
**EFFECT OF DERIVATIVES OF CYCLOHEXADIENONE
AND 1,4-BENZOQUINONE ON THE OXIDATION OF TETRALIN
AT TEMPERATURES RANGING FROM 75 TO 140°C* ****

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The oxidative transformation of phenolic antioxidants which is an integral part of the inhibition process is connected with a modification and/or loss of the antioxidative activity. It was shown by using selected model compounds that the effect of the products formed on tetralin oxidation depends on the oxidation temperature. The derivative of stilbenequinone preserves its retardative effect up to 140°C and 1,4-benzoquinones preserve it up to 75°C. At 75°C the derivatives of 4-alkylperoxy-2,5-cyclohexadienone are still without any essential effect on the course of thermal oxidation of tetralin; above this temperature they act as initiators. The derivative of 2-alkylperoxy-3,5-cyclohexadienone initiates oxidation already starting from 65°C. The initiating effect of alkylperoxycyclohexadienones is in accord with their chemical structure and thermal behaviour.

Apart from difficultly definable tarry compounds, derivatives of cyclohexadienone and benzoquinone are also formed as a result of the oxidative transformations of phenolic antioxidants modelling the participation of antioxidants in the inhibition process. An investigation of the effect of these derivatives on tetralin oxidation at 65°C has revealed¹ that quinoid compounds and hydroxy and hydroperoxy-2,5-cyclohexadienones exhibit a retardative effect of different intensity, 4-alkylperoxy-2,5-cyclohexadienones practically do not affect autoxidation, and 2-alkylperoxy-3,5-cyclohexadienone acts as a weak initiator. Owing to the observed differences in the behaviour of the individual characteristic products, experimental data were gathered providing information about their effect on the course of oxidation as a function of temperature.

EXPERIMENTAL

Analytical methods. The melting points and decomposition temperatures of cyclohexadienone derivatives were determined with a Thermal Analyzer Du Pont Model 900 at a rate of heating 5–10°C/min. The decomposition temperatures are given in Table I. For TLC, silicagel pre-

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coated aluminum foils Silufol UV 254 (Kavalier) with a fluorescence indicator were used. A 254 nm light or spraying of the foils with a solution of 0.1M-KMnO₄ in 0.05M-H₂SO₄ were used for detection.

Substrate and solvent. Tetralin was purified similarly to the preceding paper¹. Technical trichlorobenzene was purified by a modified procedure described in ref.^{2,3}. It was extracted with an aqueous KOH solution, water, repeatedly with concentrated sulphuric acid until disappearance of the brown-yellow colour of the acid layer, with water again, dried with calcium chloride and fractionated on a column with Berl saddles after distillation at atmospheric pressure. The fraction (b.p. 106°C/10 Torr) consisting of 1,2,4-trichlorobenzene with 3–9% 1,2,3-trichlorobenzene and 0–1% 1,3,5-trichlorobenzene was used in the experiments.

Additives. The phenolic antioxidants used, derivatives of cyclohexadienone *I–V* and compounds having the quinoid or quinone methide structure *VI–IX* were the same as in the preceding paper¹. α,α' -Cumyl peroxide (*X*), m.p. 39°C.

Methods of investigation of the effect of additives on the rate of oxidation and evaluation of results. The oxidation of tetralin solutions in trichlorobenzene was studied in the presence of additives at 75, 100, 120 and 140°C. The oxygen absorption was measured by means of a six-channel automatic apparatus⁴. The oxidation was carried out in vessels provided with a stirrer; silicone oil was used for thermostating. The reactors were first filled with 5 ml of trichlorobenzene, then stripped 2 min with oxygen, and trichlorobenzene was thermostated to the required temperature while stirring. After the temperatures had been balanced, a solution containing the remaining trichlorobenzene with tetralin and the dissolved compound under investigation was injected into the reactor. Owing to the technical conditions of the recording of the course of oxidation, the total amount of tetralin in the oxidized solution was varied according to the temperature used (ratio ml tetralin: ml trichlorobenzene): 75°C 5 : 5, 100°C 2 : 8, or 3 : 7, 120°C 1 : 9, 140°C 0.5 : 9.5 or 1 : 9. Oxygen consumptions thus measured were recalculated to mmol of oxygen absorbed by 1 mol of tetralin.

A comparison of the oxidation of tetralin solutions not containing additives is shown in Fig. 1. A typical course of oxygen absorption in presence of selected additives can be seen in Fig. 2 (for 75°C) and Fig. 3 (for 120°C). The effect of compounds *I–VII* and *IX* on the course of oxida-

TABLE I

Melting Points and Decomposition Temperatures of Cyclohexadienones *I–V* and of α,α' -Cumyl Peroxide (*X*) Determined by Thermal Analysis

Compound	M.p., °C	Decomposition temperature °C	Compound	M.p., °C	Decomposition temperature °C
<i>Ia</i>	114–116	120	<i>II</i>	112–113	above 200
<i>Ib</i>	86	125	<i>III</i>	66–67	75
<i>Ic</i>	103	125	<i>IV</i>	141–143	140
<i>Id</i>	35–37	130	<i>V</i>	149–154	160
<i>Ie</i>	87–91	135	<i>X</i>	39	135
<i>If</i>	5	115			

tion is characterized by the values $\tau_r = \tau_0/\tau_x$, i.e. by the ratio of data (in min) corresponding to a time during which n mmol of oxygen were consumed by 1 mmol of tetralin not containing additives (τ_0) or with an additive (τ_x) ($n = 1.0$ at 75°C and 40 at $100\text{--}140^\circ\text{C}$). The values of τ_r are summarized in Table II. The results of the investigation of the whole group of products are summarized in Table III where the retardative activity is denoted by R ($\tau_r < 1.0$), inertness in the course of oxidation is denoted by O ($\tau_r \sim 1.0$), and the initiating activity is denoted by I ($\tau_r > 1.0$).

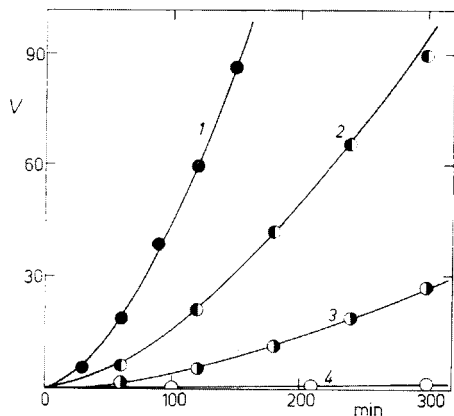


FIG. 1

Absorption of Oxygen in Tetralin (V , mmol O_2 /mol tetralin)

Temperatures, $^\circ\text{C}$: \circ 75, \bullet 100, \bullet 120, \bullet 140.

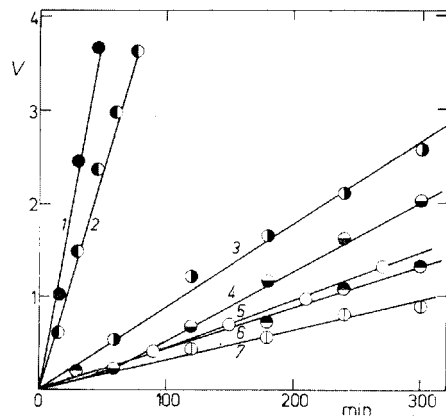


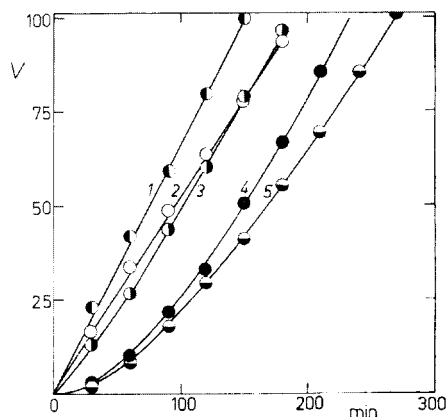
FIG. 2

Absorption of Oxygen in Tetralin (V , mmol O_2 /mol at 75°C tetralin) in Presence of Cyclohexadienones *Ia*, *Ib*, *If*, *III* and *IV* and α,α' -Cumyl Peroxide (*X*)

Additives ($5 \cdot 10^{-4}\text{M}$): \circ *Ia*, \bullet *Ib*, \bullet *If*, \bullet *III*, \bullet *IV*, \bullet *X*; \circ without additives.

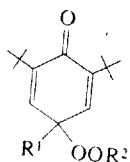
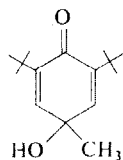
FIG. 3
Absorption of Oxygen in Tetralin (V , mmol O_2 /mol tetralin) at 120°C in Presence of Cyclohexadienones *Ib*, *If*, and *III* and Stilbenequinone (*IX*)

Additives ($5 \cdot 10^{-4}\text{M}$): \bullet *Ib*, \circ *If*, \bullet *III*, \bullet *IX* ($2.5 \cdot 10^{-4}\text{M}$); \bullet without additives.

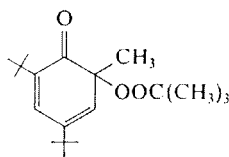
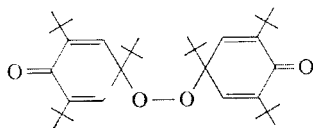
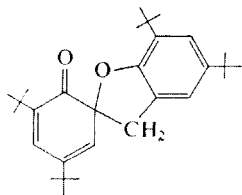
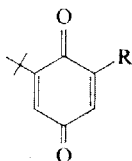
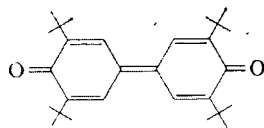


RESULTS AND DISCUSSION

We investigated the effect of 4-hydroperoxy- and 4-alkylperoxycyclohexadienones *Ia–If*, 2-tert-butylperoxy-3,5-cyclohexadienone (*III*), 4,4'-dioxycyclohexadienone (*IV*), cyclohexadienone (*V*), benzoquinones *VIa,b*, diphenoquinone (*VII*) and of the derivatives of quinonemethide *VIII* and *IX* on the course of oxidation of a tetralin solution in trichlorobenzene at 75–140°C. No initiator was added to tetralin.

*I**II*

- a*, $R^1 = \text{CH}_3$, $R = \text{H}$
b, $R^1 = \text{CH}_3$, $R^2 = \text{C}(\text{CH}_3)_3$
c, $R^1 = \text{CH}_3$, $R^2 = \alpha\text{-tetralyl}$
d, $R^1 = \text{CH}_3$, $R^2 = \text{cumenyl}$
e, $R^1 = \text{CH}_3$, $R^2 = 1\text{-cyano-1-methylethyl}$
f, $R^1 = R^2 = \text{C}(\text{CH}_3)_3$

*III**IV**V**VI**VII*

- a*, $R = \text{H}$
b, $R = \text{C}(\text{CH}_3)_3$

Changes in the rate of oxygen absorption give indications for the evaluation of differences in the role played by the structure of the individual compounds. Owing to the high oxidation temperatures, trichlorobenzene was used as the inert solvent. In order to compare oxidation in the latter solvent with that carried out in chlorobenzene (*cf.* preceding paper¹), we followed the rate of oxygen absorption at 65°C in tetralin solutions in both chloro derivatives of benzene: it was found that in presence of an antioxidant (2,6-ditert-butyl-4-methylphenol) and a retarder

TABLE II
Effect of Cyclohexadienones I–V, Quinoid Compounds VI–IX and α,α' -Cumyl Peroxide X on Tetralin Oxidation at 75–140°C
Meaning τ_r *cf.* Experimental.

Compound	$c \cdot 10^4$ mol/l	τ_r at temperature, °C			
		75	100	120	140
<i>Ia</i>	5.0	0.70	—	—	0.40
<i>Ib</i>	1.0	—	—	1.20	—
	2.0	—	1.10	—	—
<i>Ic</i>	5.0	1.00	1.40	1.60	1.90
	5.0	—	—	—	1.90
	1.0	—	—	—	2.60
<i>Id</i>	5.0	—	—	—	1.90
<i>Ie</i>	5.0	—	—	—	1.90
<i>If</i>	1.0	—	—	1.00	—
	2.0	—	1.20	—	—
<i>II</i>	5.0	1.90	1.70	1.90	2.10
	5.0	—	—	—	1.00
<i>III</i>	1.0	—	—	1.40	—
	2.0	—	1.50	—	—
<i>IV</i>	5.0	9.5–13.7	2.50	2.50	1.90
	5.0	10.30	2.70	2.10	—
<i>V</i>	5.0	—	—	0.90	—
<i>VIa</i>	5.0	—	—	0.80	—
<i>VIb</i>	2.0	—	1.00	—	—
	5.0	0.60	1.00	1.00	—
<i>VII</i>	2.5	—	—	0.80	—
<i>IX</i>	1.0	—	0.90	—	—
	2.5	0.40	0.90	0.90	0.90
	10.0	—	—	—	1.30
<i>X</i>	5.0	1.30	1.20	1.70	1.90
	10.0	—	—	—	2.60
	20.0	—	—	2.60	—

(2,6,2',6'-tetratert-butylstilbenequinone) the rate was always lower in trichlorobenzene.

Derivatives of Cyclohexadienone

For an investigation of the temperature dependence within the temperature range of 75–140°C, we chose 4-tert-butylperoxy derivatives of 2,5-cyclohexadienone differing by an alkyl in position 4 (compounds *Ib, f*) and 4,4'-dioxy-2,5-cyclohexadienone *IV*. It follows from the data in Table II and Fig. 2 that *Ib* does not influence the course of oxidation at 75°C, while the derivative *If* with a bulky alkyl in position 4 has an initiating effect. This is a difference compared to results obtained at 65°C when both compounds exhibited the same influence on the course of oxidation¹. This is a consequence of the lower thermal stability of the alkylperoxy derivative *If* compared to *Ib* (Table I). At 100°C and 120°C both compounds, *Ib* and *If*, act as initiators. (Consistent results were also found^{5,6} for polynuclear alkylperoxycyclohexadienones.) This property is concentration dependent. Within the temperature range under investigation (75–120°C) dioxycyclohexadienone has a pronounced initiating effect. At 75°C and 100°C the initiating effect is stronger than that of α, α' -cumyl peroxide; at 120°C the difference in the initiating activity of both compounds is not pronounced.

All 4-alkylperoxy-2,5-cyclohexadienones *Ib–If* investigated here accelerated the tetralin oxidation at 140°C. There is no essential difference between the effect of alkylperoxycyclohexadienones of type *I* derived from 2,6-ditertbutyl-4-methyl-

TABLE III

Indicative Data on the Retardative (R) and Initiating (I) Properties of Selected Transformation Products of Phenolic Antioxidants at 65–140°C (compounds not affecting the course are denoted by O)

The ranges of τ_r values are given in brackets.

Type of transformation product	Temperature, °C				
	65	75	100	120	140
<i>VI</i>	R (0.7–0.8)	R (0.6)	O (1.0)	O (1.0)	—
<i>IX</i>	R (0.7–0.8)	R (0.4)	R (0.9)	R (0.9)	—
<i>I</i>	O (1.0)	O (0.1)	I (1.4)	I (1.6)	I (1.9)
<i>III</i>	O–I (1.1)	I (9.5–13.7)	I (2.5)	I (2.5)	I (1.9)

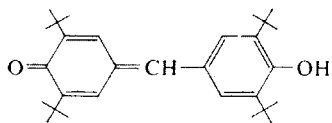
phenol or 2,4,6-tritert-butylphenol. Consequently, at such high oxidation temperature neither the character of the group R^1 nor that of the group R^2 becomes operative. α,α' -Cumyl peroxide used in tetralin at 140°C as an oxidation initiator at the same molar concentration as cyclohexadienones *I* under investigation leads to the same increase in the rate of oxidation of the tetralin solution.

A very pronounced initiating effect on the autoxidation of tetralin over the whole range of temperatures studied in this work was observed for 2-tert-butylperoxy-2-methyl-4,6-ditert-butyl-3,5-cyclohexadienone, while the cyclohexadienone derivative *V* not containing the peroxide group almost does not affect the oxidation.

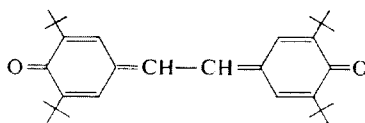
Thus, the initiating activity of the whole series of cyclohexadienone derivatives and its dependence on the oxidation temperature are evidently due to the presence of the peroxidic bond and to thermal decomposition. The thermal stability of cyclohexadienones was followed by means of DTA; it is affected by the structure. Table I shows that the decomposition temperature of all 4-alkylperoxy-4-methyl-2,6-ditert-butyl-2,5-cyclohexadienones *Ib–Ie* investigated here lies within the range of 125 to 135°C . A similar thermal behaviour was also found^{5–7} for more complicated derivatives having the structure of 4-alkylperoxy-2,5-cyclohexadienone formed from mono-nuclear and trisphenolic antioxidants. The decomposition temperature of α,α' -cumyl peroxide lies within the same range of temperatures. The experimentally determined absorption rates of oxygen in tetralin oxidized in presence of the above compounds at 140°C are in accord with the result of the DTA analysis and confirm the identical initiating effect of 4-alkylperoxycyclohexadienones *Ib–Ie* and of α,α' -cumyl peroxide.

The initiating effect of 2-tert-butylperoxy-2-methyl-4,6-ditert-butyl-3,5-cyclohexadienone, which appears already at the lowest oxidation temperature investigated here¹, *i.e.* at 65°C , can also be explained by the low temperature of its thermal decomposition (Table I); the behaviour is in accord with the analysis of the relationships existing between the decomposition temperature and the initiating effect of isomeric 4-alkylperoxy-2,5-cyclohexadienones.

4-Hydroperoxy-2,6-ditert-butyl-4-methyl-2,5-cyclohexadienone (*Ia*), which is a product of the photooxidative transformation of the technically important antioxidant, 2,6-ditert-butyl-4-methylphenol, still keeps its retardative effect at 140°C . This is due to the products of its thermal decomposition⁸, which also comprise the phenolic antioxidant mentioned above and 4-hydroxy-2,6-ditert-butyl-4-methyl-2,5-cyclo-



VIII



IX

hexadienone (*II*); the latter exhibits a retardative effect at 65°C¹ while at 140°C its presence remains virtually without influence.

In order to elucidate the influence upon the further course of oxidation of the hydrocarbon substrate by alkylperoxycyclohexadienones formed by the thermal oxidative transformation of phenolic antioxidants one needs data on the products of their thermal transformation. According to ref.⁹, the thermal decomposition of 4-tert-butylperoxy-2,6-ditert-butyl-4-methyl-2,5-cyclohexadienone (*Ib*) at 125 to 150°C gives rise to acetone which is considered to be the decomposition product of the primarily formed tert-butylalkoxyl. So far, no other products of thermal decomposition have been either isolated or defined. They form rather complicated mixtures; some of them have been partly analyzed by using the TLC method⁵. We made an attempt at a chromatographic investigation of the behaviour of cyclohexadienones *Ib,c,f, III* and *IV* under the thermal conditions used for investigating their effect on the tetralin oxidation. The compounds were heated at 65°C for 5 h in presence of oxygen in an inert solvent and in tetralin solution. It was found that cyclohexadienone *Ib* does not change at 65°C, while *If* gives rise to 3 compounds of which one corresponds by its chromatographic behaviour to 2,6-ditert-butyl-1,4-benzoquinone (*VIb*). A number of unidentified compounds are formed from 3,5-cyclohexadienone *III*. A chromatographic analysis of melts obtained after differential thermal analysis (heating completed at 200°C) has revealed that both colourless and coloured compounds are formed from cyclohexadienones *Ib, Ic, and If*; judging by the chromatographic behaviour, a mixture arising from the latter two compounds contains among others benzoquinone *VIb*, which also is a product of the thermal decomposition of dioxy cyclohexadienone. These results seem to indicate that the formation of coloured quinoid compounds is a result of a multistage reaction occurring under the conditions of thermal oxidation in a hydrocarbon substrate stabilized with a phenolic antioxidant. Consequently, the effect of quinones or quinone methides on autoxidation also deserves attention.

Quinoid Compounds

2-Tert-butyl- and 2,6-ditert-butyl-1,4-benzoquinones (*VIa,b*), diphenoquinone (*VII*) and stilbenequinone (*IX*), which exhibited¹ a retardative effect at 65°C, were studied at 120°C. The results of measurements (Table II) show that compounds *VIa, VII* and *IX* have kept their retardative activity. All have approximately the same effect; their influence is not as different as at a lower oxidation temperature. The presence of benzoquinone *VIb* does not affect the rate of oxygen absorption. Owing to the importance of 2,6-ditert-butyl-1,4-benzoquinone, a possible product of the thermal transformation of 4-alkylperoxycyclohexadienones formed from various phenolic antioxidants containing in positions 2,6 tertiary butyls and in position 4 a substituted methyl group, and of stilbenequinone *IX* which is formed from the commonly used

technical antioxidant, 2,6-ditert-butyl-4-methylphenol, and is a model for the investigation of the behaviour of more complex quinone methides (probably arising during the transformation of various polynuclear phenolic antioxidants) — similar compounds have been identified *e.g.*¹⁰ in coloured transformation products of 2,2'-methylenebis(4-methyl-6-tert-butylphenol) — the two compounds were used for investigation also at other temperatures of tetralin oxidation. According to the results, stilbenequinone retards oxidation within the whole temperature range between 65–120°C. At 140°C its effect is concentration dependent: while at a concentration corresponding to that of completely transformed 2,6-ditert-butyl-4-methylphenol it acts as a retarder, at an increased concentration its effect is slightly prooxidative.

CONCLUSION

The experimental study of the effect of the main types of products of the oxidative transformation of phenolic antioxidants on the course of thermal oxidation of tetralin has indicated a dependence on the oxidation temperature (Table III). The course of oxygen absorption in presence of all compounds investigated in this work differs from the course in presence of phenolic antioxidants when even at 120–140°C an induction period can be seen on the absorption curve. If the transformation of a polynuclear phenol leads to a product containing both quinoid and phenolic group, its properties at 65–120°C are determined by the phenolic component. This follows from an investigation of the effect of hydrogalvinoxyl VIII in the presence of which the oxygen absorption curve contained a distinct induction period longer than 600 min even at 120°C. It can be said on the whole that the unfavourable effect upon the stability of the hydrocarbon substrate exhibited by the presence of the transformation products of phenolic antioxidants increases in the series of compounds having the quinone methide structure through the derivatives of 1,4-benzoquinone and 4-alkylperoxy-2,5-cyclohexadienone to 2-alkylperoxy-3,5-cyclohexadienones. An extrapolation to the structure of the original phenolic antioxidants shows that compounds yielding 2,5-cyclohexadienones in the assumed gradual transformation can be expected to provide a more long-termed protective effect than antioxidants which are transformed into isomeric 3,5-cyclohexadienones. This finding is of course only one of the auxiliary criteria used for the selection of antioxidants.

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