Oxidation Inhibition by Interaction of Quinones with HALS (hindered amine light stabilizers)

Kazuo YAMAGUCHI, Yasukazu OHKATSU*, and Toru KUSANO

Dept. of Industrial Chemistry, Faculty of Engineering, Kogakuin University,
1-24-2 Nishishinjyuku, Shinjyuku-ku, Tokyo 163-91

(Received January 18, 1991)

The interaction of quinones with HALS (hindered amine light stabilizers) was examined in autoxidation reactions, and it was found that oxidation was little inhibited or retarded when either a quinone or HALS was used in a concentration of 10^{-4} M. A combination of a quinone with HALS in the same concentrations, however, resulted in a remarkable inhibition of oxidation, especially under the irradiation of light. Furthermore, cooperative inhibition of a quinone and HALS was enhanced by the addition of hydroperoxide. Analyses of the inhibited solutions by means of both prussian blue test and FT-IR confirmed that some phenol derivatives were formed by the interaction of a quinone with HALS.

1. Introduction

Antioxidants or stabilizers are used for many kinds of petroleum products such as fuels, lubricants, plastics, etc. In the field of polymer industries, HALS (hindered amine light stabilizers) have attracted considerable attention, because of their excellent light stabilizing abilities compared with those of other light stabilizers.

Several action mechanisms of HALS have been proposed^{1)~17)}, but these fail to explain clearly the light stabilization.

In practical stabilization of polymers, antioxidants (such as phenols) are often used together with HALS, and a synergistic effect^{18), 19)} is reported in such systems. It is well known that phenolic antioxidants are converted into quinones during autoxidation. Previously, we proposed²⁰⁾ that the synergism is due to regeneration of phenols from quinones by action of HALS. Recently, we also estimated²¹⁾, on the basis of kinetic facts, that the synergism of oxidation inhibition by interaction of quinones with HALS consists of hydrogen transfer from hydrogen donor such as HALS to quinones.

In this paper, we will report a few evidences to support that the inhibition synergism is ascribed to the generation of phenol.

2. Experimental

2.1 Materials

2.1.1 Quinones

1) 2,6-Di-tert-butyl-*p*-benzoquinone (2,6-DBBQ)

2,6-Di-tert-butylphenol (15 g, 0.07 mol) was dissolved in 75 ml of ethanol, to which 10 ml of HCl

concentrate was added and, further aqueous sodium nitrite (5.55 g, 0.08 mol) solution was added dropwise and stirred, keeping the temperature at 0—5°C. The resulting reaction solution, containing yellow crystals, was poured into cold water and 2,6-di-tert-butyl-1,4-benzoquinone-4-monooxime and then isolated by filtration. The subsequent hydrolysis of the oxime was carried out as follows: the mixture of 2,6-di-tert-butyl-1,4-benzoquinone-4-monooxime (10 g, 0.04 mol), cuprous oxide (22.5 g, 0.16 mol), HCl concentrate (100 ml), acetone (20 ml) and ethanol (125 ml) was refluxed and stirred. After one hour, the dark-colored reaction mixture was cooled at room temperature, then extracted with toluene, and washed with water. After removing the solvent, the desired product was obtained as in the form of yellow brown needle-like crystals by recrystallization from ethanol. M. p. 64—64.5°C. IR (KBr): 3,300 (—OH) cm^{-1} disappeared, and 1,650 (C=O) and 1,600 (C=C) cm^{-1} appeared. Analyses of $\text{C}_{14}\text{H}_{20}\text{O}_2$ (%): (calculated) C, 76.36; H, 9.09. (Found) C, 76.19; H, 9.13.

2) 2,5-Di-tert-butyl-*p*-benzoquinone (2,5-DBBQ)

The quinone was prepared by repeating the above-mentioned procedure except for the use of 2,5-di-tert-butyl hydroquinone as starting material. M.p. 150—151°C. IR (KBr): 3,300 (—OH) cm^{-1} disappeared, and 1,650 (C=O) and 1,600 (C=C) cm^{-1} appeared. Analyses of $\text{C}_{14}\text{H}_{20}\text{O}_2$ (%): (Calculated) C, 76.36; H, 9.09. (Found) C, 76.39; H, 9.21. The other quinones such as *p*-benzoquinone (BQ), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DCDCBQ), 2,3,5,6-tetrachloro-*p*-benzoquinone (TCBQ), were purchased from Tokyo Kasei Co., Ltd. and used without any further purification.

* To whom correspondence should be addressed.

2.1.2 HALS

The bis(2,2,6,6-tetramethyl-4-piperidiny) sebacate (ADK stab LA-77), was provided by Asahi Denka Co., Ltd. The ADK stab LA-77-NO (N-oxide)²²⁾ was synthesized by oxidation of ADK stab LA-77.

2.1.3 Others

A substrate, tetralin, 9,10-dihydroanthracene, and an initiator, AIBN (azobisisobutyronitrile) were purchased from Tokyo Kasei Co., Ltd. Phenolic antioxidant, BHT (2,6-di-tert-butyl-4-methylphenol) was used after recrystallization. tert-Butylhydroperoxide (Bu^tOH, Nakarai Chemical Co., Ltd.) was used as a model of hydroperoxide. A solvent, monochlorobenzene was used after distillation.

2.2 Procedures

2.2.1 Autoxidation

A quinone, BHT, HALS, and/or a tert-butylhydroperoxide were added to 5 ml of solution of 9,10-dihydroanthracene or tetralin in monochlorobenzene in a reaction flask. An AIBN was added as initiator, as well. Then the flask was flushed completely with oxygen and attached to an air-tight reaction system connected to a differential pressure-detecting unit (a transducer, Toyoda Koki Co., Ltd.). The oxidation was carried out at 50°C. UV light irradiation was carried out using a high pressure mercury lamp (USIO Electric Co., Ltd.). The term induction period used in this study is defined as the period preceding the condition where the rate of oxygen absorption has recovered to approximately the level of the rate observed in the absence of an inhibitor.

2.2.2 Identification of a Phenol

A phenol in reaction mixture, if produced from a quinone, was identified by a qualitative analysis carried out using FT-IR (JEOL 100 FT-IR) after separation of an oxidation solution by a thin layer chromatography (fixed bed: silica gel, eluent: toluene).

2.2.3 Prussian Blue Test

Prussian blue test^{23),24)}, as qualitative analysis of a hindered phenol, was conducted according to a conventional method. To 2 ml of a sample, 0.5 ml of 1% FeCl₃ and 0.5 ml of aqueous solution

of 1% K₃Fe(CN)₆ were added. After 5 min, 0.1 N aqueous solution of HCl was poured into the sample mixture. Phenol was determined by measuring the absorbance of a colored reaction mixture at 450 nm.

3. Results and Discussion

3.1 Synergistic Effect of a Phenol or a Quinone with HALS

As proposed in previous papers^{20),21)}, the synergistic effect of a phenol with HALS possibly relates to regeneration of a phenol from the quinone formed as result of antioxidative action of a phenolic compound. In order to further clarify the synergistic effect, however, the interaction of a quinone with HALS has been studied. In Fig. 1 is illustrated results of autoxidations of 9,10-dihydroanthracene in the presence of 2,6-DBBQ and/or ADK stab LA-77. The broken line and solid lines show the oxidation in the presence of either 2,6-DBBQ or ADK stab LA-77 and combination of both additives, respectively. In latter cases, inhibitions were observed, though they

- (1): 2,6-DBBQ 10^{-4} M or ADK stab LA-77 10^{-4} M
 (2): 2,6-DBBQ 10^{-5} M + ADK stab LA-77 10^{-5} M
 (3): 2,6-DBBQ 10^{-4} M + ADK stab LA-77 10^{-5} M
 (4): 2,6-DBBQ 10^{-5} M + ADK stab LA-77 10^{-4} M
 (5): 2,6-DBBQ 10^{-4} M + ADK stab LA-77 10^{-4} M

Fig. 1 Autoxidation of 9,10-Dihydroanthracene (0.714 M) in Presence of 2,6-DBBQ, ADK stab LA-77 and AIBN (10^{-2} M) in Monochlorobenzene under Diffused Light at 50°C

Table 1 Oxidation Rates and Induction Periods in Autoxidations of 9,10-Dihydroanthracene (0.714 M) in Presence of 2,6-DBBQ, ADK stab LA-77-NO and AIBN (10^{-2} M) in Monochlorobenzene under Diffused Light at 50°C

Run	2,6-DBBQ [$\times 10^{-5}$ M]	ADK stab LA-77-NO [$\times 10^{-5}$ M]	$(-d[O_2]/dt)_{inh}$ [$\times 10^{-5}$ Ms $^{-1}$]	Induction period [h]
1	1.0	1.0	3.70	2.31
2	1.0	10	1.49	3.13
3	10	1.0	1.49	4.39
4	10	10	0	4.55

much depended on concentrations of the 2,6-DBBQ and ADK stab LA-77. The initial rates of oxygen absorption seem to be affected by the amount of the 2,6-DBBQ added at the start, while the rates in latter stage, by the amount of ADK stab LA-77.

The great differences in $-d[O_2]/dt$ and induction period were observed when ADK stab LA-77-NO (Table 1, Run 4) was used in place of ADK stab LA-77 (Fig. 1 (5)), other being the same conditions. These phenomena are also reported in many papers^{1)~9)}, indicating that the more active species of HALS are in the N-oxide form. When the concentrations of 2,6-DBBQ and ADK stab LA-77-NO were 10^{-4} M, respectively, the oxidation was inhibited for about 5 hours under diffused light. A sample of aliquot was taken 2 hours after the start of such reaction, and it was added to a newly prepared reaction solution containing only 9,10-dihydroanthracene and an AIBN initiator in monochlorobenzene. The greater the amount of aliquot added, the less was the oxidation rate and the longer was the induction period (Table 2). From facts mentioned above and as proposed in the previous paper²⁰⁾, it is concluded that a quinone can produce some antioxidants in synergistic interaction with HALS to inhibit or retard the autoxidation.

To clarify the synergistic interaction of a quinone and HALS in more detail, more experiments were conducted using various kinds of quinones. The results are shown in Table 3.

Table 2 The Effect of Addition of Inhibited Solution* on Autoxidation System of 9,10-Dihydroanthracene (0.714 M) in Presence of BQ (10^{-4} M), ADK stab LA-77-NO (10^{-4} M), and AIBN (10^{-2} M) in Monochlorobenzene under Diffused Light at 50°C

Amount of added [ml]	$(-d[O_2]/dt)_{inh}$ [$\times 10^{-5}$ Ms $^{-1}$]	Induction period [h]
0.5	1.58	2.67
1.0	1.28	4.05
2.0	0.82	4.36

* Sampled after 2 hours from the reaction mixture of oxidation carried out under same reaction conditions.

Table 3 Effects of Quinones (10^{-4} M) on Autoxidation of 9,10-Dihydroanthracene (0.714 M) under Diffused Light at 50°C ADK stab LA-77 (10^{-4} M), AIBN (10^{-2} M)

	TCBQ	DCDCBQ	2,6-DBBQ	2,5-DBBQ	BQ
$(-d[O_2]/dt)_{inh}$ [$\times 10^{-5}$ Ms $^{-1}$]	0.66	3.06	3.22	3.44	4.20

* Absence of both quinone and ADK stab LA-77: $-d[O_2]/dt=6.06 \times 10^{-5}$ Ms $^{-1}$.

The inhibitive effect of a quinone in the presence of HALS, as described in the previous paper²¹⁾, remarkably depended on its substituent groups: a quinone having electron attracting groups was more effective than that having electron donating groups.

3.2 Effect of Adding Hydroperoxide

The effect of a hydroperoxide such as tert-butylhydroperoxide on the synergism as mentioned above, was investigated in autoxidations of 9,10-dihydroanthracene in the presence of BHT and ADK stab LA-77 (Table 4). The addition of Bu^tOOH, in adequate amounts, resulted in extended induction period and decreased rate of oxidation.

Similar experiments were repeated using 2,6-DBBQ instead of BHT (Table 5). In these cases, Bu^tOOH also acted favorably in terms of retardation of autoxidation, though the rates were slightly higher compared with that in the absence of the Bu^tOOH. These facts are highly surprising, because hydroperoxide, in general, is decomposed heterolytically to accelerate autoxidation, and may suggest positive reactivity of hydroperoxide in synergistic interaction of a quinone with HALS.

3.3 Effect of UV Irradiation

In Fig. 2 are shown results obtained in autoxidations of tetralin in the presence of BQ and/or ADK stab LA-77 as additives at 50°C.

Table 4 The Effect of Bu^tOOH on Autoxidation of 9,10-Dihydroanthracene (0.714 M) in Presence of BHT (10^{-4} M), ADK stab LA-77 (10^{-5} M) and AIBN (10^{-2} M) in Monochlorobenzene under Diffused Light at 50°C

Bu ^t OOH [$\times 10^{-5}$ M]	$(-d[O_2]/dt)_{inh}$ [$\times 10^{-5}$ Ms $^{-1}$]	Induction period [h]
0	1.15	3.42
1	2.20	—
10	0.73	3.52
100	0.43	4.28

Table 5 The Effect of Bu^tOOH on Autoxidation of 9,10-Dihydroanthracene (0.714 M) in Presence of 2,6-DBBQ (10^{-4} M), ADK stab LA-77-NO (10^{-5} M) and AIBN (10^{-2} M) in Monochlorobenzene under Diffused Light at 50°C

Bu ^t OOH [$\times 10^{-5}$ M]	$(-d[O_2]/dt)_{inh}$ [$\times 10^{-5}$ Ms $^{-1}$]	Induction period [h]
—*	6.06	0.0
0	1.93	4.4
1	3.77	>5.0
5	3.25	>5.0
10	2.72	>5.0
50	2.02	>5.0

* Absence of both 2,6-DBBQ and ADK stab LA-77-NO.

Fig. 2 Effect of UV Irradiation on Autoxidation of Tetralin (7.3 M) in Presence of BQ (6×10^{-3} M) and/or ADK stab LA-77 (2×10^{-3} M) and AIBN (10^{-2} M) in Monochlorobenzene at 50°C

The amount of oxygen absorbed in the presence of either BQ or ADK stab LA-77, under UV light, is illustrated in broken line. In the figure, it shows comparatively higher oxidation rate, indicating little inhibitive action of each individual additive. It was found, however, that the rate in the presence of combination of both additives was much lower as shown by the solid line (also see Fig. 1). The oxidation was continued under repetition of on and off, or irradiation (on) and non-irradiation (off) of UV light. Although the oxidation rate increased under the irradiation of UV light, it gradually decreased when it was turned off as may be explained reasonably by an oxidation accelerating action of UV light. It was found, however, that the inhibition effect, which was observed

○, ●: 2,5-DBBQ, □, ■: 2,6-DBBQ, △, ▲: DCDCBQ.
Open: nonpretreated. Filled: pretreated by UV light for 30 min.

Fig. 3 Effect of Pretreatment by UV Light on Autoxidation of 9,10-Dihydroanthracene (0.714 M) in Presence of Quinones (10^{-4} M), ADK stab LA-77 (10^{-4} M), Bu^tOOH (10^{-4} M) and AIBN (10^{-2} M) under Diffused Light at 50°C

clearly during the “off” period, was more notable with repetition of on-off cycles. This suggests that the light promotes the formation of an antioxidant from the quinone.

In Fig. 3 are shown the effect of UV light on the inhibitive action in a system containing quinones, ADK stab LA-77, and Bu^tOOH. There was observed pronounced differences among oxidation systems which were not pretreated and those pretreated by UV light. The UV light pretreatment inhibited the oxidation from the beginning of the reaction even in the existence of hydroperoxide. A more dramatic inhibition effect by irradiation of UV light was found in the case of a quinone which possesses electron attracting groups. Although the nonpretreated reaction solution appeared yellowish because of the inherent color of a quinone, it disappeared after pretreatment by UV light irradiation. This result, together with those mentioned before, indicates that UV light plays an important role in conversion of a quinone into some inhibitive substance such as a radical scavenger, *i.e.* phenol.

3.4 Results of Prussian Blue Test and FT-IR Measurements

After oxidation was completed, the solution was analyzed qualitatively by means of a Prussian blue test. A phenol was identified by measurement of Prussian blue color which indicates existence of a hindered phenol. As a result, it was found that the Prussian blue color became deeper with UV irradiation time, indicating formation of some phenol by interaction of a quinone and HALS, which was accelerated by UV light irradiation (Fig. 4).

The inhibitive ability of the sample, which was withdrawn at the point, A, B or C, was examined in autoxidation of 9,10-dihydroanthracene. The oxidation was not inhibited by addition of 1 ml of

2,6-DBBQ (10^{-4} M), ADK stab LA-77-NO (10^{-5} M), Bu^tOOH (5×10^{-4} M).

Fig. 4 Relationship between the Irradiation Time of UV Light and the Intensity of Prussian Blue Color

- 21) Ohkatsu, Y., Yamaguchi, K., Yamaki, A., Maruyama, Y., Kusano, T., *Sekiyu Gakkaishi*, **34**, (3), 280 (1991).
 22) Daryl, C., Hodgeman, J. *Polym. Sci., Polym. Chem. Ed.*, **19**, 807 (1981).
 23) Barton, G. M., Evance, R. S., Gardner, J. A. F., *Nature*, **170**, 249 (1952).
 24) Broumad, H., Smith, J. H., *J. Am. Chem. Soc.*, **74**, 4232 (1952).

要 旨

キノンの HALS (ヒンダードアミン系光安定剤) との相互作用による酸化防止

山口 和男, 大勝 靖一, 草野 邁

工学院大学工学部工業化学科, 163-91 東京都新宿区西新宿 1-24-2

キノンと HALS (ヒンダードアミン系光安定剤) の相互作用を両者を添加剤としている自動酸化反応において研究した。キノンまたは HALS をそれぞれ 10^{-4} M ずつ単独で添加したときにはほとんど酸化を防止する能力を示さなかった。しかし、両者を共用した場合には相乗効果が観察され、さらにこの系に光を照射することにより著しく酸化が抑制された。また、両者の共存する系にヒドロパーオキシドを添加した場合にも劇的な酸化抑制現象が観察された。酸化の抑制されている溶液を

ブルシアンブルー試験および FT-IR により分析した結果、キノンが HALS と相互作用することによって生成したと考えられるフェノール誘導体の存在を確認できた。以上の事実から、フェノール系酸化防止剤と HALS の併用による相乗効果は、前者の酸化防止後の生成物であるキノンの HALS との相互作用によるフェノール再生現象で説明でき、光およびヒドロパーオキシドが関与した相乗安定化機構を提案する。

Keywords

Quinone, Oxidation inhibition, UV light, Light stabilizer, HALS, Synergistic effect