the solvent, a Friedrich condenser was attached to the flask as a special precautionary measure to minimize the loss of product due to entrainment. The run was worked up as usual to yield 8.4 g. (68%) of reduction product, b.p. 81–81.5° (752 mm.), n^{20}D 1.4380. This proved to be a mixture of cyclohexene (75%) and cyclohexane (25%). The former was identified by conversion to 2-chlorocyclohexyl 2',4'-dinitrophenyl sulfide by reaction with 2,4-dinitrobenzenesulfenyl chloride. After crystallization from 95% ethanol, the derivative melted at 118.5–119° (reported[17] 117–118°). The infrared spectrum of an authentic cyclohexane–cyclohexene mixture was identical with the spectrum of the reduction mixture.

Reduction of Ethylbenzene by Lithium in Ethylamine. A. **At 17°.**—The reduction of 10.6 g. (0.1 mole) of ethylbenzene by 5.6 g. (0.8 g. atom) of lithium in ethylamine resulted in 7.0 g. of distillate (68%), b.p. 129°, n^{20}D 1.4438. This product proved to be a mixture of ethylcyclohexane and 1-ethylcyclohexene by comparison of the infrared spectrum with the spectrum of an authentic mixture of ethylcyclohexane and 1-ethylcyclohexene; the isolation of the nitrosyl chloride derivative of the olefin from the mixture which melted at 102° alone or in a mixed m.p. with an authentic specimen,[7] and the formation of two layers with fuming sulfuric acid. Bromine titration showed this mixture contained 42–45% 1-ethylcyclohexene and 55–58% ethylcyclohexane. A plot of refractive index *versus* percentage composition for known concentrations of ethylcyclohexane and 1-ethylcyclohexene followed a linear relationship. Analysis of the mixture by this refractometric method checked well with the value from the titration.

B. **At −78°.**—From the reduction of 10.6 g. (0.1 mole) of ethylbenzene by 5.6 g. (0.8 g. atom) of lithium in ethylamine kept at −78° by a Dry Ice slurry, there resulted 8.3 g. (75%) of 1-ethylcyclohexene, b.p. 131°, n^{20}D 1.4572 (reported[19] 1.4570). The nitrosyl chloride melted at 101–102°. No depression was observed in a mixed m.p. determination with an authentic sample.

Acknowledgment.—The authors gratefully acknowledge the assistance of Dr. Arthur Cope in interpreting the infrared absorption spectra of the octalin mixture. We also wish to express our appreciation to the Purdue Research Foundation and the Research Corporation for their financial assistance.

[19] G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 329.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Air Oxidation of Hydrocarbons.[1] II. The Stoichiometry and Fate of Inhibitors in Benzene and Chlorobenzene

BY CHARLES E. BOOZER, GEORGE S. HAMMOND, CHESTER E. HAMILTON AND JYOTIRINDRA N. SEN

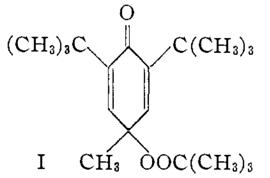
RECEIVED NOVEMBER 6, 1954

The inhibitory effects of 17 phenols and amines on the autoöxidation of cumene initiated by azo-bis-isobutyronitrile have been studied. By the measurement of the duration of the inhibition periods the relative chain-stopping capacities of the antioxidants have been determined. These relative values are then put on an absolute basis by the identification of the products derived from two of the inhibitors. The efficiency of chain initiation indicated by the stoichiometric factors thus assigned is in good agreement with initiator efficiencies measured by other methods. The significance of the individual stoichiometric factors is discussed.

Variously substituted phenols and aromatic amines are well known antioxidants for hydrocarbons. The efficiency of such antioxidants has been measured for a wide variety of substrates and experimental conditions.[2]

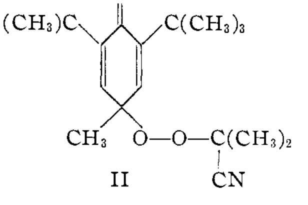
It is generally conceded that most such inhibitors function by reacting with alkyl peroxy radicals ($RO_2\cdot$) rather than alkyl radicals except at low oxygen pressures since oxidation rates become independent of the oxygen pressure at partial pressures well below one atmosphere.[3] It is, therefore, to be expected that the reactions of antioxidants may be quite unlike those of substances which are known to react with carbon radicals. Despite this fact relatively little has been done to establish the nature of these reactions.

Bolland and ten Haave[4] suggest that hydroquinones react only with $RO_2\cdot$ radicals produced in the benzoyl peroxide initiated oxidation of ethyl linoleate. Each molecule of hydroquinone was assumed to react with two radicals to produce benzoquinone and two molecules of hydroperoxide. Campbell and Coppinger[5] reported that compound I was produced as a consequence of carrying out the decomposition of *tert*-butylhydroperoxide in the presence 2,6-di-*t*-butyl-*p*-cresol. They suggested that this compound was



I

the product of the reaction(s) of two *t*-butylperoxy radicals with the phenol and drew the further inference that the reaction(s) of two $RO_2\cdot$ with this antioxidant should, in general, give analogous products. This presumption was further confirmed by the observation, which we had also made, that II



II

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[1] Part I of this series is C. E. Boozer and G. S. Hammond, THIS JOURNAL, **76**, 3861 (1954).

[2] (a) R. H. Rosenwald, J. R. Hoatson and J. A. Chenicek, *Ind. Eng. Chem.*, **42**, 162 (1950); (b) E. M. Bickoff, *J. Am. Oil Chem. Soc.*, **28**, 65 (1951); (c) R. H. Rosenwald and J. A. Chenick, *ibid.*, **28**, 185 (1951); (d) J. L. Bolland and P. ten Haave, *Disc. Faraday Soc.*, **2**, 252 (1947); (e) C. D. Lowry, Jr., G. Egloff, J. C. Morrell and C. G. Dryer, *Ind. Eng. Chem.*, **25**, 804 (1933).

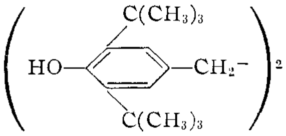
[3] L. Bateman, *Quart. Revs.*, **8**, 147 (1954).

[4] J. L. Bolland and P. ten Haave, *Trans. Faraday Soc.*, **43**, 2011 (1947).

[5] T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).

is produced by the decomposition of azo-bis-isobutyronitrile (AIBN) in the presence of oxygen and the same phenol.[6]

It also has been reported[7] that the same phenol is converted in part to the coupling product III under oxidative conditions. This product was, however, isolated in very small yield and was produced under conditions not closely analogous to those employed in our study. The formation of this product would correspond to the destruction of one oxidation chain per molecule of inhibitor. Furthermore, we have found that compounds analogous to III are themselves potent inhibitors.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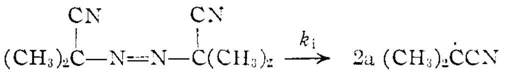
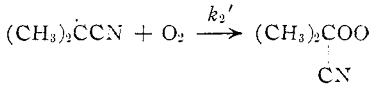
Results and Discussion

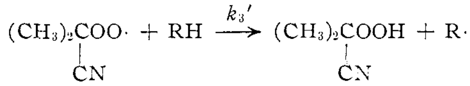
The generally accepted mechanism of initiated air oxidation is[3,8–10]



$$(CH_3)_2\underset{}{\overset{CN}{C}}{-}N{=}N{-}\overset{CN}{C}(CH_3)_2 \xrightarrow{k_i} 2a\,(CH_3)_2\dot{C}CN \quad (1)$$



$$(CH_3)_2\dot{C}CN + O_2 \xrightarrow{k_2'} (CH_3)_2\underset{CN}{C}OO\cdot \quad (2)$$



$$(CH_3)_2\underset{CN}{C}OO\cdot + RH \xrightarrow{k_3'} (CH_3)_2\underset{CN}{C}OOH + R\cdot \quad (3)$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \quad (4)$$

$$RO_2\cdot + RH \xrightarrow{k_3} RO_2H + R\cdot \quad (5)$$

$$2RO_2\cdot \xrightarrow{k_t} \text{Unknown products} \quad (6)$$

The criteria for assignment of this mechanism are the following kinetic characteristics: (1) no dependence of the oxidation rate on oxygen pressure, (2) half-order dependence of the rate on initiator concentration, and (3) first-order dependence of the rate on the concentration of the substrate (RH). It was confirmed that these conditions were met in the oxidation of both cumene and tetralin at oxygen pressures above 200 mm. in a number of solvents. The addition of a good inhibitor leads to the replacement of reaction 6 by other chain terminating steps which may be represented by equation 7.

$$In + nRO_2\cdot \longrightarrow \text{products} \quad (7)$$

Equation 7 in all probability will represent several steps with most inhibitors although if In is itself a free radical it might be a single step and n will be one. Otherwise there are a number of possibilities which lead to various values for the stoichiometric factor, n. The most important of these may be summarized in the following way: (1) The reaction of $RO_2\cdot$ with the inhibitor produced radicals of sufficient stability to permit them to survive until they eventually destroy each other by dimerization or other reactions. This would lead to n values of one. (2) The inhibitor reacts with two $RO_2\cdot$ to give products which are stable toward reaction with any of the constituents of the reaction mixture. This would give n values of two. (3) Reaction with two radicals as in (2) to give products which can react with the original inhibitor to convert it to an unreactive compound. In the case in which this is a 1:1 reaction the n value would be one. (4) Reaction as in any of the above cases to give products which are themselves inhibitors. This would lead to higher n values which would vary according to the nature of the secondary reactions.

There are two general approaches to the determination of stoichiometric factors. In the first, one carries out an accurate measurement of the initiation rate and then calculates, from the lifetime of an inhibitor which is introduced in known concentration, the number of chains which it has stopped. This is the easiest method when applied to inhibitors which produce well defined inhibition periods. It does, however, demand that one have a reliable method of estimating the rate of initiation. Finding such a method is not a trivial problem. Most of the commonly encountered initiators do not give a quantitative yield of two chain-initiating radicals per molecule when they undergo thermal decomposition.[11] It is necessary therefore, to have an independent method for counting initiating radicals from the source if the method is to be applied with confidence. The second general method is to carry out a careful study of the products of the inhibition reactions and to infer from the results the number of chains which have been terminated as was done in the previously cited investigations.[5,6] The rigorous application of the method requires a good material balance in the product study, since the isolation of a small yield of a product is no guarantee that it indicates the principal course of the inhibition reaction. A redeeming feature of the method is that a single successful product analysis goes a long way, since it constitutes a determination of the initiator efficiency and therefore permits one to apply the lifetime method to the determination of the stoichiometry of the reaction(s) of any other inhibitors under the same reaction conditions. It is important to note that the results of a comprehensive study can be checked further for reasonability by comparing the stoichiometric factors assigned to a series of inhibitors. It is reasonable to expect that certain integral values of n will occur frequently and that these will usually lead to a sensible interpretation in terms of commonly recurring mechanisms of the inhibition reactions with similarly constituted inhibitors.

All of these approaches have been applied to the present study. We chose AIBN as an initiator because an independent study of its decomposition was in progress in the laboratory.[11] In addition we have investigated the products from several

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(6) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(7) R. F. Moore and W. A. Waters, *ibid.*, 243 (1954).

(8) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949).

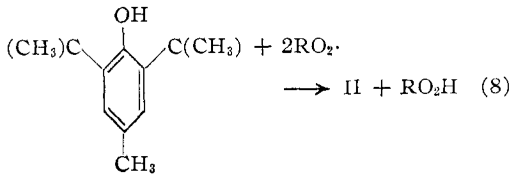
(9) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

(10) C. E. Frank, *Chem. Revs.*, **46**, 155 (1950).

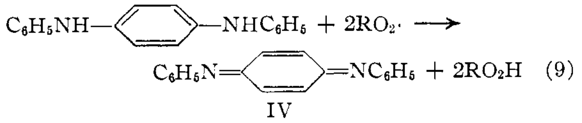
(11) G. S. Hammond, J. N. Sen and C. E. Boozer, This Journal, **77**, 3244 (1955).

inhibitors and have measured inhibition periods produced by a number of inhibitors.

The two inhibitors which yielded the most significant results in the product studies were 2,6-di-*t*-butyl-*p*-cresol and N,N'-diphenyl-*p*-phenylenediamine. As will be noted in Fig. 1 both of these compounds are very efficient inhibitors, which would lead one to expect that the products would be largely produced in the reactions of $RO_2\cdot$, derived from the initiator, with the inhibitors. Such a condition represents an obvious simplification of the product mixtures. The products isolated are consistent with the assignment of stoichiometric factors of two to both inhibitors.



(8)



(9)

The quinonimine IV was determined spectrophotometrically in the reaction mixture. Reading the optical density at various wave lengths gave values of 90–95% conversion of the original charge of the diamine to the dehydrogenation product. The product also was isolated in 50% yield. The cyclohexadienone II was isolated in approximately 50% yield and was not determined by an exact procedure. Since the isolation was achieved without great difficulty it is unlikely that other products were formed in significant amounts.

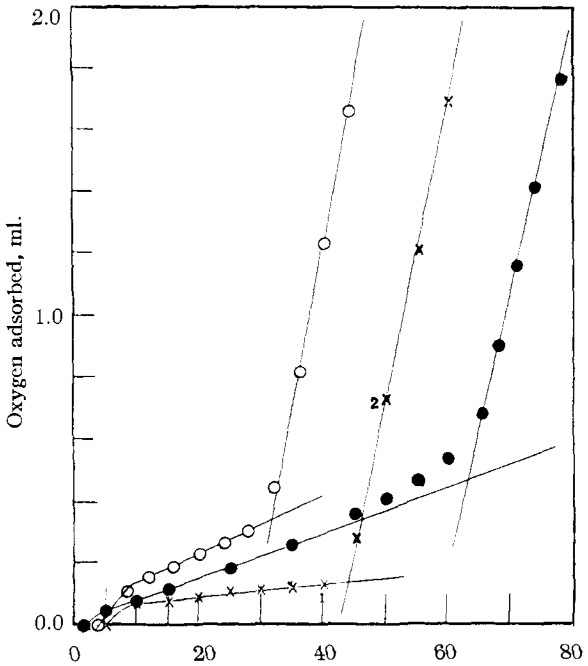


Fig. 1.—Oxidation of cumene in chlorobenzene at 62.5° with added inhibitors: ○, 10^{-5} mole of 2,6-di-*t*-butyl-*p*-cresol; ×, 1.24 × 10^{-5} mole of N,N'-diphenyl-*p*-phenylenediamine; ●, 2 × 10^{-5} mole of 2,6-di-*t*-butyl-*p*-cresol (AIBN = 6 × 10^{-4} mole).

Since both inhibitors gave sharply defined inhibition periods which are exactly proportional to the inhibitor concentrations, the assignment of the stoichiometric factors permits the calculation of initiation rates. These rates were found to be significantly smaller than the rates of decomposition of AIBN measured directly by nitrogen evolution. However, as has been discussed elsewhere, the efficiency factors calculated from the inhibition data were in quantitative agreement with those found by an independent method using iodine to trap the radicals produced by the decomposition of AIBN in the absence of oxygen.[11]

Inhibition periods were measured for the 17 inhibitors listed in Table I. Some of the less potent did not give sharply defined inhibition periods but zero-order lifetimes were estimated as shown by Fig. 2. Tangents were drawn to the oxidation

TABLE I

INHIBITION OF OXIDATION OF CUMENE IN CHLOROBENZENE BY VARIOUS INHIBITORS AT 62.5° AND ONE ATMOSPHERE OXYGEN PRESSURE

Inhibitor	*n* Factor
Chloranil and *sym*-Trinitrobenzene	No effect
2,6-Di-*t*-butyl-*p*-cresol[a]	2.0
2,5-Di-*t*-butylhydroquinone	0.85
Diphenylpicrylhydrazyl	1.98
4-*t*-Butylcatechol[a]	2.00
N-Methylaniline	2.0
p-Methoxydiphenylamine	3.3
Diphenylpicrylhydrazine	2.6
Tetraphenylpyrrole[a]	1.6
β-Naphthol	2.1
Diphenylamine	2.8
N,N'-Diphenyl-*p*-phenylenediamine	2.2
p,p'-Dihydroxyazobenzene	2.0
p-Hydroxydiphenylamine	2.1
2,2-Bis-(4-hydroxyphenyl)-propane (Bisphenol A)	4.1
p-Cresol	2.2
o-Cresol	2.2
Phenol	2.0

[a] Identical results were obtained with these inhibitors in benzene as the solvent.

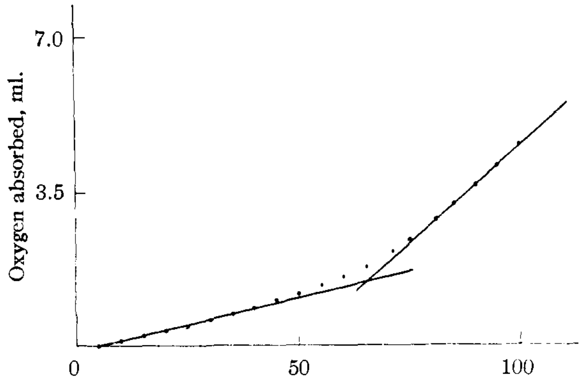
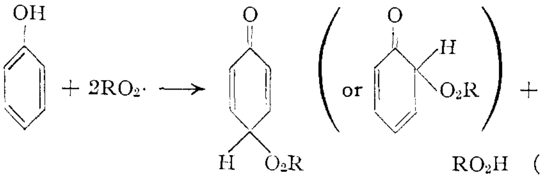


Fig. 2.—Oxidation of cumene in chlorobenzene at 62.5° containing 2 × 10^{-5} mole of N-methylaniline and 6 × 10^{-4} mole of AIBN.

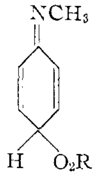
curves at an early stage in the run, and the intersection of the tangents with the straight lines drawn through the points taken late in the run, after the oxidation rate had assumed its uninhibited value, gave extrapolated zero-order lifetimes. This procedure gave lifetimes which were close to proportional to the initial inhibitor concentrations. This result indicates that very few chains are terminated by the normal process in the early parts of these runs. The assignment of stoichiometric factors is less precise than with the powerful inhibitors, but is nonetheless believed to be reasonably accurate.

Inspection of the values in Table I shows that n-values for 11 of the inhibitors are close to two. For these inhibitors, excepting α,α-diphenyl-β-picrylhydrazyl, it is easy to speculate as to the most probable products on the basis of analogy to the two cases which have been worked out. For example, the fact that phenol and its mono- and dialkyl derivatives stop two chains indicates that they probably react according to equation 10.



(10)

It is not probable that these products are converted to peroxy phenols under the conditions of our experiments as the latter should be inhibitors and their formation would increase the stoichiometric factors. The failure of Campbell and Coppinger[5] to isolate such compounds could very well be due to the fact that their experiments were conducted at a much higher temperature. The isolation of such labile compounds would be exceedingly difficult. It is also quite possible that N-methylaniline is converted to a similar product V.



V

The fact that p-hydroxydiphenylamine shows a clean stoichiometry of two whereas diphenylamine and p-methoxydiphenylamine gave a non-integral stoichiometry indicates that the former must possess a unique and effective reaction path such as dehydrogenation to benzoquinone monoanil. This is similar to the earlier suggestion as to the fate of hydroquinone.[4]

Certain of the inhibitors present special and intriguing problems which are not resolved readily on the basis of stoichiometry alone. The non-integral n-values shown by diphenylamine and its methoxy derivative indicate that there are probably at least two reaction paths which these compounds can take, with one of these leading to primary products which are themselves inhibitors. Considerable effort has been directed toward the isolation of products from oxidation mixtures which were inhibited by diphenylamine. Thus far the intractable mixtures have not been resolved into individual constituents.

Another interesting phenomenon is encountered with 2,5-di-t-butylhydroquinone. This compound shows a distinct break in the oxidation curve at a point which corresponds to the termination of one chain per mole. An extended period of weak inhibition follows this first break. Except for our current views concerning the mechanisms of inhibition reactions[12] we would be tempted to suggest that semiquinone radicals are formed and dimerize reversibly to form peroxides, as has been suggested for the tetrachlorocresoxy radical[13] and the semiquinone from phenanthrene quinone.[14] During the

$$2ArO\cdot \rightleftarrows ArOOAr \qquad (11)$$

period of weak inhibition the semiquinone radicals would react with $RO_2\cdot$ causing the eventual destruction of the dimer. This mechanism, as mentioned, has deficiencies and others may be considered. For example, it is possible that the quinone is formed and then forms a very tight quinhydrone with unreacted hydroquinone and consequently reduces the activity of the latter.

Tetraphenylpyrrole also is difficult to understand. It was used first with the view that the very labile hydrogen should be removed and that the resulting radical should stop one chain in a clean-cut fashion. Despite our current view[12] that hydrogen abstraction is not the first step in reactions with most inhibitors, it is possible that the prior abstraction mechanism does actually obtain with this particular compound. In this event it would probably be expected that some of the radicals dimerize to form some stable compound. A similar case which does not permit easy interpretation is found with α,α-diphenyl-β-picrylhydrazyl. Since it is a free radical we had hoped that it would stop only one chain per molecule. However, it is known that the hydrazyl gives variable results in other radical-counting experiments[11] and that it can, under some circumstances, react with more than one radical per molecule.

Experimental

Materials.—Tetralin was washed with concentrated sulfuric acid until the acid layer showed no more coloration and was then washed with water, dried, and distilled under nitrogen through a 4-foot Oldershaw column; b.p. 204.5–205.0°, n^{15}D 1.5444. Cumene was purified in the same way as tetralin; b.p. 152.0–152.5°, n^{15}D 1.4942. Benzene was given a treatment similar to that of tetralin and cumene. Chlorobenzene was redistilled, b.p. 130–131°. Carbon tetrachloride was dried over calcium chloride and distilled. Azo-bis-isobutyronitrile prepared by the standard method[15] was recrystallized from methanol; m.p. 105–106°. Diphenylamine, m.p. 54–55°, was recrystallized from petroleum ether. N-Methylaniline was purified by recrystallization of its acetyl derivative followed by acid hydrolysis. The pure N-methylaniline was distilled at reduced pressure and stored under nitrogen. α,α-Diphenyl-β-picrylhydrazyl, prepared by the method of Goldschmidt and Renn,[16] was recrystallized repeatedly from chloroform; m.p. 140°.

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[12] G. S. Hammond, C. E. Boozer, C. E. Hamilton and C. Peterson, This Journal, **77**, in press (1955).

[13] R. Pummerer, *Ber.*, **85**, 535 (1952).

[14] S. Goldschmidt and W. Schmidt, *ibid.*, **55**, 3197 (1922).

[15] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[16] S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

2,5-Di-*t*-butyl-*p*-cresol was purified by recrystallization from ethanol, m.p. 69–70°. After recrystallization from petroleum ether the 4-*t*-butylcatechol melted at 55–56°. Tetraphenylpyrrole was prepared by the method of Davidson.[17] It melted at 213–214° after recrystallization from alcohol. *p*-Methoxydiphenylamine was prepared by alkylation of the corresponding hydroxy compound, supplied by the B. F. Goodrich Co., with methyl sulfate. The product was recrystallized from petroleum ether; m.p. 104–105°. 1,3,5-Trinitrobenzene and chloranil were commercial materials recrystallized from acetic acid. β-Naphthol melted at 122.5–123.5° after two recrystallizations from carbon tetrachloride. Diphenylpicrylhydrazine[16] was recrystallized from acetic acid; m.p. 171–172°. The N,N'-diphenyl-*p*-phenylenediamine and *p*-hydroxydiphenylamine, obtained from the B. F. Goodrich Co., were recrystallized from a chlorobenzene–ligroin mixture. They melted at 147–149° and 72–73°, respectively. 2,2-Bis-(4-hydroxyphenyl)-propane (Bisphenol A) was recrystallized from chlorobenzene. The method of Atkinson, Morgan, Warren and Manning[18] was used to prepare *p,p'*-dihydroxyazobenzene, m.p. 215–216°. The method of Piccard[19] was used to prepare N,N'-diphenylquinonediimine (benzoquinonedianil) from N,N'-diphenyl-*p*-phenylenediamine by oxidation with chromic acid. After recrystallization from chlorobenzene, the product melted at 183–184°. The molecular compound with the *p*-phenylenediamine melted at 123–127°.

Inhibition Periods and Oxidation Rates.—An apparatus similar to that described by Bolland[20] was used to follow the rate of oxygen absorption at constant pressure. The apparatus was constructed of 8 mm. o. d. capillary tubing to keep the volume at a minimum and make the apparatus more sensitive to the absorption of small quantities of oxygen. Two thermostated, precision burets, of 5- and 30-ml. capacity, were used to read the volume changes, the smaller buret aiding in obtaining greater sensitivity for slow reactions. Myvane-20 oil was used to maintain a constant pressure in the apparatus. There was no erratic movement of the oil meniscus and the volumes read at any time were accurate to 0.01 ml. The nitrogen evolution from AIBN was followed by reducing the carbon dioxide pressure over the oil and observing the time and volume when the "standard" pressure was reached again as indicated by the pilot light on an electronic relay system. This procedure was necessary to obtain good results for very slow reactions. Inhibition periods were determined from a plot of absorbed oxygen volumes against time. The points formed straight lines both during and after the inhibition period and the time at the intersection point of these lines was taken as the inhibition period (see Figs. 1 and 2). All solutions contained 2 ml. of cumene in 4 ml. of chlorobenzene or benzene. Inhibitor concentrations were in the range 0.01–0.002 *M* and initiator concentrations ranged from 0.02 to 0.2 *M*. The inhibition periods ranged from 10 to 100 minutes. Erratic behavior was observed at the outset of every run before equilibrium was established in the vapor phase. The lag was not due to slow equilibration of the liquid but to slow gas flow through the capillary tubing.

Oxidation in the Presence of 2,6-Di-*t*-butyl-*p*-cresol.—A sample of 0.06 mole of the inhibitor was oxidized with AIBN (0.06 mole) in chlorobenzene at 62.5° by bubbling a stream of oxygen through the flask for four hours. After removal of the solvent under reduced pressure, the residue was extracted with petroleum ether. The petroleum ether was evaporated and the residue recrystallized from 95% ethyl alcohol. After several recrystallizations the product melted at 91–92° with gas evolution and had an infrared spectrum almost identical with the closely similar product isolated from the reaction of 2,6-di-*t*-butyl-*p*-cresol with *t*-butyl hydroperoxide by Campbell and Coppinger.[5] *Anal.* Calcd. for $C_{19}H_{29}O_3N$: C, 71.44; H, 9.15. Found: C, 71.74; H, 9.34. The product therefore is identified as 1-methyl-1-(2-peroxy-2-cyanopropyl)-3,5-di-*t*-butyl-2,5-cyclohexadienone-4. Bickel and Kooyman report[6] a melting point of 92–93° for the same product.

Oxidation Using N,N'-Diphenyl-*p*-phenylenediamine as Inhibitor.—A mixture of 3.75 g. (0.0229 mole) of AIBN and 2.485 g. (0.00957 mole) of N,N'-diphenyl-*p*-phenylenediamine in 200 ml. of chlorobenzene was placed in a 500-ml. round bottom flask, equipped with a bubbler tube and condenser. The flask was immersed in a constant temperature bath at 62.5°. Air was drawn through the mixture by suction. The light yellow solution soon darkened to a brown color. After 96 hours (8 half-lives of the initiator) the color had changed from reddish-brown to red and the oxidation was terminated. The chlorobenzene was removed from the reaction mixture by distilling at 50 mm. and 40°. During the distillation a small amount of solid (having an infrared spectrum similar to that of methacrylonitrile–oxygen copolymer) separated, but the amount of solid was not increased by cooling the still residue. The solids were filtered off and the remaining dark red chlorobenzene solution was evaporated by passing a stream of air over the mixture leaving a semi-crystalline residue. The solid material which was filtered off was extracted several times with a mixture consisting of one part methylene chloride and 40 parts ligroin to remove tetramethylsuccinonitrile. The solid residue then was recrystallized from methylene chloride; m.p. 183–185°, mixed m.p. with authentic N,N'-diphenylquinonediimine 184–188°. The total yield purified material obtained was 1.14 g.

In another experiment, duplicating the conditions of the kinetic runs, the reaction was stopped at the end of the inhibition period and the ultraviolet spectrum of the solution was determined. The absorption curve was the same as that for an authentic sample of N,N'-diphenylquinonediimine and the intensity of absorption indicated that this product was formed in 90–95% yield.

Acknowledgment.—We are very grateful for the generous support of this study by the B. F. Goodrich Co.

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