報 文

Syntheses of New Sulfur-Containing Complexes
as Antioxidant

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New type of complexes having both phenolic moiety and sulfur-containing chelate ring were prepared as antioxidant. The complexes exhibited both abilities to decompose hydroperoxide and to trap peroxy radicals. The coexistence of phenolic moiety and chelate ring did not considerably affect to the former ability, but increased the latter one, and made the complex more stable thermally.

It is well established^{(1),(2)} that autoxidation of organic substrates proceeds through a free radical-chain mechanism, in which a chain-propagating species is a peroxy radical and one of primary products is a hydroperoxide. The hydroperoxide is readily decomposed in the presence of some metal ions and/or under the action of heat or UV-ray to form free radicals which can further initiate the autoxidation reaction according to the radical chain mechanism. Two types of antioxidants, therefore, have been proposed and used for inhibiting autoxidation^{(3),(4)}, the one is the chain-breaking antioxidant which interrupts the propagating steps of the autoxidation reaction by trapping peroxy radicals, and the other is the peroxide-decomposer which decomposes hydroperoxides ionically.

Phenolic antioxidants belong to the former category and are widely used for various fields of industries. Sulfur-containing complexes such as metal *O,O*-dialkyl phosphorodithioates and *N,N*-dialkyl carbamates are examples of peroxide decomposers and are widely known to be much more excellent decomposers than uncomplexed sulfur-containing decomposers⁽⁵⁾. These two types of the antioxidants are also known, when used together, to exhibit, in some cases, the synergistic inhibition of autoxidation^{(6),(7)}.

This synergism is successfully utilized in industries of plastics and/or elastomers, but there remains a few important problems to be

solved in terms of thermal stability of each antioxidant. Some of excellent antioxidants, such as 2,6-di-*t*-butyl-4-methylphenol, cannot be applied to plastics and elastomers, because of their vaporizing nature at higher temperature ($\sim 150^{\circ}\text{C}$) under which plastics and elastomers are processed. This problem seems to be partly solved with the preparation of a polymeric structure having an antioxidant moiety.

In this study, new sulfur-containing complexes, which are considered to exhibit both synergistic action and thermal stability, are synthesized. The characteristic chemical and physical properties for some of these complexes are also discussed.

Experimental

Materials: New antioxidant complexes were prepared as follows:

Preparation of metal phosphorodithioates

A solution of 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-1-propanol (I) (0.0427 mol, 11.27 g) in benzene was added dropwise to phosphorus pentasulfide (0.0125 mol, 2.77 g) at about 60°C . Then the reaction mixture was stirred for 8 h under reflux at 80°C , introducing a nitrogen

stream in order to remove hydrogen sulfide evolved, until the evolution of hydrogen sulfide ceased. After removing the unreacted phosphorus pentasulfide and benzene, a pale yellow viscous liquid was obtained. This was gradually crystallized, and purified by recrystallization from petroleum ether or hexane to give phosphorodithioic acid as a colorless solid (yield: 6.7 g, 51% of theory). The infrared spectrum showed a sharp band at 2500 cm^{-1} (ν_{SH}) and a broad band at $950\sim 1050\text{ cm}^{-1}$ (ν_{POC}); mp: $93\sim 94^\circ\text{C}$.

Anal. for $\text{C}_{34}\text{H}_{55}\text{O}_4\text{PS}_2$:

Calcd.: C, 65.66; H, 8.75

Found: C, 65.75; H, 8.32

The resulting acid was converted into its sodium salt by neutralizing with aqueous sodium hydroxide at about 50°C , and aqueous zinc chloride solution was dropwise added to the solution. The precipitated product was filtered, dried and dissolved in diethyl ether. This ethereal solution was washed repeatedly with water to remove water-soluble salts and dried over anhydrous sodium sulfate. After distilling diethyl ether off, the final product, $\text{Zn-P-C}_3\text{-DTP}$ was obtained in a white-yellow solid, in which the sharp band at 2500 cm^{-1} disappeared completely; mp: $57\sim 58^\circ\text{C}$; yield: 93%.

Anal. for $\text{C}_{68}\text{H}_{108}\text{O}_8\text{P}_2\text{S}_4\text{Zn}$:

Calcd.: C, 62.39; H, 8.32

Found: C, 62.14; H, 8.31

Nickel and copper complexes were also synthesized according to the above-mentioned method except for using their metal chlorides in place of zinc chloride. They melted at $200\sim 201$ and $68\sim 69^\circ\text{C}$, respectively.

3-(3, 5-di-*t*-butyl-4-hydroxy-phenyl)-1-propanol (I) was synthesized as follows:

The methyl 3-(3, 5-di-*t*-butyl-4-hydroxy-phenyl)propionate (II) (mp $60\sim 62^\circ\text{C}$) was obtained by transesterification of Irganox 1010 (pentaerythritol ester of 3-(3, 5-di-*t*-butyl-4-hydroxy-phenyl)propionic acid made by Ciba Geigy Co.) with excess methanol for 3 h at 60°C using *p*-toluenesulfonic acid as a catalyst. The reaction mixture was then poured on ice-water and the precipitated crystals were filtered off and washed with sodium hydrogen carbonate solution and then with sufficient water. The compound (II) was obtained as white crystals,

(IR: $\nu_{\text{C=O}}$ 1730 , ν_{OH} 3620 cm^{-1} ; yield: 95%). Then the compound (II) (32.1 g, 0.11 mol) was reduced with lithium aluminum hydride (4.07 g 0.11 mol) in anhydrous ether for 1 h at room temperature. The removal of the solvent after separating yellow ethereal layer gave a crude product. It was purified by recrystallization from hexane-petroleum ether to form the compound (I) as needle-like white crystals. (mp: $66.5\sim 67.5^\circ\text{C}$; IR: ν_{OH} $3100\sim 3440$, ν_{COH} 1080 cm^{-1} ; yield: 75%).

Preparation of metal dithiocarbamates

To 3-(3, 5-di-*t*-butyl-4-hydroxyphenyl)propionitrile (III) (1.91 g, 0.00726 mol) suspended in aqueous sodium hydroxide (0.33 g) solution, carbon disulfide (0.553 g, 0.00747 mol) was added dropwise at room temperature. The resulting brown solution, containing sodium dithiocarbamate as main product, was directly reacted with aqueous zinc chloride. The white solid precipitated was washed with water repeatedly and then dried under reduced pressure. The yield of $\text{Zn-P-C}_3\text{-DTC}$ was 2.56 g (yield: 95%). mp: $142\sim 143^\circ\text{C}$.

Anal. for $\text{C}_{36}\text{H}_{56}\text{N}_2\text{O}_4\text{S}_4\text{Zn}$:

Calcd.: C, 58.24; H, 7.60; N, 3.77

Found: C, 57.65; H, 7.67; N, 3.63

$\text{Ni-P-C}_3\text{-DTC}$ was synthesized similarly. It melted at $192\sim 193^\circ\text{C}$.

The compound (III) was synthesized as follows:

The 3-(3, 5-di-*t*-butyl-4-hydroxyphenyl)propionitrile (mp: $111\sim 113^\circ\text{C}$) was prepared by the reaction of 2,6-di-*t*-butylphenol with acrylonitrile according to the method of Coffield *et al.*⁹⁾, and was reduced with lithium aluminum hydride as mentioned above. A crude product obtained as a yellow solid was recrystallized from hexane to give a white solid (III) (mp: $119\sim 121^\circ\text{C}$; yield: 45%).

Starting materials used in the preparation of new complexes were used without any purification of the highest grade of reagents. Cumyl hydroperoxide (CHP), chlorobenzene and tetralin were purified according to conventional methods.

Procedure: Decomposition of cumyl hydroperoxide was carried out using a reaction flask with stirrer and sampling neck. For hydroperoxide analysis, an iodometric method was used⁹⁾.

Autoxidation of tetralin was conducted according to the method of literature¹⁰⁾. Autoxidations were initiated by the thermal decomposition of α, α' -azobisisobutyronitrile, and rates of chain initiation were determined by induction period method using 2,6-di-*t*-butyl-4-methylphenol.

A Thermoflex TG-DTA made by Rigaku Denki Co., Ltd. was used for measurements of thermal stabilities of new complexes.

Results and Discussion

Chemical behavior of complexes

(a) Hydroperoxide-decomposing ability

Cumyl hydroperoxide (CHP) was negligibly decomposed under experimental conditions in absence of a new complex. On the other hand, the concentration of cumyl hydroperoxide decreased gradually in presence of a complex (Fig.-1).

It was found that all the complexes examined showed ability of cumyl hydroperoxide decomposition. The rate equation of decomposition is derived from the last column of Table-1 as follows:

$$-\frac{d[\text{CHP}]}{dt} = k_d[\text{CHP}][\text{Complex}] \quad (\text{A})$$

Table-1 Rate constants, k_d , of the decomposition reaction of cumyl hydroperoxide with complexes^{a)}.

[Complexes] $\times 10^3$ M		[CHP] $\times 10^2$ M	$-\frac{d[\text{CHP}]}{dt}$ $\times 10^7$ Ms ⁻¹	$\frac{d[\text{CHP}]}{dt} \frac{1}{[\text{CHP}][\text{Complex}]}$ $\times 10^2$ M ⁻¹ s ⁻¹
Zn-P-C ₃ -DTP	1.00	1.25	1.63	1.3
	6.25	"	9.38	1.2
	5.00	2.50	16.3	1.3
	10.00	"	35.0	1.4
Cu(I)-P-C ₃ -DTP	0.625	1.25	3.44	4.4
Ni-P-C ₃ -DTP	2.50	"	3.75	1.2
Zn-P-C ₃ -DTC	1.00	"	3.88	3.1
	2.50	"	9.38	3.0
Zn-Pr ₂ ⁱ -DTP ^{b)}	"	"	2.88	0.92
Zn-Pr ₂ ⁱ -DTC ^{b)}	"	"	0.33	0.11
Ni-Pr ₂ ⁱ -DTP ^{b)}	"	"	4.69	1.5

a) in chlorobenzene at 50°C.

b) These complexes are known. They were prepared, according to the procedure for the new complexes, using the corresponding metal salt and alcohol, for example zinc chloride and isopropyl alcohol for Zn-Pr₂ⁱ-DTP.

Fig.-1 Decomposition of cumyl hydroperoxide with new complexes in chlorobenzene at 50°C.

where k_d means the rate constant of decomposition reaction. This equation is in good agreement with that of the decomposition of cumyl hydroperoxide with zinc *O, O*-diisopropylphosphorodithioate (Zn-Pr₂ⁱ-DTP)⁹⁾ possessing no phenolic moiety in the molecule. Rate constants, k_d , are shown in Table-1; those of similar known complexes are also shown for comparison. The values of k_d for the new complexes prepared were found to be $1.2 \sim 4.4 \times 10^{-2}$ M⁻¹ s⁻¹ at 50°C. The values are well comparable with those ($0.1 \sim 1.5 \times 10^{-2}$ M⁻¹ s⁻¹) for known complexes. The phenolic moiety of the new complexes does not seem to affect considerably on

their abilities to decompose cumyl hydroperoxide.

(b) Free radical-trapping ability

The liquid phase oxidation of tetralin was carried out in the presence of α, α' -azobisisobutyronitrile as initiator at 50°C. The addition of a new complex slowed much down the rate of oxygen absorption until the complex was consumed.

In general, autooxidation of hydrocarbons in the presence of an effective antioxidant, AH, can be written as follows:

Initiation: formation $R^\cdot$ from AIBN (R_i)

(1)

Propagation: $R^\cdot + O_2 \longrightarrow RO_2^\cdot$ (2)

$RO_2^\cdot + RH$

$\xrightarrow{k_p} ROOH + R^\cdot$ (3)

Termination: $RO_2^\cdot + AH$

$\xrightarrow{k_{inh}} ROOH + A^\cdot$ (4)

$A^\cdot + ROO^\cdot \longrightarrow AOOR$ (5)

R_i : rate of initiation, k_p and k_{inh} : rate constants of the corresponding steps, and AH: inhibitor.

The rate of oxidation inhibited is given by Eq. (B),

$$-\left(\frac{d[O_2]}{dt}\right)_{inh} = R_{inh} = \frac{k_p[RH]R_i}{n k_{inh}[AH]} \quad (B)$$

n : numbers of peroxy radical trapped per mole of an inhibitor.

and n can be calculated by the following equation (C) in the case of sufficient long chain:

$$n = \frac{R_i \times \text{induction period}}{[AH]} \quad (C)$$

Table-2 shows AIBN-initiated autooxidation

Table-2 Autooxidation of tetralin in the presence of Zn-P-C₃-DTP at 50°C in chlorobenzene.

Tetralin M	Inhibitor $\times 10^5$ M	AIBN $\times 10^3$ M	R_{inh} $\times 10^6$ M/s	Induction period $\times 10^{-3}$ s	Calculated value of n	$k_{inh} = \frac{k_p[RH]R_i^*}{n[AH]R_{inh}}$ $\times 10^{-4}$ M ⁻¹ s ⁻¹	Chain length
7.3	1.0	9.0	8.25	0.65	11.1	2.04	48
"	2.0	"	4.14	0.86	7.3	2.04	24
"	3.0	"	4.75	1.23	7.0	1.18	28
"	4.5	"	1.50	2.09	7.9	2.50	9
"	6.0	"	1.38	3.03	8.9	2.04	8
"	8.0	"	1.10	4.37	9.3	1.92	7
"	4.5	4.5	1.07	3.17	6.0	1.75	13
"	4.5	2.25	0.49	6.35	6.0	1.92	12
5.1	6.0	9.0	1.15	2.29	6.5	1.71	7
3.7	6.0	"	0.79	2.33	6.6	1.80	5
2.9	6.0	"	0.59	2.26	6.4	1.89	4

* calculated as $n=10$

Table-3 Rate constants (k_{inh}) of inhibition reaction with some inhibitors.

Inhibitors	Peroxy radical	Theoretical n value	$k_{inh} (\times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})$		Ref.
			30°C	50°C	
Zn-P-C ₃ -DTP	Tetralyl	10	0.13	18.9	This work
Zn-P-C ₃ -DTC	"	6		24.0	"
ZnPr ₂ ⁱ -DTP	"	2		3.9	10)
Zn-Et ₂ -DTC	"	2		"	"
<i>t</i> -Butyl	2	0.13	11.5	11)
"	Styryl	2		7.0	12)
"	2		6.4	"

of the tetralin in the presence of Zn-P-C₃-DTP at 50°C. It can be seen from the Table that the inhibited autoxidation obeys the rate equation (B) and proceeds via steps (1) to (5). The mean values of k_{inh} at 50°C are summarized in **Table-3**, along with the data obtained for the other types of inhibitors. In the calculation of k_{inh} from Eq. (B), it was assumed that the values of n^{*1} were 10 and 6 for Zn-P-C₃-DTP and Zn-P-C₃-DTC, respectively. The rate constant, k_p , was taken as $13.6M^{-1}s^{-1}$ from the literature¹³⁾. R_i was experimentally determined as $1.7 \times 10^{-7}s^{-1}$ from the inhibited period in autoxidation of tetralin in the presence of 2,6-di-*t*-butyl-4-methylphenol. The value of k_{inh} of a new complex is much higher than that of either the corresponding phenolic antioxidant or known chelate complexes. This fact supports the synergism of both phenolic moiety and sulfur-containing chelate ring which coexist in a new type of complex.

Thermal stabilities of complexes

Some of complexes synthesized were subjected to DTA and TGA analyses. In every case, there was observed endothermic reaction with the decrease of weight of a new complex. Results are shown in **Table-4**. The decompo-

Table-4 Thermal stabilities of complexes.

Complexes	Decomposition temperature* (°C)	Ref.
Zn-P-C ₃ -DTP	250	This work
Zn-P-C ₃ -DTC	220	"
Cu(II)-P-C ₃ -DTP	190	"
Zn-Pr ₂ ⁱ -DTP	196	14
Zn-(<i>n</i> -amyl) ₂ -DTP	212	14
Zn-(4-methyl-pentyl) ₂ -DTP	185	15

* Temperatures at which a complex starts to decompose.

sition temperature of zinc dialkylphosphorodithioates depends on the kind of their substituents. The complex having a simple alkyl substituent such as *n*-pentyl were decomposed at 212°C or

lower, while Zn-P-C₃-DTP and Zn-P-C₃-DTC did not start to decompose up to 250°C and 220°C, respectively. This fact indicates considerable improvement of thermal stability of the new complexes. Cu(II)-P-C₃-DTP was found to decompose at 190°C or higher.

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酸化防止剤としての新しい含硫黄錯体の合成

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フェノール性残基及び含硫黄キレート環の両方を有する新しい種類の錯体を酸化防止剤として合成した。この錯体はヒドロペルオキシドの分解及びペルオキシラジカルの捕捉の両能力を有した。フェノール性残基及びキレート環の共存は前者の能力にあまり影響を与えなかったが、後者の能力を増大させ、また錯体を熱的により安定させた。

*1 The theoretical assignment for n 's of phenolic moiety¹¹⁾ and sulfur-containing ring¹⁰⁾, were 2 and 1, respectively. The theoretical value of n was 10, for example, for Zn-P-C₃-DTP.