EFFECT OF SELECTED TRANSFORMATION PRODUCTS OF PHENOLIC ANTIOXIDANTS ON TETRALIN OXIDATION AT 65°C* **

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The effect of the most important types of products of the oxidation transformation of phenolic antioxidants on the autoxidation of tetralin initiated at 65°C with 2,2'-azobis(isobutyronitrile) was investigated. It was found that under these conditions 4-alkylperoxy derivatives of 2,5-cyclohexadienone do not virtually influence autoxidation at all; 2-alkylperoxy-3,5-cyclohexadienone has a weak initiating effect. A retardative effect was observed for 4-hydroperoxy and 4-hydroxy-2,5-cyclohexadienones and coloured oxidation products, *i.e.* 1,4-benzoquinones and above all stilbenequinone. The properties of mixtures of phenolic antioxidants with the individual types of transformation products are additive.

In the oxidation of hydrocarbon substrates stabilized with phenolic antioxidants the autoxidation chain reaction is interrupted by binding of the ROO• radicals. The antioxidants used undergo a chemical change during the process, which results in a modified effect upon the course of autoxidation. A kinetic analysis of the autoxidation reaction carried out in presence of the antioxidant cannot give information on the effect of the individual main transformation products on the autoxidation process. A solution is seen in a model study and in the application of defined compounds derived from the phenols under investigation.

In the oxidation transformations of phenolic antioxidants[1] the primary formation of aryloxyl radicals is followed by reactions giving rise to mixtures of coloured and colourless reaction products. Defined compounds were prepared by model reactions; some of them were also detected in hydrocarbons oxidized in presence of antioxidants. The investigation carried out up to now[2-4] of the effect of defined transformation products on the oxidation of hydrocarbons confirmed the need for a detailed study of the behaviour of the individual groups of compounds. In this paper results are reported which were obtained by using selected compounds of the group of alkylperoxycyclohexadienones, benzoquinones and quinone methides investigated at 65°C.

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EXPERIMENTAL

Tetralin (b.p. 207°C) and cumene (b.p. 152·5°C) (substrates) were purified according to ref.[5]; purity was checked by the GLC method, the hydroperoxides content was checked by Nozaki's method[6]. Chlorobenzene (b.p. 132·1°C) was purified after ref.[7,8] 2,2'-Azobis(isobutyronitrile). nitiator, m.p. 103—104°C (acetone).

Phenolic antioxidants. Compounds recrystallized from heptane or methyl alcohol were used; their purity was checked by the TLC method (silicagel precoated aluminium foils Silufol UV 254 Kavalier): 2,6-ditert-butyl-4-methylphenol (*I*), m.p. 70°C, 2,4,6-tritert-butylphenol (*II*), m.p. 131·5°C, 2-methyl-4,6-ditert-butylphenol (*III*), m.p. 48—50°C, 2,2'-methylenebis(4-methyl--6-tert-butylphenol (*IV*), m.p. 131°C, 2,2'-methylenebis(4,6-ditert-butylphenol) (*V*), m.p. 151 to 152°C, 4,4'-methylenebis(2,6-ditert-butylphenol) (*VI*), m.p. 154—156°C, 4,4'-ethylenebis(2,6-ditert-butylphenol) (*VII*), m.p. 170—171°C, 1,3,5-trimethyl-2,4,6-tris(3,5-ditert-butyl-4-hydroxybenzyl) benzene (*VIII*), m.p. 200°C.

Derivatives of cyclohexadienone. The compounds were prepared by using literary data and purified by crystallization from methyl alcohol (compounds *IX* and *XIV* from heptane). 4-Methyl--4-hydroperoxy-2,6-ditert-butyl-2,5-cyclohexadienone[9] (*IXa*), m.p. 114—116°C, 4-methyl-4-tert-butylperoxy-2,6-ditert-butyl-2,5-cyclohexadienone[10] (*IXb*), m.p. 86°C (ref.[10] 87°C), 4-methyl--4-α-tetralylperoxy-2,6-ditert-butyl-2,5-cyclohexadienone[10] (*IXc*), m.p. 103—104°C (ref.[10] 104°C), 4-methyl-4-cumylperoxy-2,6-ditert-butyl-2,5-cyclohexadienone[10] (*IXd*), m.p. 35—37°C, (ref.[10] 42·5°C), 2,6-ditert-butyl-4-methyl-4-(1-cyano-1-methyl-ethylperoxy)-2,5-cyclohexadienone[10](*IXe*) m.p. 87—91°C (ref.[10] 92·5°C), 4-tert-butylperoxy-2,4,6-tritert-butyl-2,5-cyclohexadienone[10] (*IXf*), m.p. 5°C, 2-methyl-2-tert-butylperoxy-4,6-ditert-butyl-3,5-cyclohexadienone[10] (*X*), m.p. 66—67°C (ref.[10] 70°C), 2,2'-methylenebis(4-methyl-4-tert-butylperoxy-6-tert-butyl-2,5-cyclohexadienone)[11] (*XI*), m.p. 139—142°C, 1,3,5-trimethyl-2,4,6-tris(1-tert-butylperoxy-3,5-ditert--butylcyclohexa-2,5-diene-4-onylmethyl)benzene[12] (*XII*), m.p. 134—138°C, decomp., 1,3,5-tritert-butyl-2,5-cyclohexadiene-4-one peroxide[13,14] (*XIII*), m.p. 142°C, decomp. (ref.[13,14] 148—149°C), 4-methyl-4-hydroxy-2,6-ditert-butyl-2,5-cyclohexadienone[9] (*XIV*), m.p. 110—112°C (ref.[9] 111—112°C), 5,7,3',5'-tetratert-butylspiro[2,3-dihydrobenzofuran-2,1'-cyclohexa-3',5'-diene-2'-one][15] (*XV*), m.p. 149—154°C (ref.[15] 153—155°C).

Quinones and quinone methides. All compounds were prepared according to literature and purified. 2-Tert-butyl-1,4-benzoquinone[16] (*XVI*), m.p. 52—55°C (heptane), 2,6-ditert-butyl--1,4-benzoquinone[17] (*XVII*), m.p. 64—66°C (sublimed), (ref.[17] 67—68°C), 3,5,3',5'-tetratert--butyl diphenoquinone[18] (*XVIII*), m.p. 245—246°C (ethyl alcohol), (ref.[18] 240—241°C, ref.[9] 246°C), 2,6-ditert-butyl-4-(3,5-ditert-butyl-4-hydroxybenzylidene)-2,5-cyclohexadiene-1-one[19] (*XIX*), called hydrogalvinoxyl, m.p. 157·5—158·5°C (85% ethyl alcohol), (ref.[19] 157—158°C), 3,5,3',5'-tetratert-butylstilbenequinone[20] (*XX*), m.p. 317—318·5°C (toluene), (ref.[20] 315—316°C).

Methods of investigation of the effect of additives on the rate of oxidation of tetralin and evaluation of results. The effectivities of phenolic antioxidants and of their oxidation transformation products were followed at 65°C in the oxidation of tetralin initiated with 2,2'-azobis(isobutyronitrile) (AIBN). The oxidation was carried out in thermostated glass cells with magnetic stirring. A solution of sodium alizarinsulphonate in a Kolthoff–Vleeschhouwer's regulator, pH 10 (light isolation within an extent of 390—560 nm) was used as the thermostating liquid. The oxidation cells were filled with 5 ml of chlorobenzene in which 8·21 mg AIBN was dissolved (total AIBN concentration in the reactor was $5 . 10^{-3}$M) and 5 ml of tetralin with the compound under investigation dissolved in it. Oxygen absorption was measured volumetrically with an automatic oxidation apparatus[21]. The oxygen consumptions thus obtained were recalculated to millimol of O_2 consumed by 1 mol of tetralin.

TABLE I

Effect of Phenolic Antioxidants *I*— *VIII* and 2,6-Ditert-butyl-4-(3,5-ditert-butyl-4-hydroxybenzylidene)-2,5-cyclohexadiene-1-one(*XIX*) on Tetralin Oxidation at 65°C

c Antioxidant concentration in mol . l^{-1} . 10^4. Oxidation conditions and meaning of symbols *cf.* Experimental.

Antioxidant	*c*	A_r	v_r
I	5·0	1·00	0·93
	10·0	1·00	0·83
II	10·0	0·97	0·82
III	10·0	0·74	0·92
IV	2·5	0·92	0·81
	5·0	1·10	0·73
V	5·0	0·60	0·87
VI	5·0	0·94	0·79
VII	5·0	1·03	0·77
VIII	3·3	1·01	0·74
XIX	5·0	0·97	0·82

TABLE II

Effect of Cyclohexadienones *IX*— *XV* and Quinoid Compounds *XVI*— *XX* on Tetralin Oxidation

c Concentration of the compound in mol . l^{-1} . 10^4. Oxidation conditions and meaning of symbols *cf.* Experimental.

Compound	*c*	v_r	Compound	*c*	v_r
IXa	5·0	0·64	*XII*	3·3	1·00
	10·0	0·35	*XIII*	10·0	1·00
IXb	5·0	1·00	*XIV*	5·0	0·86
	10·0	0·99	*XV*	5·0	0·99
	25·0	1·00	*XVI*	10·0	0·76
IXc	10·0	0·96	*XVII*	5·0	0·87
IXd	10·0	1·01		10·0	0·89
IXe	10·0	0·99	*XVIII*	5·0	0·91
IXf	10·0	0·94	*XX*	2·5	0·80
X	10·0	1·13		5·0	0·70
XI	2·5	0·98		12·5	0·37
	5·0	1·01			

The induction period (IP) was determined graphically as time data in minutes corresponding to the intersection of two straight lines of the curve representing the dependence of oxygen consumption on time. The effectivities of compounds having an IP were compared with that of 2,6-ditert-butyl-4-methylphenol (*I*) as a standard. The relative effectivity A_r was calculated as the ratio of the IP of a given antioxidant to the IP of the standard used in the same concentration (for polynuclear compounds the concentration was related to one phenolic ring). For all compounds the rate of oxygen absorption was evaluated in the straight part of the oxidation curve on completion of the induction period. The rate of absorption was calculated in $mmolO_2 \times mol\ tetralin^{-1} \times h^{-1}$ and v_r was calculated as the ratio of the rate of oxidation of tetralin initiated with AIBN in presence of the compound under investigation to the rate of oxidation of tetralin initiated with AIBN in the absence of another additive. The τ_r values were calculated as the ratio of values indicating time in min needed for the absorption of 15 mmol of oxygen by 1 mol of tetralin with and without additive. A_r, v_r and τ_r values are given in Tables I—III. Typical examples of the course of oxygen absorption in presence of some compounds under investigation and their mixtures are in Figs 1*a*—1*d*.

RESULTS AND DISCUSSION

The investigation of the effects of the transformation products of phenolic antioxidants was carried out with compounds having the cyclohexadienone and benzoquinone structure formed from phenols in the process of inhibited oxidation or in model reactions (Scheme). A mixture of tetralin with chlorobenzene at 65°C and 2,2′-azobis(isobutyronitrile) (AIBN) as initiator were used in the experiments. The effect of the transformation products on the oxidation course was compared with that of phenolic antioxidants used in the same concentrations.

TABLE III

Effect of Mixtures of Phenolic Antioxidants (*A*), Cyclohexadienones (*B*) and Quinoid Compounds (*C*) on Tetralin Oxidation at 65°C

c Concentration of the compound in $mol \cdot l^{-1} \cdot 10^4$. Oxidation conditions and meaning of symbols *cf.* Experimental.

Components of the mixture						A_r	v_r	r
A	*c*	*B*	*c*	*C*	*c*			
I	5·0	*IXa*	5·0	—	—	1·27	0·68	0·30
I	5·0	*IXb*	5·0	—	—	1·07	0·88	0·40
I	5·0	*XIV*	5·0	—	—	1·20	0·70	0·35
IV	2·5	*XI*	2·5	—	—	1·00	0·78	0·36
I	5·0	—	—	*XVII*	5·0	1·20	0·79	0·36
I	5·0	—	—	*XX*	2·5	1·20	0·72	0·35
—	—	*IXb*	5·0	*XVII*	5·0	—	0·95	0·91
—	—	*IXb*	5·0	*XX*	2·5	—	0·85	0·80
—	—	—	—	*XVII* + *XX*	5·0 + 2·5	—	0·70	0·61

Phenolic Antioxidants

Antioxidants from the group of mononuclear phenols *I–III*, bisphenols *IV–VII* and trisphenol *VIII* were selected for investigation. They were compared with each other at an equivalent concentration of the phenolic groups acting as scavengers in the radical process, with 2,6-ditert-butyl-4-methylphenol (*I*) as standard. The trend of influencing the effectivity by substitution agrees with conclusions obtained by studying the effectivity of large series of mono and binuclear phenols at 60°C in a comparable concentration of antioxidants in tetralin[22,23]. The course of oxygen absorption in oxidized tetralin containing antioxidants *I – VIII* is typical of inhibited

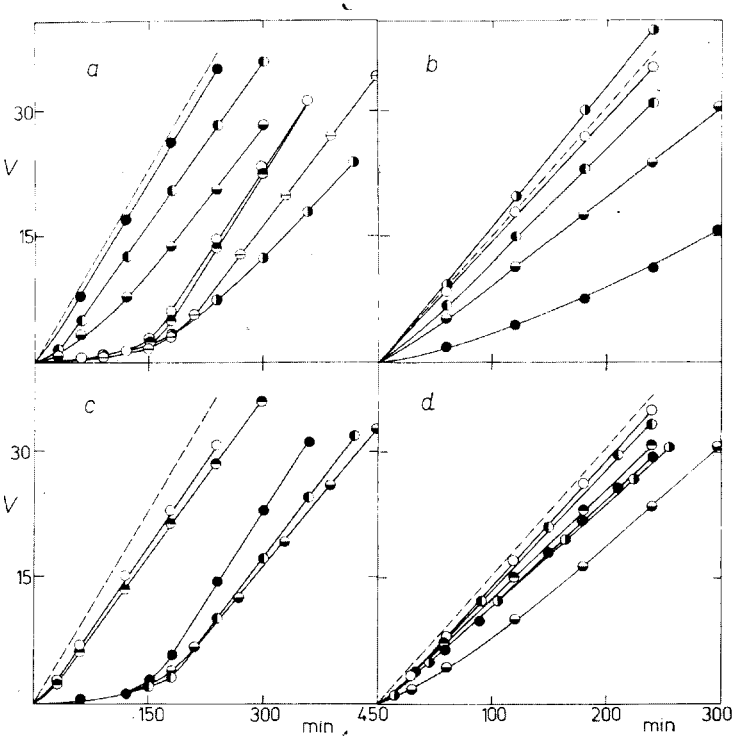
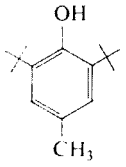


FIG. 1

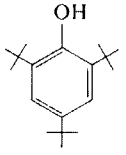
Course of Oxygen Absorption in Tetralin at 65°C (*V*, mmol O_2/mol tetralin) in Presence of Additives

Additives (if not indicated otherwise, concentration $5 \cdot 10^{-4}$M refers to each additive): *a* ○ *I*, ◒ *IXa*, ● *IXb*, ◐ *XIV*, ◓ *I* + *IXa*, ◑ *I* + *IXb*, ⊖ *I* + *XIV*; *b* ● *IXa*, ○ *IXb*, ◑ *X*, ◐ *XVII*, always $1 \cdot 10^{-3}$M), ◒ *XX*; *c* ● *I*, ○ *XVIII*, ◓ *XX* ($2{\cdot}5 \cdot 10^{-4}$M), ◐ *I* + *XVIII*, ◒ *I* + *XX* ($2{\cdot}5 \cdot 10^{-4}$M); *d* ○ *IXb*, ◓ *XVII*, ◑ *XX* ($2{\cdot}5 \cdot 10^{-4}$M), ◐ *IXb* + *XVI*, ● *IXb* + *XX* ($2{\cdot}5 \cdot 10^{-4}$M), ◒ *XVII* + *XX* ($2{\cdot}5 \cdot 10^{-4}$M); – – – – – tetralin without additives.

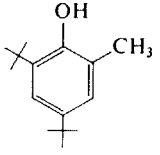
oxidation. With the exception of oxidation in presence of antioxidant *III* the rate of tetralin oxidation after completion of the IP in presence of all the other antioxidants mentioned above varies from 6·57 to 7·87 mmol O_2 × mol tetralin^{-1} × h^{-1}. An increased rate of oxidation in this part of the reaction was recorded in presence of *III* (*cf.* v_r values, Table I). It can be explained on the basis of different properties of the derived alkylperoxycyclohexadienone (discussed in another part of this paper). For all compounds under investigation with phenolic hydroxyl in their molecule, including hydrogalvinoxyl *XIX*, the rate of oxidation on completion of the IP is lower than that of tetralin alone (v_r values are always lower than unity, Table I). This is for the antioxidant concentration in question an indication of the generally weak retardative effect of the sum of transformation products remaining in the oxi-



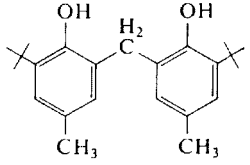
I



II



III



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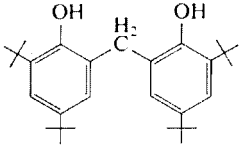

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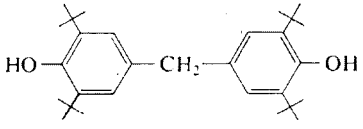
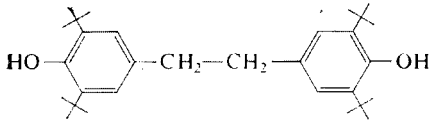
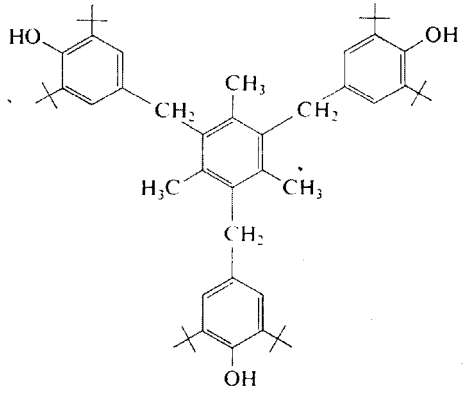


VI



VII

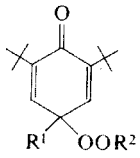


VIII

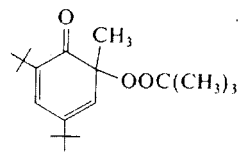
dized hydrocarbon. This property also follows from the finding about the effect of the antioxidant concentration on the rate of oxidation: at a lower concentration (*cf.* antioxidants *I* and *IV*), when a smaller accumulation of products having a retardative effect can be assumed, the rate of oxidation on completion of the IP becomes closer to the rate of tetralin oxidation.

Cyclohexadienones

The reaction of sterically hindered phenols (mono- and polynuclear) with alkylperoxyls gives rise to 4-alkylperoxy-2,4,6-trialkyl-2,5-cyclohexadienones and their analogs (compound *IX*, *XI*, *XII*). These compounds were synthesized, and in order to examine the effect on the course of oxidation they were supplemented by other important and structurally analogous derivatives of 2,5-cyclohexadienone, *i.e.* model

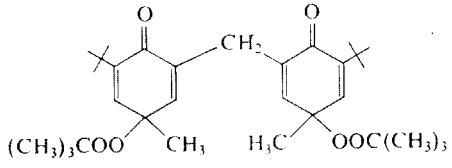


IX

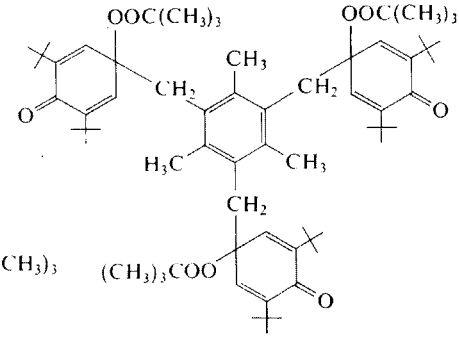


X

a, $R^1 = CH_3$, $R^2 = H$
b, $R^1 = CH_3$, $R^2 = C(CH_3)_3$
c, $R^1 = CH_3$, R = α-tetralyl
d, $R^1 = CH_3$, R^2 = cumenyl
e, $R^1 = CH_3$, R^2 = 1-cyano-1-methylethyl
f, $R^1 = R^2 = C(CH_3)_3$



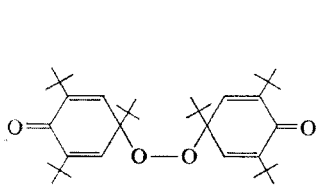
XI



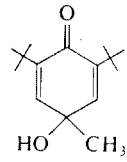
XII

compounds *IXa*, *XIII* and *XIV*. Cryptophenol *III* yields 2-tert-butylperoxy-2-methyl--4,6-ditert-butyl-3,5-cyclohexadienone (*X*). Another compound having the 3,5-cyclohexadienone structure is obtained by an intramolecular reaction from antioxidant *V* and has the structure *XV*.

4-Alkylperoxycyclohexadienones of type *IX* (R^1 = methyl) derived from 2,6-ditert-butyl-4-methylphenol were compounds studied in greatest detail. Compounds *IXb*–*IXd* differ by the character of the group R^2 derived from the oxidized substrate. Compound *IXe* is the product of a reaction between antioxidant *I* and radicals formed from the initiator AIBN in the oxidizing medium[10]. It follows from data in Table II that the group R^2 does not affect the course of oxidation. It is a characteristic feature that on the oxygen absorption curves recorded during the oxidation of tetralin in presence of cyclohexadienones *IXb*–*IXe* no induction period can be seen (examples *cf.* Fig. 1*a*,*b*). Such course of the oxygen absorption is also characteristic of other 2,5-cyclohexadienones: mononuclear *IXf*, binuclear *XI* and trinuclear *XII*. A similar behaviour has been observed[24] for triscyclohexadienone derived from 1,3,5-tris(2,6-ditert-butyl-4-hydroxybenzyl)cyanuric acid. The behaviour of cyclohexadienones derived from the triphenolic antioxidant *VIII* and from the cyanuric acid derivative mentioned above can be used for the demonstration of the disappearing of the induction period on the oxygen absorption curve during the



XIII



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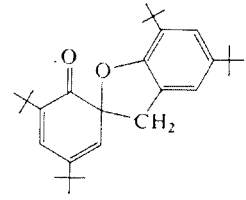
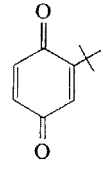
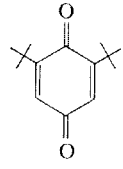


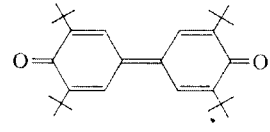
XV



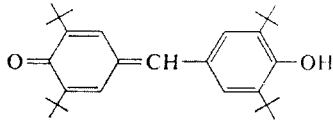
XVI



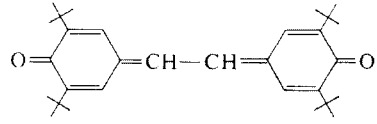
XVII



XVIII



XIX



XX

gradual transformation of phenolic rings into 2,5-cyclohexadienone groups[12,24]. The total transformation of a polynuclear phenolic antioxidant by a reaction of each phenolic ring with two alkylperoxyls to yield polynuclear alkylperoxycyclohexadienone is reflected (for the temperature 65°C used) in a total loss of antioxidative effectivity.

Under the conditions used, *i.e.* at 65°C, the rate of thermal oxidation is still not affected unfavourably by the oxidation product, as happens at higher oxidation temperatures[25]. Neither does an increase in the alkyl R^1 volume have any effect in this respect, as illustrated (Table II) by the investigation of 4-tert-butylperoxy-2,4,6-tritert-butyl-2,5-cyclohexadienone (*IXf*). An indication of the possibility of acceleration of the oxidation process by the substituent's volume can be seen only from the course of oxygen absorption in presence of 1,3,5-tritert-butyl-2,5-cyclohexadiene-4-one peroxide (*XIII*), $\tau_r = 1{\cdot}05$.

The relative rates of oxygen absorption in tetralin for all 4-alkylperoxy-2,5-cyclohexadienones *IX*, *XI*, and *XII*, and for cyclohexadienone *XIII* vary between 0·94—1·01. Thus, they can be regarded as compounds which at 65°C do not influence the course of tetralin oxidation even if present in the oxidized mixture in a concentration equivalent to that of the originally present antioxidant. A similar conclusion was drawn from the study of the oxidation of cumene carried out at 65°C in presence of AIBN: also in this case 4-cumylperoxy-2,6-ditert-butyl-4-methyl-2,5-cyclohexadienone (*IXd*) remains practically without influence on the rate of oxygen absorption.

With respect to the products of sensitized photooxidation of 2,6-ditert-butyl-4-methylphenol[26] we also investigated the effect of 4-hydroperoxy and 4-hydroxy-4-methyl-2,6-ditertbutyl-2,5-cyclohexadienones (*IXa*, *XIV*) on tetralin oxidation: the hydroxy derivative *XIV* has only a low retardative effect while the retardative effect of the hydroperoxy derivative *IXa* is very distinct (Fig. 1*a*,*b*). The retardative effect of hydroperoxide *IXa* in thermal oxidation is the greatest difference ever observed in comparison with the whole series of alkylperoxy-2,5-cyclohexadienones. The reason of the strong retardative effect of *IXa* is the slow thermal decomposition[26] to yield 2,6-ditert-butyl-4-methylphenol and 4-hydroxycyclohexadienone *XIV*, of which the former is an antioxidant and the latter is a weak retarder.

Transformation of phenolic antioxidants of the cryptophenol type, *i.e.* 2-methyl-4,6-ditert-butylphenol (*III*), gives rise to cyclohexadienone isomeric with the preceding group, that is, to 2-tert-butylperoxy-2-methyl-4,6-ditert-butyl-3,5-cyclohexadienone (*X*). In accord with the different thermal behaviour of both types of isomeric cyclohexadienones *X* has a slightly prooxidative effect already at 65°C (Table II, Fig. 1*b*); this property becomes pronounced at an elevated temperature of oxidation[25].

The investigation of the effect of compounds with the cyclohexadienone structure was supplemented by 5,7,3′,5′-tetratert-butylspiro[2,3-dihydrobenzofuran-2,1′-cyclohexa-3′,5′-diene-2′-one] (*XV*) which arises without interaction with another alkylperoxyl from aryloxyl derived from 2,2′-methylenebis(4,6-ditert-butylphenol) (*V*). Unlike all preceding cyclohexadienones it does not contain the alkylperoxidic group and is virtually without any effect on thermal oxidation.

Quinoid Compounds

Several compounds having a typical structure and whose formation in the transformation of phenolic antioxidants was proved or is very likely were selected for investigation, namely, alkylated 1,4-benzoquinones *XVI* and *XVII*, 3,5,3′5′,-tetratertbutyldiphenoquinone (*XVIII*), hydrogalvinoxyl *XIX* (which at the same time can be regarded as a model phenolic antioxidant), and 3,5,3′,5′-tetratert-butylstilbenequinone (*XX*). The investigation has revealed (Table I) that the properties of hydrogalvinoxyl *XIX* are predominantly affected by the presence of a sterically hindered phenolic group. Its relative antioxidative activity can be compared with that of 2,6-ditertbutyl-4-methylphenol; the induction period is well visible on the absorption curve of oxygen. Thus, the 1,4-benzoquinonemethinoid group has no unfavourable effect on the antioxidative property of sterically hindered phenol. This suggests that also in other types of polynuclear antioxidants, in which partial transformation of some phenolic group will give rise to the quinonemethine group, there will be no other change in activity than a decrease due to the relative decrease in the content of sterically hindered phenolic groups.

The total transformation of polynuclear phenolic antioxidant into a quinonemethinoidic system is demonstrated by the behaviour of the pair of compounds 4,4′-ethylenebis(2,6-ditertbutylphenol) (*VII*) and stilbenequinone *XX* (the latter quinone methide is formed in the process of inhibited oxidation from 2,6-ditert-butyl-4-methylphenol[20]). The antioxidative properties of *VII* will be changed to the retardative effect of *XX* (Table II, Fig. 1*b*,*c*), which depends on the concentration of stilbenequinone in the oxidized substrate. However, the retardative properties appear already at a low concentration corresponding to that of the originally present antioxidant. The types of antioxidant which can form quinone methinoid systems during the transformation owing to interactions in the inhibition process may have a retardative effect after IP, according to the results of our investigation. Consequently, the transformation into quinone methides is more favourable from the viewpoint of polymer stabilization than the transformation into alkylperoxycyclohexadienones.

The retardative activity has also been observed at 65°C for 2-tert-butyl and 2,6-ditert-butyl-1,4-benzoquinones (*XVI*, *XVII*); the effect was weaker than that of stilbenequinone *XX*. The effect of diphenoquinone *XVIII* is still weaker than that of benzoquinones *XVI* and *XVII*.

Mixtures of Phenolic Antioxidants with the Transformation Products

The preceding investigation carried out with individual compounds has revealed that the oxidative transformation of phenols leads to a loss of their antioxidative activity: 1,4-benzoquinoidic products still keep their retardative properties at 65°C to various degree, while alkylperoxy-2,5-cyclohexadienones have no effect on the

oxidation rate at this temperature. The thermally less stable 3,5-cyclohexadienone acts as an initiator.

The transformation of the phenolic antioxidant during inhibited oxidation proceeds gradually, taking place in the course of IP. During this time the concentration of the original antioxidant is reduced and the transformation products start accumulating. We examined the behaviour of model mixtures of antioxidants with their transformation products. Concentrations of the mixtures were chosen so as to make possible an evaluation of their relations. The investigation was based on the effects upon the properties of 2,6-ditert-butyl-4-methylphenol which is the source of cyclohexadienones of type *IX*, of stilbenequinone *XX*, and under suitable conditions also of benzoquinone *XVII*.

The plot of oxygen absorption (Fig. 1*a*) and data on the oxidation rate of duration of IP (Table III) indicate that the course of reaction during the oxidation of tetralin carried out in presence of the mixture of phenol *I* with alkylperoxycyclohexadienone *IXb* is completely identical with that in presence of the same concentration of phenol *I*. In this way we demonstrated the inert character of 2,5-cyclohexadienone; the phenolic antioxidant gradually transformed into such a compound further acts as an antioxidant in the substrate depending on its concentration (quite similarly, alkylperoxycyclohexadienone *XI* has no unfavourable effect upon IP due to bisphenol *IV*; the presence of the former is reflected in a small retardation after IP). If hydroperoxycyclohexadienone *IXa* or hydroxycyclohexadienone *XIV* are formed from phenol *I*, their retardative activity is reflected in a slowing-down of the rate of oxygen absorption after completion of IP, the duration of which is not affected unfavourably; there is only a less sharp transition between the phase characterizing inhibited oxidation and that after completion of IP. The retardative effect is also clearly visible in mixtures of phenol *I* and benzoquinone *XVII*, and particularly stilbenequinone *XX* (Fig. 1*c*).

A retardative effect is also observed for benzoquinone *XVII* or stilbenequinone *XX* in a mixture with cyclohexadienone *IXb* (Fig. 1*d*). The intensity of the retardative effect of the mixture is proportional to the retardative effect demonstrated by means of pure model compounds. The retardative effect of benzoquinone *XVII* and stilbenequinone *XX* used in the mixture is an additive one.

It follows from the investigation of tetralin oxidation in chlorobenzene at 65°C that under the conditions used the least unfavourable properties for the further course of thermal oxidation are exhibited by quinoid compounds (which however stain the substrate) and by hydroperoxy derivatives of 2,5-cyclohexadienone. Another important group of the transformation products, *i.e.* 4-alkylperoxy-2,5-cyclohexadienones, still has no effect on the course of oxidations carried out at 65°C, but the initiating activity of the less stable 2-alkylperoxy-3,5-cyclohexadienone indicates their behaviour at higher oxidation temperatures.

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