[Regular Paper]

Interaction between Nitroxide of Hindered Amine Light Stabilizers and Phenol

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(Received June 26, 2006)

The antagonism between nitroxides of hindered amine light stabilizers (HALS NO) and phenolic antioxidants, such as 2,6-di-*t*-butyl-4-methylphenol (BHT), was investigated. Identification of the reaction products of HALS NO and BHT clarified the formation of HALS hydroxylamine (HALS NOH) and HALS amine (HALS NH) by the reduction of HALS NO, and the formation of quinone methide and stilbene quinone by the oxidation of BHT. The identification of these products in the reaction of HALS NO with BHT suggests a new antagonism between HALS NO and BHT: two molecules of HALS NO form HALS nitrosonium by electron transfer. The nitrosonium has strong oxidation power, and uselessly oxidizes a phenol such as BHT to quinone methide and finally stilbene quinone, while the nitrosonium and HALS NO are reduced to HALS NOH and HALS NH.

Keywords

HALS, Phenol, Antagonism, HALS nitrosonium, HALS nitroxide

1. Introduction

Polymer materials, such as a plastics, rubbers, and fibers, have an extremely wide variety of applications. However, these organic materials suffer the major defects of deterioration during use. Another defect is the social problem caused by the disposal of waste polymer materials. Increased stability of these materials would extend the service life and improve both of those defects. In general, the degradation of polymer materials results from the actions of light, heat, and oxygen, and is essentially caused by autoxidation. Therefore, the prevention of autoxidation is extremely important for polymer materials.

Although hindered amine light stabilizers (HALS) have been used as light stabilizers, they are utilized widely, at present, as multifunctional stabilizers with actions of light stabilizing, radical trapping, hydroperoxide decomposition, and heavy metal trapping^{1)~4)}. It is pointed out as a feature of HALS, however, that they must be taken notice of the compatibility with other additives.

Phenolic antioxidants are polymer additives which can trap peroxy radicals, and are used widely to stabilize almost all polymer materials. The HALS and phenolic antioxidants are frequently used together practically. Therefore, the interaction of these additives is very important, but previous studies have shown either antagonism or synergism. Consequently, the inter-

action remains unclear⁵⁾.

Previously we proposed a synergistic action mechanism of these additives for preventing the photo-degradation process of plastics⁶⁾. The phenolic antioxidant forms a quinone as a result of trapping peroxy radicals. The quinone absorbs light and is excited to initiate or promote a homolytical chain reaction or autoxidation. However, the photo-excited quinone, in the presence of HALS, abstracts hydrogen atoms from the HALS or HALS derivatives such as HALS hydroxylamine (HALS NOH) to go back to a phenol. Therefore, HALS not only prevent the deterioration acceleration by a quinone, but also make good use of the light absorption of the quinone to regenerate a phenol. Consequently, synergism is observed.

The antagonism of HALS and phenolic antioxidants is explained by the mechanism that a HALS derivative, HALS nitroxide (HALS NO), abstracts a hydrogen from the phenol, and the resulting phenoxy radical couples with another HALS NO, resulting in useless consumption of both additives (**Scheme 1**)⁷⁾. This mechanism has been accepted for the last 20 years, but some characteristics remain unclear, such as the identity of the final coupled product shown in **Scheme 1**.

The present study investigated the possible antagonistic mechanism using phenols such as BHT in detail, and has identified a new antagonistic mechanism between HALS and phenols.

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2. Experiment

2.1. Reagents

2.1.1. Commercial Reagents

3,5-Di-*t*-butyl-4-hydroxy-toluene (BHT), 2-*t*-butyl-*p*-cresol, and *p*-cresol (Tokyo Chemical Ind. Co., Ltd.) were purified by recrystallization of the commercial phenols from hexane. Chlorobenzene (Takahashi Pure Chemical) was used as a solvent after distillation.

2.1.2. Synthesis of Bis(1-oxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate (HALS NO)

Bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate (13 g; ADEKA, ADK stab LA-77) (HALS NH) was dissolved in 200 cm³ of methanol, and 7 cm³ of acetonitrile was added. Then, 3.6 g of potassium hydrogen carbonate, 0.5 g of sodium tungstate and 20 cm³ of 35% hydrogen peroxide were added. The mixture was stirred at room temperature for one day. After the reaction, the solvent was removed under reduced pressure, and the residue was extracted with chloroform. The product was purified by column chromatography (stationary phase: silica gel, mobile phase: chloroform) and recrystallized from hexane. Yield: 6.10 g (44.17%), melting point: 103.5–104.2°C, FT-IR (KBr): around 3300 cm⁻¹ (NH) disappeared, 1732 cm⁻¹ (ester), 1285 cm⁻¹ and 985 cm⁻¹ (NO).

2.1.3. Synthesis of Bis(1-oxo-2,2,6,6-tetramethylpiperidinium-4-yl)sebacate Nitrate/Nitrite Mixture (HALS N⁺=O NO₃⁻/NO₂⁻)

This compound was synthesized by the method of G. Kaupp *et al.*⁸⁾. Nitrogen dioxide (*ca.* 7.2 × 10³ cm³ at 0°C) was passed over 0.60 g of HALS NO at -10°C for 2 h. The mixture was then stirred for 2 h. Remaining nitrogen dioxide was released by warming up to 50°C. Water-soluble and highly viscous crimson oil was obtained. Yield 0.56 g (75%), FT-IR (NaCl): 988 cm⁻¹ (nitroxide) disappeared; 2940, 1620, 1350, 1240, 1160, and 1100 cm⁻¹ (nitrosonium salt⁴⁾), and 1736 cm⁻¹ (ester).

2.1.4. Synthesis of 4-Acetoxy-2,2,6,6-tetramethylpiperidine (acetate HALS NH)

4-Hydroxy-2,2,6,6-tetramethylpiperidine (15.7 g; Tokyo Chemical Ind. Co., Ltd.) was dissolved in 36 cm³ of acetic acid, and 1 cm³ of concentrated sulfuric acid was added. The mixture was stirred for 4 h at 100°C. After the reaction, the solution was added to ice water and the basicity raised a little with sodium hydroxide. The solution was extracted with dichloromethane. The solvent was removed under a reduced pressure, and a pale yellow oil was obtained. Yield: 11.76 g (59.12%), FT-IR (NaCl): 3327 cm⁻¹ (NH), 1732 cm⁻¹ (ester), 3400 cm⁻¹ (OH) disappeared, ¹H-NMR (CDCl₃, TMS): 1.6 ppm (CH₃ 12H), 5.3 ppm (CH₂ 4H).

2.1.5. Synthesis of 1-Oxy-4-acetoxy-2,2,6,6-tetramethylpiperidine (acetate HALS NO)

Acetate HALS NH (1.99 g) was dissolved in 30 cm³ of methanol. Then, 0.8 g of potassium hydrogen carbonate, 0.1 g of sodium tungstate and 4 cm³ of 35% hydrogen peroxide were added. The mixture was stirred at room temperature for one day. After the reaction, the solvent was removed under reduced pressure, and the residue was extracted with chloroform. This product was purified by column chromatography (stationary phase: silica gel, mobile phase: chloroform) and recrystallization from hexane. Yield: 0.50 g (23.36%), melting point: 51.6–52.5°C, FT-IR (KBr): around 3300 cm⁻¹ (NH) disappeared, 1732 cm⁻¹ (ester), 982 cm⁻¹ (NO).

2.2. Reaction of HALS NO and Phenol

The reaction was carried out by dissolving a HALS NO and a the phenol at a predetermined concentration ratio in chlorobenzene in a reaction vessel at 120°C in an oil bath, and the reaction products were identified by gas chromatography-mass spectrometry (GCMS).

2.3. Instrumental Analysis

Model GC-17A or GC-14B manufactured by Shimadzu Corp. was used as a gas chromatograph with a flame ionization detector (FID). The gas chromatograph-mass spectrometer was a Model QP5050A made by Shimadzu Corp. The 400-1HT column (Quadrex Corp.) was used in both systems.

3. Results and Discussion

3.1. Identification of Reaction Products

The reaction products of HALS NO and BHT were analyzed. **Figure 1** shows the gas chromatogram of various reaction products at 6 h after the reaction at 120°C. The main products A-F were identified by GCMS and by comparison with authentic samples, if available, as follows:

Product A: 2,6-di-*t*-butyl-*p*-quinone methide (QM)

MS: *m*⁺/*e* = 218 (P, 41), 175 (40), 91 (18), 203 (54), 161 (100), 41 (29)

Product B: 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (FP)

MS: *m*⁺/*e* = 234 (P, 28), 191 (35), 219 (100), 57 (60)

[HALS NO] : [BHT] = 1×10^{-2} mol/l : 2×10^{-2} mol/l in chlorobenzene at 120°C.

Fig. 1 Gas Chromatogram after Reaction of HALS NO and BHT for 6 h

Product C: 4,4'-ethylenebis(2,6-di-*t*-butylphenol) (BHT dimer)

MS: m^+/e = 438 (P, 10), 204 (10), 219 (100), 57 (25)

Product D: HALS NH

MS: m^+/e = 343 (1), 124 (100), 140 (9), 58 (26)

Product E: 3,3',5,5'-tetra-*t*-butyl-4,4'-stilbene quinone (SQ)

MS: m^+/e = 434 (P, 60), 124 (15), 419 (5), 57 (100)

Product F: bis(1-hydroxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate (HALS NOH)

MS: m^+/e = 343 (3), 140 (13), 58 (26), 154 (10), 124 (100)

The following features are characteristic of the main products:

- (1) The coupling product of a phenoxy radical with a HALS NO as shown in **Scheme 1** is not detected.
- (2) The nitroxide-reduced product D (HALS NH) is produced in the reaction system of HALS NO and BHT, although BHT has no strong reducing power.
- (3) The 4-methyl group of BHT is oxidized, although the hydroxyl group would be oxidized more easily

(product B).

(4) The main products from BHT were compounds, QM, BHT dimer, and SQ.

In fact, the reaction solution of HALS NO and BHT became yellow as the reaction proceeded, and finally was very deep orange. This observation corresponds with the formation of SQ.

The discoloration of plastics containing BHT in air is well known. Such coloring by the reaction of BHT with NO_x gas is explained in **Scheme 2**⁹⁾. Interestingly, the colored products, quinone methide and stilbene quinone, are the same main products (QM and SQ) as obtained in this study. This suggests that a substance with very strong oxidizing power, like NO_x gas, is formed in the reaction of HALS NO and BHT.

Nitrosonium compounds containing a piperidine moiety are reported to have strong oxidation power, in particular the power to oxidize alcohols to the corresponding ketones or aldehydes^{10)~12)}. Considering these facts, HALS nitrosonium ($\text{HALS N}^+=\text{O}$) may be a candidate for such a substance formed in the reaction of HALS NO and BHT. To confirm this idea, bis(1-oxo-2,2,6,6-tetramethyl-4-piperidyl)sebacate salt ($\text{HALS N}^+=\text{O NO}_3^-/\text{NO}_2^-$) was prepared, and reacted with BHT.

Figure 2 shows gas chromatograms at an earlier stage of the reactions of HALS NO with BHT and $\text{HALS N}^+=\text{O NO}_3^-/\text{NO}_2^-$ with BHT at room temperature. The latter reaction was carried out at the nitrosonium concentration of only 5% of that of HALS NO for the former reaction, because only a small part of the HALS NO is assumed to become $\text{HALS N}^+=\text{O NO}_3^-/\text{NO}_2^-$. Both chromatograms show the same products, QM and HALS NOH. This result indicates that HALS nitrosonium is formed in the reaction of HALS NO and BHT, and shows that the nitrosonium oxidizes BHT to QM to be HALS NOH. That is, HALS nitrosonium is the active oxidation species of BHT.

3. 2. Formation Mechanism of Reaction Products

The HALS NO was reacted with BHT at 120°C. The reaction products are shown in **Fig. 3**. The left figure in **Fig. 3** shows reaction products derived from BHT, and the right one, those from HALS. The BHT was consumed first just after the start of reaction and

QM was formed at the same time, and the formation of BHT dimer followed. Then, SQ and FP were formed parallelly and gradually.

In contrast, HALS NOH was formed first, followed by HALS NH. The formation of HALS NH increased monotonically, in contrast to HALS NOH. Comparing formation curves of products, the formation of HALS NH seems to correspond to the formation of FP. Moreover, the amount of HALS NOH was only a few percents of that of QM, due to the consumption of HALS NOH by donating hydrogen to other various intermediates.

According to **Fig. 3**, no detailed changes of products from BHT could be observed clearly with time because of the disturbance caused by the large quantity of unreacted BHT. Therefore, a similar reaction was repeated under the same conditions except for the relative increase in HALS NO concentration (**Fig. 4**). As a result, the BHT was finally consumed completely.

Figure 4 shows that QM and BHT dimer are reaction intermediates, and the amount of SQ starts to increase,

Scheme 1 Antagonism between HALS Nitroxide and Phenolic Antioxidant

especially about the same time as the decrease in BHT dimer. All BHT was converted into SQ, QM, and other products after 12 h. Therefore, BHT dimer is the precursor of SQ, in agreement with the mechanism for the reaction of NO_x with BHT (**Scheme 2**).

3.3. Reaction between HALS NO and Phenol

The generally accepted antagonism between HALS and phenols is shown in **Scheme 1**. We investigated the interaction of HALS NO and BHT as a representative phenol, and found a new antagonism between them. To confirm the antagonism further, 2-*t*-butyl-4-methylphenol and 4-methylphenol with less steric hindrance were reacted with HALS NO. The reaction of 2-*t*-butyl-4-methylphenol was considerably slower than that of BHT, and 4-methylphenol did not react at all at 120°C.

Figure 5 shows the gas chromatogram of reaction products at 23 h after reacting acetate HALS NO with 2-*t*-butyl-4-methylphenol at 120°C. Similar products were detected to those from BHT, but a few differences were observed. That is to say, acetate HALS NH and 1-hydroxy-2,2,6,6-tetramethyl-4-piperidyl acetate (acetate HALS NOH) were formed from acetate HALS

Scheme 2 Colorization Mechanism of BHT by Nitrogen Dioxide Gas

[HALS NO] : [BHT] = $1 \times 10^{-2} \text{ mol/l}$: $1 \times 10^{-2} \text{ mol/l}$ in chlorobenzene at r.t

[HALS N⁺=O] : [BHT] = $5 \times 10^{-4} \text{ mol/l}$: $1 \times 10^{-2} \text{ mol/l}$ in chlorobenzene at r.t.

Fig 2 Initial Gas Chromatogram of Reaction Mixture of HALS and BHT

[HALS NO] : [BHT] = 1.0×10^{-2} mol/l : 1.0×10^{-2} mol/l in chlorobenzene at 120°C .

Fig 3 Products in Reaction of HALS NO and BHT

NO, and a dimer from 2-*t*-butyl-4-methylphenol was identified, but quinone methide regarded as precursor of the dimer and stilbene quinone derived from oxidation of the dimer were not detected. These observations suggest that such undetected compounds are unstable, even if formed, or are little formed. However, the order of reactivity of HALS NO with these three types of phenols was the same as that of the reactivity of HALS nitrosonium¹³. Therefore, the antagonism of HALS NO with a phenol seems to relate to the oxidation potential of the phenol¹³: a phenol with higher oxidation potential is more difficult to react with HALS NO.

Interestingly, the product shown as G in Fig. 5 was observed only in the case of 2-*t*-butyl-4-methylphenol. The G is identified as a phenoxy dimer of the phenol, although the substituted position cannot be specified:

MS: $m^+e = 326$ (P, 50), 270 (15), 120 (40)
311 (13), 255 (100), 57 (60)

Previously¹³, a phenol with no substituent on 2- or 4-position, for example 2-*t*-butyl-4-methylphenol, was reported to be nitrated to 2-*t*-butyl-4-methyl-6-nitrophenol, if HALS $\text{N}^+ = \text{O} \text{ NO}_3^-/\text{NO}_2^-$ is used. If this fact is applicable to this study, an intermediate

is estimated to occur in the reaction of HALS NO with 2-*t*-butyl-4-methylphenol.

[HALS NO] : [BHT] = 2.0×10^{-2} mol/l : 5.0×10^{-3} mol/l in chlorobenzene at 120°C .

Fig 4 Products from BHT in Reaction of HALS NO and BHT

3. 4. Antagonism between HALS NO and Phenol

Based on results mentioned before, three stages in the interaction of HALS NO and phenol can be proposed.

Initial stage: formation of HALS NOH and quinone methide.

Middle and final stages: formation of stilbene quinone from quinone methide, in parallel with the formation of formyl phenol (FP) and HALS NH.

Therefore, the mechanism for the interaction (antagonism) between HALS NO and phenol is proposed as in Scheme 3.

In the initial stage, two molecules of HALS NO react with each other through electron transfer to form the active species, HALS nitrosonium (Eq. (1)). The nitrosonium reacts with phenol to form HALS NOH and another nitrosonium with a phenoxy anion as counter ion (Eq. (2)). The resulting HALS nitrosonium phenolate undergoes an intramolecular redox reaction to

[acetate HALS NO] : [phenol] = 1×10^{-2} mol/l : 1×10^{-2} mol/l in chlorobenzene at 120°C .

Fig 5 Gas Chromatogram of Reaction Mixture of Acetate HALS NO and 2-*t*-Butyl-4-methylphenol after 23 h

Scheme 3 New Antagonism between HALS Nitroxide and Phenolic Antioxidant

form HALS NOH and quinone methide (Eq. (3)).

In the middle stage, the HALS NOH from the initial stage reacts further with quinone methide to form HALS NO and benzyl radical (Eq. (4)), as reported in the reaction of HALS NOH with *p*-benzoquinone⁶⁾. The two benzyl radicals are coupled together to form a dimer such as BHT dimer. The dimer produces stilbene quinone by further oxidation (Eq. (5)).

In the final stage, the benzyl radical is combined with

HALS NO in parallel with the middle stage, and finally produces formyl phenol (FP) and HALS NH (Eq. (6)). This mechanism can well explain the observations of this study.

The reaction of HALS NO with BHT was also studied kinetically. As a result, the consumption rate equation of BHT was obtained as follows:

$$-\frac{d[\text{BHT}]}{dt} = k[\text{HALS NO}]^{1.7}[\text{BHT}]^0$$

in the concentration ranges of 7.5×10^{-3} to 2.5×10^{-2} M for HALS NO and of 5.0×10^{-3} to 2.0×10^{-2} M for BHT. Interestingly, the BHT consumption rate does not depend on the BHT concentration, which implies no participation of BHT in the rate-determining step of the reaction of HALS NO with BHT, as well as the rate-determining step consisting of the reaction of 1.7 moles, roughly 2 moles of HALS NO. These findings agree with the mechanism shown in **Scheme 3**. Equation (1) in the initial stage will be probably slow due to the stability of HALS NO.

4. Conclusion

The widely accepted antagonism mechanism between HALS NO and phenols is based on the direct hydrogen abstraction of HALS NO from a phenol, followed by a useless coupling of the resulting phenoxy radical with another nitroxide. In this study, a new antagonism mechanism has been proposed. The active species, HALS nitrosonium, formed by electron transfer between two HALS NO molecules, oxidizes and consumes a phenol uselessly.

This result is very important for clarifying the overall interaction between HALS and phenolic antioxidants

used in plastics. Furthermore, it is also useful for developing and constructing a combination of both additives with less antagonism. As a result, additive systems emphasizing the synergism of HALS and phenols⁶⁾ will be studied and established in the future.

References

- 1) Wiles, D. M., Carlsson, D. J., *Polym. Deg. and Stab.*, **3**, 69 (1981).
- 2) Allen, N. S., Padron, A. C., Henman, T. J., *Polym. Deg. and Stab.*, **13**, 31 (1985).
- 3) Fairgrieve, S. P., MacCallum, J. R., *Polym. Deg. and Stab.*, **15**, 81 (1986).
- 4) Ohkatsu, Y., "Theory and Practice of Autoxidation (in Japanese)," Kagaku-Kogyosha, Tokyo (1986), p. 141.
- 5) Ohkatsu, Y., ed., "The Base and Applicative Technology of Polymer Functional Materials (in Japanese)," Gijyutsu-kyoiku-shyuppan, Tokyo (2000), p. 278.
- 6) Ohkatsu, Y., Yamaguchi, Y., Sengoku, T., Sato, T., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **37**, (4), 405 (1994).
- 7) Allen, N. S., Hamid, A., *Plas. Rub. Pro. Appl.*, **5**, 259 (1985).
- 8) Kaupp, G., Schmeyer, J., *J. Org. Chem.*, **60**, 5494 (1995).
- 9) Smeltz, K. Z., *Textile Chem. Color.*, **15**, (4), 52 (1983).
- 10) Zhenkun, Ma, Bobbitt, J. M., *J. Org. Chem.*, **56**, (21), 6110 (1991).
- 11) Chang, P. S., Robyt, J. F., *J. Carbohydr. Chem.*, **15**, (7), 819 (1996).
- 12) Bobbitt, J. M., *J. Org. Chem.*, **63**, (25), 9367 (1998).
- 13) Yamashita, H., Bannno, K., Ohkatsu, Y., *J. Appl. Polym. Sci.*, **102**, 1310 (2006).

要 旨

ヒンダードアミン光安定剤のニトロキシドとフェノールの相互作用

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ヒンダードアミン光安定剤ニトロキシド (HALS NO) とフェノール系酸化防止剤の拮抗作用を検討した。両者の反応生成物を詳細に検討したところ, HALS NO からはそれが還元された HALS ヒドロキシルアミン (HALS NOH) および HALS アミン (HALS NH) が生成し, 一方, フェノール, たとえば 2,6-ジ-*t*-ブチル-4-メチルフェノール (BHT) からは主にそのキノンメチドおよびスチルベンキノンなどが生成することが分かった。

これらの生成物は初めての発見である。この結果に基づいて, 新しい HALS NO とフェノールの拮抗作用が提案される。HALS NO は 2 分子間の電子移動反応によって HALS ニトロソニウムとなる。このニトロソニウムは強い酸化力を持ち, フェノール, たとえば BHT をキノンメチド, そして最終的にスチルベンキノンに酸化し, 無益に消費する。一方, HALS NO は HALS アミンおよび HALS ヒドロキシルアミンへ還元される。