Inhibitory Action of Phenols and Amines in the Photo-Oxidation of Tetralin

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Synopsis

The inhibitory efficiences of antioxidants (phenols and aromatic amines) were determined under irradiation for elucidation of their behavior in photo-oxidation. We determined the ratio of termination rate constant to propagation rate constant and compared the ratio under irradiation with that in the dark. Phenols are classified into two categories with respect to their behavior under irradiation. The first is as antioxidants that have the same ratios under both conditions; the second, as antioxidants that have smaller ratios under irradiation than in the dark. We assumed the smaller ratios to be due to the following: quinones formed via the excited state of phenols by light absorption, in addition to the original phenols, participate in radical capture. Aromatic amines were also classified into two categories relative to their behavior under irradiation.

INTRODUCTION

In the thermal oxidation of hydrocarbon polymers, the process of inhibition with phenols or aromatic amines has been widely investigated.[1] In photo-oxidation, however, little attention is paid to the inhibitory action of antioxidants.

In the present paper, we compare the efficiencies of antioxidants under irradiation with those in the dark. We used tetralin as a model compound, which facilitates the estimation of rate constants.

EXPERIMENTAL

Materials

Tetralin was purified by refluxing over sodium in a nitrogen stream and by distilling twice under reduced pressure. Immediately before use it was passed through a 20-cm alumina column. The purified tetralin (bp 78°C/10 mm Hg, $n_D^{20} = 1.5402$) showed a negligible rate of oxidation in the absence of an initiator both under irradiation and in the dark. Azobisisobutylonitrile (AIBN) was recrystallized from ethanol (mp 103°C). p-Phenylenediamine, N,N'-disubstituted p-phenylenediamines, N-phenylnaphthylamines, 2,6-di-$tert$-butyl-4-methylphenol, and bisphenols were recrystallized from commercial compounds. Other hindered phenols, naphthols,

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and hydroquinones were of the highest purity available and were not purified further.
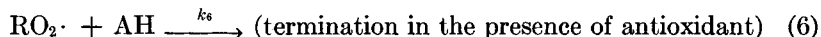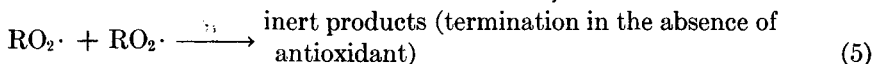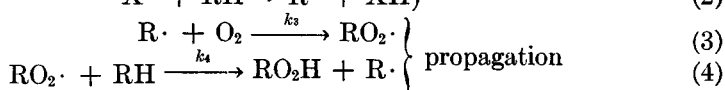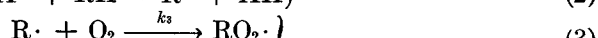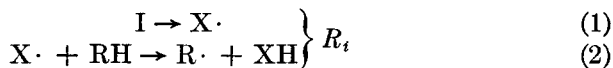
Quinones were prepared as follows. A mixture of 2,6-di-*tert*-butylphenol (5 g) and nickel peroxide[2] (10 g) in benzene (300 ml) was stirred for 2 hr at room temperature. After the reaction mixture was filtered, the crude product obtained by removal of the solvent was recrystallized from ethanol to give 3.90 g (78.8% yield) of 2,2,6,6-tetra-*tert*-butyldiphenoquinone, mp 246°C. Benzoquinone and 2,5-di-*tert*-butyl-*p*-benzoquinone were prepared by the same procedure as 2,6-di-*tert*-butylphenol.

Method

An aliquot (15 ml) of the stock solution containing AIBN (0.1M) in tetralin was poured into a plane-faced silica cell. To this was added 1 ml of a solution of an antioxidant in tetralin (0.01M) by a microsyringe. This method enables very small quantities of antioxidant (6.25 $\times$ 10^{-4} mole) to be accurately introduced. The oxidation was carried out at 50°C and 760 mm Hg oxygen pressure under irradiation and in the dark. The oxygen absorption was volumetrically measured at a constant pressure of 760 mm Hg. Unfiltered light from a high-pressure mercury lamp (Toshiba SHL-100 UV lamp) was used as a light source.

RESULTS AND DISCUSSION

It has been established that thermal oxidation proceeds via the following steps,[3] where I is an initiator, RH is the hydrocarbon, and AH is antioxidant:

$$I \rightarrow X \cdot \left.\begin{array}{l} \\ \end{array}\right\} R_i \qquad (1)$$

$$X \cdot + RH \rightarrow R \cdot + XH \qquad (2)$$

$$R \cdot + O_2 \xrightarrow{k_3} RO_2 \cdot \left.\begin{array}{l} \\ \end{array}\right\} \text{propagation} \qquad (3)$$

$$RO_2 \cdot + RH \xrightarrow{k_4} RO_2H + R \cdot \qquad (4)$$

$$RO_2 \cdot + RO_2 \cdot \xrightarrow{} \begin{array}{l}\text{inert products (termination in the absence of}\\ \text{antioxidant)}\end{array} \qquad (5)$$

$$RO_2 \cdot + AH \xrightarrow{k_6} \text{(termination in the presence of antioxidant)} \qquad (6)$$

Oxidation Kinetics

We determined the rate constant for reaction (6) by following the kinetic method used by Gupta and co-workers.[4] Application of the stationary state method to the above reaction scheme in the presence of antioxidant leads to the following equation:

$$-d[O_2]/dt = R_i\{1 + k_4[RH]/k_6[AH]\} \qquad (i)$$

Assuming the relation*

$$[AH] = [AH]_0 - R_i \cdot t \tag{ii}$$

where AH_0 is the initial concentration, and combining eq. (i) with eq. (ii) leads to

$$\frac{1}{(-d[O_2]/dt) - R_i} = \frac{k_6}{k_4[RH]} \left\{ \frac{[AH]_0}{R_i} - t \right\}. \tag{iii}$$

For most practical purpose, R_i is negligible as compared with $d[O_2]/dt$. Hence,

$$\frac{1}{-d[O_2]/dt} = \frac{k_6}{k_4[RH]} \left\{ \frac{[AH]_0}{R_i} - t \right\}. \tag{iv}$$

The slope, $k_6/k_4[RH]$, of the $1/(-d[O_2]/dt)$ versus time curve allows the calculation of the constant ratio k_6/k_4 (because RH is not a variable), as only a small fraction of tetralin is allowed to auto-oxidize.

Decomposition of AIBN

If the value of k_4 under irradiation were different from that in the dark, we could not compare k_6 values under both conditions. If the excited tetralin molecule reacted with peroxy radicals, its rate constant k_4* would be larger than k_4. It is, therefore, necessary to examine whether the excited tetralin molecule reacts with peroxy radicals under irradiation.

Firstly, the decomposition of AIBN in tetralin was examined under irradiation and in the dark both at 50°C. The result is shown in Table I. The ratio of the decomposition rate under irradiation to that in the dark was 7.1. The oxidation of tetralin containing AIBN as an initiator was carried out under irradiation and in the dark, and is indicated in Figure 1. The ratio of the oxidation rate under irradiation to that in the dark is equal to the square root (2.7) of the ratio of AIBN decomposition, within experimental error; i.e., under irradiation as well as in the dark, the oxidation rate is only proportional to the square root of the initiation rate. The result shows that acceleration of oxidation rate under irradiation is attribut-

TABLE I
Decomposition of AIBN in Tetralin at 50°C[a]

Time, min	AIBN decomposed, %	
	Under irradiation	In the dark
60	12.7	1.8
80	14.6	2.1
90	17.5	
100	18.9	2.7

[a] (AIBN decomp.)$_{h\nu}$/(AIBN decomp.)$_{dark}$ = 7.1.

* In thermal and photochemical autoxidation, this eq. (ii) is valid (our unpublished work).

able only to the accelerated decomposition of AIBN. Consequently, the
value of k_4 under irradiation is the same as in the dark.

Figure 2 shows that, at constant $[AH]_0$, the initial rate of oxidation under
irradiation increases in proportion to the increase of [AIBN] as well as
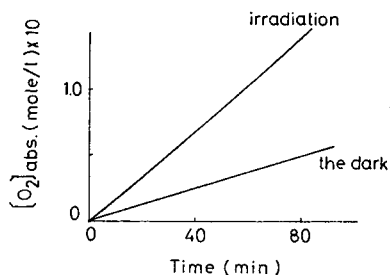that in the dark.

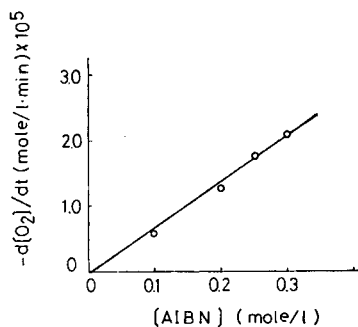Fig. 1. Oxidation of tetralin initiated by AIBN at 50°C and 760 mm Hg oxygen pressure.

Fig. 2. Plot of initial rate of oxidation vs. initiator concentration under irradiation;
AH = N,N'-diphenyl-p-phenylenediamine, 6.25 × 10^{-4} mmole/l.

Determination of the Relative Value of the Rate Constant k_6

The ratio k_6/k_4 was determined both under irradiation and in the dark
for a series of phenols and aromatic amines. The values of the ratio k_6/k_4
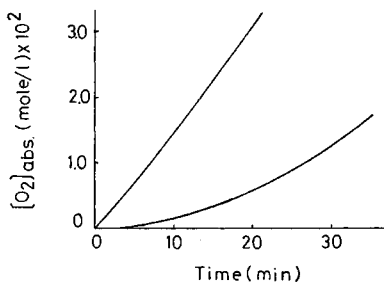of phenols are summarized in Table II. Naphthols and bisphenols possess

Fig. 3. Photo-oxidation of tetralin containing 2,6-di-$tert$-butyl-4-methylphenol at 50°C
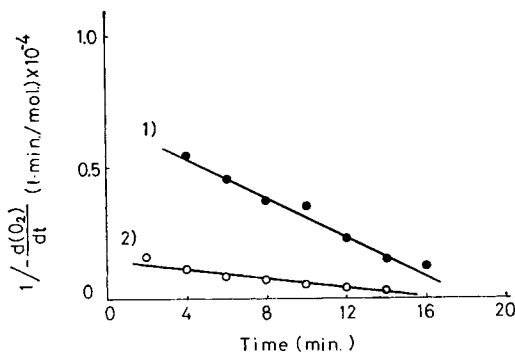and 760 mm Hg oxygen pressure; AH = 6.25 × 10^{-4} mmole/l.

Fig. 4. Plot of $1/(-d[O_2]/dt)$ vs. time under irradiation for phenols: (1) 2,6-di-*tert*-butyl-4-methylphenol; (2) hydroquinone.
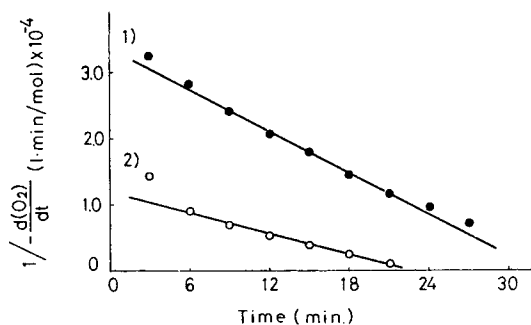

Fig. 5. Plot of $1/(-d[O_2]/dt)$ vs. time in the dark for phenols: (1) 2,6-di-*tert*-butyl-4-methylphenol; (2) hydroquinone.

the same value under both conditions. Hindered phenols and hydroquinones, on the other hand, have smaller values under irradiation than in the dark.
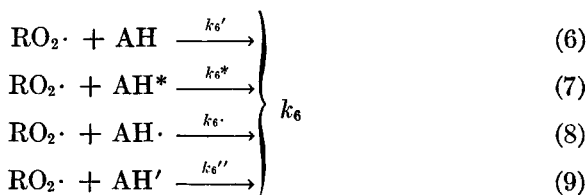
TABLE II
Ratio k_6/k_4 of Phenols Under Irradiation and in the Dark

Phenol	$(k_6/k_4) \times 10^{-3}$	
	Under irradiation	In the dark
2,4-Dimethylphenol	4.08	5.50
3,5-Dimethylphenol	0.56	6.97
2,6-Di-*t*-butylphenol	1.31	4.80
2,6-Di-*t*-butyl-4-methylphenol	3.21	8.10
α-Naphthol	7.32	8.69
β-Naphthol	0.44	0.52
Hydroquinone	0.41	4.71
2,5-Di-*t*-butylhydroquinone	1.71	8.09
2,2'-Methylenebis(4-methyl-6-*t*-butylphenol)	10.3	11.8
4,4'-Thiobis(6-*t*-butyl-3-methylphenol)	6.98	7.61

In the case of hindered phenols and hydroquinones, the literature reports[5] that these phenols easily produce quinone-type compounds from phenoxy radicals via their excited state by light absorption. We, also, observed quinone-type compounds formed during the photo-oxidation of tetralin containing them:

(A)   (B)   (C)
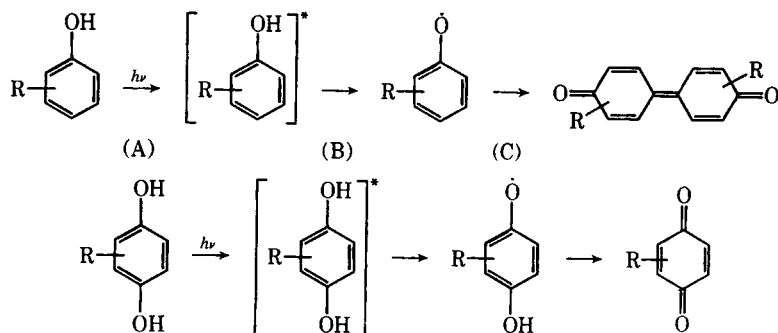
When we assume that the excited molecule, radical, or quinone derived from the phenol reacts with peroxy radicals under irradiation, we can write the following four reactions:

$$RO_2\cdot + AH \xrightarrow{\ k_6{}'\ } \tag{6}$$

$$RO_2\cdot + AH^* \xrightarrow{\ k_6{}^*\ } \tag{7}$$

$$RO_2\cdot + AH\cdot \xrightarrow{\ k_6\cdot\ } \tag{8}$$

$$RO_2\cdot + AH' \xrightarrow{\ k_6{}''\ } \tag{9}$$

k_6

where $RO_2\cdot$ signifies peroxy radical, AH is ground state antioxidant, AH^* is excited state antioxidant resulting from light absorption, $AH\cdot$ is phenoxy radical, and AH' is quinone.

Since the above four reactions (6) to (9) are considered to proceed in parallel under irradiation, the apparent rate constant k_6 is written as

$$k_6 = ak_6{}' + bk_6{}^* + ck_6\cdot + dk_6{}'' \tag{v}$$

where a, b, c, and d are factors for each rate constant. Clearly, $k_6 = k_6{}'$ in the dark ($a = 1$, $b = c = d = 0$).

If reaction (7) or (8) participates in radical capture besides reaction (6), k_6 should be larger than k'_6 owing to higher reactivity of AH^* or $AH\cdot$, even if $a = 0$. However, our results indicate that the observed ratios k_6/k_4 under irradiation are smaller than those in the dark. Therefore, reactions (7) and (8) should be eliminated from the radical capture reaction. Indeed, steps (A), (B), and (C) are very rapid, and hence concentration of AH^* and $AH\cdot$ in the system may be small. Consequently, reaction (9) should be introduced into the radical capture reaction. It is clear from Table III that the ratio $k_6{}''/k_4$ for quinones is smaller than $k_6{}'/k_4$ for the corresponding phenols.

TABLE III
Ratio k_6/k_4 of Quinones in the Dark

| Quinone	k''_6/k_4	Phenol	k_6'/k_4
2,2,6,6-Tetra-t-butyldiphenoquinone	3.8×10^2	2,6-Di-t-butylphenol	4.8×10^3
p-Benzoquinone	3.5×10^2	Hydroquinone	4.8×10^3
2,5-Di-t-butylbenzoquinone	2.9×10^2	2,5-Di-t-butylphenol	8.7×10^3

When we assume $a \doteqdot b \doteqdot c \doteqdot 0$ and substitute the relation $k_6'' < k_6'$ in eq. (v), we can interpret our results to mean that the ratio k_6/k_4 under irradiation is smaller than the ratio k_6/k_4 in the dark. The above assumption seems to be reasonable.

TABLE IV
Ratio of Aromatic Amines Under Irradiation and in the Dark

Amine	$(k_6/k_4) \times 10^{-4}$	
	Under irradiation	In the dark
N,N'-Diphenyl-p-phenylenediamine	4.2	5.5
N-Isopropyl-N'-phenyl-p-phenylenediamine	3.4	4.3
N-Cyclohexyl-N'-phenyl-p-phenylenediamine	4.1	4.4
N,N'-Di-β-naphthyl-p-phenylenediamine	6.0	6.3
p-Phenylenediamine	1.5	1.5
N-Phenyl-β-naphthylamine	0.05	2.6
N-Phenyl-α-naphthylamine	0.13	2.8

Table IV indicates that amines are classified into two categories with respect to behavior under irradiation. For p-phenylenediamines, the values of k_6/k_4 under both conditions are almost the same. For naphthylamines, on the contrary, k_6/k_4 values under irradiation are smaller than those in the dark.

For naphthylamines, there is little possibility of energy transfer from excited singlet state amine (AH*) to tetralin (RH), and besides, products which react with peroxy radicals cannot be easily formed via the excited state at the initial oxidation stage. Therefore, their smaller values of k_6/k_4 may be explained by the assumption that the excited amine AH* reacts with oxygen to give active radicals which are able to initiate the auto-oxidation:

$$AH(ArNH) \xrightarrow{h\nu} AH^*(ArNH^*)$$

$$ArNH^* + O_2 \rightarrow ArN\cdot + \cdot O_2H$$
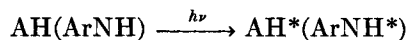
When the oxidation rate increases according to additional factors except reactions (1)–(6) in the scheme, $1/(-d[O_2]/dt)$ in eq. (iv) becomes small. Thus, the observed ratio k_6/k_4 under irradiation is smaller than that in the dark, even if the ratio k_6/k_4 is the same under both conditions. But more detailed study is necessary.

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