilizer differ widely. The chemistry of the hindered phenolic antioxidants, of which 2,6-di-*tert*-butyl-4-methylphenol (I) is a typical example, has been extensively studied [1] in



both polymeric and model autoxidizing systems, largely as a basis to understanding the mechanism of antioxidant action. In autoxidizing media, phenolic antioxidants react with intermediate peroxy radicals to form a relatively stable phenoxy radical [1]. The final products from reaction of the phenols are phenolic coupling products and peroxy-cyclohexadienones, the relative proportions depending on the reaction conditions and structure of the phenol [2].



In contrast to the phenolic antioxidants, relatively few reports have appeared in the literature on reactions of the two major classes of phenolic light stabilizers, the 2'-hydroxy-2-phenylbenzotriazoles (II),



and the 2-hydroxybenzophenones (III). The formation of peroxycyclohexa-2,5-dienones in the reaction of 2'-hydroxy-2-phenylbenzotriazoles has been reported [3] in a previous publication.

A preliminary report is presented here on the reaction of some phenolic light stabilizers during initiated autoxidation of cumene and a comparison of the thermal decomposition of some peroxycyclohexa-2,5-dienones derived from phenolic antioxidants and phenolic light stabilizers.

RESULTS AND DISCUSSION

Reactions of Phenolic Light Stabilizers in Initiated Autoxidation of Cumene

Phenolic light stabilizers are introduced into the polymer at the processing stage during which the polymer is subjected to high temperatures and undergoes some oxidation. Further thermal oxidation at lower temperatures occurs throughout the useful life of the polymer. To investigate reactions of phenolic light stabilizers in autoxidizing media, the reaction of the stabilizers in azobisisobutyronitrile (AIBN)-initiated autoxidation of cumene in chlorobenzene at 65°C was examined.

Consumption of the 2'-hydroxy-2-phenylbenzotriazole light stabilizers IIa, IIb, and IIc during the AIBN-initiated autoxidation of cumene in chlorobenzene at 65°C is shown in Fig. 1. Each of the hydroxyphenylbenzotriazoles examined was found to react readily during the autoxidation reaction, the rate of reaction depending on the substitution pattern of the phenolic ring.

2'-Hydroxy-2-phenylbenzotriazoles have been shown to react with the tert-butyl peroxy radical in solution with formation of relatively stable tert-butylperoxycyclohexa-2,5-dienones [3] (IV). An analogous

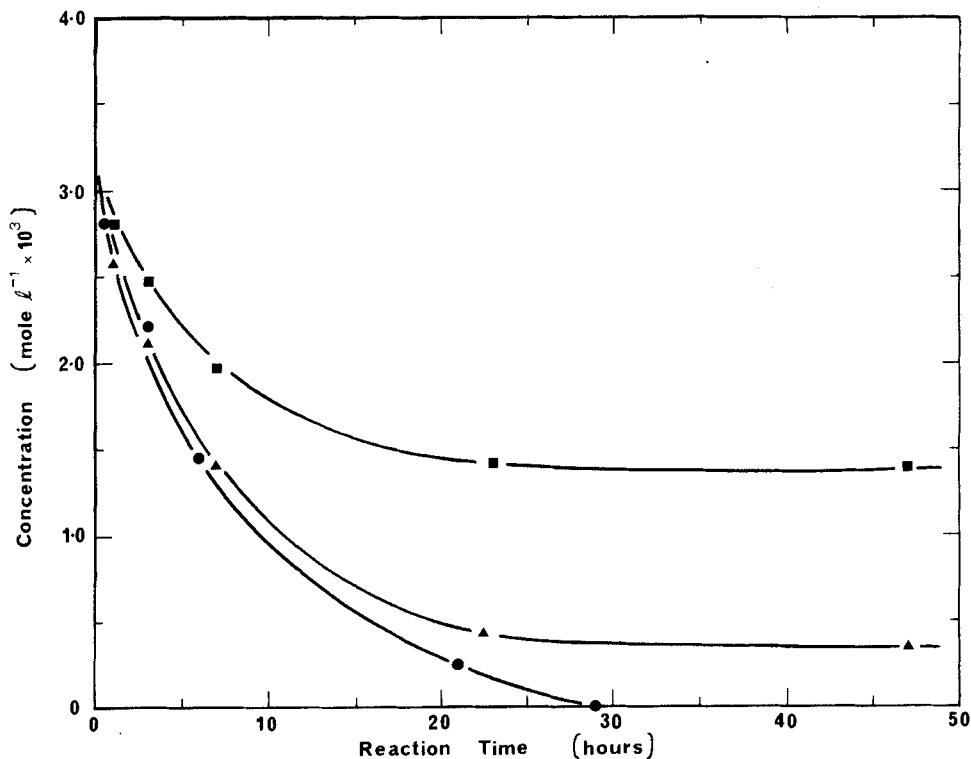
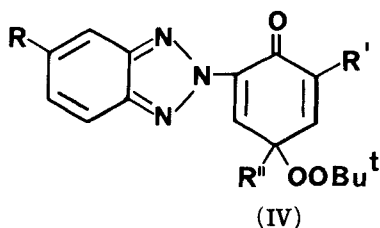
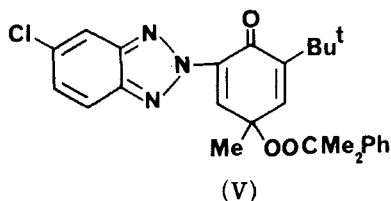
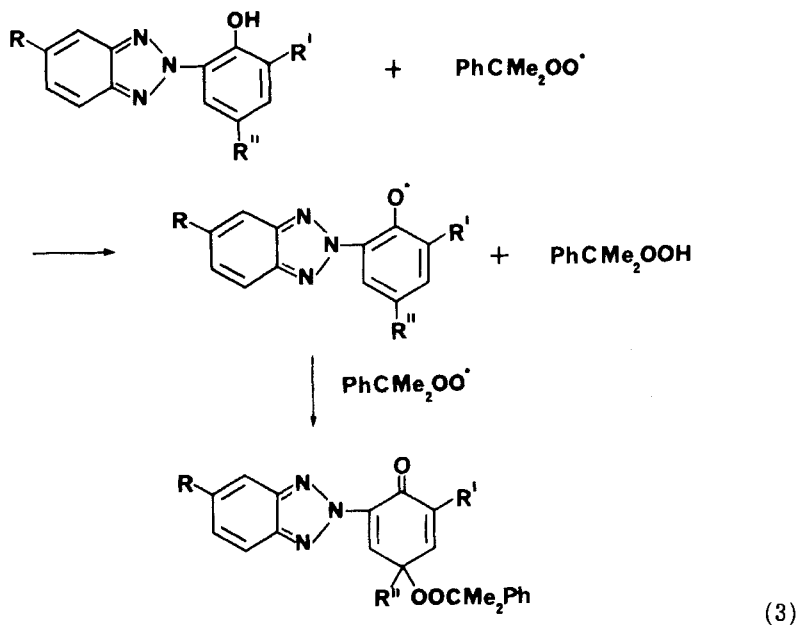
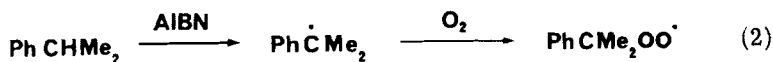


FIG. 1. Consumption of 2'-hydroxy-2-phenylbenzotriazoles during AIBN-initiated autoxidation of cumene in chlorobenzene at 65°C: (■) IIa; (●) IIb; (▲) IIc.



reaction would be expected with the intermediate cumyl peroxy radical in the cumene autoxidation reaction [Eqs. (2) and (3)].

Formation of the cumylperoxycyclohexa-2,5-dienone (V) from the hydroxyphenylbenzotriazole (IIb) during autoxidation of cumene was confirmed by independent synthesis of V by the cobalt(II) acetylacetonate-catalyzed reaction of cumyl hydroperoxide with IIb.



Compound V was obtained as colorless needles, mp 99.5-101.5°C (from hexane) and the structure confirmed from infrared (bands at 1683, 1663 and 1627 cm^{-1} consistent with the cyclohexadienone structure [4]) and NMR (in CDCl_3 : δ 1.31, 9H, *t*-Bu; 1.45, 3H, CH₃; 1.59, 6H, C(CH₃)₂; 6.73, doublet, $J = 3.0$ Hz, vinylic H; 7.1-8.0, aromatic H and remaining vinylic H) spectra. High-pressure liquid chromatographic analysis of the reaction of IIb during the autoxidation of cumene showed that, after a reaction time of 28 hr, no IIb remained, and (V) was obtained in 88% yield. The other hydroxyphenylbenzotriazoles examined would be expected to react in a similar manner.

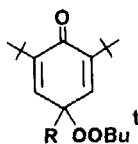
As seen from Fig. 1 the relative rates of reaction for IIa-c are

consistent with the combined effects of relative stabilities of the intermediate phenoxy radical and steric hindrance to approach of the cumyl peroxy radical to the 5'-position.

Thermal Decomposition of Peroxycyclohexa-2,5-dienones

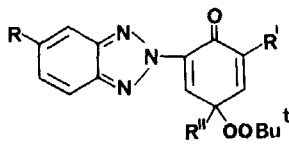
Peroxycyclohexa-2,5-dienones, which have been shown to form from phenolic antioxidants in oxidized polypropylene [5], are thermally and photolytically unstable. These reactions would be expected to play an important role in the ageing of stabilized polymers. In the present section, the thermal decomposition of several peroxycyclohexa-2,5-dienones derived from phenolic antioxidants and light stabilizers as studied by pyrolysis-gas chromatography-mass spectrometry, electron spin resonance, and reactions in solution, is discussed.

Pyrolysis-GC-MS Studies. The nature of the volatile products from thermal decomposition of the tert-butylperoxycyclohexa-2,5-dienone VIa, VIb, and VIIa-c was examined by pyrolysis-GC-mass spectrometry. Products were identified by comparison of retention times and mass spectra with those of authentic compounds.



(VI)

- a: R = Me
b: R = t-Bu

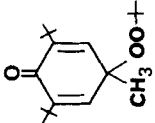
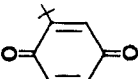
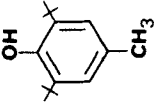
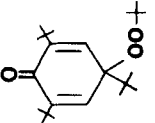
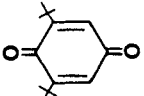
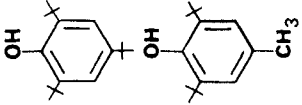


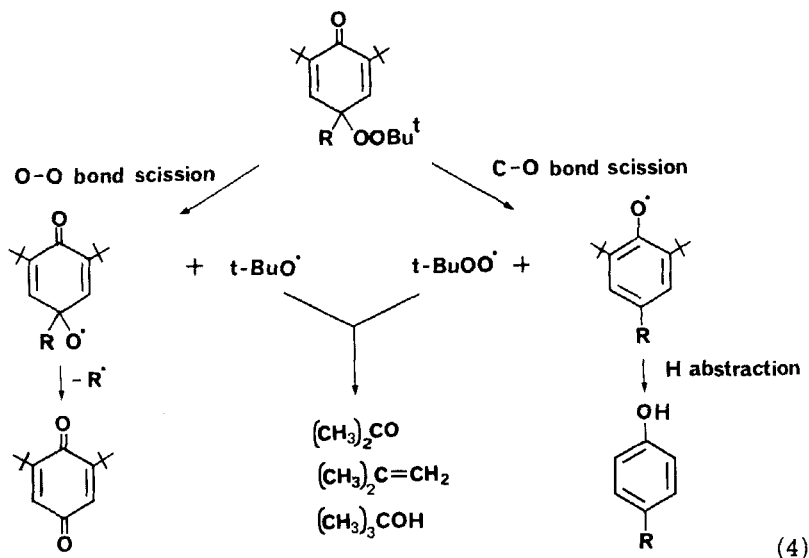
(VII)

- a: R = H ; R' = H ; R'' = Me
b: R = Cl ; R' = t-Bu ; R'' = Me
c: R = H ; R' = t-Bu ; R'' = t-Bu

The volatile products, together with their relative yields, from the thermal decomposition of the neat peroxycyclohexa-2,5-dienones (VIa and VIb) at 80-200°C are listed in Table 1. VIa and VIb were observed to undergo thermal decomposition by both O-O and C-O bond scission mechanisms, the relative proportions of the two fragmentation reactions depending on the nature of the 4'-substituent and, in the case of VIa, on the temperature of thermal decomposition. Most of the products formed on thermal decomposition of VIa are accounted for by the reactions of Eqs. (4) (R = CH₃). Acetone, tert-butanol and isobutene are obtained from secondary reactions of the tert-butoxy and tert-butyl peroxy radicals. 2,6-Di-tert-butyl-benzoquinone and 2,6-di-tert-butyl-4-methylphenol arise from O-O and C-O bond

TABLE 1. Products Obtained on Pyrolysis-GC-MS of tert-butylperoxycyclohexa-2,5-dienones (VIa) and (VIb)

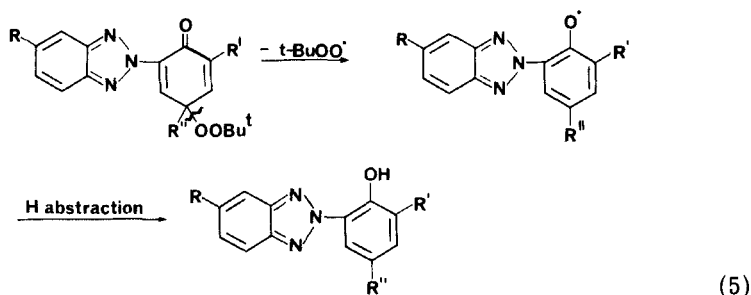
COMPOUND	PYROLYSIS TEMPERATURE	MAJOR	RELATIVE YIELDS OF PRODUCTS INTERMEDIATE	MINOR
	200 °C	$(\text{CH}_3)_2\text{C}=\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CH}_2$ UNIDENTIFIED CPD. MW. 234	$(\text{CH}_3)_3\text{COH}$,  UNIDENTIFIED CPD. MW. 234	
	200 °C & 100 °C	$(\text{CH}_3)_2\text{C}=\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_3\text{CH}$, 	$(\text{CH}_3)_3\text{COH}$	



scission reactions, respectively. The major product of molecular weight 234 obtained on pyrolysis of VIa at 200°C (Table 1) has not yet been identified. Koch [6] has reported the formation of 2,6-di-tert-butylbenzoquinone, 3,5-di-tert-butyl-4-hydroxybenzaldehyde, acetone and tert-butanol on thermal decomposition of VIa at 170°C and Buben and Pospisil [7] have reported no change in VIa at 65°C but at 200°C obtained several unidentified products, among which 2,6-di-tert-butylbenzoquinone was not detected.

Thermal decomposition of VIb at both 100 and 200°C occurred mainly by O-O bond scission [Eq. (4), R = t-Bu] with formation of the quinone reflecting the greater stability of the tert-butyl radical as a leaving group. (Buben and Pospisil [7] have reported formation of the quinone on thermal decomposition of VIb at both 65 and 200°C.) A small amount of 2,4,6-tri-tert-butylphenol was obtained via C-O bond scission on thermal decomposition of VIb at both temperatures. The reaction leading to formation of low yields of 2,6-di-tert-butyl-4-methylphenol is uncertain.

On pyrolysis of the benzotriazolyl-substituted peroxy-cyclohexa-2,5-dienones (VIIa-c) at temperatures above 150°C, the only volatile product resulting from the benzotriazolyl moiety which could be detected was the corresponding phenol resulting from C-O bond scission [Eq. (5)]. No quinone or other products were detected although reference compounds were not available for comparison. Examination of the pyrolysis probe after heating at 200°C showed a solid residue remaining, possibly due to phenolic coupling reactions. On heating to 700°C this residue decomposed with formation of a small amount of the corresponding phenol.



Thermal Decomposition in Solution. Semiquantitative studies of thermal decomposition of the benzotriazolyl substituted peroxy cyclohexa-2,5-dienones (VIIa) and (VIIb) were carried out in both inert and hydrogen donor solvents. Thermal decomposition of VIIa at 132°C in refluxing chlorobenzene gave the phenol IIIa in 36% yield, together with unidentified highly colored compounds resulting from phenoxy coupling and disproportionation reactions. Under the same conditions, the benzotriazolyl-substituted peroxy cyclohexa-2,5-dienone (VIIb) gave the phenol IIb in approximately 50% yield. One of the minor products from this latter reaction, although not fully characterized, showed an infrared spectrum consistent with the aldehyde (II, R = Cl, R' = t-Bu, R'' = CHO).

On thermolysis of VIIb in the hydrogen donor solvents tetralin (at 150°C) and cumene (at 110°C), the phenol IIb was obtained in 86% and 87% yield, respectively, due to hydrogen abstraction by the intermediate phenoxy radical from the solvent. These experiments confirm that the principal pathway for thermal decomposition of the benzotriazolyl-substituted peroxy cyclohexa-2,5-dienone VIIb is by C-O bond scission rather than by O-O bond scission, giving the corresponding phenol in the presence of a suitable hydrogen donor.

Electron Spin Resonance Studies. Phenoxy radicals formed on thermal decomposition of the peroxy cyclohexa-2,5-dienones (VIa) and (VIb) by C-O bond scission were observed by ESR on in situ thermolysis of the peroxy cyclohexadienones in *m*-dichlorobenzene solution. When degassed solutions of (VIa) were heated at temperatures above 90°C, the 2,6-di-tert-butyl-4-methyl phenoxy radical (a_{H} 1.11 (3H), 0.17 mT (2H); lit. [8] a_{H} 1.10 (3H), 0.175 mT (2H)) was observed and, at higher temperatures and higher concentrations of (VIa) secondary radicals arising from coupling reactions were also observed (Fig. 2). On in situ thermolysis of the peroxy cyclohexa-2,5-dienone (VIb) under the same conditions, the 2,4,6-tri-tert-butyl phenoxy radical was observed at temperatures above 90°C. In the case of VIb the ESR signal intensity of the phenoxy radical was much weaker than that for VIa, due to the higher proportion of O-O bond scission in the case of VIb.

Thermal decomposition studies of VIIa-c have shown that C-O bond

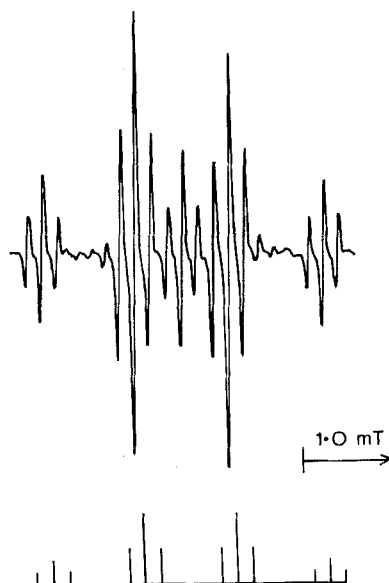


FIG. 2. ESR spectrum observed on thermal decomposition of 0.2 M VIa in *m*-dichlorobenzene at 130°C.

scission is a major fragmentation pathway. However, no phenoxy radicals were detected on in situ thermolysis of VIIa-c at temperatures greater than 100°C. This observation suggests that the benzotriazolyl-substituted phenoxy radicals are much more reactive to coupling, disproportionation, and hydrogen abstraction reactions than the 2,6-di-*tert*-butyl substituted phenoxy radicals, resulting in a steady-state concentration of the phenoxy radical too low to detect by ESR. (The fact that the 2'-hydroxy-2-phenylbenzotriazoles are only weak retarders and not inhibitors of cumene autoxidation [9] shows that the phenoxy radical is very reactive.)

CONCLUSIONS

The results described in this paper show that the 2'-hydroxy-2-phenylbenzotriazole light stabilizers undergo reaction with intermediate peroxy radicals in the initiated autoxidation of cumene at 65°C. The resultant peroxycyclohexadienones are shown to undergo thermal decomposition at polymer processing temperatures (> 100°C) mainly by C-O bond scission with, in the presence of a suitable hydrogen donor, re-formation of the phenolic light stabilizer. At the lower temperatures of autoxidation and photo-oxidation prevailing

during the useful life of the polymer these peroxycyclohexadienone products are thermally stable, and the reactions described may play an important role in the chemistry of the induction period of polymer ageing.

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