433. *Alkylperoxy-radicals. Part II.* Kinetics of Autoxidations retarded by 2 : 4 : 6-Trialkylphenols.*

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By use of a competitive method involving reactions of alkylperoxy-radicals either with a 2 : 4 : 6-trialkylphenol (AH) or with a standard hydrocarbon (RH = 9 : 10-dihydroanthracene), the relative reactivities at 60° of various phenols were determined by measuring initial rates of oxidation. Alkylperoxy-radicals were generated by the dissociation of 2 : 2 : 3 : 3-tetraphenylbutane and reaction of the resulting radicals with oxygen.

Three types of kinetics were found to occur, depending on the phenol investigated, and were interpreted on the basis of three different reaction mechanisms.

It appeared that phenolic antioxidants can be characterized (1) by the antioxidant efficiency, *i.e.*, the ratio of the rates of hydrogen abstraction by alkylperoxy-radicals from the phenol and from the hydrocarbon respectively, and (2) by the rate of the chain-transfer reaction $A\cdot + RH \longrightarrow AH + R\cdot$. All phenolic antioxidants reacted much faster than the standard hydrocarbon, differing among themselves by a factor of about 20. The rate of the chain-transfer reaction decreased with increasing size of *ortho*-substituents. The presence of two *o-tert.*-butyl groups completely prevented the starting of new oxidation chains by transfer.

The nature of the products formed by interaction of 2 : 4 : 6-trialkylphenols and independently generated alkylperoxy-radicals was established in Part I.* This provided the necessary basis for the quantitative comparison of the activities of the various alkylphenols, which is the subject of the present paper.

Our approach to this investigation resembles that of Bolland and ten Have [1] who carried out comparative kinetic measurements on a series of phenols acting as retarders for the autoxidation of ethyl linoleate initiated by benzoyl peroxide. Whilst the latter method had an advantage in so far as the kinetics of the uninhibited oxidation had been worked out in some detail, it also has some notable drawbacks. Benzoyl peroxide, for instance, is known to suffer induced decomposition, whilst initiation by thermal decomposition of the unstable linoleate hydroperoxide should become faster as the reaction proceeds. 1 : 4-Dienes such as ethyl linoleate are not readily obtained pure and are, moreover, not stable to atmospheric oxidation, even at room temperature.

To avoid these difficulties another competitive system was developed for the comparison of the alkylphenols (AH), using 9 : 10-dihydroanthracene (RH) as reactive standard hydrocarbon, 2 : 2 : 3 : 3-tetraphenylbutane as oxidation initiator, and bromobenzene as inert solvent. The main reactions can be represented :

$$RO{\cdot}O\cdot + RH \longrightarrow RO{\cdot}OH + R\cdot$$
$$RO{\cdot}O\cdot + AH \longrightarrow RO{\cdot}OH + A\cdot$$

antioxidant and hydrocarbon competing for the alkylperoxy-radicals.

The kinetics were studied by measuring initial rates of oxidation as a function of intakes of initiator, hydrocarbon, and phenol.

The kinetics to be derived are based on the formation of hydroperoxides which are stable at the reaction temperatures employed. 2 : 2 : 3 : 3-Tetraphenylbutane seemed to possess useful properties for the present study. Its preparation is relatively simple; it is stable in the solid state up to 80°, which makes it suitable for use in ampoules. It dissociates in solution to two diphenylethyl radicals at a suitable rate at 60° and in a strictly unimolecular manner in the presence of a suitable radical scavenger. The results

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* Part I, *J.*, 1953, 3211.

[1] Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, No. 2, p. 252.

of Ziegler,[2] who determined the dissociation rate by measuring rates of oxygen consumption in presence of pyrogallol ($k_D = 2{\cdot}057 \times 10^{-4}$ sec.$^{-1}$ at 60·05°), have been verified by us by measuring the rate of oxidation in the presence of 2 : 6-di-*tert.*-butyl-4-methylphenol ($k_D = 2{\cdot}065 \times 10^{-4}$ sec.$^{-1}$ at 60·06°). Thus, 60° was selected as the most convenient reaction temperature.

The choice of 9 : 10-dihydroanthracene as a standard hydrocarbon was prompted by its stability towards oxygen in the absence of initiators up to 100° as well as by its rapid reaction with alkylperoxy-radicals.

The stability of the hydroperoxides derived from the initiating radicals as well as from the 9 : 10-dihydroanthracene at the reaction temperature of 60° was established by isolating these products in good yields in similar runs at 80°. Hence, initiation is brought about by the dissociation of the tetraphenylbutane added rather than by the thermal decomposition of hydroperoxides.

The initiating diphenylethyl radicals are not identical with the radicals formed as intermediates in the autoxidation of dihydroanthracene. Unfortunately, 1 : 1-diphenylethane, which gives diphenylethyl radicals on removal of hydrogen from the α-position, could not be used in view of its low reactivity towards alkylperoxy-radicals. In view of the structural similarity of diphenylethyl radicals and the radicals formed from dihydroanthracene, it was assumed throughout that the corresponding alkylperoxy-radicals would behave kinetically in the same manner. Judging from the kinetic results, this approximation appeared to be satisfactory.

Kinetics.—From measurements of the initial rate of oxidation at different relative amounts of initiator (R_2), phenol (AH), and standard hydrocarbon (RH) it appeared that the alkylphenols can be arranged in several groups exhibiting different kinetic behaviours :

(*a*) For 2 : 4 : 6-tri-*tert.*-butylphenol (I), 2 : 6-di-*tert.*-butyl-4-methylphenol (II), 2-*tert.*-butyl-4 : 6-dimethylphenol (IV), and 2-*tert.*-butyl-4-methylphenol (VIII) the initial oxidation rate is a strictly linear function of the [RH]/[AH] ratio (Figs. 1 and 2).*

(*b*) For 4-*tert.*-butyl-2 : 6-dimethylphenol (V) and 2 : 4-di-*tert.*-butyl-6-methylphenol (III) the initial rates of oxidation pass through a minimum with increasing retarder concentration (Fig. 3).

(*c*) The initial rates of oxidations retarded by 2 : 4 : 6-trimethylphenol (VI) or *p*-*tert.*-butylphenol (VII) are found to be linear functions of [RH] (Fig. 4) as well as of 1/[AH] (Fig. 5); they may be represented as a linear function of [RH]/[AH] + *c*[RH], where *c* is a constant.

The retarding action of the phenols mentioned under (*a*) can be interpreted in terms of one of the following mechanisms :

(*a*,1) Termination by dimerization of benzyl-type radicals (A·). Since termination by interaction of R· and/or RO·O· radicals will be of no importance in the presence of an active retarder, the reaction equations will be the following :

$$R_2 \xrightarrow{k_D} 2R\cdot \qquad R\cdot + O_2 \longrightarrow RO{\cdot}O\cdot$$

$$RO{\cdot}O\cdot + RH \xrightarrow{k_r} RO{\cdot}OH + R\cdot$$

$$RO{\cdot}O\cdot + AH \xrightarrow{k_b} RO{\cdot}OH + A\cdot$$

$$2A\cdot \xrightarrow{k_d} A_2$$

A· represents a 3 : 5-dialkyl-4-hydroxybenzyl radical formed by hydrogen abstraction from the *p*-methyl group of the phenol.

The rate of oxidation is given by :

$$-\mathrm{d}[O_2]/\mathrm{d}t = 2k_D[R_2]\left\{1 + k_r[RH]/k_b[AH]\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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* Throughout this paper, square brackets [] are used to denote concentrations in moles per 300 ml. (= 446 g.) of bromobenzene, this being the volume used in all experiments. $\mathrm{d}[O_2]\mathrm{d}t$ is in mole/sec.

[2] Ziegler, *Annalen*, 1942, **551**, 150.

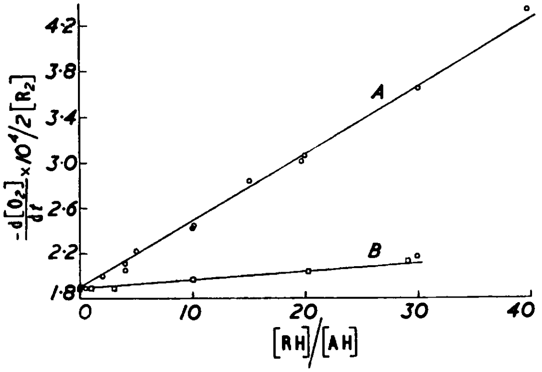


FIG. 1.
A, 2 : 4 : 6-*Tri*-tert.-*butylphenol.*
B, 2-tert.-*Butyl*-4 : 6-*dimethylphenol.*

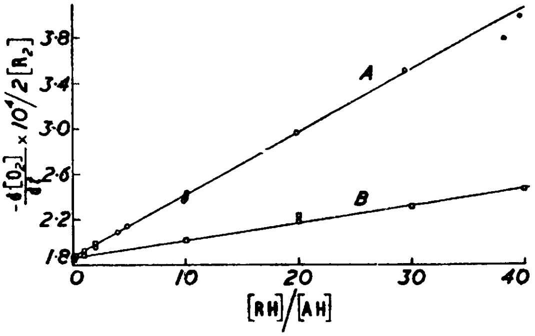


FIG. 2.
A, 2 : 6-*Di*-tert.-*butyl*-4-*methylphenol.*
B, 2-tert.-*Butyl*-4-*methylphenol.*

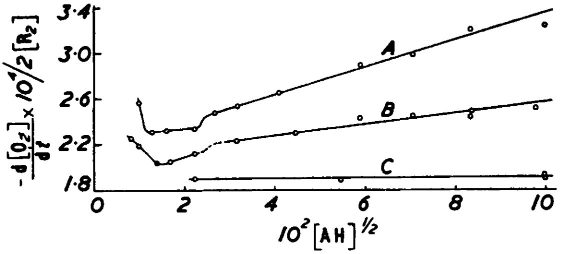


FIG. 3. 4-tert.-*Butyl*-2 : 6-*dimethylphenol*: [RH] = *A*, 5×10^{-3}; *B*, 2×10^{-3}; *C*, 0.

FIG. 4. *Mesitol*: [AH] = *A*, $0{\cdot}25 \times 10^{-3}$; *B*, $0{\cdot}5 \times 10^{-3}$; *C*, $5{\cdot}0 \times 10^{-3}$.

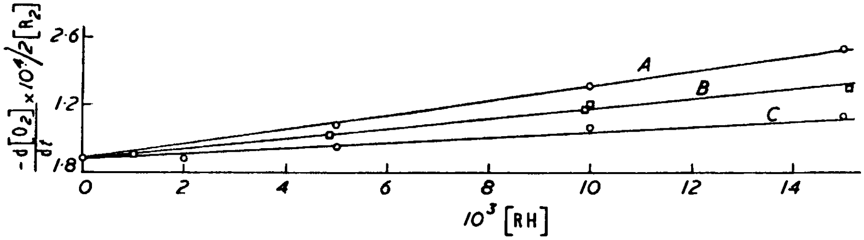
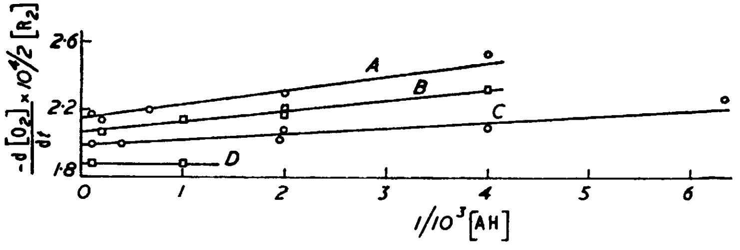


FIG. 5. *Mesitol*: [RH] = *A*, 15×10^{-3}; *B*, 10×10^{-3}; *C*, 5×10^{-3}; *D*, 0.



Since the initial rate is linearly dependent on the ratio [RH]/[AH] the validity of eqn. (1) can be tested by measuring the initial oxidation rates for different values of [RH] and [AH] and plotting the results against [RH]/[AH]. The ratio k_b/k_r, termed antioxidant efficiency, can be evaluated from the slope of the line and the values thus obtained may serve for the comparison of antioxidants with regard to their chain-stopping properties.

(*a*,2) Termination by combination of inhibitor radical (A·) with peroxy-radical (RO·O·) to form a stable peroxide (RO·OA). A· now represents a mesomeric 2 : 4 : 6-trialkylphenoxy-radical and the reactions involving A· radicals are :

$$\mathrm{RO{\cdot}O{\cdot}} + \mathrm{AH} \xrightarrow{k_a} \mathrm{RO{\cdot}OH} + \mathrm{A{\cdot}} \qquad \mathrm{RO{\cdot}O{\cdot}} + \mathrm{A{\cdot}} \xrightarrow{k_t} \mathrm{RO{\cdot}OA}$$

The rate of oxidation is expressed by :

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = 2k_D[\mathrm{R_2}]\left\{1 + k_r[\mathrm{RH}]/2k_a[\mathrm{AH}]\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(*a*,3) Simultaneous occurrence of terminations (*a*,1) and (*a*,2). In this case the rate of oxidation can be represented by :

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = 2k_D[\mathrm{R_2}]\left\{1 + k_r[\mathrm{RH}]/(2k_a + k_b)[\mathrm{AH}]\right\} \quad . \quad . \quad . \quad . \quad (3)$$

Obviously, it is impossible to distinguish kinetically between dimerization and formation of a stable peroxide. Hence, the production of peroxide and/or dimer is in agreement with kinetics showing a linear relation between oxidation rate and [RH]/[AH] ratio.

Our product studies (Part I) make it very probable that retardation by phenols (I) and (II) follows mechanism (*a*,2) (exclusive formation of peroxides RO·OA), whilst phenol (IV) might act in accordance with mechanism (*a*,3) (simultaneous formation of peroxide and stilbenequinone). No product studies have been made for phenol (VIII), but it may be assumed to operate in nearly the same manner as phenol (IV). The respective antioxidant efficiencies were calculated from the slopes in Figs. 1 and 2 and are presented in the Table.

	Alkylphenol with alkyl groups in positions			Antioxidant efficiency	Chain transfer
	2	4	6		
(I)	Bu^t	Bu^t	Bu^t	32·0 *	0
(II)	Bu^t	Me	Bu^t	33·5 *	0
(III)	Bu^t	Bu^t	Me	? *	Small
(IV)	Bu^t	Me	Me	250 †	0
(V)	Me	Bu^t	Me	16—31 *	Large
(VI)	Me	Me	Me	260—350 †	0·0035 ‡
(VII)	—	Bu^t	—	80—100 *	0·0086 ‡
(VIII)	Bu^t	Me	—	118 †	0

* $2k_a/k_r$. † $(2k_a + k_b)/k_r$. ‡ $k_c/k_d^{\frac{1}{2}}$.

The phenols (V) and (III) probably act in accordance with mechanism (*b*) outlined below.

(*b*) Chain transfer of retarder radical with hydrocarbon ($\mathrm{A{\cdot}} + \mathrm{RH} \xrightarrow{k_c} \mathrm{AH} + \mathrm{R{\cdot}}$) and termination by combination of (A·) with a peroxy-radical (RO·O·). The general equation for $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t$ that can be derived is too complicated to be correlated with experimental results. It can, however, be simplified by assuming predominant chain transfer ($k_c[\mathrm{RH}] \gg k_t[\mathrm{RO{\cdot}O{\cdot}}]$). The rate of oxidation is then given by :

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = 2k_D[\mathrm{R_2}] + \left\{k_r[\mathrm{RH}] + k_a[\mathrm{AH}]\right\}[\mathrm{RH}]^{\frac{1}{2}}[\mathrm{AH}]^{-\frac{1}{2}}(k_c k_D[\mathrm{R_2}]/k_a k_t V)^{\frac{1}{2}} \quad . \quad (4)$$

where V is the volume of solution.

For [RH] = constant, equation (4) becomes :

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = 2k_D[\mathrm{R_2}] + c_1[\mathrm{AH}]^{-\frac{1}{2}} + c_2[\mathrm{AH}]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (5)$$

where c_1 and c_2 are constants.

Equation (5) can easily be checked with experimental results by writing it in the form

$$\left\{-\mathrm{d}[O_2]/\mathrm{d}t - 2k_D[R_2]\right\}[AH]^{\frac{1}{2}} = c_1 + c_2[AH] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and plotting the left-hand part against [AH]. The antioxidant efficiency $2k_a/k_r$ can then be calculated from the values of c_1 and c_2 by $2k_a/k_r = 2c_2[RH]/c_1$. Successive differentiation of eqn. (5) shows that there should be a minimum in the rate of oxidation for $[AH] = k_r[RH]/k_a$ and a point of inflexion at $[AH] = 3k_r[RH]/k_a$.

The experimental results for 4-*tert.*-butyl-2 : 6-dimethylphenol (V) are shown in Fig. 3. The linear dependence of $-\mathrm{d}[O_2]/\mathrm{d}t$ on $[AH]^{\frac{1}{2}}$ corresponds to an overwhelming influence of the $k_a[AH]$ term in eqn. (4); the $k_r[RH]$ term becomes relatively important only as [AH] becomes low, and an increasing rate of oxidation then results. Plots in the manner of eqn. (6) are shown in Fig. 6. Slopes and intercepts give values for $2k_a/k_r$ of 31 and 16. The experimental results do not allow of the calculation of a reliable value for the antioxidant efficiency of 2 : 4-di-*tert.*-butyl-6-methylphenol (III): here the chain-transfer reaction plays a less important role than for 4-*tert.*-butyl-2 : 6-dimethylphenol (V). On the whole, eqn. (4) accounts qualitatively for the experiments with these two phenols. It should be realized that quantitative agreement cannot be expected since eqn. (4) has been derived for the limiting case of predominant chain transfer.

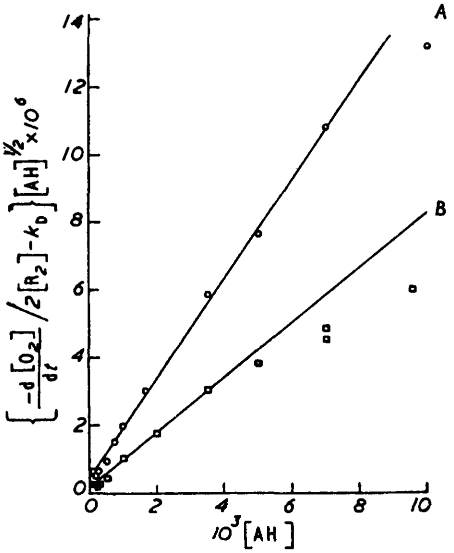


FIG. 6. 4-tert.-*Butyl*-2 : 6-*dimethylphenol*: *A*, $[RH] = 5 \times 10^{-3}$, $2k_a/k = 31$; *B*, $[RH] = 2 \times 10^{-3}$, $2k_a/k_r = 16$.

p-*tert.*-Butyl- and 2-*tert.*-butyl-4-methylphenol (VII) and (VIII) seem to follow the kinetics of scheme (*c*).

(*c*) Chain transfer of retarder radical with hydrocarbon ($A\cdot + RH \xrightarrow{k_c} AH + R\cdot$) and termination by dimerization of (A·). The following equation can be derived in the usual way:

$$-\mathrm{d}[O_2]/\mathrm{d}t = 2k_D[R_2]\left\{1 + k_r[RH]/k_b[AH]\right\} + k_c(2k_D[R_2]/k_dV^{\frac{1}{2}})[RH] \quad . \quad (7)$$

For [RH] = constant, eqn. (7) becomes:

$$-\mathrm{d}[O_2]/\mathrm{d}t = c_1 + c_2[AH]^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The antioxidant efficiency k_b/k_r can be determined from the slopes of plots of eqn. (8) (Fig. 5).

Since

$$c_1 = 2k_D[R_2] + k_c(2k_D[R_2]/k_d V)^{\frac{1}{2}}[RH]$$

the intercept in a plot of $-d[O_2]/dt$ against $[AH]^{-1}$ is linearly dependent on [RH]. The equation for c_1 can be used to calculate $k_c/k_d^{\frac{1}{2}}$, a measure of the chain transfer (Table).

For [AH] = constant, eqn. (7) becomes:

$$-d[O_2]/dt = c_3 + c_4[RH] \quad \ldots \ldots \quad (9)$$

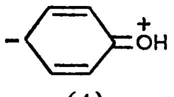
In a plot of $-d[O_2]/dt$ against [RH], the intercept is the same for all values of [AH].

It should be borne in mind that the products isolated (Part I) also indicated the formation of small amounts of a peroxide in the case of mesitol. For *p*-*tert*.-butylphenol (VII) the nature of the products is unknown, but the formation of 5 : 5′-di-*tert*.-butyl-2 : 2′-dihydroxydiphenyl is conceivable, since a similar product was obtained by Moore and Waters [3] on oxidation of cumene inhibited by *p*-cresol.

Relations between Structure and Reactivity of Alkylphenols.—Since the present measurements are limited to a single temperature, interpretation remains speculative. Both classical steric hindrance and steric inhibition of resonance will be invoked in this discussion.

The nearly identical values of $2k_a/k_r$ found for the two phenols (I) and (II) having *tert*.-butyl groups in both *ortho*-positions, *viz*., 32 and 33·5 respectively, show that these two react with alkylperoxy-radicals at nearly the same rates. They were found (Part I) to give analogous reaction products, *viz*., *cyclo*hexadienones carrying a RO·O group in the 4-position. Since *addition* of RO·O· as the primary step would probably involve quite different steric requirements it seems likely that the primary step consists in removal of hydrogen from the hydroxyl group; the substituent effects of a *p*-methyl group and a *p*-*tert*.-butyl group are known to be very similar, whereas the hydroxyl group is flanked by the same *ortho*-substituents.

Removal of hydrogen from the hydroxyl group by an approaching alkylperoxy-radical will be interfered with by the shielding effect of bulky *ortho*-substituents, lower reactivity resulting. On the other hand, bulky groups may prevent coplanarity of the hydroxyl bond and the ring, thereby lowering resonance stabilization due to structural contributions of the type (*A*). Since this effect disappears in the radical, the *strength* of the O–H bond will be lower in strongly hindered phenols than in less hindered phenols. Thus, bulky *ortho*-substituents should cause both a retarding and an accelerating effect, the net result of which cannot be predicted. In this way, we may account for the fact that phenols (I) and (V) show roughly the same reactivity (32 and ~31) in the first step.


(*A*)

The absence of chain-transfer effects with strongly hindered phenols is probably attributable both to shielding and to a lower strength of the O–H bond to be formed. Further, the radical A· from 2 : 4-di-*tert*.-butyl-6-methylphenol (III) will react more slowly with RH than that from 4-*tert*.-butyl-2 : 6-dimethylphenol (V). According to these arguments, phenols having the same *ortho*-substituents should show a similar behaviour in chain transfer. However, mesitol (VI) shows little transfer and 2-*tert*.-butyl-4 : 6-dimethylphenol (IV) none at all, although the corresponding phenols (V) and (III) are quite reactive in this respect. Possibly, the *p*-methyl groups are attacked as well; dimerization of these benzyl type radicals causes formation of stilbenequinones (Part I). The above discrepancy might be therefore explained by assuming that chain transfer only occurs by means of aryloxy-radicals.

Summing up, it appears that the special technical merits of strongly hindered phenols are due to the absence of chain transfer with compounds to be protected rather than to an outstandingly high reactivity towards alkylperoxy-radicals. Differences in reactivity may be interpreted as being due to two opposing influences, a lowering of reactivity caused by a classical shielding effect and an increase attributable to steric inhibition of resonance in the phenol, which is released in the radical.

Conclusions with Regard to the Nature of the Hydrocarbon.—The data on the occurrence of

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[3] Moore and Waters, *J.*, 1954, 243.

chain transfer suggest that the behaviour of antioxidants such as 2 : 6-di-*tert.*-butyl-4-methylphenol (II) and of the chain-transfer type may be different for different hydrocarbon substrates. Thus the contribution of the chain-transfer reaction will probably be less important for unreactive paraffins than for very reactive hydrocarbons. This suggests that, for the latter, inhibitors of the chain-transfer type should be inferior to antioxidants such as (II).

EXPERIMENTAL (with W. ROEST)

Starting Materials.—Bromobenzene was shaken with changes of concentrated sulphuric acid until the acid layer remained colourless. It was then washed with 5% sodium hydroxide and distilled water, dried ($CaCl_2$), and fractionated at 30 mm. in a 1-m. Vigreux column, the fraction of n_D^{20} 1·5600 being collected.

2 : 2 : 3 : 3-Tetraphenylbutane and the trialkylphenols were prepared as described in Part I. 4-*tert.*-Butylphenol and 2-*tert.*-butyl-4-methylphenol were prepared similarly and had m. p. 98·5° and 53°, respectively.

9 : 10-Dihydroanthracene was obtained by hydrogenation of anthracene in ethanol with Adkins catalyst at 160°/140 atm. Recrystallized from ethanol, it had m. p. 109—109·5°.

Reaction of 2 : 2′-*Azo*iso*butyronitrile or* 2 : 2 : 3 : 3-*Tetraphenylbutane with Oxygen and* 9 : 10-*Dihydroanthracene.*—Dihydroanthracene (0·1 mole) and the azo-compound or the butane (0·01 mole) were dissolved in dry, thiophen-free benzene (250 ml.), and oxygen was bubbled through the solution at 80° for 7 hr. or at 70° for 3 hr. The mixture was evaporated at 40°/1 mm. The residue was freed from dihydroanthracene by treatment with ethanol and filtration, then evaporated, and the residue was recrystallized from toluene. In this manner 9 : 10-*dihydro*-9-*anthryl hydroperoxide* was obtained pure [m. p. 108·5—109° (decomp.)] in yields of 7 g. (33%) and 5 g. (24%), respectively (Found: C, 79·5, 79·7; H, 6·0, 5·7. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%).

Measurement of Initial Rates of Oxidation.—The apparatus consisted essentially of a cylindrical Pyrex-glass vessel (diam. 9 cm., height 16 cm.), fitted with a mercury-sealed Vibromixer, a capillary for oxygen supply, a support for an ampoule, and a rod which could be used to crush the ampoule by a 90° turn. The capillary was connected to a manometric system, consisting of an octyl phthalate manometer and a graduated gas-burette containing mercury provided with a levelling tube. The reaction vessel was placed in a thermostat at 60·06° ± 0·01°.

The thin-walled glass ampoules had a volume of 0·4 ml. and contained 362·5 ± 0·3 mg. (1 mmol.) of 2 : 2 : 3 : 3-tetraphenylbutane in a nitrogen atmosphere at a pressure of 66 cm. of mercury at room temperature. In this manner a pressure of about 76 cm. of mercury was attained at 60°.

The procedure was as follows: The oxidation vessel containing an ampoule was closed with a rubber stopper, evacuated, and filled with pure, dry oxygen twice in succession. Weighed quantities of 9 : 10-dihydroanthracene and phenol, and 446 g. of pure bromobenzene were introduced. The Silicone-greased glass stopper with stirrer was brought in position and the slot was filled with 25 ml. of mercury and 10 ml. of bromobenzene. The apparatus was placed in the thermostat, the Vibromixer and oxygen supply were connected, and when temperature equilibrium was established stirring was started. Usually a constant-volume reading was attained within 12 min. The ampoule was crushed by a 90° turn of the rod, and volume and time were read every minute for 20 min.

The initial rate in ml. of O_2 per min. was obtained from a plot of volume against time. In most cases it had a constant value (error <2%) for the first 10 min. The results are expressed as $-d[O_2]/2[R_2]dt$ sec.$^{-1}$. The reproducibility is within 2—3%.

The authors thank the Management of the Koninklijke/Shell-Laboratorium, Amsterdam (N.V. De Bataafsche Petroleum Maatschappij) for permission to publish this paper.

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM.
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[*Received, August* 9*th*, 1955.]