THE OXIDATION OF PHENOLS

I. THE OXIDATION OF 2,6-DI-*t*-BUTYL-4-METHYLPHENOL, 2,6-DI-*t*-BUTYLPHENOL, AND 2,6-DIMETHYLPHENOL WITH PEROXY RADICALS¹

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ABSTRACT

Previous work on the oxidation of alkyl phenols with peroxy radicals is summarized. The yields of the peroxy-cyclohexadienones formed from 2,6-di-*t*-butyl-4-methylphenol in the α, α' -azo-bis-isobutyronitrile-initiated oxidation of tetralin at 40 °C have been measured quantitatively. The results suggest that not all the oxidation chains are initiated by iso-butyronitrile peroxy radicals.

The products from the oxidation of 2,6-di-*t*-butylphenol and 2,6-dimethylphenol with *t*-butyl peroxy radicals are found to be mainly dialkyl-*p*-benzoquinones and tetraalkyl diphenoquinones.

Although the kinetics of the phenol – peroxy radical reaction² have been investigated intensively in recent years, comparatively little attention has been paid to the products of this reaction. About 10 years ago the products from 2,4,6-trialkyl phenols were examined by several groups of workers (1–6), but there has been very little activity in this field since that time. Peroxy radicals generated by the cobalt-catalyzed decomposition of hydroperoxides (1, 2) or by the thermal decomposition of compounds such as α, α' -azobis-isobutyronitrile (AIBN) in the presence of oxygen (2, 3) generally gave mainly 4-peroxy-cyclohexadienones (1–3), the yields of which depended upon the phenol, the peroxy radical, and the experimental conditions. Extremely high yields approaching 100% were obtained with 2,6-di-t-butyl-4-methylphenol (BMP) and t-butyl peroxy radicals. After the initial abstraction of the phenolic hydrogen (cf., however, ref. 7), the reaction can be represented, for example, as



Under certain conditions phenols containing a p-methyl group gave stilbenequinones (e.g. see ref. 2),



This product is formed from two phenoxy radicals by a very complicated sequence of reactions (8). The less highly oxidized dihydroxy bibenzyl dimers have been isolated after

²That is, the kinetics for the inhibition of hydrocarbon autoxidation by phenols.

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the high-temperature air oxidation of hydrocarbons retarded with phenols containing a p-methyl group, e.g. 2,6-di-t-butyl-4-methylphenol (4, 5), 2-t-butyl-4,6-dimethylphenol (5), and 2,4,6-trimethylphenol (5). With a n-alkyl group in the para position trialkyl phenols generally give 4-hydroxyaryl ketones (6).

In contrast to the wealth of information on trialkyl phenols only two di- and one mono-alkyl phenol have been examined. When cumene was oxidized, Moore and Waters (5) identified traces of 2,2'-dihydroxy diphenyls from p-cresol and 2,4-dimethylphenol, while 2,6-dimethylphenol gave the tetramethyl 4,4'-dihydroxy diphenyl and 4,4'-diphenoquinone (see also ref. 9).

Our interest in this subject arose from our studies of the kinetics of the inhibition of hydrocarbon autoxidation by phenols (10). In particular, we felt that more information on the products from phenols other than trialkyl phenols would be a great help in further elucidating the overall mechanism of this reaction. The present paper describes the products formed by the t-butyl peroxy radical oxidation of two dialkyl phenols, 2,6-di-tbutyl- and 2,6-dimethyl-phenol. In addition, the development of a thin-layer chromatographic (t.l.c.) method for separating and tentatively identifying oxidation products prompted us to look for a compound having structure I under the conditions actually employed in kinetic studies of inhibition. That is, no compound of this structure in which R is derived from an oxidizing hydrocarbon RH has ever been identified. The actual formation of such a product is of importance in connection with the assumptions involved in determining rates of chain initiation by the induction-period method of Boozer et al. (3). That is, rates of chain initiation in hydrocarbon autoxidation are generally determined by measuring the induction period produced by small quantities of BMP (3, 10), it being assumed that each molecule of the phenol reacts with just two peroxy radicals (see, however, ref. 11). This plausible assumption is based on the identification of 2,6-di-tbutyl-4-methyl-4-peroxy-isobutyronitrile-2,5-cyclohexadiene-1-one $(I, R = (CH_3)_2(CN)C)$ hereafter referred to as IBN-1) after the decomposition of AIBN in chlorobenzene containing BMP in the presence of oxygen (3).

A somewhat better justification for this assumption is provided by the present results on the products formed from BMP during the oxidation of tetralin at 40 °C under conditions fairly typical of those normally used in induction-period studies. The reaction mixture in these experiments consisted of 3 ml of tetralin and 10 ml of chlorobenzene with 2.7×10^{-4} mole/l BMP and 0.66 g (2.94×10^{-1} mole/l) AIBN. The oxygen absorption curve is shown in Fig. 1. The induction period is 2 760 s, giving an efficiency of chain initiation, e, equal to 0.64. (The rate constant, k_1 , for AIBN decomposition at 40 °C was taken to be 5.2×10^{-7} s⁻¹.) The reaction was stopped at various times between 3 600 and $5\,500$ s, since all the BMP should by now be consumed as the oxidation rate is equal to its uninhibited value. Work-up of the reaction mixtures for t.l.c. analysis is described in the Experimental section. The t.l.c. plates showed three well-resolved spots travelling ahead of a long streak which started at the origin and is due to residual AIBN and tetralin hydroperoxide. The spot with the largest R_t is formed from AIBN and chlorobenzene rather than from BMP or tetralin. The second spot corresponded in position to the expected a-tetralyl peroxy derivative of BMP (hereafter referred to as TET-1). Positive identification was achieved by extracting this spot (from a large sample) with CCl_4 and comparing its infrared spectrum with that of an authentic sample prepared by the method of Bickel and Kooyman (2). The third spot, which was relatively weak, corresponded in position to IBN-1. There was no spot corresponding to the stilbenequinone nor to either its di- or tetra-hydro derivatives. The yield of TET-1 was estimated by running the reaction

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mixture and several standard solutions on the same thin-layer sheet. The chromatogram was photographed and analyzed with a photodensitometer, as this proved to be more satisfactory than direct measurement on the chromatogram (see Experimental section). There was an excellent straight-line relation between the sample weight and the area under the densitometer curve in the range of concentrations from 5 to 40 g/l. From this calibration line the best estimate of the yield of TET-1 (based on the starting phenol) was $86 \pm 10\%$ (standard deviation) at 3 600 s and $84 \pm 5\%$ at 5 500 s. The IBN-1 spot

was too faint for this method to be applied. Its yield was estimated to be $10 \pm 3\%$ by visual comparison with spots from solutions of known strength. The overall yield of compounds with structure I is, therefore, $\sim 95 \pm 10\%$. This provides a sound justification for the assumption that each molecule of BMP reacts with two peroxy radicals under normal kinetic conditions.



FIG. 1. Oxygen absorption by 3 ml tetralin in 10 ml chlorobenzene with 0.66 g AIBN and 2.7 \times 10⁻⁴ mole/l BMP at 40 °C.

The relative yields of IBN-1 and TET-1 can roughly be predicted by comparing the rate of chain initiation $(2ek_1[AIBN] = 2 \times 10^{-7} \text{ mole/l s})$ with the amount of oxygen absorbed at the point where the rate reaches its uninhibited value (i.e. 3.10×10^{-3} mole/l at 3 600 s).³ If the rate of isobutyronitrile peroxy radical production is equal to the rate of chain initiation, then $2 \times 10^{-7} \times 3600 = 7.2 \times 10^{-4}$ mole/l of these radicals was formed by the end of the induction period. Since 3.1×10^{-3} mole/l of α -tetralyl peroxy radicals was formed in this time, the expected yield of TET-1 is $(3.1/3.1 + 0.72) \times 100 = 81\%$, and of IBN-1 $(0.72/3.82) \times 100 = 19\%$. The fact that only about half the expected IBN-1 was formed indicates that fewer isobutyronitrile peroxy radicals

³The measured change in gas volume amounts to 3.25×10^{-3} mole/l. This must be corrected for nitrogen evolution by the AIBN and oxygen absorption by the initiator radicals (10). This correction is $-(2e - 1)k_1$ [AIBN] $\times 3600 = -0.15 \times 10^{-3}$ mole/l.

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are involved in the main reaction sequence than is suggested by this simple calculation, since it seems unlikely that these radicals would add to the phenoxy radical any less readily than α -tetralyl peroxy radicals. A possible explanation for the low yield of IBN-1 is that two isobutyronitrile peroxy radicals can frequently be formed while they are still in the same solvent cage in which their precursors were produced. Mutual interaction would give two tertiary alkoxy radicals, which could both initiate oxidation but probably could not add to the phenoxy radical (cf. the reaction of *t*-butoxy radicals with this phenol (12)). An alternative possibility would be the formation of an unstable peroxide from a single molecule of oxygen and its subsequent decomposition to the same two alkoxy radicals. That is,



In this connection, the yield of IBN-1 in the absence of tetralin, but otherwise under the same experimental conditions, was only $62 \pm 4\%$ at 3 600 s and $71 \pm 4\%$ at 5 500 s, which also suggests that BMP is a relatively ineffective trap for the radicals formed from AIBN and oxygen.

The 2,6-di-*t*-butylphenol and 2,6-dimethylphenol were oxidized by the method of Bickel and Kooyman (2). That is, 0.1 mole of *t*-butyl hydroperoxide in 50 ml of benzene containing 0.05 mole of the phenol was catalytically decomposed by the slow addition of powdered cobalt toluate, the temperature being kept below 30 °C. Unfortunately, this simple procedure does not give very reproducible product yields. However, this disadvantage is more than offset when unstable products are formed by the low temperature of the reaction. After all the hydroperoxide had been decomposed, the products were separated by column chromatography on silica gel, mixtures of hexane, benzene, and ethyl acetate being used as eluents. Every fraction was checked for purity by t.l.c. on silica before being worked up for the products.

The principal products from 2,6-di-*t*-butylphenol and 2,6-dimethylphenol result from two competing radical coupling reactions. That is, the initially formed phenoxy radical can react with either a peroxy radical



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or a second phenoxy radical



The 2,6-dimethylphenol-hydroperoxide solution turns the deep red color characteristic of diphenoquinones (VI) almost immediately after the addition of the cobalt catalyst. In contrast, the 2,6-di-*t*-butylphenol-hydroperoxide solution turns only light yellow, which is characteristic of *p*-benzoquinones (IV), although gas chromatography shows that all the starting phenol has been consumed. This yellow color very gradually darkens and finally becomes a deep red after several hours. This suggests that the tetra-*t*-butyl VI is not formed by the direct oxidation of V under these conditions.⁴ Instead, this keto compound must first rearrange to its enol tautomer, the bis-phenol Va.



This rearrangement is catalyzed by the *t*-butanol formed in the oxidation (cf. refs. 13 and 14). The bis-phenol is then oxidized to VI by the peroxy radicals. The rearrangement of V to Va must be a much faster process for the methyl than for the *t*-butyl compound. It is therefore not surprising that, although tetra-*t*-butyl V was a minor product ($\sim 1\%$) from 2,6-di-*t*-butylphenol, none of the tetramethyl compound was isolated or identified from 2,6-dimethylphenol. Compound III was not identified in either case, but its similarity to I provides a logical path for the production of the *p*-benzoguinone IV.

The relative importance of IV and VI in the products depends on the nature of the alkyl group. The dimethylphenol yields approximately 12% IV⁵ and up to 75% VI, whereas the dibutylphenol yields approximately 59% IV and 31% VI. The higher yield of IV in the latter case can probably be attributed to the greater stability of the 2,6-di-*t*-butyl phenoxy radical. Both phenols also gave some brown polymeric material and a few additional crystalline products that were not isolated in sufficient quantity for identification.

EXPERIMENTAL

2,6-Di-t-butyl-4-methylphenol

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When the oxidation was stopped after the rate had reached its uninhibited value, the reaction mixture was placed overnight in a freezer at -30 °C to crystallize the unreacted AIBN. After filtration the tetralin and chlorobenzene were removed under high vacuum with gentle warming. The semisolid residue, which consisted mainly of unreacted AIBN and tetralin hydroperoxide, was extracted with 5–10 ml of cold *n*-hexane (in which both these compounds are very insoluble). The hexane was removed under vacuum, and the very small oily residue was dissolved in toluene and made up to 0.1 ml. Handling losses were probably not more than 2–3% unless some compound was strongly adsorbed on the surface of the AIBN crystals.

A 1 μ l sample of the toluene solution was spotted on an Eastman Chromagram sheet (with fluorescent indicator) along with the same volumes of three known concentrations of TET-1 (e.g. 5, 10, and 20 g/l). After t.l.c. was carried out in trichloroethylene, a transverse strip of the TET-1 spots was excised and evaluated on a Spinco model R Analytrol. This instrument was modified by using the ultraviolet light source to excite the fluorescent strip and the visible-sensitive photocell as the detector. To reduce the visible light from

⁴However, the tetra-t-butyl V does inhibit the α, α' -azo-bis-isobutyronitrile-initiated oxidation of cumene at 65 °C. This inhibition may be due to the promotion by the higher temperature of either an isomerization to Va or a direct reaction of V with peroxy radicals.

⁵All product yields are based on the percentage conversion of the starting phenol.

the source a Corning 7-54 filter was used between the light and fluorescent strip. The sensitivity of this method was later increased by photographing the uncut fluorescent chromatogram under ultraviolet light. An enlarged positive transparency was then prepared, cut into strips lengthwise, and evaluated in the Analytrol in visible light, to which the machine is more sensitive.

The average of triplicate (three t.l.c.) determinations of the yield of TET-1, based on the starting phenol concentration, was $86\pm10\%$ after $3\ 600$ s and $84\pm5\%$ after $5\ 500$ s. In the absence of tetralin the yield of IBN-1 (t.l.c. in benzene) was $62 \pm 4\%$ after 3 600 s and 71 $\pm 4\%$ after 5 500 s.

The IBN-1 and TET-1 were both prepared by the methods of Bickel and Kooyman (2). The purified materials melted at 92-93.5° (lit. m.p. 92.5° (2) and 91-92° (3)) and 105-106.5° (lit. m.p. 104°(2)) respectively.

2,6-Dimethylphenol

The precipitate of reacted cobalt and of most of the deep red compound VI was filtered and weighed. Benzene was removed from the filtrate under vacuum. The residue was eluted through a 4 ft silica column with mixtures of benzene and ethyl acetate; the fractions were automatically collected in the order IV, VI, and p-toluic acid from the cobalt catalyst. Compounds IV and VI were identified by comparison with authentic samples of these compounds by means of melting point, mixed melting point, and X-ray powder pattern. The yield of IV was confirmed by gas-liquid chromatography on a polyester succinate column at 185 °C.

2,6-Di-t-butyl-phenol

The cobalt precipitate was filtered off and the benzene removed under vacuum. The products were eluted in the order V, VI, IV, and p-toluic acid. The products were identified by comparison with authentic samples by means of melting point, mixed melting point, X-ray powder pattern, and infrared spectra. Authentic V was prepared by the oxidation of 2,6-di-t-butylphenol with silver oxide (14). The melting point is $152-156^{\circ}$ (lit. m.p. 151-152° (13, 14)); at 156° there is a sudden dendritic growth of red crystals of VI which do not melt until 249°. In separate experiments, it was shown that, at its melting point, V decomposed to VI and 2.6-di-t-butylphenol. The infrared spectrum of V shows the doublet characteristic of p-quinolides at 1 637 and 1 661 cm⁻¹, and the nuclear magnetic resonance spectrum of V shows protons with chemical shifts (in parts per million to low field of tetramethylsilane) of 1.18 (t-butyl), 3.36 (4H), and 6.33 (3H and 5H).

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