

ANTIOXIDATIVE ACTIVITY OF PHENOLS CONTAINING SUBSTITUENTS WITH HETEROATOMS O, S AND N IN THE OXIDATION OF TETRALIN*

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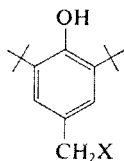
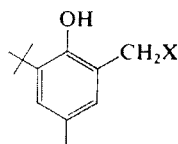
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The relationship between the structure and antioxidative activity of derivatives of 2,6-di-tert-butyl-4-methylphenol and 2,4-dimethyl-6-tert-butylphenol containing in their molecule atoms of oxygen, sulphur, or nitrogen as another heteroatom was studied during the oxidation of tetralin at 65°C. The results obtained were compared with the activities measured for the stabilization of isotactic polypropylene at 180°C. The results indicate the probability of a bifunctional mechanism of the antioxidative effect of sulphur-containing derivatives.

The results obtained by examining relationships between the structure and activity of bisphenols in the oxidation of isotactic polypropylene at 180°C and tetralin at 60°C pointed out the specific position of compounds containing sulphur in their molecule^{1,2}. Thiobisphenols were highly active and retarded the oxidation of the substrate in the phase after completion of the induction period. This fact can be explained by the complex mechanism of their action. As phenols, they interrupt the propagation chain of radical autoxidation by reacting with the ROO• radicals; as sulphides, they decompose into nonradical products, hydroperoxides, arising either in the propagation reaction of autoxidation or *via* the above reaction between antioxidants and the ROO• radicals. The former mechanism becomes operative predominantly in the initial steps and at lower temperatures of autoxidation and appears as the induction period in the absorption of oxygen. The latter mechanism plays role in later stages (after accumulation of hydroperoxides) and at higher oxidation temperatures. It also leads to a retardation of the process on completion of the induction period in which probably there also participate some compounds formed during the inhibited oxidation by the transformation of thiobisphenols. The specific effect of sulphidic sulphur on the total activity was investigated by means of bisphenols with a molecule modified by partial or total etherification of phenolic hydroxyl groups³. A considerable effect of temperature was observed.

In order to find out whether the sulphidic sulphur atom in the molecule of the antioxidant has the same influence on the course of oxidation if it is present in thio-bisphenols or if it is separated from the phenolic ring by a methylene group, we investigated⁴, in the oxidation of isotactic polypropylene at 180°C, mono- and poly-nuclear compounds of type *I* and *II* derived from 2,6-di-tert-butyl-4-methylphenol

and 2,4-dimethyl-6-tert-butylphenol. The group X contained a sulphidically bonded sulphur; for the sake of comparison we also studied properties of some other compounds in which this group contained oxygen or nitrogen atoms. Owing to the effect of temperature on the total antioxidative effect of the phenols under investigation we supplemented the results obtained with compounds of type *I* and *II* at a high temperature by an investigation of the relationship between the structure and activity at a lower oxidation temperature.

*I**II**Ia*, X = H*Ib*, X = OH*Ic*, X = OCH₃*Id*, X = NH₂*Ie*, X = NHCH₃*If*, X = N(CH₃)₂*Ig*, X = N(CH₃)R¹*Ih*, X = NR¹₂*Ii*, X = SH*Ij*, X = SCH₃*Ik*, X = SR¹*Il*, X = SSR¹*IIa*, X = H*IIb*, X = OH*IIc*, X = OCH₃*IId*, X = OR²*IIe*, X = N(CH₃)₂*IIf*, X = SCH₃*IIg*, X = SR²R¹ = 3,5-di-tert-butyl-4-hydroxybenzylR² = 5-methyl-3-tert-butyl-2-hydroxybenzyl

EXPERIMENTAL

Materials. Antioxidants of type *I* and *II* were chromatographically pure. Tetralin (substrate) was purified by a procedure described in ref.² and distilled in an inert atmosphere, b.p. 204–6°C. 2,2'-Azobis(isobutyronitrile) used as initiator was recrystallized from acetone, m.p. 103°C.

Determination of antioxidative activity and evaluation of results. The absorption of oxygen was followed volumetrically in tetralin at 65°C. The experiments were carried out under atmospheric pressure on an automatic oxidation apparatus with recording of the oxygen consumption⁵. The concentration of antioxidants related to one phenolic ring was $5 \cdot 10^{-4}$ mol/l. 2,6-Di-tert-butyl-4-methylphenol in the same concentration served as standard. The concentration of the initiator was $5 \cdot 10^{-3}$ mol/l. Table I summarizes the relative activities of antioxidants, $A_r = (\tau_x - \tau_0) / (\tau_s - \tau_0)$, where τ is time (min) needed for the absorption of 10 ml of oxygen per one mol of tetralin (τ_x holds for the stabilization with the antioxidant under investigation, τ_s holds for the stabilization with the standard, and τ_0 holds for nonstabilized tetralin). The rate of tetralin oxidation on completion of the induction period expressed as the slope S of the straight intercept of the absorption curve was calculated from the relationship $S = 5 / (\tau_{15} - \tau_{10})$, where τ_{10} and τ_{15} give time in minutes needed for the absorption of 10 or 15 ml of oxygen per one mol of tetralin. Table I gives the values of S_r representing the ratio of the S values calculated for the stabilized and unstabilized tetralin.

RESULTS AND DISCUSSION

In order to determine the relationship between the structure and activity of phenolic antioxidants containing in their molecule another heteroatom N, O or S we measured the antioxidative activity of compounds of type *I* and *II* in the oxidation of tetralin initiated with 2,2'-azobis(isobutyronitrile). The results were compared with the activity of these compounds determined in the oxidation of isotactic polypropylene at 180°C (ref.⁴). The relative activities A_r (definition *cf.* Experimental) of polynuclear antioxidants were determined and discussed after recalculation to one phenolic ring, similarly to the stabilization of polypropylene (Table I). With the exception of N,N-dimethyl-2-hydroxy-3-tert-butyl-5-methylbenzylamine (*Ile*), an induction period was recorded on the absorption curves of oxygen measured in tetralin stabilized with all the other compounds under investigation. Typical absorption curves of oxygen are given in Fig. 1 for illustration.

Compounds *I* are derivatives of a technically widely applied antioxidant, 2,6-di-tert-butyl-4-methylphenol (*Ia*), which was selected as standard for the set of compounds examined in this work. Substitution of one hydrogen atom in the methyl group of *Ia* with the hydroxyl or methoxyl group reduces the activity similarly to the stabilization of isotactic polypropylene. However, at a lower temperature of tetralin oxidation of the two compounds thus obtained, that is, 3,5-di-tert-butyl-4-hydroxybenzyl alcohol (*Ib*) and 2,6-di-tert-butyl-4-methoxymethylphenol (*Ic*), *Ib* is the more active one.

While the activity of mononuclear nitrogen derivatives of 2,6-di-tert-butyl-4-methylphenol in polypropylene⁴ depended on the number of hydrogen atoms on the nitrogen atom and decreased with their substitution each time by approximately the same value, no such dependence was observed in the stabilization of tetralin. N-Methyl-3,5-di-

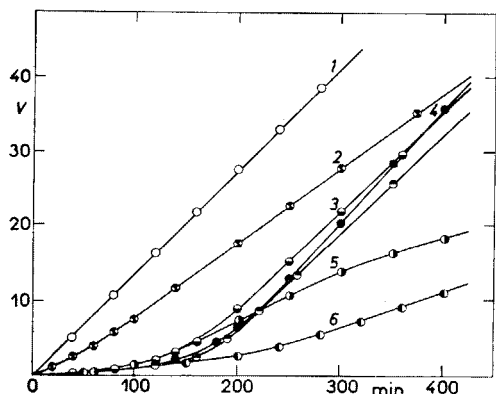


FIG. 1

Absorption Curves of Oxygen in the Inhibited Oxidation of Tetralin (65°C) in Presence of 2,2'-Azobis(isobutyronitrile)

V Denotes ml O_2 /mol tetralin. Antioxidants: ● 2,6-di-tert-butyl-4-methylphenol (*Ia*), ● 3,5-di-tert-butyl-4-hydroxybenzyl alcohol (*Ib*), ● bis(3,5-di-tert-butyl-4-hydroxybenzyl)methylamine (*Ig*), ● bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulphide (*Ik*), ● 3,5-di-tert-butyl-4-hydroxybenzylmethyl sulphide (*Ij*), ⊙ N,N-dimethyl-2-hydroxy-3-tert-butyl-5-methylbenzylamine (*Ile*); ○ without antioxidant.

-tert-butyl-4-hydroxybenzylamine (*Ie*) is less active than N,N-dimethyl-3,5-di-tert-butyl-4-hydroxybenzylamine (*If*). Two other compounds containing the tertiary amino group, *i.e.* bis(3,5-di-tert-butyl-4-hydroxybenzyl)methylamine (*Ig*) and tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine (*Ih*) are reckoned among polynuclear antioxidants. Their activity is approximately the same as that of the mononuclear amine *If* and of the standard. It is obvious that the substituent X containing a tertiary nitrogen atom does not influence the antioxidative activity of phenols under the conditions used. No increase in the activity with increasing number of phenolic rings in one molecule of amines of type *I* as observed in the stabilization of polypropylene at 180°C could be seen in the stabilization of tetralin. The likely reason consists in the low temperature of tetralin oxidation at which there are no losses of the antioxidant from the stabilized system owing to the evaporation of compounds having a lower molecular weight.

TABLE I

Antioxidative Activity of Phenols of Type *I* and *II* in Tetralin Oxidation initiated with 2,2'-Azobis(isobutyronitrile) at 65°C

Meaning of symbols *cf.* Experimental Part. Standard: 2,6-di-tert-butyl-4-methylphenol.

| Compound | A_r | S_r |
|--|-------|-------|
| <i>Ia</i> 2,6-Di-tert-butyl-4-methylphenol | 1.00 | 0.96 |
| <i>Ib</i> 3,5-Di-tert-butyl-4-hydroxybenzyl alcohol | 0.86 | 0.96 |
| <i>Ic</i> 2,6-Di-tert-butyl-4-methoxymethylphenol | 0.61 | 1.14 |
| <i>Id</i> 3,5-Di-tert-butyl-4-hydroxybenzylamine | 1.47 | 0.75 |
| <i>Ie</i> N-Methyl-3,5-di-tert-butyl-4-hydroxybenzylamine | 0.77 | 1.02 |
| <i>If</i> N,N-Dimethyl-3,5-di-tert-butyl-4-hydroxybenzylamine | 0.96 | 0.78 |
| <i>Ig</i> Bis(3,5-di-tert-butyl-4-hydroxybenzyl)methylamine | 0.99 | 1.10 |
| <i>Ih</i> Tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine | 0.92 | 0.75 |
| <i>Ii</i> 3,5-Di-tert-butyl-4-hydroxybenzylmercaptan | 0.97 | 0.67 |
| <i>Ij</i> 3,5-Di-tert-butyl-4-hydroxybenzylmethyl sulphide | 1.26 | 0.52 |
| <i>Ik</i> Bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulphide | 1.90 | 0.35 |
| <i>Il</i> Bis(3,5-di-tert-butyl-4-hydroxybenzyl) disulphide | 2.67 | 0.22 |
| <i>IIa</i> 2,4-Dimethyl-6-tert-butylphenol | 0.87 | 0.96 |
| <i>IIb</i> 2-Hydroxy-3-tert-butyl-5-methylbenzyl alcohol | 1.08 | 0.90 |
| <i>IIc</i> 2-tert-Butyl-4-methyl-6-methoxymethylphenol | 0.69 | 0.88 |
| <i>IId</i> Bis(2-hydroxy-3-tert-butyl-5-methylbenzyl) oxide | 0.70 | 0.88 |
| <i>IIe</i> N,N-Dimethyl-2-hydroxy-3-tert-butyl-5-methylbenzylamine | 0.31 | 0.78 |
| <i>IIf</i> 2-Hydroxy-3-tert-butyl-5-methylbenzylmethyl sulphide | 1.05 | 0.49 |
| <i>IIg</i> Bis(2-hydroxy-3-tert-butyl-5-methylbenzyl)sulphide | 1.24 | 0.55 |

For compounds of type *I* containing an O or N atom in the group X, slopes of straight intercepts of the absorption curves of oxygen were calculated on completion of the induction period, which represent the rate of oxidation of the substrate in the given intercept. The S_r values (definition *cf.* Experimental) approach unity within the limits of experimental error, that is, a value for an unstabilized substrate. Consequently, compounds formed from these antioxidants during the inhibited oxidation in the stabilization of tetralin do not influence, similarly to polypropylene, the further oxidation of the substrate on completion of the induction period.

In the stabilization of polypropylene⁴, all compounds of group *I* containing sulphur were highly active at a high temperature. On the other hand, under the conditions of tetralin oxidation the activity of 3,5-di-*tert*-butyl-4-hydroxybenzylmercaptan (*Ii*) was only approaching standard *Ia*; a somewhat higher activity was found for 3,5-di-*tert*-butyl-4-hydroxybenzylmethyl sulphide (*Ij*). The values of their relative slopes S_r are also comparatively high. Thus, the transformation products of *Ii* and *Ij* have only a weak retardative effect on the initiated oxidation. Both binuclear thio derivatives, *i.e.* bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) sulphide (*Ik*) and bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) disulphide (*Il*) are highly active antioxidants and their activity strongly increases with the sulphur content in the molecule similarly to thiobisphenols^{1,2}. The retardative activity of these compounds is also high and increases with the sulphur content in the molecule in accordance with earlier results.

The compounds of group *II* are derivatives of 2,4-dimethyl-6-*tert*-butylphenol (*IIa*). The number of oxygen derivatives by far outweighed the other ones in this series. 2-Hydroxy-3-*tert*-butyl-5-methylbenzyl alcohol (*IIb*), A_r of which is approximately unity, is the most active of the oxygen derivatives. However, its activity is far below that determined in isotactic polypropylene⁴ where A_r is 1.8. The activities of bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl) oxide (*IIc*) and 2-*tert*-butyl-4-methyl-6-methoxymethylphenol (*IIc*) are the same in tetralin. Similarly to the tertiary amines of group *I*, in the case of these derivatives the volatility of mononuclear antioxidants cannot play any important role at a reduced oxidation temperature. This volatility is probably one of the causes of the different activity of mono- and polynuclear antioxidants determined at a high oxidation temperature of polypropylene.

The only aminic representative of the group of compounds of type *II*, *i.e.* N,N-dimethyl-2-hydroxy-3-*tert*-butyl-5-methylbenzylamine (*IIe*) exhibits only a low activity. It is the only compound of the whole set of compounds investigated in this work for which no induction period can be found on the absorption curve of oxygen recorded in tetralin stabilized with this antioxidant (Fig. 1).

The activity of sulphur-containing compounds, 2-hydroxy-3-*tert*-butyl-5-methylbenzylmethyl sulphide (*IIf*) and bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl) sulphide (*Ilg*) is not markedly higher in tetralin, similarly to the stabilization of polypropylene, although both sulphur-containing derivatives are more active than the standard. It has been confirmed for bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl) sulphide (*Ilg*)

that its stabilization activity is lower than that of an analogous position isomer *Ik*. As can be seen from the S_r values, in the group of compounds of type *II* only the transformation products of the sulphur-containing antioxidants cause the retardation of the further oxidation of the substrate on completion of the induction period.

The relative activity values, A_r , and the slope values, S_r , determined in the oxidation of tetralin, and their comparison with the results obtained in the oxidation of isotactic polypropylene⁴ at 180°C allow us to summarize that the participation of the oxygen and nitrogen atoms (separated from the phenolic ring by the methylene group) as another active centre of the phenolic antioxidant is not likely in the mechanism of antioxidation. The presence of such groups affects the stabilization activity in rather a negative manner. The activity of compounds containing the O or N atoms in the group X is mostly lower than or close to the activity of the standard; during the inhibited oxidation, their transformation products do not retard the oxidation of the substrate on completion of the induction period. On the other hand, sulphur derivatives of 2,6-di-tert-butyl-4-methylphenol (*Ia*) and 2,4-dimethyl-6-tert-butylphenol (*IIa*) usually have a higher activity than the standard and distinctly retard oxidation after the induction period. Consequently, a bifunctional mechanism is likely to be operative in their case even at 65°C.

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