Active Species in Hydroperoxide Decomposition by Hindered Amine Light Stabilizers and Its Reactivity with Phenol

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ABSTRACT: Hydroperoxide decomposition by hindered amine light stabilizers (HALSs) is an important process producing active HALS derivatives and has been studied energetically. The decisive active species of the decomposition, however, has not been proposed yet. In this article, HALS nitrosonium that forms in the decomposition of a hydroperoxide by HALSs and a ring-opening product of the nitrosonium, a nitroso compound, are proposed as active species for hydroperoxide decomposition. Furthermore, the reactivity of the nitrosonium with phenols is discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1310–1317, 2006

Key words: antioxidants; HALS

INTRODUCTION

Nowadays, polymeric materials such as plastics, rubbers, and fibers are necessary for our lives. However, they have defects of degradation by autoxidations. Therefore, many kinds of polymer stabilizers are added to polymeric products. Among them, hindered amine light stabilizers (HALSs) and phenolic antioxidants are important as stabilizers. However, both types of stabilizers sometimes show apparent antagonism, although they also exhibit synergism under light.[1] We have already reported a new antagonism caused by hydroperoxide decomposition by HALSs.[2] That is, in the presence of phenolic antioxidants, HALSs also accelerate the homolytic and catalytic decomposition of a hydroperoxide and form free radicals able to initiate autoxidation. In addition, the same article reveals that the decomposition reaction consists of two phases: an early phase corresponding to an induction period forming an active species for hydroperoxide decomposition and a later phase in which fast decomposition occurs. The induction period is shortened by the interaction of HALSs with protons obtained by acidic compounds, such as carboxylic acids and phenols. Few studies, however, have been published discussing the active species of hydroperoxide decomposition.

In this article, hydroperoxide decomposition by HALS derivatives is studied in detail. An active species for such decomposition is proposed, and its reactivity with phenols is discussed.

EXPERIMENTAL

Reagents

Commercial materials

2,6-Di-*tert*-butyl-*p*-cresol, 2,6-di-*tert*-butyl-*p*-methoxyphenol, *p*-cresol, 2-*tert*-butyl-*p*-cresol, 2,4,6-trimethylphenol, *p*-methoxyphenol, and 2-*tert*-butyl-*p*-methoxyphenol were used as phenolic antioxidants. They were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) The solid compounds at room temperature were purified by recrystallization from *n*-hexane, and phenols with melting-point ranges within ±0.5°C were used. Bis(2,2,6,6-tetramethylpiperidinyl) sebacate (ADK Stab LA-77, Adeka Corp.) and 4-hydroxy-2,2,6,6-tetramethylpiperidine (Tokyo Kasei Kogyo, Tokyo, Japan) were used as HALSs. Cumene hydroperoxide (CHP; Nacalai Tesque, Inc.) was used as a hydroperoxide.

Bis(1-oxo-2,2,6,6-tetramethylpiperidinyl) sebacate dinitrate (sebacate HALS $N^{+}{=}O$ NO_2^-/NO_3^-)

Bis(1-oxy-2,2,6,6-tetramethylpiperidinyl) sebacate (0.5 g) was allowed to react with dried nitrogen dioxide (ca. 7.7 L) over 2 h at −10°C. Then, the reaction mixture was kept at −10°C and stirred for 1 h. After the end of the reaction, it was brought to room tempera-

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ture and then warmed to 40°C to remove the residual nitrogen dioxide. A brown, viscous oil was left. The yield was 0.68 g (stoichiometric). The Fourier transform infrared (FTIR; NaCl) measurement results were the same as those described in ref. 3.

1-Oxo-4-acetyloxy-2,2,6,6-tetramethyl-4-piperidinium nitrate (acetate HALS $N^+{=}O$ NO_2^-/NO_3^-)

The previous procedure was repeated, except that 0.6 g of 1-oxy-4-acetyloxy-2,2,6,6-tetramethylpiperidine was used instead of bis(1-oxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate. After the end of the reaction, a yellow liquid was obtained. The yield was 0.83 g (stoichiometric). The FTIR (NaCl) results were the same as those in ref. 3.

1-Oxy-4-acetoxy-2,2,6,6-tetramethylpiperidine as a starting substance was synthesized as follows. 1-Oxy-4-hydroxy-2,2,6,6-tetramethylpiperidine (3.4 g) was dissolved in 30 mL of benzene. Triethylamine (3 mL) was added, and 1 mL of acetyl chloride in 20 mL of benzene was dropped into the solution. After the completion of the reaction, the triethylammonium chloride that formed was filtered off, and the solvent was distilled off *in vacuo*. The product was purified by column chromatography (stationary phase = silica gel, mobile phase = 9 : 1 chloroform/methanol). The yield was 2.2 g (52%), and the melting point was 51.7–52.7°C. In FTIR (NaCl), 3416 cm^{-1} (OH) disappeared, and 1742 cm^{-1} (ester) appeared.

1-Oxy-4-hydroxy-2,2,6,6-tetramethylpiperidine was synthesized as follows. 4-Hydroxy-2,2,6,6-tetramethylpiperidine (9.6 g) was dissolved in 200 mL of methanol. An aqueous 35% hydrogen peroxide solution (20 mL), 7 mL of acetonitrile, 3.6 g of sodium hydrogen carbonate, and 0.5 g of sodium tangstate were added. The mixture was stirred for 3 days. Then, the solvent was distilled off *in vacuo*. The residue was washed with saturated brine and water and was extracted with diethyl ether. After dehydration, the ether was removed, and a deep orange product was obtained. The compound was used directly for the following synthesis without purification. The yield was 9.1 g (86%). In FTIR (NaCl), 962 and 1240 cm^{-1} (NO) appeared.

1-Oxo-4-acetoxy-2,2,6,6-tetramethylpiperidinium bromide (acetate HALS $N^+{=}O$ Br^-)

1-Oxy-2,2,6,6-tetramethyl-4-piperidinyl acetate (0.43 g) was dissolved in 100 mL of *n*-hexane. Bromine dissolved in 50 mL of carbon tetrachloride was dropped into the solution over 1 h. Then, it was filtered, and a mulberry powder was obtained. The yield was 0.13 g (22%), and the melting point was 74.5–76.5°C. The FTIR (KBr) results were the same as those in ref. 3.

Synthesis of 4-acetyloxy-2,2,6,6-tetramethylpiperidine (acetate HALS)

4-Hydroxy-2,2,6,6-tetramethylpiperidine (4.7 g) and 10 mL of acetic acid were stirred at 100°C for 4 h. After the completion of the reaction, an aqueous saturated sodium hydrogen carbonate solution (100 mL) was added, and then the pH was made about 8 by the addition of sodium hydrogen carbonate. The resulting solution was extracted with dichloromethane and dried. The solvent was distilled off *in vacuo*, and a yellow liquid was obtained. The yield was 2.2 g (37%). In FTIR (NaCl), 3264 cm^{-1} (OH) disappeared, and 1732 cm^{-1} (ester) appeared. In FT ^{1}H-NMR ($CDCl_3$, tetramethylsilane, δ), 0.94 (1H, NH) and 1.5 ppm (1H, OH) disappeared, and 2.0 ppm (3H, acetyl) appeared.

Procedure

CHP decomposition by HALSs in the presence of phenol

CHP (1×10^{-2} mol/L) decomposed in a mixture of 5×10^{-4} mol/L 4-acetyloxy-2,2,6,6-tetramethylpiperdine and 5×10^{-4} mol/L 2,4,6-trimethylphenol. Chlorobenzene was used as the solvent. The HALS derivatives that formed in the CHP decomposition were identified and determined by gas chromatography/mass spectrometry (GC–MS).

Thermal decomposition of HALs nitrosonium

Acetate HALS $N^+{=}O$ NO_2^-/NO_3^- (0.06 g) was dissolved in 200 mL of benzene, and the solution was stirred at 80°C under a nitrogen atmosphere for 5 h. The decomposition product was yellow oil. It was analyzed by GC–MS (GCMS-QP5050A, Shimadzu Corp.).

Decomposition of CHP by HALS nitrosonium

CHP (1×10^{-2} mol/L) was decomposed by acetate HALS $N^+{=}O$ NO_2^-/NO_3^- (in several concentrations) under a nitrogen atmosphere at 120°C. Chlorobenzene was used as the solvent. A sample was taken out at every predetermined time, and the remaining CHP was determined by iodometry. The components of the reaction solution were identified by GC–MS. Furthermore, CHP decomposition by acetate HALS $N^+{=}O$ NO_2^-/NO_3^- was also examined in a polar solvent, such as benzonitrile or methyl benzoate.

Measurement of the oxidation potential of phenols and the reaction of HALS nitrosonium with phenols

The oxidation potentials of phenols were measured by cyclic voltammetry. A solution of a phenol (1×10^{-3} mol/L) and tetra-*n*-butylammonium perchlorate

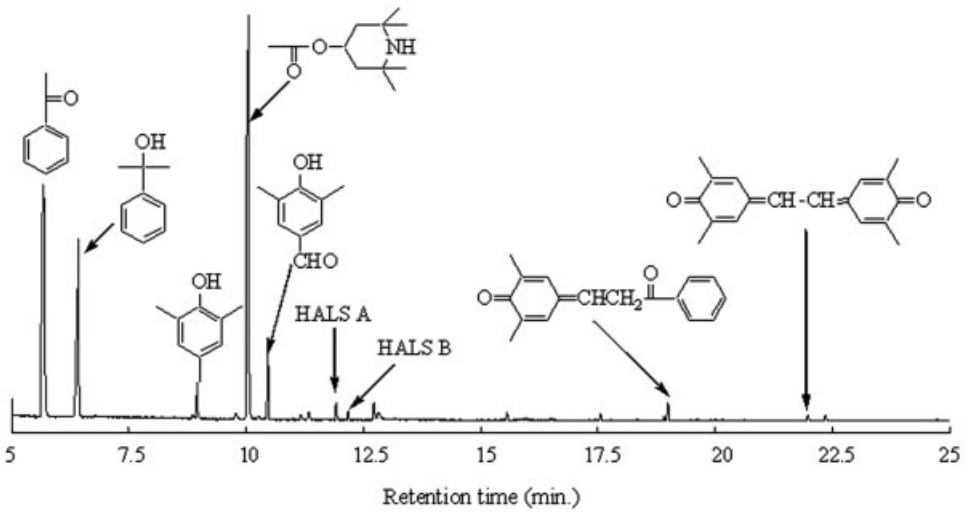


Figure 1 Gas chromatogram of a reaction solution for CHP decomposition by acetate HALS with 2,4,6-trimethylphenol after 25 h in chlorobenzene under N_2 at 120°C.

(TBAP; 0.1 mol/L) in acetonitrile was used for the measurements. The conditions were room temperature, a nitrogen atmosphere, a saturated calomel electrode (SCE) as a reference electrode, and Pt as work and cathode electrodes. On the other hand, the reactivity of HALS nitrosonium with phenol was carried out as follows. *p*-Cresol, 2-*tert*-butyl-*p*-cresol, 2,4,6-trimethylphenol, *p*-methoxyphenol, 2-*tert*-butyl-*p*-cresol, or 2,6-di-*tert*-butyl-*p*-methoxyphenol (5×10^{-4} mol/L) and sebacate HALS $N^+{=}O$ NO_2^-/NO_3^- (1.25×10^{-4} mol/L) were allowed to react in air at room temperature. After the reaction, the products were analyzed with GC–MS.

RESULTS AND DISCUSSION

Active species in CHP decomposition by HALS

CHP decomposition by acetate HALS has been studied in the presence of 2,4,6-trimethylphenol. Figure 1 shows a gas chromatogram of the reaction solution. The decomposition products of CHP, such as acetophenone and cumyl alcohol, suggest that CHP is decomposed homolytically by the HALS. In addition, 2,4,6-trimethylphenol is oxidized during CHP decomposition, and the HALS gives two new products detected by GC–MS (HALS A and HALS B). Figures 2 and 3 show the mass spectra of the two products. The product shown in Figure 2 has been identified as 2-nitroso-2,6-dimethyl-5-hepten-4-yl acetate (nitroso compound), and that in Figure 3 has been as identified as 2-nitro-2,6-dimethyl-5-hepten-4-yl acetate (nitro compound). These products seem to be simple ring-opening compounds of oxidized HALSs.

It has been reported that a nitrosonium derived from a compound having a piperidine moiety gives ring-opening compounds, as shown in Figure 2. According to Abakumov et al.,[4] Scholl et al.,[5] and van Bekkum et al.,[6] a nitroso compound is produced from the nitrosonium by a reaction similar to Hofmann degradation by the action of a basic compound when the nitrosonium has an oxygen- or nitrogen-containing double bond at the 4-position. Bobbitt and Flores[7] reported that a nitrosonium having a chloric ion as a counteranion opens its ring by the action of sodium benzoate or silver benzoate, even if it does not have a double bond at the 4-position.[7] Abakumov et al. also reported that the same compound is formed in the reaction of a nitroxyl radical with trichloroacetic acid: in this reaction, trichloroacetic acid catalyzes the hydrogen transfer, as a proton, at the 3-position of the nitrosonium to the oxyamino anion, and the resulting deprotonated nitrosonium gives a nitroso compound.

We have also confirmed that the ring-opening compound is formed by a thermal action on a nitrosonium salt. When a nitrosonium compound is left in chlorobenzene at 80°C, the HALS nitrosonium is completely

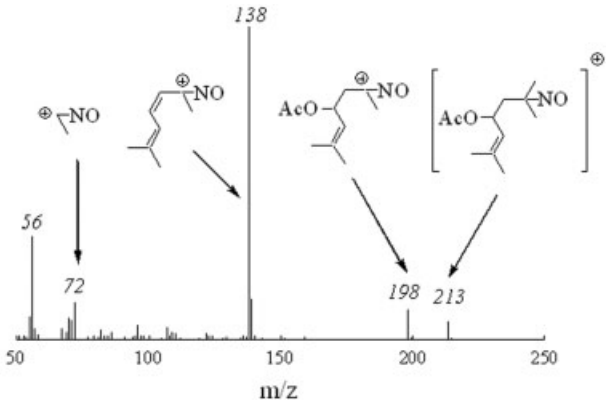


Figure 2 Mass spectrum of HALS A.

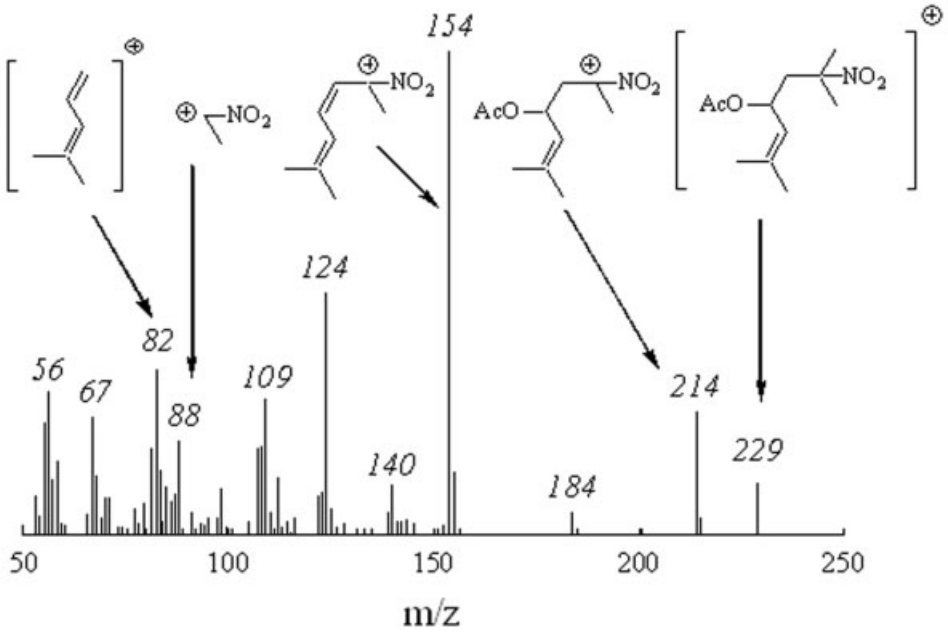
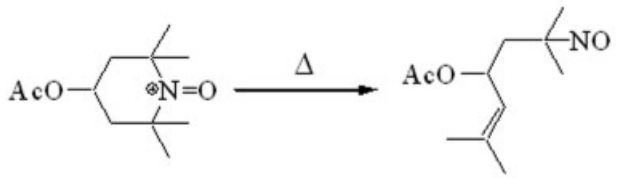


Figure 3 Mass spectrum of HALS B.

decomposed after 5 h and gives a product with ring-opened 2,2,6,6-tetramethylpiperidine:



This suggests that a nitrosonium is present before the formation of the ring-opening compounds.

Figure 4 shows CHP decomposition by acetate HALS in the presence of 2,4,6-trimethylphenol and also shows the relationship between the formation of the ring-opening compound and the decomposition of CHP. The decomposition of CHP is accelerated at the same time with the formation of ring-opening compounds. The result may mean that the nitrosonium is an active species or an active-species-forming precursor of CHP decomposition. When CHP decomposition was repeated without 2,4,6-trimethylphenol, a longer induction period (ca. 120 h)

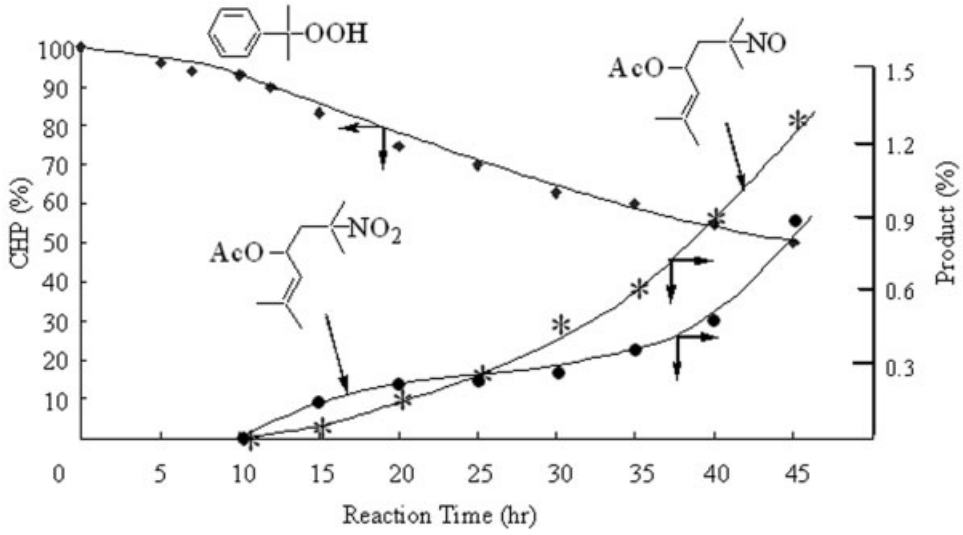


Figure 4 Decomposition of CHP by acetate HALS in the presence of phenol and reaction products in chlorobenzene under N_2 at 120°C (CHP concentration = 10 mmol/L, acetate HALS concentration = 5.0 mmol/L, 2,4,6-trimethylphenol concentration = 5.0 mmol/L).

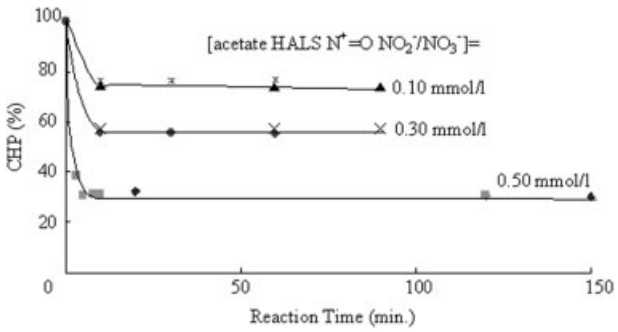


Figure 5 Decomposition of CHP by acetate HALS $N^+{=}O$ NO_2^-/NO_3^- in chlorobenzene under N_2 at 120°C (CHP concentration = 10 mmol/L).

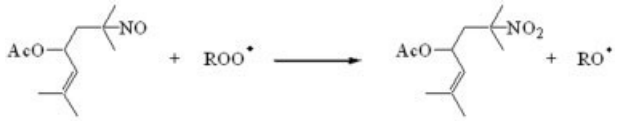
was observed before fast decomposition. In this case, however, the same ring-opening product was detected at the same time with the start of fast decomposition.

Thus, it can be concluded that the nitrosonium is a possible active species of CHP decomposition and that 2,4,6-trimethylphenol works as an accelerator for nitrosonium formation.

Confirmation of the effect of HALS nitrosonium on CHP decomposition

Shown in Figure 5 is CHP decomposition by HALS nitrosonium. When the CHP concentration is fixed at 1.0×10^{-2} mol/L, acetate HALS $N^+{=}O$ NO_2^-/NO_3^- decomposes CHP very quickly, regardless of the nitrosonium concentration. In addition, Figure 5 shows that acetate HALS $N^+{=}O$ NO_2^-/NO_3^- decomposes CHP catalytically (i.e., ca. 15–25 mol of CHP/mol of nitrosonium). This may suggest that nitrosonium decomposes a hydroperoxide in a redox mode.

In this reaction, it has been confirmed that the product from the nitrosonium obtained after the decomposition reaction is the same product found in the thermal decomposition of the nitrosonium. These results support further the idea that HALS nitrosonium exists as a possible active species in the decomposition of a hydroperoxide by HALSs. However, the resulting ring-opening product, a nitroso compound, cannot be denied as an active species of hydroperoxide decomposition because such a compound has been reported to decompose hydroperoxides quickly and catalytically.[2] Ultimately, the nitroso compound is converted to the nitro compound as shown:



The decomposition of CHP by HALS nitrosonium is affected by the kind of solvent. As shown in Figure 6, the decomposition of CHP is delayed and becomes quite slow in comparison with that shown in Figure 5 when the solvent is changed from chlorobenzene to a polar solvent (benzonitrile or acetophenone). This fact shows that hydrophilic substrates, such as HALS nitrosonium and CHP, are gathered in a nonpolar solvent, chlorobenzene, and this results in the acceleration of CHP decomposition. In fact, in the case of benzonitrile, only an increased concentration of HALS nitrosonium has been found to dramatically enhance the decomposition speed of CHP beyond expectations.

Reactivity of HALS nitrosonium with phenol

The characteristics of a nitrosonium were summarized in various aspects by Bobbitt et al.[7] and van Bekkum et al.[6] The aforementioned nitrosonium reaction, however, is limited exclusively to the oxidation of alcohols. A nitrosonium compound can oxidize primary and secondary alcohols to the corresponding aldehydes and ketones. Golubev et al.[8] reported the oxidation of a secondary alcohol in 1965. According to Bobbitt et al., alcohol oxidation by a nitrosonium proceeds via different mechanisms depending on the pH of the reaction system. When the pH is less than 3, a nitrosonium compound and hydroxylamine are formed from two molecules of nitroxyl radicals, and when the pH is greater than 3, two molecules of nitrosonium are produced. Correspondingly, the intermediate of alcohol oxidation differs, depending on the pH of the reaction solution:[9]

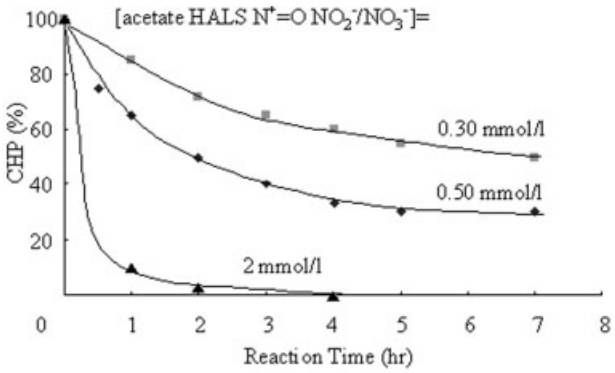
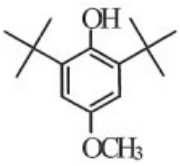
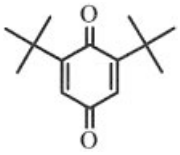
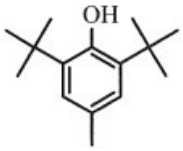
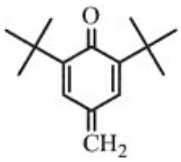
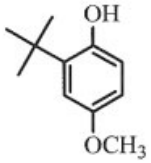
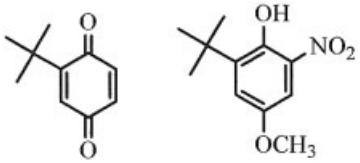
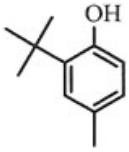
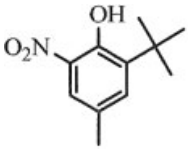
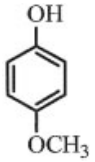
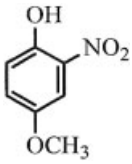
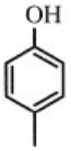
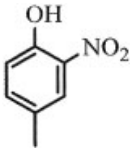
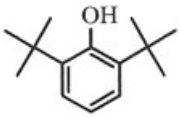
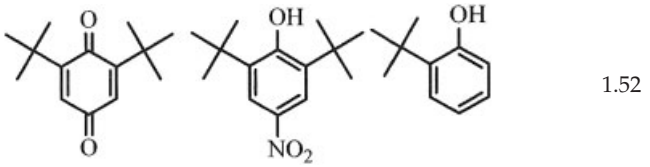
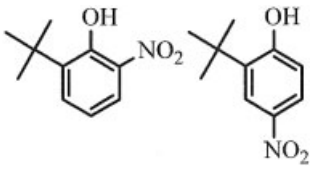
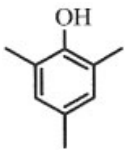
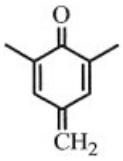


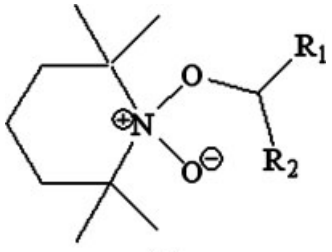
Figure 6 Decomposition of CHP by acetate HALS $N^+{=}O$ NO_2^-/NO_3^- in benzonitrile under N_2 at 120°C (CHP concentration = 10 mmol/L).

TABLE I
Reaction of Sebacate HALS N^+═O NO_2^-/NO_3^- with Phenols

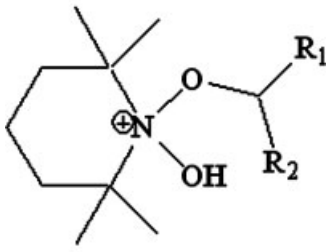
Phenol	Oxidation potential (V) vs SCE[a]	Reaction product	Phenol	Oxidation potential (V) vs SCE[a]	Reaction product
	0.94			1.24	
	0.98			1.29	
	1.05			1.40	
	1.15			1.52	
					

The reaction was performed in chlorobenzene at room temperature under N_2 (sebacate HALS N^+ ═ O NO_2^-/NO_3^- concentration = 0.125 mmol/L; phenol concentration = 0.50 mmol/L).

[a] Taken in a 0.1 mol/L TBAP acetonitrile solution at room temperature under N_2 (phenol concentration = 1.0 mmol/L).



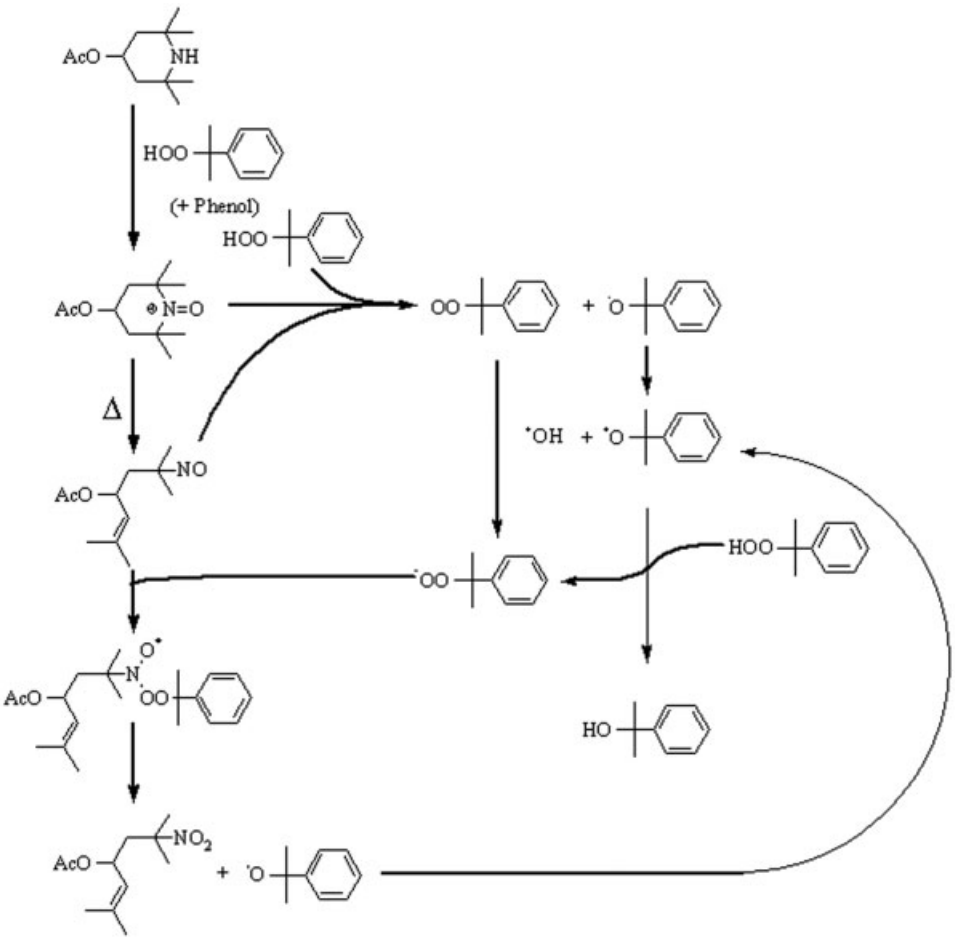
(a)



(b)

In general, polymer materials contain many kinds of stabilizers, such as HALSs, phenolic antioxidants, and UV absorbers. These stabilizers do not work independently but interact with one another in many cases. Thus, it is very interesting from the standpoint of polymer stabilization to clarify the interaction of HALS nitrosonium with phenols. The oxidation of a phenolic compound by a nitrosonium, however, has been reported in few publications. Bobbitt et al.[7] reported that a quinone dimer is formed in the oxidation of 2,4-di-*tert*-butylphenol by a nitrosonium.[10] However, this article reports the results only briefly and does not describe the detailed reaction mechanism.

Therefore, the reaction of HALS nitrosonium with phenols has been examined in this study. Shown in Table I is the reaction of sebacate HALS N^+═O NO_2^- / NO_3^- with a phenol at room temperature. The reaction was carried out with equivalent amounts of nitroso-



Scheme 1 Reaction mechanism of HALS nitrosonium salt.

nium and phenol. Table I shows the products only qualitatively. From Table I, the reactions can be classified into the following three groups:

1. Oxidation of phenol to quinone (including quinone methide).
2. Nitration of phenol.
3. Combination of reactions 1 and 2.

The oxidation of a phenol entirely depends on the redox potential of the phenol. 2,6-Di-*tert*-butyl-4-methoxyphenol or 2-*tert*-butyl-4-methoxyphenol, having a lower redox potential, is oxidized more easily to give the corresponding quinone. On the other hand, such an oxidation reaction also takes place for a phenol having a slightly higher redox potential, but it does not proceed as easily as that of a phenol having a lower redox potential.

On the other hand, the formation of a nitro compound does not seem to depend on the redox potential of phenol, but a phenol having no substituents at the ortho and/or para positions goes into a nitration reaction. In terms of the oxidation reaction and the nitration reaction at the ortho or para position, it can be concluded that the nitration reaction at the ortho position occurs more easily than the oxidation reaction, and the oxidation reaction occurs more easily than the nitration reaction at the para position. When a similar reaction was repeated with acetate HALS $N^+{=}O\ Br^-$ in place of sebacate HALS $N^+{=}O\ NO_2^-/NO_3^-$, the corresponding bromo compound was obtained. Therefore, it can be understood that nitration takes place through the attack of a species derived form NO_2^- as a counteranion of sebacate HALS $N^+{=}O\ NO_2^-/NO_3^-$.

It is not important in this article to discuss what the attacking species of nitration is. Considering the orientation of a substitute (ortho or para position) in the aforementioned reaction, however, we have estimated that a cation (NO_2^+) or a radical ($NO_2\cdot$) is formed by the oxidation of the counteranion (NO_2^-) by the nitrosonium and attacks a vacant ortho or para position electrophilically.

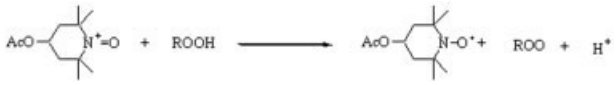
CONCLUSIONS

A HALS nitrosonium is formed in the process of hydroperoxide (CHP) decomposition by HALSs, and its

formation is accelerated by the coexistence of a phenol. The resulting HALS nitrosonium promotes the homolytic decomposition of a hydroperoxide while it goes into a ring-cleavage reaction. A cleaved product, a nitroso compound, also promotes the decomposition of a hydroperoxide. Summarizing the experimental results, Scheme 1 explains the aforementioned reaction process clearly; the reaction of the HALS and phenol, however, is not shown.

In this report, we have made it clear that HALS nitrosonium is an extremely strong oxidant formed during a hydroperoxide decomposition, and it is an active species able to oxidize and deactivate a phenolic antioxidant.

In HALS chemistry, the decomposition of a hydroperoxide by HALSs is an important reaction forming active derivatives of HALSs, such as HALS nitroxide and hydroxide. The results obtained in this study never deny such well-known facts. On the basis of the CHP decomposition rates shown in Figures 4 and 5, a nitrosonium is considered to exist only in a very small amount in an actual reaction system (Fig. 4), compared with the initially added amount of HALSs. On the other hand, HALS nitroxide will be formed from a nitrosonium by one electron oxidation:



This reaction may occur mainly.

References

1. Yamaguchi, K.; Ohkatsu, Y.; Kusano, T. J Jpn Pet Inst 1991, 34, 458.
2. Yamashita, H.; Ohkatsu, Y. Polym Degrad Stab 2003, 80, 421.
3. Miyazawa, T.; Endo, T.; Shiihashi, S.; Okawara, M. J Org Chem 1985, 50, 1332.
4. Abakumov, G. A.; Tikhonov, V. D. Bull Acad Sci Div Chem Sci 1969, 724.
5. de Ilarduya, J. I. M.; Krzyczmonik, P.; Scholl, H.; Grabowski, G. Electroanalysis 1991, 233, 3.
6. de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. Synthesis 1996, 1153, 8.
7. Bobbitt, J. M.; Flores, M. C. L. Heterocycles 1988, 509, 27.
8. Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. Bull Acad Sci Div Chem Sci 1965, 1898.
9. Ma, Z.; Bobbitt, J. M. J Org Chem 1991, 6110, 56.
10. Bobbitt, J. M.; Ma, Z. Heterocycles 1992, 641, 33.