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Kinetic Evaluation of Reactivity of Phenolic Derivatives as Antioxidants for Polypropylene

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ABSTRACT

Reactivity of commercial phenols as antioxidants for plastics, especially polypropylene, was examined under kinetic considerations. Inhibitive rate constants, k_{inh}, were found to decrease in the order: SWP $\gtrsim$ Topanol CA $\gg$ BMP $>$ Ionox 330 $>$ Irganox 1076 $>$ Irganox 1010, while numbers n' of free radicals trapped by the phenolic moiety decreased in the order: Irganox 1076 $\gtrsim$ Irganox 1010 $\gtrsim$ Ionox 330 $>$ BMP $\gg$ Topanol CA $>$ SWP (the structures of these antioxidants are given in the text). In practical use of phenols for polypropylene, it was found that effective phenols are not those having higher values of of k_{inh}, but n' values nearly two. The effect of substituents, especially para substituents, of phenols on their activities was elucidated.

INTRODUCTION

Antioxidants such as phenols are generally evaluated by two methods. One of these is to evaluate inhibitive activities of phenols based on kinetic studies, namely to measure inhibition rate constants

k_{inh} of reactions between phenols and peroxy radicals. Ingold and Howard measured the rate constants k_{inh} of a number of phenols of low molecular weights, and elucidated the inhibition mechanism as well as the effect of substituents of phenols on their activities [1-3]. No fundamental study, however, is available for commercial phenols in terms of the determination of k_{inh} value as a measure of ability as antioxidants for high polymers.

The second method for evaluation of phenols as antioxidant consisted of the measurement of inhibiting periods of autoxidation in the presence of phenols, corresponding to the determination of number of moles of peroxy radical trapped by mole of the relevant phenol.

There have been available several studies in which each of these two methods was applied to elucidate the mechanism of a particular reaction, but no comparative study has been available with respect to the scope and limitation of these two methods. In the present study, the two methods are applied to the evaluation of some commercial phenols as antioxidant for high polymers. Activities of these phenols are compared with special reference to the effect of substituents of phenols on the antioxidant activities.

EXPERIMENTAL

Materials

Commercial phenols were used after recrystallization and are listed in Table 1. Phenols VII-IX were synthesized in these laboratories.

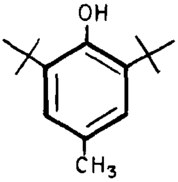
Irganox ketone was obtained by a reaction of 2,6-di-tert-butylphenol with 1-dimethylamino-3-butanone in dimethyl sulfoxide in the presence of potassium hydroxide at 60°C for 18 hr and distilling the reaction mixture. The phenol was identified by NMR and IR spectra: mp, 49.5-50°C; bp, 157-159°C/0.45 Torr; yield, 46.6%.

1-Diethylamino-3-butanone was synthesized by stirring a mixture of diethylamine hydrochloride (70.4 g), paraformaldehyde (27.6 g), acetone (240 ml), methanol (32 ml), and water (100 ml) under reflex for 10 hr. The mixture was neutralized with potassium hydroxide (26.4 g), extracted with diethyl ether, and distilled: bp, 60-61°C/8 Torr; yield, 57%.

Irganox ketone-d_2 and Irganox ketone-d_5 were prepared by a procedure similar to that given above, except for the use of deuterated paraformaldehyde and deuterated acetone, respectively. Irganox ketone-d_2 showed mp, 49.0-50.0°C; yield, 43.2%; d_2-deuterated

TABLE 1. Phenols Used

Phenol structure	Name	Source
I	BMT	
II	Irganox 1010	Ciba-Geigy Co. Ltd.
III	Irganox 1076	Ciba-Geigy Co. Ltd.
IV	Ionox 330	Shell Chemical Co. Ltd.
V	Topanol C. A.	Imperial Chemical Industries Ltd.
VI	SWP	Yoshitomi Pharmaceutical Co. Ltd.
VII	Irganox ketone	Synthesized
VIII	Irganox ketone-d_2	Synthesized
IX	Irganox ketone-d_5	Synthesized



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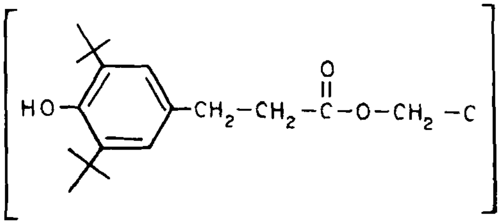

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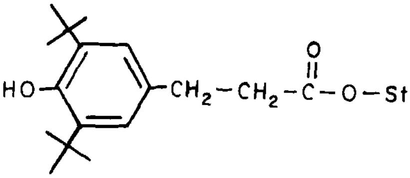
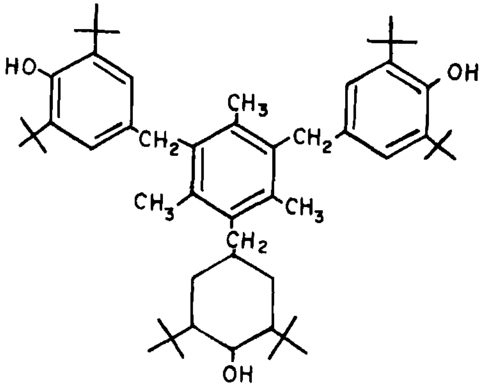


III

component, ca. 100% determined by NMR. Irganox ketone-d_5 showed mp, 47.5-49.0°C; yield, 40.1%; d_5-deuterated component, ca. 67% determined by NMR.

Styrene was used after distillation under reduced pressure just before the reaction. Chlorobenzene as solvent and α,α'-azobisisobutyronitrile (AIBN) as initiator were purified by conventional methods.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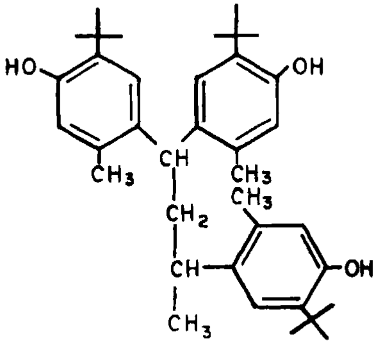
IV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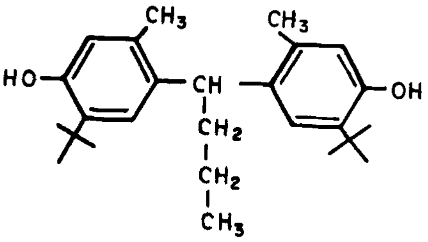
V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CH3

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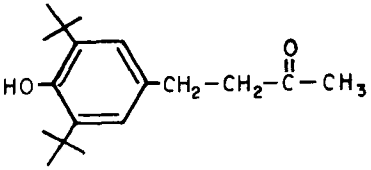

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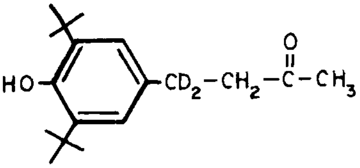

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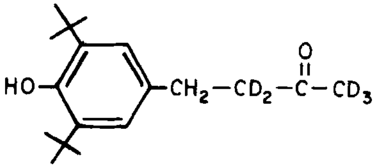


IX

Procedure

AIBN-induced autoxidation reactions were followed by means of an automatic recording apparatus. The reactions were performed with and without the inhibitor at 50-70° C. The rates of oxygen absorption were measured at the stationary state of the reactions. Concentrations of phenols and kinetic and thermodynamic data were calculated based on one unit of the phenolic moiety of phenols when they have two or more phenolic moieties in their molecules.

RESULTS

Autoxidation of Styrene in Absence of Inhibitor

Styrene was oxidized with oxygen at 50°C in chlorobenzene in the presence of α,α'-azobisisobutyronitrile (AIBN) as initiator. The rates of oxygen absorption are shown in Table 2. The results in Table 2 show that the autoxidation reaction proceeds according to the rate expression (1), which is most common formula for autoxidation reactions:

TABLE 2. AIBN-Initiated Autoxidation of Styrene in Chlorobenzene at 50°C

Styrene ($\underline{M}$)	AIBN $\times 10^2$ ($\underline{M}$)	R_i $\times 10^8$ ($\underline{M}$/sec)	$-d[O_2]/dt$ $\times 10^6$ ($\underline{M}$/sec)	$\frac{-d[O_2]/dt}{R_i^{1/2}[RH]}$ $\times 10^3 (M^{1/2}/sec^{1/2})$
1.74	1.0	3.35	3.42	10.4
3.48	1.0	3.35	6.43	10.0
6.96	1.0	3.35	12.2	9.57
8.70	1.0	3.35	14.9	9.35
3.48	0.3	1.01	3.65	10.5
3.48	0.5	1.68	4.67	10.37
3.48	2.0	6.70	8.25	9.16
3.48	1.0	3.35	6.20	9.76[a]
3.48	1.0	3.35	6.25	9.80[b]

[a] O_2 = 600 Torr.
[b] O_2 = 400 Torr.

$$-d[O_2]/dt = k_p/(2k_t)^{1/2}\ [\text{styrene}]R_i^{1/2} \tag{1}$$

Equation (1) is known to be derived from the chain reactions (2)-(5), in which I_2 represents AIBN, RH represents styrene, and $\dot{R}H$ means a free-radical species arising from the reaction of RH with I•

$$I_2 \longrightarrow 2I\bullet$$

$$I\bullet + RH \longrightarrow \dot{R}H \qquad \text{rate} = R_i \tag{2}$$

$$\dot{R}H + O_2 \longrightarrow HRO_2^\bullet \tag{3}$$

$$HRO_2^\bullet + RH \xrightarrow{k_p} HROO\dot{R}H \tag{4}$$

$$2HRO_2^\bullet \xrightarrow{k_t} \text{inert products} \tag{5}$$

In the case of [styrene] = 3.48 M and [AIBN] = 2×10^{-2} M, the inhibitor method using BMP gave the rates of initiation R_i as follows: 6.70×10^{-8} mole/liter-sec at 50°C, 3.45×10^{-7} mole/liter-sec at 60°C, and 1.28×10^{-6} mole/liter-sec at 70°C.

Kinetic Study of Commercial Inhibitors

The above-mentioned autoxidation of styrene was repeated in the presence of a commercial inhibitor (Tables 3 and 4). The last columns in Tables 3 and 4 show that the inhibited rates, $[-(d[O_2]/dt)_{inh}]$, of oxidations can be expressed by the generally accepted equation, (6):

$$-(d[O_2]/dt)_{inh} = k_p[RH]\,R_i/nk_{inh}\,[AH] \qquad (6)$$

in which n represents the number of moles of peroxy radicals trapped by one mole of phenol, and AH represents an inhibitor. The kinetic law indicates that the termination reactions are (7) and (8),

$$HROO\cdot + AH \xrightarrow{k_{inh}} HROOH + A\cdot \qquad (7)$$

$$A\cdot + HROO\cdot \xrightarrow{fast} HROOA \qquad (8)$$

in place of the reaction (5). When the propagating rate constants k_p are estimated as 96.1 liter/mole-sec at 50°C, 143.3 liter/mole-sec at 60°C, and 207.3 liter/mole-sec at 70°C from Eq. (9) [4],

$$k_p = 4.7 \times 10^7 \exp\{-8{,}400/RT\} \qquad (9)$$

the inhibitive rate constants, k_{inh}, can be calculated from Eq. (6). The result is shown in Table 5. Values of k_{inh} decreased in the order: SWP $\gtrsim$ Topanol CA $\gg$ BMP $>$ Ionox 330 $>$ Irganox 1076 $>$ Irganox 1010. The constant k_{inh} for phenols can be expressed in terms of the Arrhenius equation as follows:

$$k_{inh}(\text{BMP}):\ 3.8 \times 10^6\{\exp\ -3{,}700/RT\}(\text{liter/mole-sec})$$

$$k_{inh}(\text{Irganox 1010}):\ 2.4 \times 10^8\{\exp\ -6{,}600/RT\}(\text{liter/mole-sec})$$

TABLE 3. AIBN-Initiated Autoxidation of Styrene in the Presence of Irganox Ketone in Chlorobenzene at 50°C

AH $\times 10^3$ (M)	Styrene (M)	AIBN $\times 10^2$ (M)	$(d[O_2]/dt_{inh}$ $\times 10^7$ (M/sec)	$\frac{(d[O_2]/dt)_{inh}[AH]}{[RH]R_i}$ $\times 10^2$
1.0	3.48	6.0	24.5	3.50
1.0	3.48	4.0	15.6	3.38
1.0	3.48	2.0	8.02	3.44
1.0	3.48	1.0	3.67	3.14
1.0	1.74	2.0	4.41	3.78
1.0	5.22	2.0	12.5	3.56
1.0	6.96	2.0	16.7	3.58
0.2	3.48	2.0	33.2	2.84
0.4	3.48	2.0	19.3	3.32
0.8	3.48	2.0	9.93	3.40
			Avg.	3.40

k_{inh} (Ionox 330): 1.2×10^7 exp $\{-5,000/RT\}$ (liter/mole-sec)

k_{inh} (SWP): 1.4×10^7 exp $\{-5,100/RT\}$ (liter/mole-sec)

Measurement of n Values

Relative n values in Eq. (6) can be calculated from induction periods in the presence of an inhibitor:

$$n = R_i\tau/[AH] \tag{10}$$

in which τ is the induction period. In Table 6, n' values are calculated with respect to one unit of phenolic moiety, because the inhibitors examined have one to four phenolic moieties in a molecule. The n' value for phenols having tert-butyl substituents on both ortho positions were found to be nearly two, while those for less hindered phenols, such as Topanol CA and SWP, were considerably lower than two.

TABLE 4. The AIBN-initiated Autoxidation of Styrene in the Presence of SWP in Chlorobenzene at 50° C

AH × 10^3 (M)	Styrene (M)	AIBN × 10^2 (M)	$(d[O_2]/dt)_{inh}$ × 10^7 (M/sec)	$\frac{(d[O_2]/dt)_{inh}[AH]}{[RH]R_i}$ × 10^2
1.0	3.48	2.0	2.32	9.96
1.0	3.48	3.0	3.55	10.16
1.0	3.48	4.0	5.42	11.62
1.0	3.48	6.0	7.23	10.34
1.0	5.22	2.0	2.86	8.19
1.0	6.96	2.0	4.10	8.79
0.2	3.48	2.0	9.74	8.35
0.4	3.48	2.0	4.65	7.97
0.8	3.48	2.0	2.40	8.25
			Avg.	9.29

TABLE 5. Inhibition Rate Constants k_{inh} of Available Phenols

	Rate constants k_{inh} × 10^3 (liter/mole-sec)		
Phenols	50°C	60°C	70°C
BMP	15.8	20.6	21.8
Irganox 1010	8.75	11.7	15.8
Irganox 1076	10.4	-	-
Ionox 330	13.0	18.1	19.8
SWP	48.6	66.0	77.4
Topanol CA	45.4	-	-

TABLE 6. n' Values of Phenols[a]

Phenols	Induction period (min)	n'
BMP	108	1.71
Irganox 1010	125	1.97
Irganox 1076	129	2.00
Ionox 330	121	1.92
SWP	70	1.13
Topanol CA	80	1.26

[a] Reaction conditions: [Styrene] = 3.48 M, [Phenol] = 1×10^{-3} M, in chlorobenzene at 50° C.

TABLE 7. Kinetic and Thermodynamic Data of Activities of Irganox Ketones

Phenols	Rate constants k_{inh} $\times 10^{-3}$ (liter/mole-sec) 50° C	60° C	70° C	$\Delta H^‡$ (kcal/mole)	$\Delta S^‡$ (cal/deg)	$\Delta G^‡$ (kcal/mole)
Irganox ketone	14.1	15.7	17.5	2.56	-31.8	12.9
Irganox ketone-d_2	13.2	15.4	19.3	3.60	-28.7	12.8
Irganox ketone-d_5	12.8	19.2	22.3	3.86	-27.9	12.9

Isotope Effect of Para Substituents

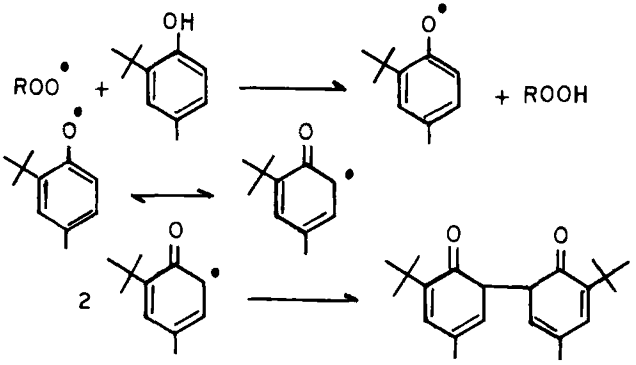
Inhibitive activities of Irganox ketone and deuterated derivatives are shown in Table 7. It is seen from Table 7 that the rate constants for inhibition k_{inh} were affected by the deuteration of the para substituent of the phenols. The order of k_{inh} was Irganox ketone > Irganox ketone-d_2 $\gtrsim$ Irganox ketone-d_5 at 50° C, while the reverse order, Irganox ketone-d_5 > Irganox ketone-d_2 > Irganox ketone, was obtained at 70° C. The deuteration, however, had little influence upon the value of activation free energy, $\Delta G^‡$, for step (7), which means the compensation rule to be established between $\Delta S^‡$ and $\Delta H^‡$. The thermodynamic data also show that the reaction of step (7) is controlled by the entropy term, $\Delta S\ddagger$, rather than the enthalpy term, $\Delta H\ddagger$. These results strongly imply that the observed secondary isotope effect should be interpreted in terms of the difference in the extent of electronic stabilization in activated complexes from Irganox ketone and its deuterated derivatives for step (7). (When the phenolic hydroxyl was deuterated, the $k_{inh,H}/k_{inh,D}$ was reported [5] as above ca. 10 in a similar autoxidation of styrene to that of this work.)

DISCUSSION

Action of Inhibitors

As seen from the results mentioned above, it is very important to elucidate effect of substituents of phenols for the evaluation of their inhibitive activities, because significantly different values of k_{inh} and n' have been found even with phenols having similar structures.

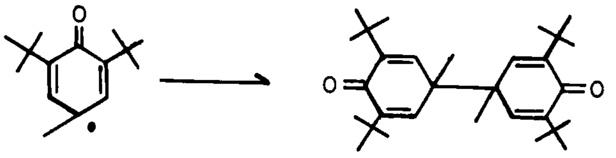
It is well known [6] that a less-hindered phenol having a substituent on the ortho position has higher value of k_{inh} than a hindered phenol having two ortho substituents, because of the easier access of a peroxy radical to the hydroxy group in reaction (7), as is also observed in this study (Table 5). However, the less hindered phenol could not catch two peroxy radicals, as shown by the n' value in Table 6. The low n' values for less hindered phenols are explained by the coupling reaction of phenoxy radicals [7], for example.



(7)

(11a)

The coupling reaction of phenoxy radicals may also be observed for a hindered phenol having small substituent on the para position even if it has two bulky substituents such as tert-butyl on both ortho positions; [for example Eq. (12)].



(12)

BMP (n' = 1.71)

Since para-substituents of BMP, Irganox 1010 and 1076, and Ionox 330 are regarded as $-CH_3$, $-n-C_5H_{11}$, and $-CH_2-C_6H_5$, respectively, the corresponding Tafts steric substituent constants should be 0.00, -0.40, and -0.38, respectively; this order agrees well with that of n values (Table 6), in harmony with the above consideration on steric requirement in terms of the reaction (12).

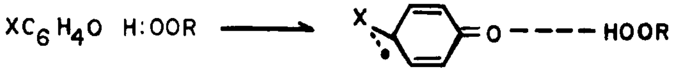
There has been reported, however, another effect of para substituents which is claimed to arise from electronic origins. Howard and Ingold showed [2] that the rate constants k_{inh} of some para-substituted phenols could be correlated with the substituent constants of Brown and Okamoto:

$$\log [k_{inh}/(k_{inh})_0] = a + \rho^+\sigma^+ \tag{13}$$

Howard and Ingold proposed that the transition state for the reaction (7) consists of three resonance forms:

$$XC_6H_4O{:}H\ OOR \longleftrightarrow XC_6H_4O^+\ H^-{:}OOR \longleftrightarrow XC_6H_4O\ H{:}OOR \tag{14}$$

Equation (13) must be very reasonable for phenol derivatives having a sterically similar para substituent. In addition, the secondary isotope effect for Irganox ketones observed in this study may be an excellent example for the electronic participation of the para substituents. A phenoxy radical is considered to be formed through reactions (14) including the electronic state shown in Eq. (15).



(A)

(15)

TABLE 8. Evaluation of Phenols as Stabilizer for Polypropylene by an Oven Test [8][a,b]

	Period in which phenols are still active (hr)[c]		
	0.2 parts added		0.5 parts added
Phenols	At 150°C	At 160°C	at 160°C
Irganox 1010	960	240	400
Irganox 1076	264	72	170
Ionox 330	240	72	180
SWP	48	24	70
Topanol CA	120	48	120
BMP	48	24	

[a] Polypropylene used: Profax 6501 (MW: 250,000), manufactured by Hercules Corporation.

[b] Oven test: according to a conventional method, in which polypropylene is rolled in presence of a phenol for 5 min at 180°C and pressed under 250 kg/cm^2 for 5 min at 180°C to produce test specimens. The specimen then is subjected to the oven test.

[c] The period in which the specimen is degraded by oxidation to become brittle.

The para substituent in the intermediate (A) may stabilize the quinoid form of radical, which will cause reaction (8) to proceed more easily, resulting in the higher n value.

Phenolic Antioxidants as Stabilizers for Polypropylene Plastics

When phenols studied in this work were used for stabilization of polypropylene plastics, they made the plastic withstand oxidation even at the concentration of 0.2-0.5 parts by weight (Table 8). In practical use, the phenols can be classified into two groups: group 1 (Irganox 1010, Irganox 1076, Ionox 330) and group II (SWP, Topanol CA). (As BMP is highly volatile, it does not show its real antioxidative activity. Therefore, it is omitted in the discussion in terms of results of oven tests.) The phenols of group I are much more effective than those of group II. On comparison of the classification with the results shown in Tables 5 and 6, it seems necessary for effective phenols not to have higher values of k_{inh}, but to have n' values of nearly two. In other words, to be effective, phenols, in practical use, must be able to trap two free radicals but not necessarily to trap them quickly. To satisfy this condition, the phenols should have bulky substituents such as tert-butyl, especially at both ortho positions, and, preferably should have a para substituent, which has higher electophilic substituent constant and stabilizes the intermediate radical (A).

Finally, it should be emphasized that antioxidative activities of several phenols have been discussed in this paper without regard for other ingredients in the stabilization recipe, such as a sulfur-containing antioxidant which may strengthen the activity of phenol synergistically (commonly used for commercial polypropylene plastic), and that the phenols of group II may be used in the presence of sulfur-containing antioxidant too.

In future, this study must be continued to develop new phenolic antioxidants, considering the vaporizability and mobility of phenols in polypropylene and the synergistic effect of co-additives for polypropylene.

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We wish to express our thanks for Dr. G. Minagawa of Adeka Argus Chemical Co. Ltd. for giving us samples of phenols and data of oven tests. The work was carried out with the help of advice and discussion with Prof. Teiji Tsuruta, University of Tokyo.

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