ANTIOXIDANTS AND STABILIZERS. XXXIV.*
ANTIOXIDATIVE ACTIVITY OF BISPHENOLS DURING STABILIZATION OF TETRALIN

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An investigation was made of the antioxidative activity of 59 biphenyldiols (*I, II*), alkylidene-bisphenols (*III— VI*), and thiobisphenols (*VII, VIII*) in oxidation of tetralin initiated with 2,2′-azobis(isobutyronitrile) (AIBN) at 60°C. In the first two groups of compounds the 4,4′ isomers are more active than the 2,2′ isomers. Thiobisphenols are at low temperature of oxidation rather weak antioxidants. The antioxidative activity is discussed on the basis of the relative activity values in relation to 2,2′-methylenebis(4-methyl-6-tert-butylphenol) as a standard.

The oxidation stability of low-molecular and high-molecular hydrocarbons depends upon their structure and on conditions under which the oxidation is carried out. This property determines the lifetime and applicability of various technical products, such as various kinds of fuels, lubricating oils, or products made from polyolefins and rubbers. The internal oxidation stability which is affected by the chemical structure or the present impurities can be increased by using appropriate antioxidants. Bisphenols are used with advantage at temperatures up to 200°C. They are able to react with ROO˙ or RO˙ radicals which propagate the oxidation chain reaction. By modifying the bisphenol structure, it is possible to achieve the deactivation of hydroperoxides. This property can be expressed at elevated oxidation temperatures, in the first place.

   The application of bisphenols for the stabilization of various organic compounds has been suggested in a number of patents. However, these data do not allow to obtain a complete picture of the effect of structure upon the activity of bisphenols in the stabilization of hydrocarbons under
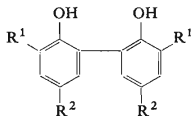
I, IIa, R¹ = R² = CH₃
I, IIb, R¹ = C(CH₃)₃, R² = CH₃
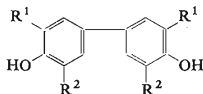
Ic, R¹ = CH₃, R² = C(CH₃)₃
I, IId, R¹ = R² = C(CH₃)₃

I
II

*   Part XXXIII: J. Chromatog., *65*, 279 (1972).

certain conditions. In most cases, the data on the antioxidative activity were compared by dealing with a randomly selected and limited number of commercially available compounds. No deeper conclusions can be drawn from these data. Above all, the results obtained by various authors cannot be properly compared owing to the different character of the experimental conditions and of the stabilized organic compounds. Partial results concerning the effect of structure
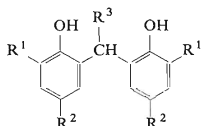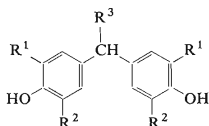
III, IVa, $R^1 = R^2 = CH_3$, $R^3 = H$ *III, IVe,* $R^1 = C(CH_3)_3$, $R^2 = R^3 = CH_3$

III, IVb, $R^1 = C(CH_3)_3$, $R^2 = CH_3$, $R^3 = H$ *IIIf,* $R^1 = R^3 = CH_3$, $R^2 = C(CH_3)_3$

III c, $R^1 = CH_3$, $R^2 = C(CH_3)_3$, $R^3 = H$ *III, IVg,* $R^1 = R^2 = C(CH_3)_3$, $R^3 = CH_3$

III, IVd, $R^1 = R^2 = C(CH_3)_3$, $R^3 = H$ *III, IVh,* $R^1 = C(CH_3)_3$, $R^2 = CH_3$,

$R^3 = CH_2CH_2CH_3$

III, IVi, $R^1 = C(CH_3)_3$, $R^2 = CH_3$, $R^3 = C_6H_5$
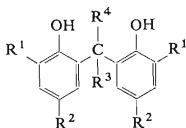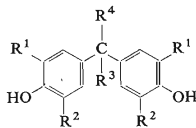
V, VIa, $R^1 = R^2 = R^3 = R^4 = CH_3$

V, VIb, $R^1 = C(CH_3)_3$, $R^2 = R^3 = R^4 = CH_3$

Vc, $R^1 = R^3 = R^4 = CH_3$, $R^2 = C(CH_3)_3$

V, VId, $R^1 = R^2 = C(CH_3)$, $R^3 = R^4 = CH_3$

VIe, $R^1 = C(CH_3)_2CH_2—C(CH_3)_3$, $R^2 = R^3 = R^4 = CH_4$

V, VIf, $R^1 = C(CH_3)_3$, $R^2 = R^3 = CH_3$, $R^4 = CH_2CH_3$

V, VIg, $R^1 = C(CH_3)_3$, $R^2 = CH_3$, $R^3 = R^4 = (CH_2)_5$
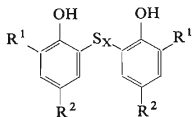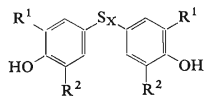
VII, VIIIa, $R^1 = R^2 = CH_3$, $x = 1$

VII, VIIIb, $R^1 = C(CH_3)_3$, $R^2 = CH_3$, $x = 1$

VIIIc, $R^1 = CH_3$, $R^2 = C(CH_3)_3$, $x = 1$

VII, VIIId, $R^1 = R^2 = C(CH_3)_3$, $x = 1$

VII, VIIIe, $R^1 = C(CH_3)_3$, $R^2 = CH_3$, $x = 2$

VIIIf, $R^1 = C(CH_3)_3$, $R^2 = CH_3$, $x = 3$

follow from the investigation of the activity of alkylidenebisphenols in the stabilization of rubber[1] and polyethylene[2,3] or the activity of thiobisphenols in oxidized rubber[4]. A comparison between alkylidene- and thiobisphenols in polymeric materials has been described[2,5,6]. A detailed study of selected compounds has been carried out in hydrocarbon fractions prepared from sulphur containing crude oil[7].

IX
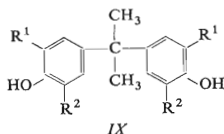
a, $R^1 = R^2 = R^3 = H$
b, $R^1 = CH_3$, $R^2 = R^3 = H$
c, $R^1 = C(CH_3)_3$, $R^2 = R^3 = H$
d, $R^1 = C(CH_3)_2CH_2C(CH_3)_3$, $R^2 = R^3 = H$
e, $R^1 = C(CH_3)_2CH_2C(CH_3)_2CH_2C(CH_3)_3$, $R^2 = R^3 = H$
f, $R^1 = R^3 = CH_3$, $R^2 = H$
g, $R^1 = R^3 = C(CH_3)_3$, $R^2 = H$
h, $R^1 = R^3 = C(CH_3)_2CH_2C(CH_3)_3$, $R^2 = H$
i, $R^1 = R^3 = C(CH_3)_2CH_2C(CH_3)_2CH_2C(CH_3)_3$, $R^2 = H$
j, $R^1 = R^3 = C_6H_5$, $R^2 = H$
k, $R^1 = R^3 = Br$, $R^2 = H$
l, $R^1 = R^3 = Cl$, $R^2 = H$
m, $R^1 = R^2 = C(CH_3)_3$, $R^3 = H$
n, $R^1 = R^2 = R^3 = CH_3$
o, $R^1 = R^2 = R^3 = C(CH_3)_3$

X   *XI*
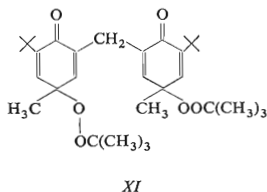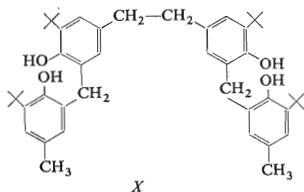
To obtain deeper information on the effect of the bridge type and its position on the phenol nucleus, we prepared extensive series of bisphenols *I−IX* and studied their antioxidative properties in the stabilization of isotactic polypropylene[8−10]. The same compounds were used in the present work to stabilize tetralin oxidized at 60°C in the presence of AIBN. The results obtained are discussed together with our previous data concerning the antioxidative activity of methylenebisphenols in tetralin[11] on the basis of relative activity values calculated from the oxygen absorption in oxidized tetralin. The slope values of absorption curves in the region of the stationary oxidation rate were also taken into consideration.

EXPERIMENTAL

Materials used

Tetralin was purified by shaking with conc. sulphuric acid, dried with sodium and distilled in an inert atmosphere. 2,2'-Azobis(isobutyronitrile) was freshly recrystallized from acetone, m.p. 103°C. Antioxidants — diphenyldiols *I* and *II*, alkylidenebisphenols *III— VI* and *IX* and thiobisphenols *VII— VIII* were chromatographically pure[8-10].

Determination of the Antioxidative Activity

The oxygen absorption in tetralin at 60°C was followed volumetrically under an atmospheric pressure of oxygen. The examples of typical absorption curves are given in Fig. 1. 2,2'-Azobis (isobutyronitrile) in a concentration of $5 \cdot 10^{-3}$ mol/l was used as initiator. The concentration of antioxidants was $2 \cdot 10^{-4}$ mol/l; in some cases it was $5 \cdot 10^{-3}$ mol/l. The activities of the individual phenolic compounds were compared on the basis of the time needed for the absorption of 50, 100, and 200 ml oxygen per one mol of tetralin (τ_{50}, τ_{100}, τ_{200}). The relative activities of antioxidants (given in the Tables) were calculated using always the values of τ_{100} from the expression $A_{rel} = (\tau' - \tau)/(\tau° - \tau)$, where τ' is the value of τ_{100} of the inhibitor under investigation, τ is the value for an unstabilized tetralin, $\tau°$ is the value obtained in the presence of the standard, *i.e.* 2,2'-methylenebis(4-methyl-6-tert-butylphenol). The value of the slope of an intercept of the curve in the region of a stationary rate of oxidation after the induction period, S, was calculated from the relationship $S = 100/(\tau_{200} - \tau_{100})$. The relative value S_{rel} represents the the ratio of S to the value $2 \cdot 32$ ml mol^{-1} min^{-1} determined in the absence of the antioxidant. The stoichiometric coefficient n was calculated from a relationship (used already in an earlier paper[12])

$$n = 2e(c_i - c_i e^{-k_i \tau_0})/c_a, \qquad (1)$$

where e is the activity factor of the initiator (the value 0·6 was determined[13] by means of 2,6-di-tert-butyl-4-methylphenol), k_i is the rate constant of decomposition of the initiator, $1·0 \cdot 10^{-5}$ s^{-1} (the mean from the data in refs[14,15] was used), τ_0 is the induction period (s), and c_i, c_a are the initial concentrations of the initiator and antioxidant resp. (mol/l); all these values hold for 60°C.

RESULTS

We investigated the autoxidation of tetralin initiated at 60°C with 2,2'-azobis(isobutyronitrile) and followed the antioxidative properties of bisphenols *I— IX* under these conditions; thus, with the exception of 4,4'-isopropylidenebisphenols, only tetraalkylated derivatives were investigated. 2,2'-Methylenebis(4-methyl-6-tert-butylphenol) (*IIIb*) was the standard compound used to compare activities; the results are summarized in Tables I and II.

Biphenyldiols I, II. The absorption curves of oxygen in the presence of all compounds under investigation exhibit an induction period. Under the conditions studied, 3,3-dimethyl-5,5-di-tert-butyl-4,4'-biphenyldiol (*IIb*) is the most active compound; its activity approaches that of the standard. The activities of all the other compounds under investigation are lower, and no marked effect of the position of the connection of both phenolic rings can be seen (Table I).

Alkylidenebisphenols III *and* IV — *with ring-connecting secondary and tertiary carbon atoms* (Table I). The course of the absorption curves is similar in the whole group of compounds. Methylenebisphenols (R^3 = H) were discussed in detail in ref.[11]. Similarly to the inhibition

of the oxidation of polypropylene[9], it cannot be determined which of the positions of the methylene bridge is of greater importance. In the series of ethylidenebisphenols ($R^3 = CH_3$) and butylidenebisphenols ($R^3 = C_3H_7$), the most active compound was always the 4,4′-isomer derived from 2-methyl-6-tert-butylphenol. It approaches by its activity the chosen standard. An opposite activities ratio was found with benzylidenebisphenols, where the isomer 2,2′ is the more active.

Alkylidenebisphenols V, VI *and* IX — *with ring-connecting quaternary carbon atom* (Tables I and II). The largest number of compounds was investigated in the series of 4,4′-isopropylidenebisphenols (VI, R^3, $R^4 = CH_3$; IX). The absorption curves of oxygen in the presence of monoalkylated derivatives are characterized by the fact that they have no clearly outlined induction period. The individual compounds do not differ much in their activities caused by the character of the alkyl group. 2-Tert-butyl-4,4′-isopropylidenebisphenol was the most active; however, also this compound is considerably less active than the chosen standard. In the tetralin inhibited with 4,4′-isopropylidenebis(2-alkylphenols), a considerable absorption of oxygen can be observed from the very beginning of oxidation. The activity is not affected by substitution to any essential degree. It is, however, somewhat higher than in the case of the monoalkyl derivatives, owing to

TABLE I

Activity of Antioxidants *I— VI* During Stabilization of Tetralin at 60°C

Concentration of the antioxidant $2 . 10^{-4}$ mol l^{-1}, the initiator $5 . 10^{-3}$ mol l^{-1}. Definition of the parameters A_{rel} and S_{rel} *cf.* Experimental.

Compound	A_{rel}	n	S_{rel}	Compound	A_{rel}	n	S_{rel}
Ia	0·64	3·0	0·74	IVa[a]	1·05	4·6	0·80
Ib	0·55	2·75	0·72	IVb[a]	1·16	5·4	0·72
Ic	0·53	2·55	0·72	IVd[a]	0·92	4·6	0·72
Id	0·74	3·6	0·67	IVe	1·01	4·8	0·86
				IVg	0·83	4·0	0·64
IIa	0·72	2·7	0·42	IVh	1·00	4·6	0·78
IIb	0·99	4·64	0·83	IVi	0·82	3·9	0·81
IId	0·58	2·76	0·74				
IIIa[a]	0·58	3·0	0·72	Va	0·53	3·3	0·59
IIIb[a]	1·00	4·4	0·625	Vb	0·04	—	0·58
IIIc[a]	0·80	3·6	0·63	Vc	0·28	—	0·78
IIId[a]	0·93	3·7	0·62	Vd	0·02	—	0·83
IIIe	0·85	3·9	0·57	Vf	0·03	—	0·77
IIIf	0·83	3·6	0·66				
IIIg	0·78	3·5	0·72	VIa	0·91	4·4	0·88
IIIh	0·77	3·4	0·63	VIb	0·98	4·6	0·86
IIIi	1·06	5·0	0·77	VId	0·68	3·4	0·86
				VIe	0·82	4·0	0·88
				VIf	0·91	4·2	0·69
				VIg	0·87	4·2	0·90

[a] Values of the parameters taken from ref.[11].

the presence of the second alkyl group in the bisphenol ring. In the series of symmetrically disubstituted derivatives, the compounds having substituents exhibiting a negative inductive effect were also studied and found to be inactive. 2,6-Di-tert-butyl-4,4′-isopropylidenebisphenol (*IXm*) was very little active. Of the whole series of the 4,4′-isopropylidenebisphenols under investigation, the tetraalkyl derivatives were the most active. They are the only ones approaching by their activity 2,2′-methylenebis(4-methyl-6-tert-butylphenol). A similar activity have 4,4′-sec-butylidene(*VIf*) and 4,4′-cyclohexylidenebisphenol(*VIg*). Of the series of 2,2′-isopropylidenebisphenols, only the tetraalkyl derivatives have been studied. They are of very weak activity compared with the tetraalkylated 4,4′-isopropylidenebisphenols. Absorption curves of oxygen in tetralin stabilized by them do not exhibit any induction period at all. A similar behaviour was observed with 2,2′-sec-butylidenebis(4-methyl-6-tert-butylphenol) (*Vf*). Of this group, an extraordinarily weak activity was found for the derivatives substituted with the tertiary butyl group in the position *ortho* to the hydroxyl group.

Thiobisphenols VII and VIII (Table II) have a comparatively weak relative activity; with the exception of 4,4′-trithiobis(2-methyl-6-tert-butylphenol) (*VIIIf*), it does not attain the activity of the chosen standard. In monothiobisphenols series, the inhibition activity is not affected to any marked degree by the position of the sulphide bridge or the character of the alkyl substitution. The induction period is indicated on the absorption curves of oxygen in tetralin stabilized by all the compounds investigated here. The exception to this is 2,2′-dithiobis(4-methyl-6-tert-butylphenol) (*VIIe*), which exhibits only retardation property from the very beginning of the oxidation.

TABLE II

Antioxidative Activity of Bisphenols *VII—IX* During Stabilization of Tetralin at 60°C

Conditions *cf*. Table I.

Compound	A_{rel}	n	S_{rel}	Compound	A_{rel}	n	S_{rel}
VIIa	0·74	3·4	0·72	*IXg*	0·78	3·8	0·43
VII b	0·63	3·1	0·40	*IXh*	0·79	3·4	0·43
VIIc	0·73	2·5	0·69	*IXi*	0·86	3·8	0·57
VIId	0·87	2·5	0·32	*IXj*	0·35	—	0·53
VIIe	0·68	—	0·29	*IXk*	0·05	—	0·86
				IXl	0·05	—	0·77
VIIIa	0·71	2·8	0·50	*IXm*	0·38	2·0	0·86
VIIIb	0·63	2·4	0·45	*IXn*	0·74	3·5	0·58
VIIId	0·63	2·1	0·41	*IXo*	0·74	3·6	0·56
VIIIe	0·99	3·5	0·33				
VIIIf	1·11	4·2	0·32				
IXa	0·27	—	0·58				
IXb	0·43	—	0·60				
IXc	0·58	—	0·49				
IXd	0·53	—	0·54				
IXe	0·57	—	0·47				
IXf	0·76	3·8	0·47				

DISCUSSION

Biphenyldiols and Alkylidenebisphenols

While investigating the effects of the character and position of bridge, our main attention was paid to the tetraalkylated bisphenols containing methyl or tert-butyl groups or combinations thereof. These compounds were found[10] to be most effective inhibitors in isotactic polypropylene. At 60°C in the oxidized tetralin, the differences in activities due to the character of the ring substitution in both isomeric series were not so great as in polypropylene. However, it can be seen that also here 4,4'-bis-phenols *II* and most of 2,2'-bisphenols *I* substituted with alkyls R^1 = tert-butyl and R^2 = methyl were most active. Thus substituted compounds were also used for the discussion of the effect of the bridge.

The series of activities of tetrasubstituted bisphenols having rings connected at positions 2,2' to the hydroxyl group is (with respect to the character of the bridge) as follows: sec-butylidene, isopropylidene < direct connection Ar-Ar (bisphenyldiols) < butylidene < ethylidene < methylene < benzylidene. Bisphenols under study form two distinctly separated groups. Compounds with a bridge containing a qua-ternary carbon atom possess the lowest activity. All compounds having at least one hydrogen atom at the carbon atom connecting both phenol rings or compounds with directly connected rings (biphenyldiols) are much more active. With the excep-tion of benzylidenebisphenol, the above order of the influence of bridges is in full agreement with the results obtained in the stabilization of polypropylene[10].

The activity series of bisphenols having bridges at 4,4' is not characterized by a pronounced differentiation caused by the effects of different bridges as in the pre-ceding case. This is an essential difference in comparison with the results obtained in isotactic polypropylene[10]. An increase in the volume of substituents on the bridge, however, causes a decrease in the activity also in the stabilization of tetralin.

It follows from a comparison between the activities of tetraalkylated 2,2'- and 4,4'-biphenyldiols and alkylidenebisphenols that position 4,4' is more favourite for all types of the compounds under investigation with the only exception of benzylidene-bisphenols. These isomers have been stronger antioxidants in tetralin at 60°C. At a comparatively low oxidation temperature, the steric effect of an alkylidene group connecting both rings is evidently much pronounced. At a high oxidation temperature (180°C, polypropylene[10]) the decrease in activity of 2,2'-alkylidenebisphenols caused by a reduced accessibility of the ROO• radicals to the hydroxy groups due to the steric effect of the bridge could be observed only with the compounds having the bulkiest bridges (isopropylidene and sec-butylidene). Therefore, with the exception of these compounds, all other 2,2'-alkylidenebisphenols were strong antioxidants.

In the series of 4,4'-isopropylidenebisphenols derivatives substituted with one to four alkyl groups were investigated (*VIa–e, IX*, Tables I and II). Generally, the tetraalkyl derivatives exhibited very low activity in the stabilization of polypropy-

lene[8]. In tetralin, however, the activity is affected to a high degree by the character of alkyl groups: the tetramethyl derivative is the most active in the series of methyl derivatives, and the activity decreases with the number of the methyl groups in the molecule. In the series of the tert-butyl derivatives, the trend of the effect of the number of the alkyl groups is the same as in the case of polypropylene[8]. The activity decreases in the series of the derivatives as follows: sym-di-tert-butyl > tri-tert-butyl > tetra-tert-butyl > mono-tert-butyl > unsym-di-tert-butyl. The most active compound of the whole series in tetralin was 4,4'-isopropylidenebis(2-methyl-6-tert-butylphenol), which was almost equal to the standard. The order of activities generally observed while evaluating the effect of the number of substituents and comparing the most active representatives of the individual groups was tetraalkyl > sym-dialkyl > trialkyl > monoalkyl > unsym-dialkyl > unsubstituted 4,4'-isopropylidenebisphenol.

Thiobisphenols

Antioxidants *VII* and *VIII*, Table II, were investigated at the same molar concentration as alkylidenebisphenols and biphenyldiols. They resemble biphenyldiols by their activity, and by their value of the stoichiometric coefficient, n (compare Table I).
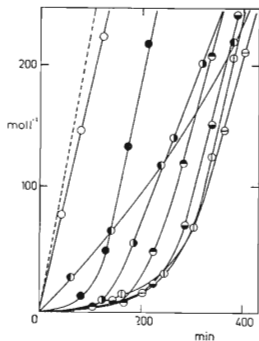
FIG. 1

Absorption of Oxygen During Oxidation of Stabilized Tetralin Initiated with 2,2'-Azobis(isobutyronitrile) $(5 . 10^{-3} \text{ mol } l^{-1})$ at 60°C

Antioxidants $(2 . 10^{-4} \text{ mol } l^{-1})$: ○ *Vb*, ● *IXm*, ◑ *VIIe*, ◐ *VIIIb*, ◕ *IIIh*, ◔ *VIf*, ◓ *IIb*, ◒ *IIIb*; — — — unstabilized tetralin.

FIG. 2

Dependence of the Antioxidative Parameter n on the Sulphur Content in the Molecule of Thiobisphenols

● 2,2'-Thiobisphenols: *1 VIIa*, *2 VIIb*, *3 VIIc*, *4 VIId*; ○ 4,4'-thiobisphenols: *5 VIIIa*, *6 VIIIb*, *7 VIIId*, *8 VIIIe*, *9 VIIIf*.

While at a high oxidation temperature the activity of thiobisphenols[10] was markedly affected by an increase in the sulphur content in the molecule, the same factor leads but to a slight increase in activity at the relatively low oxidation temperature of tetralin. It i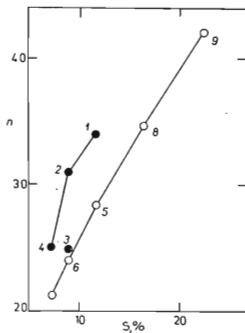s expressed only when trithiobisphenol *VIIIf* is applied. This fact is to be related to the lower extent of deactivation of hydroperoxides by their decomposition by the sulphur atom in the molecule at a low oxidation temperature. Here, the ability to inhibit oxidation by reacting with the ROO· radicals plays its part in the first place. In comparison with alkylidenebisphenols, this ability is lower, probably as a consequence of a modified inhibition mechanism. This is why under the conditions used by us the thiobisphenols were in tetralin even at an elevated concentration always less active than with alkylidenebisphenols.

The values of induction periods in tetralin stabilized with thiobisphenols are low and only very little affected by their structure. This is another difference in comparison with the stabilization of polypropylene[10]. However, the retardation ability still persists when the induction period is over, due to some of transformation products of thiobisphenols. The retardation ability does not depend on the position of the bridge with respect to the hydroxyl group, but increases with the sulphur content in the molecule of thiobisphenol.

In our experiments, we did not observe any prooxidative effect which appeared instead of the antioxidative properties in the presence of 2,2'-thiobis-, 2,2'-selenobis- or 2,2'-dithiobis(4-methyl-6-tert-butylphenols) in some oils[7]. In particular, the latter compound caused the formation of undesirable asphaltenes and cokes. The prooxidative action of thiobisphenols was also observed in the case of their application in polyacrylates[16].

The position of thiobisphenols among the other phenolic binuclear antioxidants is therefore determined by the composition of the stabilized substrate (in the first place, by the sensitivity of various hydrocarbons to the action of inhibitors[7] and by the contents of compounds which may affected the optimum function of thiobisphenols in the mechanism of inhibited oxidation), and also by the oxidation temperature. There are evidently less suitable to be applied at lower temperatures, because they have the reduced ability to decompose alkyl hydroperoxides.

Stoichiometric Coefficient of Bisphenols

For antioxidants (AH) acting as scavengers of radicals propagating the autoxidation chain of the oxidation of hydrocarbons (RH) according to

$$R· + O_2 \rightarrow ROO·, \quad RH + ROO· \rightarrow R· + ROOH \quad (A, B)$$

deactivation of the ROO· radical is assumed[17] by reactions

$$AH + ROO· \rightarrow A· + ROOH, \quad A· + ROO· \rightarrow products . (C, D)$$

An important parameter of the antioxidant activity is therefore the stoichiometric coefficient *n* which gives the total number of peroxyls with which the antioxidant molecule reacts during inhibited autoxidation. The determination of *n* from the overall reaction mechanism is exact, but experimentally difficult. Therefore, only main

products formed from molecular phenols under conditions modelling the inhibited autoxidation have so far been studied[17-21].

In our investigations, we simulated the composition of a reaction mixture obtained in the oxidation of hydrocarbons inhibited with mononuclear dihydric phenols[22] and 2,2'-methylenebis(4-methyl-6-tert-butylphenol)[23]. It should be pointed out that the nature and ratio of the individual reaction products from which the value of n was thus derived is a function of the oxidation conditions of phenols. The value of n varies for the above compounds between 0·5 and 3·0 (related to one phenolic nucleus only).

The determination of the stoichiometric coefficient n from the induction period is experimentally less difficult. The value thus determined includes all the processes in which the antioxidant takes part during the inhibited oxidation. It is therefore also dependent upon the antioxidant concentration[13]. The stoichiometric coefficient is an integral value. To calculate it, it is supposed that the antioxidant concentration is zero at the end of the induction period and that all ROO· radicals formed in the propagation reaction (A) are deactivated by reaction (C) and (D) only. Owing to the complexity of the reactions involved, it cannot be expected, that n will be an integer. When calculating n, some authors[13,20,24-27] used a relationship in which the rate of initiation due to the decomposition of initiator is considered to be constant throughout the induction period. However, this assumption is valid only for an induction period shorter than 13,000 s (ref.[13]). We therefore used relationship (I) respecting the change in the initiation rate with time[12].

Using relationship (I), we calculated for biphenyldiols I and II the stoichiometric coefficients n in the range from 2·6 to 3·0 (Table I). The only exception was 3,3',5,5'-tetra-tert-butyl-2,2'-biphenyldiol having the value $n = 3·6$. It should be noted that Howard and Ingold[24] determined from the data of cumene oxidation at 65°C for the same compound value $n = 1·4$ (this value refers to one phenolic ring only), while $n = 2·0$ was calculated for its isomer, 3,3', 5,5'-tetra-tert-butyl-4,4'-biphenyldiol, at 65°C in styrene[28].

In the bisphenol IV series, all the derivatives have $n \geqq 4·0$ (it is referred[28] the value $n = 4·0$ for IVb, determined at 65°C during styrene oxidation). All 2,2'-methylene-, 2,2'-ethylidene and 2,2'-benzylidenebisphenols III have $n < 4·0$. The exception form derivatives substituted with $R^1 = $ t-Bu, $R^2 = $ Me for which $n \geqq 4·0$. From this group, derivative $IIIb$ has been investigated earlier in more detail[12,23]. It has followed[23] from the products of the model investigation of its transformation by ROO· and RO· radicals generated from tert-butyl hydroperoxide or tert-butyl peroxide that in a mixture where the concentration of tert-butyl hydroperoxide does not exceed an equimolar ratio with respect to bisphenol $IIIb$, dimer X and trimer are formed as the main phenolic reaction products of reaction (E). At the same time
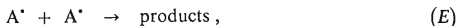
$$A· + A· \rightarrow \text{products}, \qquad (E)$$

another three phenolic compounds and several intensively coloured compounds of quinoid character (derived[29] from oligomers of bisphenol $IIIb$) were detected. The amount of brown products increases at a higher content of tert-butyl hydroperoxide. If the latter is present in a considerable molar extent, 2,2'-methylenebis-(4-methyl-4-tert-butylperoxy-6-tert-butylcyclohexa-2,5-dienone) (XI) is formed as

the main reaction product. This indicates the complex character of the participation of bisphenol *IIIb* in reactions (C), (D), and (E) whose stoichiometry varies in various stages of inhibited oxidation. The formation of dimer X is characterized by $n = 1.0$, the formation of trimer has $n = 1.33$. In the case of oxidative coupling of a larger amount of molecules of bisphenol *IIIb*, n converges two. Above mentioned phenolic oligomeric compounds react with further ROO˙ radicals to oxidation products of a stilbenequinone type[29], or to peroxy derivatives of cyclohexadienones[23]. Such reactions considerably increase n in an unidentifiable manner. For instance, the stoichiometric coefficient for the formation of cyclohexadienone XI is $n = 4.0$. If all the reactions involved are taken into account, n can become as high as 6.

Bisphenols with a quaternary carbon atom connecting both phenolic rings in positions 2,2′ form a special group. From the shape of the oxygen absorption curve during oxidation of tetralin stabilized with 2,2′-isopropylidenebisphenols *Va—d* and 2,2′-sec-butylidenebisphenol *Vf* the induction period cannot be determined with reliability. This makes it impossible to calculate the stoichiometric factor *n*. A value $n \geqq 4.0$ was calculated (with the only exception) for analogous compounds having bridges bonded at positions 4,4′.

The stoichiometric coefficient of thiobisphenols was determined under our experimental conditions within the range from 2.2 to 3.0. It can be seen from the Fig. 2 that the value of n increases with the sulphur content in the molecule of compounds under investigation. The possibility of decomposition of alkyl hydroxy peroxides into non-radical products can also be considered, along with a reaction with the ROO˙ radicals according to (C) and (D).

In accordance with the values of the stoichiometric coefficients n determined for bisphenols during tetralin oxidation (Tables I and II), the compounds under investigation can be on the whole divided into several groups. It can be assumed that the compounds in each of these groups can react with alkyl peroxyls in a similar manner. These groups consist of bisphenols *IV* and *VI* with $n \geqq 4$, the majority of bisphenols *III* with $n = 3.0$ to 3.6, biphenyldiols *I* and *II* and thiobisphenols *VII* and *VIII* with n approximately 2.8 and of bisphenols *V* which are very weak antioxidants under the conditions studied here and do not cause any induction period on the oxygen absorption curve.

Influence of the Character of Antioxidant upon the Stationary Rate of Oxidation after the Induction Period

The value of the slope of an intersection of the absorption curve of oxygen in the area of stationary rate of tetralin oxidation after the induction period in the presence of all the alkylidenebisphenols and biphenyldiols under investigation is lower than the same value calculated from the oxygen absorption curve in stabilized tetralin (the ratio of these values, S_{rel} is given in Tables I and II). This fact can be explained by the participation of transformation products of antioxidants formed during the induction period an by their different ability to retard the further oxidation process. The character of the transformation products remains unknown, with the exception of some products formed from 2,2′-methylenebis(4-methyl-6-tert-butylphenol). It can be deduced from

results obtained in the oxidation of stabilized isotactic polypropylene[10] carried out at 180°C that these newly formed compounds have a limited thermal stability, because they did not affect the oxidation after the induction period.

A strong decrease in the value of slopes of the curve in the phase of the stationary rate of oxidation of tetralin after induction period can be seen in most cases in the presence of bisphenols if the carbon bridge is replaced by the sulphur bridge. The decrease in the slope is also evident if the number of sulphur atoms in the bridge is increased. The same phenomenon was observed in the stabilization of isotactic polypropylene[10]. Its cause lies in the pronounced retardation ability of compounds formed from thiobisphenols during oxidation. This ability is especially strong at higher oxidation temperatures.

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