DEVELOPMENT OF A COMPETITIVE TECHNIQUE FOR THE COMPARISON OF STRONG OXIDATION INHIBITORS

Thesis by

Richard Steve Tunder

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ABSTRACT

The mechanism of the inhibited chain oxidation of cumene has been carefully investigated in previous studies. A competitive technique for determining relative efficiencies of strong inhibitors was to be tried in this study. Such a study might extend and verify work of a similar nature on weaker inhibitors. However the relative efficiencies determined were not constant. They varied because of possible side reactions of N,N'-diphenyl-p-phenylenediamine, the inhibitor chosen as a standard. For the same reason variation of the initial concentration of the standard inhibitor caused slight unexpected deviations in the results.

Hydroquinones were found to reduce N,N-diphenyl-p-quinonimine, the oxidation product of the standard inhibitor, back to the inhibitor while stopping chains at the same time. As in previous studies, the strength of an inhibitor was found to increase with increasing ortho steric hindrance as well as with increasing electron density in the aromatic ring. Initiator concentration was found to be first order with respect to termination rate as would be expected in a chain reaction in which an inhibitor molecule stops two radical chains. The oxidation product formed from a phenolic inhibitor was found not to affect the standard inhibitor.

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INTRODUCTION

The first instance of the inhibition of oxidation by oxygen was observed by Berthelot in 1797 when he found that traces of the vapors of sulfur compounds prevented the luminescence of phosphorus in a dilute atmosphere of oxygen (33). Other early research included the discovery that traces of ethylene or carbon monoxide inhibit the reaction of hydrogen and oxygen. These gases were observed to inhibit the oxidation of chloroform also. At the beginning of this century studies of the inhibition of sulfite oxidation were started. Substances like hydroquinone and resorcinol were found to be effective in the inhibition of the oxidation of oxalic acid by air. Inhibitors of the oxidation of fats and paraffins were discovered (33).

During the First World War phenolic inhibitors were found to be useful in rubber. By 1922 the observation was made that many antioxidants were phenols. The problem of stabilizing acrolein was solved by adding small amounts of phenols, especially hydroquinone, to acrolein. By the time Moureu and Dufraisse wrote their review on antioxidants (33), antioxidants were defined to be any easily oxidized substance. Antioxidants were also thought to function as accelerators under different conditions. They were regarded as catalyst poisons. Antioxidants were supposed to neutralize the positive catalyst thought to be necessary for the oxidation reaction to

occur. Other possible modes of antioxidant behavior considered were: (1) inactivation of oxygen by the inhibitor and (2) inactivation by the inhibitor of a species composed of oxygen and substrate (33).

In 1926 the suggestion was made that there is a relationship between inhibitory efficiency and oxidation potential of the inhibitor (29). This relationship might reasonably exist if the inhibitor functioned by losing hydrogen. However the controversy at this time concerned whether or not the antioxidant functions by stopping chains, particularly energy chains (1,3,19,23,26,31).

Bäckstrom (3) argued that these negative catalysts are effective in both photochemical and thermal oxidations, that both are chain reactions and that inhibitors function by breaking energy or reaction chains. Christiansen produced a theoretical analysis which showed that if a small amount of a substance inhibits a reaction, it must work by breaking a reaction chain (19).

Dhar (23) objected to the chain theory. He said oxygen and substrate react to give an activated form of oxygen which oxidizes the inhibitor. Although this explanation appears to have an element of truth in it from the viewpoint of present-day explanations, it overlooks the fact that only small amounts of a substance are required for it to be effective as an inhibitor.

Work on the inhibition of sulfite oxidation by butyl alcohols (1) backed the chain theory. This work indicated that two molecules of alcohol are required to stop one reaction chain. The alcohol is inductively oxidized to an aldehyde or ketone in the process of stopping chains. This explanation was verified by showing that tert-butyl alcohol does not act as an inhibitor. The investigators emphasized the fact that the inhibitors affect the number of chains broken rather than the number started. Hydroquinone was also tried as an antioxidant. Although it too inhibits by being inductively oxidized, it is also directly oxidized under the reaction conditions. Specifically, inhibitors of sulfite oxidation were found to work by terminating the reaction chain prematurely. Oxidation of the alcohols produced no chain-continuing species.

Milas proposed that inhibitors must have loosely bound valence electrons (30). He assumed that these electrons absorb the excess energy of the just-reacted peroxide molecules thereby stopping the reaction chain. The activiated inhibitor molecules are then oxidized. Milas preferred this theory to the earlier one which said that inhibitors act by destroying peroxidic compounds formed by the oxidation substrate. He also looked with disfavor upon the idea that inhibitors function by forming a loose complex with a reactive species in solution. This last idea was proposed when

substances like quinones were found to have inhibitory power (31).

After studying the relationship between oxidation potential and inhibitor efficiency, Egloff (26) said that inhibitors are foreign molecules which deactiviate the hot molecules in a reaction mixture by absorbing their excess energy. Once the hot molecules are deactivated, the energy chain needed to keep the reaction going is stopped. Egloff's theory was based on the idea that more readily oxidizable substances are more effective inhibitors, unless they are so reactive that they are directly oxidized by oxygen. Egloff found the most effective inhibitors to be those with oxidation potentials of 0.609-0.797v while those with potentials of 0.799-1.943v were moderately efficient. Those with potentials above 1.064v had little or no inhibitory value.

The only irregular inhibitors were hydroquinones. They showed less effective inhibition than their oxidation potentials indicate. Since the inhibition experiments were done in an oxygen pressure bomb, some direct oxidation of the hydroquinones may have occurred. Inhibitory activity is also reported for quinones. This phenomenon, Egloff suggested, may be due to traces of water which convert the quinones to aromatic trihydroxy compounds which are inhibitors. Another explanation for the inhibitory activity of

quinones was developed later (16). Ortho- and para-substituted phenols and amines were found to be more effective inhibitors than meta-substituted phenols and amines. This greater effectiveness occurs because ortho- and para-substituents have a greater effect on the oxidation potential of an inhibitor than do meta-substituents. However meta-substituted nitrophenols are almost as effective as ortho-substituted nitrophenols and more effective than para-substituted nitrophenols.

Bolland and Ten Haave (10) related relative efficiency of inhibitor to oxidation potential for phenols and hydroquinones. As did Egloff, these investigators found an inverse linear relationship between the logarithm of relative efficiency and oxidation-reduction potential. Since oxidation-reduction potential gives a measure of the relative ease of removal of phenolic hydrogen, Bolland and Ten Haave interpreted the inhibition mechanism as consisting of removal of phenolic hydrogen by an alkylperoxy radical. A more recent study also relates oxidation potential and inhibitory efficiency again using cracked gasoline as substrate in the oxygen pressure bomb (35). The results are virtually the same as those of Egloff. However only those inhibitors with oxidation potentials below 0.7v are said to be good inhibitors while those at 0.7-0.8v are considered to be fair. Those above 0.8v are said to have low inhibitory

activity. Again the effectiveness of hydroquinone as an inhibitor was less than predicted from its oxidation potential. Substituted hydroxyanisoles gave higher efficiencies than were expected from their oxidation potentials.

In order to explain the inhibitory activity of quinones Calkins and Mattill said that quinones might be reduced by traces of substances present, to semiquinones which could act as inhibitors (16). This explanation was referred to in another paper by Bolland and Ten Haave (11) in which they incidentally reported that quinones show inhibitory activity. However this latter paper is important mainly because Bolland and Ten Haave showed that hydroquinone inhibits autoxidation of hydrocarbons by reacting with alkylperoxy radicals rather than by reacting with alkyl radicals. This proof was kinetic in nature and freed subsequent investigators from having to consider the possibility that the inhibitor interferes directly with the alkyl radicals as they are produced. Mono-olefins and 1,4-dienes were substrates for this study.

Other studies using cracked gasoline and the oxygen pressure bomb pointed to ortho- and para-substitution of aromatic inhibitors by alkyl groups as a way to increase inhibitor efficiency (25). Two or more hydroxyl groups as substituents on the aromatic ring were found to be more effective yet. The hydroxyls were most effective if they were not meta to one another. Addition of amino groups to

the phenolic ring also gave good inhibitors. Nitro substitution gave weaker inhibitors. Bulky groups showed steric hindrance effects only when ortho-substituted on phenols and amines. Alcohols and aliphatic amines were ineffective as inhibitors while aromatic diamines were very effective. Halogen substituents had no effect on inhibitor potency.

Before the discovery that inhibitors react with alkylperoxy radicals rather than alkyl radicals, one study revealed that autoxidation rates of hydrocarbons in the presence of an inhibitor are independent of oxygen concentration (27). The initial rate depends on inhibitor concentration and also on the second power of hydrocarbon concentration. The latter dependence is probably second power because of involvement of hydrocarbon in the initiation step. The length of the induction period itself was independent of oxygen pressure and inversely proportional to hydrocarbon concentration. The investigators for this thought that inhibitors act by breaking an energy chain. The possibility that the inhibitor may function by interfering with a chain precursor was also brought up.

Substitution studies of a practical nature were made by Rosenwald and co-workers (38). Amounts by weight of inhibitor needed to bring the induction period to a standard value were determined. By this technique qualitative estimates of the relative efficiency of inhibitors were made. Alkyl phenols were rated in the oxygen pressure bomb with cracked gasoline

as substrate. Substitution of two or more alkyl groups on the phenolic ring had a more than additive affect on the strength of phenolic inhibitors. The length of an alkyl substituent had no affect on inhibitor potency. Introduction of the first substitution in the ortho-position was more effective than placing it in the para-position. The position of the second substitution made little difference although the para-position was slightly favored. This finding seems to contradict a previously mentioned study (25). Branching of a substituent is effective at the ortho-position but not at the para-position. Work reported a year later confirmed the results of this study (9). A report at the same time by Rosenwald extends his research to hydroxyanisoles as inhibitors (36). Alkyl substitution in the 3-position of 4-hydroxy anisole was found to give most effective inhibition. The tert.-butyl group was the most effective alkyl substituent.

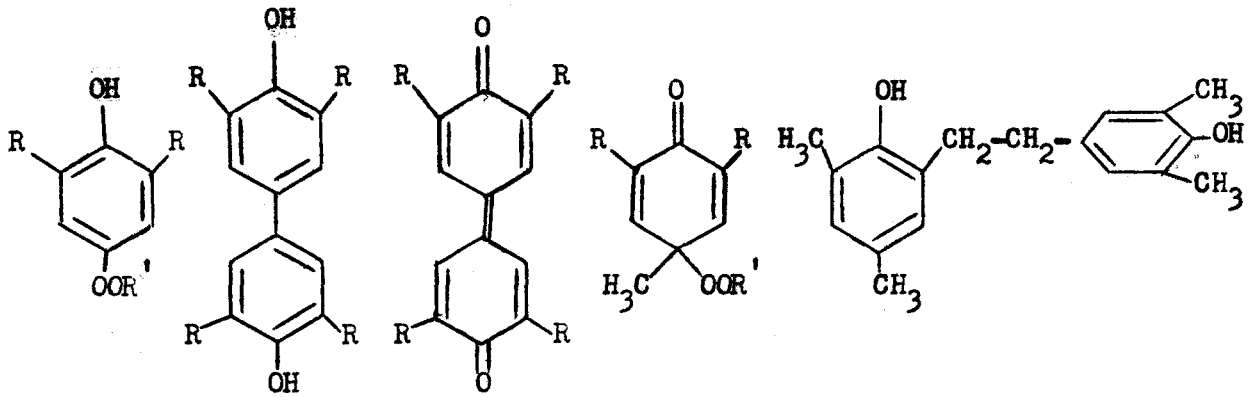
Kinetic studies of the inhibited oxidation of rubber were done by Shelton and co-workers (40,41). In amine-inhibited rubber the rate of oxygen absorption is a function of the square root of oxygen pressure (40). This is expressed as; rate = $k(P_{O_2} + a)^{\frac{1}{2}}$. Except at high temperatures, a is negligible for strongly inhibited rubber. This result led Shelton to conclude that amines, instead of stopping chains, interfere with initiation by decomposing the initiator into stable substances. Since oxygen must be involved in the

initiation step for a rate dependence on oxygen to occur, the rate equation suggests that there is initiation involving oxygen as well as initiation by decomposition of peroxides already present (40).

Shelton's other study at this period (41) found an optimum inhibitor concentration beyond which oxygen absorption increases during the induction period. The result was expressed in the law; rate = $a(1 + (1 + bP_{O_2})^{\frac{1}{2}}$; a and b are constants. Inhibitors have four functions in the mechanism proposed: (1) initiation by direct oxygen attack on the inhibitor (2) chain transfer without termination (3) termination by inhibitor radical and another radical (4) conversion of peroxides to stable products thereby reducing the quantity of initiator present. Step one is considered to be more common for amines than phenols. Chain transfer also occurs more commonly for amines. Phenols seem to be more efficient than amines in stopping reaction chains. Step four is more common for amines than phenols and is more effective if carbon black is present. Step three is inserted to account for the formation of certain products which indicate that termination occurs both by reaction of inhibitor with alkylperoxy radicals and by dimerization of inhibitor radicals. Obviously the inhibitor is now considered to interfere with a radical chain mechanism.

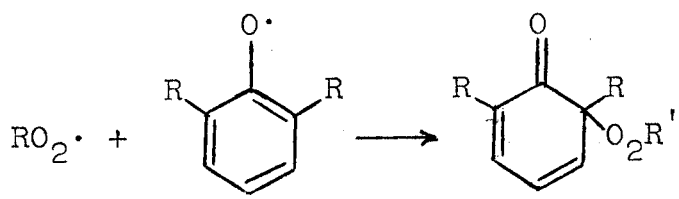
Previous to this last investigation, study of products formed from oxidation inhibitors had been begun. Cosgrove

and Waters (21,22) discovered that 2,6-dialkyl phenols give a 4-substituted product (I) but give mostly diphenols or diphenoquinones (II and III). They also found that 4-methyl-2,6-dialkylphenols give 4-substituted cyclohexadienones (IV)



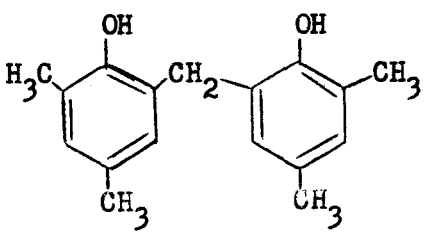
I II III IV V

and a little dimer. Later investigation revealed that alkylperoxy radicals also attack the ortho-position of a phenol:



Cosgrove and Waters suggested that this may always be the initial mode of attack on phenoxy radicals with subsequent rearrangement of the alkylperoxy group to the para-position (22). Oxidation of mesitol gave the unsymmetrical bibenzyl (V). The dimethylated product 4,4'-dihydroxy-3,5,3',5'-tetramethyldiphenylmethane (VI) was a minor product. Cosgrove and Waters concluded that phenolic inhibitors are oxidized to resonance stabilized phenoxy radicals as inter-

mediates followed by attack of alkylperoxy radicals at the para-position if the ortho-position is blocked.



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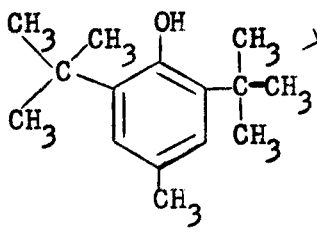

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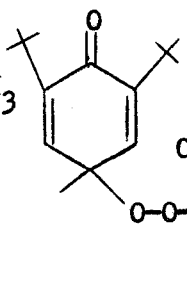

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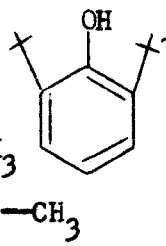

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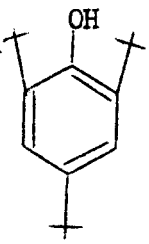


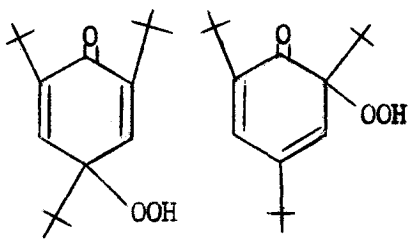
X

Campbell and Coppinger (17) sought to shed light on the mechanism of inhibition by reacting phenolic inhibitors with tert.-butyl hydroperoxide. The reactions were conducted at the decomposition temperature of the hydroperoxide and were followed spectroscopically. Most phenols tested gave resins or uncrystallizable substances. However 2,6-di-tert.-butyl-p-cresol (VII) gave the solid product 1-methyl-1-tert.butyl-peroxy-3,5-di-tert.butylcyclohexadienone-4 (VIII). Campbell and Coppinger concluded that the inhibitor first loses a hydrogen, becoming a reasonably stable free radical; then it reacts with an alkylperoxy radical to form the stated product. Bickel and Kooyman analyzed the products formed from 2,4,6-trimethyl phenol and found more than one alkylperoxy cyclo-hexadienone as well as dimer and a little stilbenequinone (5).

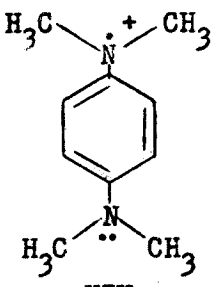
Moore and Waters (32) recovered only dimers of phenols in their studies. A biphenyl derivative was obtained whenever

the phenol was unsubstituted at an ortho- or para-position. Dihydroxydibenzyls were always obtained from 2,4,6-trisubstituted phenols if one of the substituents was a methyl group. This indicates that a hydroxybenzyl radical was the intermediate rather than a phenoxy radical. Phenoxy radicals and hydroxybenzyl radicals are not interconvertible.

Cook (20) confirmed the formation of dimer from 2,6-di-tert.-butyl-p-cresol (VII) and showed that a phenoxy radical probably forms first. It is then converted to a benzyl radical which can dimerize. Rather recently Bickel (4) performed some oxidations of phenols by base and oxygen. He obtained a stilbenequinone from 2,6-di-tert.-butyl phenol (IX). Tri-tert.-butyl phenol (X) gave XI and XII. These two compounds were interconvertible at 40°. The cresol (VII) gave only XIII. However, these oxidations occur by a polar mechanism.



XI XII XIII



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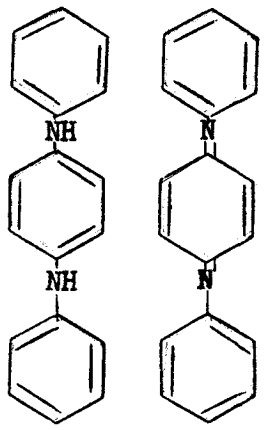


XV XVI

In 1954 Hammond and Boozer (12) introduced the idea that inhibition of oxidation proceeded not by preliminary hydrogen

abstraction but by reversible formation of a complex between an inhibitor molecule and an alkylperoxy radical. The complex was believed to react subsequently with a second alkylperoxy radical to form products. Hammond found that deuteration of the labile hydrogen of an amine inhibitor did not give an increased oxidation rate during the inhibition period as expected for a hydrogen abstraction mechanism. Furthermore substances with no labile hydrogen like tetramethyl-*p*-phenylenediamine have inhibitory power. In nitromethane this inhibitor shows the color typical of Wurster's cation (XIV). This color disappears by the end of the inhibition period. With water present the color of Wurster's cation develops during the first half of the inhibition period, and then disappears. This phenomenon is interpreted as meaning that the alkylperoxy-inhibitor complex is readily and reversibly hydrolyzed to Wurster's cation.

Hammond was led to do further work in order to develop a comprehensive picture of inhibitor action (14,15). First a list of inhibitors was investigated to determine their chain-stopping capacities (*n* values). Most of the inhibitors investigated stopped two chains per molecule of inhibitor. This fact is interpreted to mean that most inhibitors function by first becoming a radical product which then reacts with a second alkylperoxy radical to give stable products. If $n = 1$, the intermediate radicals produced by reaction of inhibitor molecules with alkylperoxy radicals may

dimerize. Higher n values are obtained when the first non-radical products of the inhibition reaction are inhibitors themselves. The n values were based on product studies with two inhibitors; 2,6-di-tert.-butyl-p-cresol (VII) and N,N'-diphenyl-p-phenylenediamine (XII). The cresol gave an alkyl-peroxy-substituted cyclohexadienone (XIII) while the diamine gave the corresponding diimine (XVI). Product analysis was used to obtain reference n values since the inhibition period method suffers from uncertainties due to the inefficiency of the initiator (azobisisobutyronitrile, ABN). Independent determination of the efficiency of ABN using iodine as a scavenger gave good agreement with values based on the assigned stoichiometric factors of the inhibitors.

Hammond and co-workers (14) tested seventeen phenols and amines in this way. Eleven had n values of 2. The products from phenol and of N-methyl aniline were assumed to be of the same type as that from 2,6-di-tert.-butyl-p-cresol (VII). With 2,5-di-tert.-butyl hydroquinone, some direct oxidation probably occurred since it gave an n value of 0.85. This inhibitor is characterized by strong inhibition during the time which represents the stopping of one chain. An extended period of weak inhibition follows. Hammond speculated that the resulting quinone may form a tight quinhydrone with hydroquinone thereby reducing the activity of the hydroquinone. Alternatively the semiquinone might form and dimerize to give a product which is a weak

inhibitor. p-Hydroxydiphenylamine has an n value of 2. It is thought to form benzoquinone monoanil, in imitation of hydroquinone. Other diphenylamines have non-integral n values near 3. Product analysis with these inhibitors was not successful. Tetraphenylpyrrole is apparently an unusual inhibitor since Hammond says that it may act by direct hydrogen abstraction with subsequent dimerization.

Hammond believed that complex formation is the most common mechanism for inhibition (15). Evidence cited in favor of this idea included the fact that N-methylaniline-N-D and diphenylamine-N-D showed no isotope effect. Furthermore dihydrophenazine, hydrazobenzene, and dimethylaniline are all weak inhibitors. If hydrogen abstraction is the mechanism involved in inhibition, dihydrophenazine and hydrazobenzene should be strong inhibitors while dimethylaniline should not inhibit at all. In addition, a Hammett plot done with relative efficiencies of these inhibitors, as well as those reported for other inhibitors in the literature (σ vs. log relative efficiency) gave a rather crude fit to the Hammett equation with a ρ value of -3.7, indicating that inhibitor reactivity is a sensitive function of electron density in the aromatic nucleus of amines and phenols. Moreover, the rate of ABN-initiated oxidation of cumene and tetralin, in the presence of weak antioxidants, showed an inverse square root dependence on inhibitor concentration whereas previous investigators found an inverse first order dependence (10,37).

Work with tetramethyl-p-phenylenediamine was cited again including work concerning the appearance of Wurster's cation coloring with water present.

Hammond (15) emphasizes that lack of an isotope effect in deuterated inhibitors, lack of abstractable hydrogens in some inhibitors, ready availability of hydrogens in some non-inhibitors, and the great dependence of inhibitory efficiency on electron density argue against preliminary hydrogen abstraction as a mechanism. Furthermore the first step in the inhibition mechanism must be reversible to account for the observed dependence of rate on inhibitor concentration. Hydrogen abstraction is not very likely to be reversible. Alkylperoxylation is unlikely as a first step since bulky para-substituents show no steric effects. Moreover, the phenylenediamines would then require a separate mechanism. However, reversible complex formation by inhibitor molecule with an alkylperoxy radical fits all the observations. With this mechanism no isotope effect upon deuteration is expected and no steric effects are expected either.

Hammond and co-workers (13) also reported some work as interesting but unexplained observations. They found that the n value of an inhibitor is affected by both the nature of the solvent and the nature of the oxidation substrate. In an attempt to see if alkylperoxy-solvent complexes exist, much of the aromatic solvent was replaced by aliphatic hydrocarbon solvent but without effect. When the substrate was

also made non-aromatic, there was a change in the behavior of 4-tert.-butyl catechol but not in that of 2,6-di-tert.-butyl-p-cresol.

Bickel and Kooyman reported comprehensive studies with inhibitors (6,7,8). A competitive method of study was used. Two inhibitors per run were present as well as substrate and initiator (6). If the substrate to inhibitor ratio was a linear function of initial oxidation rate (rate during inhibition), dimerization of phenoxy radicals was proposed to occur. At the same time phenoxy radicals may also terminate alkylperoxy radicals. If the oxidation rate during inhibition passed through a minimum with increasing inhibitor concentration, chain transfer by the phenoxy radical was believed to occur. If initial oxidation rates were directly proportional to substrate concentration and inversely proportional to inhibitor concentration, the inhibitor was believed to act as a chain transfer agent with termination by dimerization. Whereas bulky ortho-groups hinder hydrogen removal sterically, they favor it by providing greater resonance stabilization for the phenoxy radical. In addition strongly hindered phenols do not participate in chain transfer. Therefore strongly hindered phenols are the best phenolic inhibitors because they do not undergo chain transfer with the substance they are supposed to protect.

Bickel and Kooyman later presented results of an investigation of amine inhibitors similar to the investigation

of phenols described above (7). Tertiary amines increased rather than retarded the oxidation rate, perhaps by forming an oxygen-absorbing radical. Isolation of products from reactions of amine inhibitors was found to be impossible. As with phenols, one group of amines was found which terminates by dimerization or by reaction of an initial radical intermediate with alkylperoxy radical. N-methyl anilines probably induced chain transfer as well as termination. N,N'-di-sec.-butyl-p-phenylenediamine showed a true inhibition period even in competition with a weak standard like dihydroanthracene. Alkylperoxy radicals may react exclusively with this phenylenediamine until its concentration becomes very low. Therefore a measurement of its efficiency is not possible. Steric hindrance, with consequent resonance stabilization of the intermediate radical, accounts for the strength of amine inhibitors as well as for the strength of phenolic inhibitors.

In a third paper Bickel and Kooyman argue that previous work with deuterated amines is inconclusive since the energy of activation for the hydrogen abstraction step in the preliminary hydrogen abstraction mechanism is low (8). These investigators claimed that when a radical such as diphenylpicrylhydrzyl reacts with 2,6-di-tert.-butyl-p-cresol, more activation energy is required than if the inhibitor reacted with alkylperoxy radical. In accordance with this hypothesis they found an isotope effect for the reaction

of deuterated amine with diphenylpicryhydrazyl. The implicit assumption was that only reactions involving at least a moderate activation energy are capable of showing isotope effects.

About this time Pedersen (34) discovered that dideuterated N,N'-diphenyl-p-phenylenediamine gave no isotope effect. He proposed an electron transfer mechanism of inhibition wherein alkylperoxy radical becomes alkylperoxy anion and the amine inhibitor becomes a radical-cation. Pedersen did not think that a unified theory of inhibition was possible. He took as evidence for his mechanism the fact that electron-releasing alkyl groups on the nitrogen of an amine inhibitor increase the efficiency of the inhibitor. He also found that steric hindrance around the nitrogen of an amine inhibitor gave greater inhibitory efficiency. Steric hindrance may prevent undesired side reactions. However Pedersen also discovered a free radical hydrogen exchange that occurs in spite of strong steric hindrance. Diphenylpicrylhydrazine reacts with 2,4,6-tri-tert.-butyl phenoxy radical to give diphenylpicrylhydrazyl and 2,4,6-tri-tert.-butyl phenol. The quinonediimine produced from Pedersen's dideuterated inhibitor, as well as the corresponding N,N'-dioxide, had inhibitory action although their mode of action is unknown. Pedersen concluded that the electron donation mechanism is operative in some cases, hydrogen abstraction in others, and still unknown mechanisms in other cases.

Walling and Hogden (45), using benzoyl peroxide as initiator and phenolic inhibitors, confirmed previous findings that electron-supplying groups on phenol increase inhibitory efficiency but found no evidence for a simple Hammett relationship. A clear relationship of relative efficiency to steric hindrance about the phenolic function exists which precludes the establishment of any simple Hammett relationship. Moreover when deuterium was substituted for the hydrogen of the phenolic function, a small constant isotope effect was noted. This observation was taken as evidence for the hydrogen abstraction mode of inhibition. In this work the rate of oxidation during the inhibition period varied with the nature of the particular peroxidic initiator used and with the nature of the solvent as well.

The latest work with inhibitors has been done with rubber as substrate (2,24,39,42,43,44). Because of the shorter reaction chains in rubber and because of the low diffusion coefficient of inhibitors in rubber, the concentration of inhibitor needed for inhibition work with rubber is much higher than for ordinary hydrocarbons. Otherwise the inhibited oxidation of rubber is like that of any other hydrocarbon.

Aldehydes rather than peroxides are the products of the inhibited oxidation of rubber according to Angert and Kuzminski (2). Hydroperoxides do not react with inhibitors to give aldehydes. Similar results were later found for uninhibited oxidation. Angert and Kuzminski conducted infra red

studies which indicated that the N-H bond of amine inhibitors is replaced by C-N or N-N bonds after inhibition occurs. An increase in inhibitor content above saturation concentration, the concentration where a reduction of oxidation rate or a prolongation of inhibition period no longer occurs with addition of more inhibitor, results in a slight increase of oxidation rate during the inhibition period. This phenomenon could occur if the inhibitor and oxygen interact to produce an initiator.

Work was also done with specific inhibitors by this same team (2). Inhibitors with no abstractable hydrogen gave no inhibition. While N-phenyl-β-naphthylamine inhibits oxidation, it does not inhibit polymerization. Apparently it reacts only with peroxy radicals. To test the idea that a secondary amine radical might stop an oxidation chain but not a growing polymer chain, Angert and Kuzminski heated tetraphenylhydrazine to high temperatures and the resulting diphenylamino radicals were used as inhibitors. They were slightly better oxidation inhibitors than diphenylamine itself; however they did not inhibit polymerization at all. The reaction of secondary amines with diphenylpicrylhydrazyl to give hydrazines was also reported. Tertiary amines did not react at all. These observations were construed as favoring hydrogen abstraction as the key step in inhibition by secondary amines. Relative reactivities of diphenylamine, phenylnaphthylamine, and dinaphthylamine were determined to

be 1:4.5:11. Electron-releasing substituents on the phenyl group of N-phenyl-β-naphthylamine increased its inhibitory power.

Shelton (42) worked with butadiene-styrene copolymer as substrate and used deuterated 2,6-di-tert.-butyl-p-cresol and deuterated N-phenyl-2-naphthylamine as inhibitors. He obtained a normal isotope effect with the phenol although he reported no effect at low phenol concentration. The amine gave a normal isotope effect at intermediate concentrations. Shelton concluded that hydrogen abstraction is the mechanism at work here. The π-complex mechanism may be applicable to cases where the inhibitor has no abstractable hydrogen.

At this point amines were found to photosensitize the degradation of natural rubber. Using ultraviolet radiation Shelton and McDonel (42) found that high concentrations of amine inhibitors accelerate the degradation of rubber while low concentrations retard it. Phenols give at least weak inhibition at all concentrations (24).

Shelton recently reviewed the field and did some clarifying work in the area (39,44). He worked with thin films of latex copolymer, films thin enough so that oxidation was not diffusion controlled. He used a Warburg-like oxygen apparatus to follow the reactions (43). Shelton classified inhibitors as: (1) light absorbers, such as secondary aryl amines which inhibit thermal oxidation (see class 4) but promote photo-oxidation, (2) deactivators (by

chelation) of metal catalysts of oxidation, (3) peroxide decomposers or substances which decompose potential initiators into stable, non-radical products, and (4) chain stoppers like hindered phenols and secondary aryl amines. Class 3 inhibitors are phenols, mercaptans, and other organosulfur compounds. Their particular mode of action has not been determined. Inhibition occurs because of a reduction in the rate of initiation. Zinc dimethyldithiocarbamate, present in vulcanized rubber, may be such an inhibitor since extraction of the compound from rubber removes the aging resistance of the rubber (39).

Shelton considers hydrogen abstraction, electron donation to alkylperoxy radical, addition of alkylperoxy radical to the aromatic ring of the inhibitor, and formation of a π-complex between inhibitor and alkylperoxy radical as possible modes of action of class 4 inhibitors; but he favors hydrogen abstraction (39). He states that all previous product studies are consistent with any of the mechanisms. To account for all observations inhibitors must be considered to act as initiators, chain transfer agents, and chain-stoppers. Class 3 type inhibition is common for amine inhibitors. This is especially true if carbon black is also present. However class 3 inhibition does not occur with phenols.

Shelton (39) mentions his own work in which he obtained isotope effects for both deuterated hindered phenols and

deuterated secondary aryl amines. This work was done with rubber substrate. Differences in oxidation rates during the induction periods in the presence of the deuterated and undeuterated inhibitors were observed. Shelton refers to his most recent work (44) in which he found no isotope effect or a reverse isotope effect in some cases. These results, he says, can be accounted for by temperature changes, changes in concentration of inhibitor, and the nature of the particular antioxidant used. Shelton concludes that hydrogen abstraction is not the only mechanism by which inhibitors act since inhibition by tertiary amines must be accounted for among other things. The other suggested mechanisms are considered to be possible in certain cases.

Shelton's last investigation in this area (44) dealt with diphenylamine and N-phenyl-2-naphthylamine as deuterated inhibitors. Reactions were carried out at 90° with a thin layer of crumb latex as substrate. The latex had the inhibitor milled into it and the mixture was pressed onto an aluminum screen. Deuterated diphenylamine gave a reverse isotope effect. At lower temperature and lower inhibitor concentration this reverse effect was considerably lessened. In both cases the inhibition period was longer with the deuterated amine. High inhibitor concentrations at 90° gave no isotope effect. The deuterated naphthylamine gave a normal isotope effect at 90°. As the inhibitor concentration was increased, the isotope effect was reversed. Therefore the isotope effect seems to depend upon temperature and concentration.

The reverse isotope effect at high inhibitor concentrations might occur because the inhibitor participates in initiation at these high concentrations. Deuteration would be expected to slow down this initiation (44). The influence of temperature on the isotope effect could be due to the fact that the energy of activation for termination is smaller than that for initiation by inhibitor radicals. A temperature increase would then affect the initiation reaction more and would cause a reverse isotope effect to occur at the higher temperature, with the deuterated inhibitor. Although hydrogen abstraction may not be the only mechanism by which inhibitors operate, Shelton argues that it is the most common one.

Other oxidation studies and studies on inhibition of oxidation have been carried out at very high temperatures (360°) (18,28,37). Diisopropyl ether was the substrate and substances like xylene and aniline were used as inhibitors. The efficiency of aromatic compounds as inhibitors was related to the first ionization potential of the compounds. The electron density of the aromatic ring was important to inhibitor efficiency. The aromatic compounds were inductively oxidized in acting as inhibitors (18).

In similar studies Rosenwald (37) and Hoatson found the inhibition period to be directly proportional to inhibitor concentration. Variations of inhibitor concentration at low initial inhibitor concentrations caused a greater change

in inhibition period than changes at higher initial concentrations. The empiricial relation: $\log y = r + s \log x$ (y = inhibition period, x = initial inhibitor concentration) was developed. The semi-theoretical expression: $y = a + bx + c \log x$ was also derived. Both of these equations were tested with benzofuroxan and both were valid to about the same precision. The logarithmic or exponential relationship is said not to be due to removal of a loosely bound hydrogen. These relationships do not hold for pure hydrocarbons as substrates although they hold for mixtures of hydrocarbons. With cyclohexane and diisobutylene the first equation was found to hold for three inhibitors.

Lloyd and Lippincott (28) found an exponential relationship between inhibitor concentration and inhibition period that held for tetralin as substrate if a strong branching catalyst was present. They stated that all of this work is in the field of non-steady state kinetics.

The subject of this thesis is related to the work of Hammond and co-workers (15). Hammond has already determined relative efficiencies for weak and moderately strong inhibitors. Attempts to determine relative efficiencies for strong inhibitors were made as well. A better technique for comparing strong inhibitors was desired in order to check these efficiencies and extend or verify the Hammett plot of the previous work (15). The basic purpose of this work was

to study the feasibility of a competitive method for comparing inhibitors wherein the disappearance of one of the inhibitors is followed spectrometrically.

EXPERIMENTAL

Reagents: Cumene used in this study was Eastman red label. The cumene was repeatedly washed with concentrated sulfuric acid until the acid layer showed no further yellow coloration. Washing with a saturated solution of sodium bicarbonate followed and was continued until no further bubbling occurred upon washing with fresh solution. This was followed by washing with distilled water and drying overnight with anhydrous sodium sulfate. The dried cumene was distilled through a thirty-inch packed column. The fraction boiling at 150.0-150.5° was collected.

A vapor-phase chromatogram of the distilled cumene showed only one negligibly small peak occurring before the main peak. This peak was also present in the cumene taken directly from the bottle; however in the distilled product it was reduced in size. The cumene taken directly from the bottle showed, in addition, two peaks not present in the distilled product. Comparison of the vapor-phase chromatograms of the distilled cumene with those of technical cumyl hydroperoxide and a mixture of cumene and cumyl hydroperoxide seemed to indicate that the small peak for the distilled cumene was not cumyl hydroperoxide. The vapor-phase chromatograms were done at 140°.

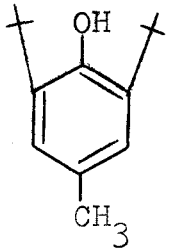
Chlorobenzene was used as the solvent in this study. Reagent grade chlorobenzene was used directly from the bottle without further purification.

Azobisisobutyronitrile (ABN) used in this study as a free radical initiator was recrystallized twice from reagent grade methanol. The ABN was dissolved in methanol at room temperature and then more ABN was dissolved upon heating the solution to about 35°. This solution was cooled in an ice bath and the crystals which formed were removed by filtration. This operation was performed twice. The resulting crystals, dried, melted with decomposition at 100.0 to 100.5°.

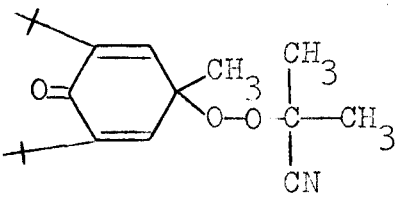
The N,N'-diphenyl-p-phenylenediamine, referred to as the standard inhibitor in this work, was obtained in suitably pure form by alternate recrystallization from dimethylformamide and benzene (three times with each) followed by leaching with petroleum ether, b.p. 30-40°. The original material was obtained from K & K Laboratories, Inc. of New York City. The inhibition period given by a standard solution of the unpurified material (the standard solution was made with the assumption that all the material had the same molecular weight as the pure material would) in a normal oxygen absorption run with cumene as substrate. ABN as initiator, and chlorobenzene as solvent showed that the unpurified material was 70% pure. Thus run was at 70° and 1 atm. pressure.

The alternate recrystallization of the 70% pure material with dimethylformamide and benzene was followed by leaching with petroleum ether in order to remove any remaining oxidation product of the diamine (the diimine). Petroleum ether

seems to dissolve the diimine more readily than it does the diamine. The purified diamine gave a satisfactory inhibition period which indicated a chain-stopping value of 2.2. This agrees with the value obtained in work with this inhibitor by Boozer, Hammond, Hamilton, and Sen (14).



VII



XVII

A cyanoisopropylperoxylated product of 2,6-di-tert.-butyl-p-cresol (VII) having the structure XVII was also prepared and used in this study. ABN and 2,6-di-tert.-butyl-4-methylphenol (VII) in the proper ratio (5 g. of ABN and 6.2 g. of VII) were dissolved in benzene. This solution was poured into a three-necked, round-bottom flask and a stream of oxygen was bubbled through the solution. The reaction was allowed to proceed for ten hours. (This is similar to a procedure reported by Boozer (14) and to a method used by Bickel and Kooyman (5) in an attempted preparation of the compound.) The originally colorless solution became yellow as the reaction proceeded. After ten hours the product was crystallized out of the solution by stripping off the solvent with a stream of air followed by

further evaporation of the solvent under vacuum. The crude yield was 85%. The product was recrystallized from ethanol and gave an essentially white product. It was stored in the refrigerator in a brown bottle under nitrogen. The product was characterized by its infrared spectrum which was the same as that reported in the research notebook of Boozer. An ultra violet spectrum of the compound also helped to verify its structure.

The inhibitors 2,6-di-tert.-butyl-p-cresol, 2,4,6-tri-tert.-butyl phenol, 2,6-di-tert.-butyl-4-methoxy phenol, and phenothiazine were recrystallized twice from ethanol. Hydroquinone, mono-tert.-butyl hydroquinone, 4-methoxy phenol, 2-methyl-4-methoxy phenol, hydroquinone dibenzyl ether, hydroquinone monobenzyl ether, and 2-tert.-butyl-4-methoxy phenol were recrystallized twice from either benzene or petroleum ether or mixtures thereof. These inhibitors, except for the 2,6-di-tert.-butyl-p-cresol which was Eastman red label, were obtained from B. F. Goodrich Company or Universal Oil Company.

Apparatus: The Beckmann DU spectrophotometer was used in the visible region in this investigation. The one centimeter quartz cells used were checked with chlorobenzene in both cells; the absorbance was 0.002. The decision to use the 440 mu absorption to follow production of the diimine of N,N'-diphenyl-p-phenylenediamine was based upon data reported by C. E. Hamilton (unpublished thesis, Iowa

State College). He observed production of a clean peak at 440 mu upon oxidation of the diamine to the diimine.

The gas apparatus used to follow oxidation of cumene by oxygen uptake was essentially the same as that used by Hammond and co-workers (14).

Procedures: All runs were made at 70° and one atmosphere pressure. Except where noted, all runs were made with oxygen as the gas and oxygen uptake was observed on the buret of the gas apparatus. The total volume of liquid in the reaction cell was six ml. Inhibitor solutions were 0.01 M chlorobenzene solutions except where noted. ABN solutions were 0.25 M except where noted. Preliminary runs to determine whether the two inhibitors combined would show additive inhibition periods were done with two ml. cumene, two ml. ABN solution, and one ml. of each of the inhibitor solutions.

The runs which were concluded by absorbance readings were done as follows: two ml. of cumene and two ml. of ABN solutions were used with one ml. of each inhibitor solution. When only one inhibitor was used, the solution was brought up to a volume of six ml. with chlorobenzene. In all runs the gas apparatus was evacuated and then flushed with oxygen; this was done three times before oxygen was admitted for the run itself. Time zero was when water from the 70° bath was

diverted through the jacket of the reaction cell and stirring was begun in the cell. Readings on the gas buret were taken to make sure that inhibition was occurring.

Fifteen seconds before the time desired for the absorbance reading, stirring was stopped and the apparatus was shut down except for circulation of water from the 70° bath. The reaction cell was opened and a sample removed with a five ml. hypodermic syringe. This solution was immediately ejected into an Erlenmeyer flask sitting in an ice bath. The stopwatch was stopped as this operation was performed. In a volumetric flask 1.5 ml. of the cooled solution was diluted to 25 ml. with chlorobenzene. The absorbance of this solution at 440 mu was read in the Beckmann DU spectrophotometer; a slit width of 0.075 was used. Cooling water was circulated through the carriage of the Beckmann DU while the quartz cells containing the solution were in the carriage.

The 0.01 M hydroquinone solution used in this work contained 10% acetonitrile. Hydroquinone is not soluble in pure chlorobenzene.

RESULTS

The immediate data obtained from this project were mostly absorbances at given times of solutions containing initiator, substrate, and standard inhibitor (N,N'-diphenyl-p-phenylenediamine) and of solutions containing initiator, substrate, standard inhibitor, and a second inhibitor (see Table I). The absorbances were read at 440 mu. These absorbances were converted to diimine concentrations (concentrations of the oxidation product of the standard inhibitor) using the value of 6.69×10^3 as the molar extinction coefficient. Since the initial concentration of the standard inhibitor was known (1×10^{-4} M) and the diimine concentration was measured, the concentration of standard inhibitor remaining in those solutions not having a second inhibitor present, $[In_1]$, was calculated for a given time.

In the competitive runs the residual concentration of the second inhibitor was calculated in the following way. The amount of diimine produced in the competitive runs was always smaller than the amount produced in noncompetitive runs during the same time interval. The difference was taken to be equal to the amount of the second inhibitor consumed during the interval $[In_2]$. The concentrations $[In_1]$ and $[In_2]$ were used to calculate the relative efficiencies of the inhibitors recorded in Table I:

TABLE I

Inhibitor Compared and Time (t) of Removal of Sample	A_1 (Absorbance of solution containing only standard inhibitor)	A_2 (Absorbance of solution containing 2 inhibitors)	$[In_1]_t$ (Concentration of standard at time t) x 10^5	$[In_2]_t$ (Concentration of second inhibitor at time t) x 10^5	$\log[In_1]_o - \log[In_1]_t$	$\log[In_2]_o - \log[In_2]_t$	Relative Efficiency
1. 2,6-di-tert.-butyl-p-cresol;t=6 min.	0.312	0.278	5.34	9.50	0.273	0.023	0.094
2. 2,6-di-tert.-butyl-p-cresol;t=8 min.	0.422	0.375	3.70	9.30	0.432	0.032	0.074
3. 2,6-di-tert.-butyl-p-cresol;t=10 min.	0.526	0.472	2.13	9.18	0.672	0.037	0.055
4. 2,4,6-tri-tert.-butyl-phenol; t = 6 min.	0.312	0.277	5.34	9.50	0.273	0.023	0.084
5. 2,4,6-tri-tert.-butyl-phenol; t = 10 min.	0.526	0.484	2.13	9.37	0.672	0.028	0.042
6. 2,6-di-tert.-butyl-4-methoxyphenol;t=6min.	0.312	0.218	5.34	7.92	0.273	0.102	0.374
7. 2,6-di-tert.-butyl-4-methoxyphenol;t=10 min.	0.526	0.339	2.13	7.21	0.672	0.142	0.212
8. phenothiazine;t= 8 min.	0.422	0.387	3.70	9.50	0.432	0.022	0.051
9. phenothiazine;t=10 min.	0.526	0.479	2.13	9.29	0.672	0.032	0.048
10. 2-methyl-4-methoxy-6-tert.-butylphenol;t = 10 min.	0.526	0.465	2.13	9.09	0.672	0.041	0.061
11. 2-tert.-butyl-4-methoxy-phenol;t = 10 min.	0.526	0.503	2.13	9.64	0.672	0.016	0.024
12. 2-methyl-4-methoxy-phenol; t = 10 min.	0.526	0.511	2.13	9.76	0.672	0.011	0.016
13. hydroquinone monobenzyl ether; t = 10 min.	0.526	0.519	2.13	9.89	0.672	0.005	0.007
14. hydroquinone dibenzyl ether; t = 10 min.	0.526	0.510	2.13	9.76	0.672	0.011	0.016

$\text{Log}[In_2/\ \text{Log}\ In_1]$ = relative efficiency compared to N,N'-diphenyl-p-phenylenediamine (standard)

$[In_1]_o = [In_2]_o = 1 \times 10^{-4}$ M

(1) $2RO_2\cdot + In_1 \xrightarrow{k_{t1}}$ Products

(2) $2RO_2\cdot + In_2 \xrightarrow{k_{t2}}$ Products

(3) $-d[In_1]/dt = k_{t1}[In_1][RO_2\cdot]^2$

(4) $-d[In_2]/dt = k_{t2}[In_2][RO_2\cdot]^2$

(5) $d[In_2]/d[In_1] = (k_{t2}/k_{t1})[In_2]/[In_1]$

(6) $\{\log[In_2]_0 - \log[In_2]_t\}/\{\log[In_1]_0 - \log[In_1]_t\}$
$= k_{t2}/k_{t1}$ = Relative Efficiency

In the final expression the subscripts of the concentrations $[In_2]$ and $[In_1]$ refer to time. For example $[In_2]_0$ is the initial concentration of the second inhibitor while $[In_2]_t$ is the concentration of the second inhibitor at the given time t.

The calculated relative efficiencies are listed in Table I. Only the relative efficiency of 2,6-di-tert.-butyl-4-methoxyphenol is notably different from the others. The relative efficiency of 4-methoxyphenol is not included in this table since it was too low to be measured. According to Table I the calculated relative efficiency of an inhibitor decreases with time. However if only the calculated relative efficiencies for a given time such as 10 minutes are considered, they seem to fall into two groups (except for 2,6-di-tert.-butyl-4-methoxyphenol). For example, 2,6-di-tert.-butyl-p-cresol, 2,4,6-tri-tert.-butylphenol, phenothiazine, and 2-methyl-4-methoxy-6-tert.-butylphenol constitute one group of inhibitors with similar relative efficiencies. The other group with similar relative

efficiencies would consist of 2-tert.-butyl-4-methoxyphenol, 2-methyl-4-methoxyphenol, hydroquinone dibenzyl ether, and hydroquinone monobenzyl ether.

Figure 1 is a calibration curve for those solutions containing only standard inhibitor. This graph shows that there is a normal linear relationship between increasing diimine concentration (as measured on the time scale) and the absorbance of the solutions. Figure 2 shows that this linear relationship also is valid in the presence of a second inhibitor (2,6-di-tert.-butyl-p-cresol) except for a slight curvature when nearly all of the standard inhibitor has been converted to diimine.

According to figure I the inhibition period of the standard inhibitor is 12 3/4 minutes. This agrees exactly with the inhibition period obtained in oxygen absorption runs where the end of the inhibition period is the time at which the rate of oxygen uptake becomes that of the uninhibited reaction. Oxygen absorption runs with initiator, substrate, and two inhibitors in solution (standard inhibitor plus one other) showed that the inhibition periods of the inhibitors are additive. Oxidation rates during the inhibition period were measured for the standard inhibitor and two other inhibitors in order to calculate relative efficiencies in the same manner as Hammond and co-workers (15). Relative efficiencies of 0.71 for 2,4,6-tri-tert.-butylphenol and of 0.66 for 2,6-di-tert.-butyl-p-cresol

2 ml. cumene
2 ml. 0.25 M ABN
1 ml. 0.01 M N,N'-diphenyl-p-phenylenediamine
1 ml. chlorobenzene

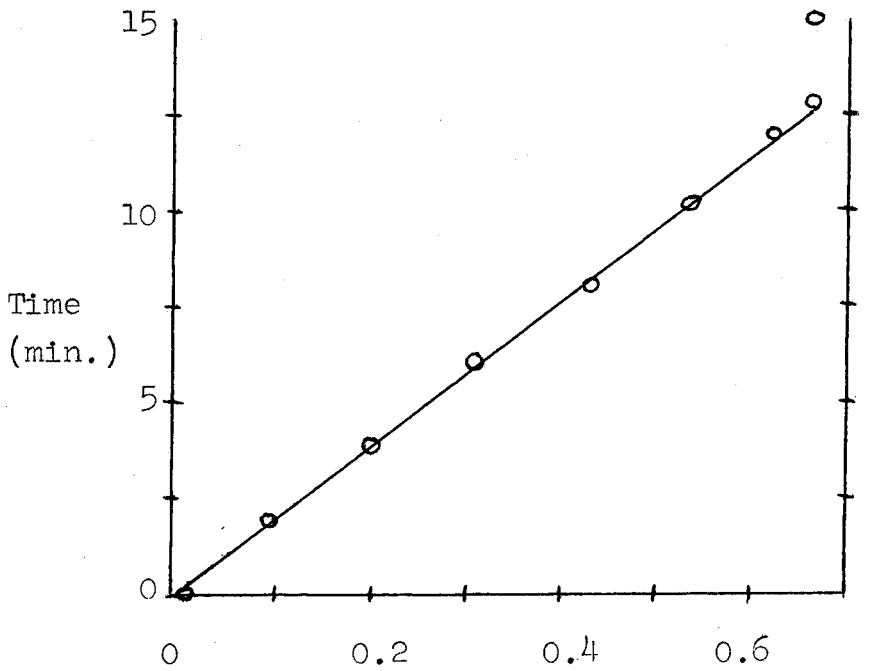


FIGURE 1

2 ml. cumene
2 ml. 0.25 M ABN
1 ml. 0.01 M N,N'-diphenyl-p-phenylenediamine
1 ml. 0.01 M 2,6-di-tert.-butyl-p-cresol

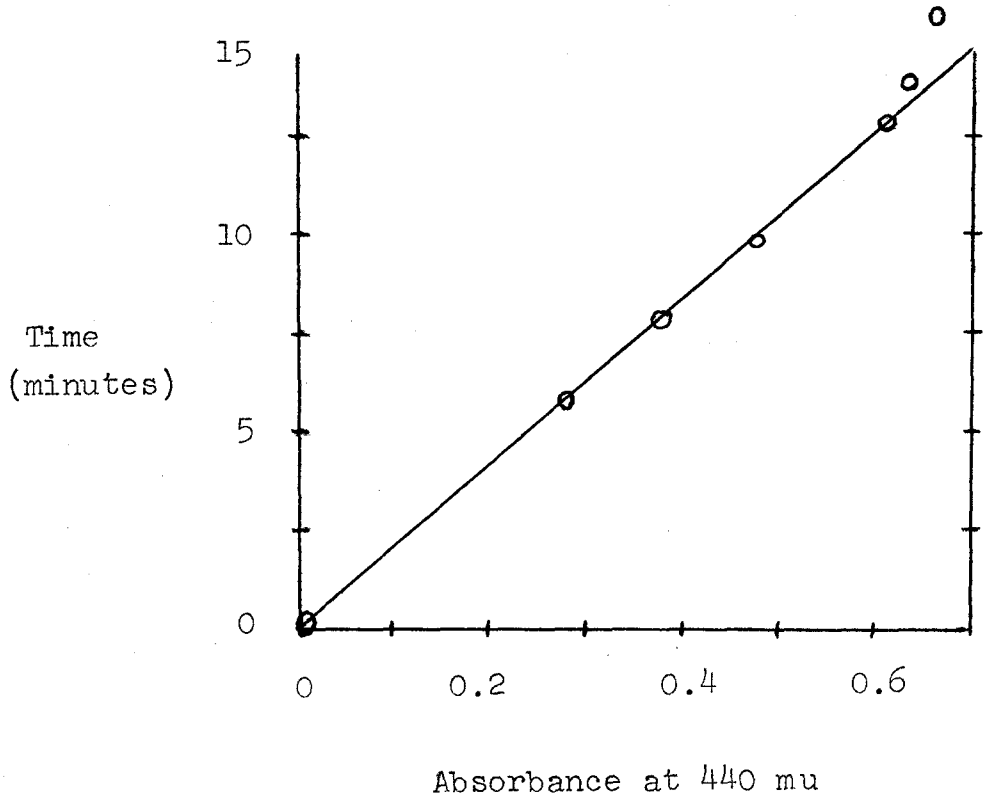


FIGURE 2

were obtained. These relative efficiencies compare poorly with those reported in table I for the competitive technique.

Some competitive runs in which initial concentrations of the inhibitors were varied were also carried out (Table II). All other runs in this investigation involved initial concentrations of 1×10^{-4} M for any inhibitor present. Variation in the initial concentration of 2,6-di-tert.-butyl-p-cresol does not seem to affect the diimine concentration. Variations in the initial concentration of the standard inhibitor do seem to have a slight affect on the diimine concentration at a given time.

The initiator concentration was also varied in some runs in which the diamine was the only inhibitor (Table III). The results seem to indicate that initiator concentration is first order with respect to termination rate as measured by the diimine concentration at different times. (The last two items in Table III indicate exactly a first order relationship while the first two items indicate approximately a first order relationship.)

Competitive runs in which the second inhibitors were hydroquinone and mono-tert.-butyl hydroquinone gave unusual results. No quinonediimine appeared until nearly all of the hydroquinone was used up. Diimine appeared in the solution only when that part of the inhibition period attributable to one inhibitor alone was over. The diimine concentration then increased linearly with time. Mono-tert.-butyl

TABLE II

Initial Inhibitor concentrations			
Standard (N,N'-diphenyl-p-phenylenediamine)	2,6-di-tert.-butyl-p-cresol	Time (minutes)	Concentration of quinonediimine
1×10^{-4} M	1×10^{-4} M	8	5.60×10^{-5} M
1×10^{-4} M	2×10^{-4} M	8	5.60×10^{-5} M
2×10^{-4} M	1×10^{-4} M	8	5.71×10^{-5} M
1×10^{-4} M	1×10^{-4} M	6	4.16×10^{-5} M
5×10^{-5} M	1×10^{-4} M	6	3.46×10^{-5} M
1×10^{-4} M	----	8	6.30×10^{-5} M
2×10^{-4} M	----	8	6.98×10^{-5} M
1×10^{-4} M	----	6	4.66×10^{-5} M
5×10^{-5} M	----	6	4.09×10^{-5} M
5×10^{-5} M	----	8	6.03×10^{-5} M

TABLE III

Initial Concentration of Azo-bis-isobutyronitrile	Time (minutes)	Concentration of quinonediimine
0.250 M	6	4.66×10^{-5} M
0.380 M	6	6.53×10^{-5} M
0.250 M	12	9.30×10^{-5} M
0.125 M	12	4.65×10^{-5} M

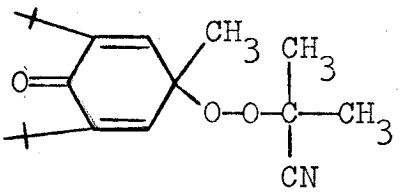
hydroquinone gave the same results. A 50% increase in the initial concentration of mono-tert.-butyl hydroquinone in solution increased by 50% the time preceding the appearance of any diimine in the solution.

A run with cumene, initiator, and only the standard inhibitor was allowed to proceed until the inhibition period was over and all of the diamine had been converted to quinone-diimine. Only at this point was a second inhibitor, hydroquinone, added. The bright orange coloring of the solution faded immediately. The diimine concentration dropped from 1×10^{-4} M to 1.30×10^{-5} M. Apparently hydroquinone has the power to reduce diimine to diamine. This could explain the unusual results of the competitive runs with hydroquinones.

Some runs were made with XVII in order to determine whether or not the oxidation product of an inhibitor would have any effect on the competitive runs. When XVII was heated to 70° in solution with only the standard inhibitor, no diimine appeared in solutions blanketed with either oxygen or nitrogen. A solution of the standard inhibitor by itself under oxygen at 70° did give a very faint yellow color after 12 minutes although there was no detectable absorption at 440 mu. In competitive runs with XVII as the second inhibitor, the diimine concentration was always somewhat lower at a given time than expected. At eight minutes the diimine concentration was measured as

5.73×10^{-5} M and 5.95×10^{-5} compared with an expected value of 6.30×10^{-5} M which was obtained in a noncompetitive run with the standard inhibitor being the only inhibitor present. At ten minutes the diimine concentration was 7.47×10^{-5} M as compared to the expected value of 7.77×10^{-5} M.

XVII



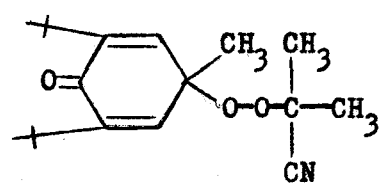
A run was made with equimolar amounts of standard inhibitor and XVII present as well as initiator and substrate. The inhibition period was 13.75 minutes whereas it should have been 12.75 minutes if the standard was the only inhibitor present. A run with initiator, substrate, and XVII gave no inhibition period. However if the inhibition period attributable to XVII had been only one minute, it might not have been detectable.

Table IV contains data which indicates the degree of reproducibility of the experimental data. The runs grouped together contained the same materials in solution at the same concentrations; as shown in the table, the absorbances of these solutions were also read at the same times. The largest deviation is for runs B and III whose solutions at 16 minutes have a mean absorbance value of $0.659 \pm .009$ at 440 mu.

TABLE IV

Run number	Time (minutes)	Absorbance of solution at 440 mu	Diimine Concentration x 10^5 (M)
	Runs with only N,N'-diphenyl-p-phenylenediamine present as inhibitor		
D	0	0.012	0.18
IV.b.	0	0.012	0.18
XIV	0	0.004	0.06
XXVI	8	0.415	6.21
XXII	8	0.422	6.29
VII	8	0.432	6.45
C	6	0.316	4.72
VI	6	0.312	4.67
	Runs with N,N'-diphenyl-p-phenylenediamine and compound XVII present		
XXI	8	0.383	5.72
XXIX	8	0.398	5.95
	Runs with N,N'-diphenyl-p-phenylenediamine and 2,6-di-tert.-butyl-p-cresol present		
B	16	0.650	9.72
III	16	0.668	9.97
	Runs with only N,N'-diphenyl-p-phenylenediamine (Since these times are over 12.75 minutes, the inhibition period, the absorbances should be the same.)		
X	13	0.669	10.0
XI	15	0.669	10.0

XVII

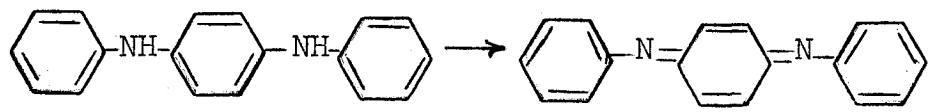


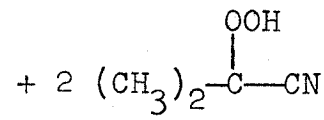
DISCUSSION

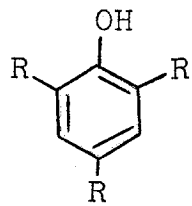
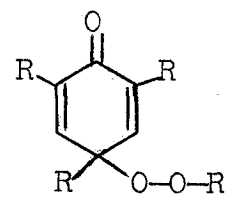
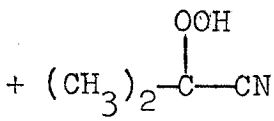
Relative efficiencies obtained by the competitive technique developed in this study compare poorly with relative efficiencies obtained by measurement of oxidation rates during the inhibition period. However, estimation of relative efficiencies by comparison of the slopes of oxidation curves during the inhibition period is somewhat arbitrary since the graph of oxygen uptake during inhibition may be a continuous curve instead of a straight line. In any case there is some curvature (gradual increase in oxidation rate) near the end of the inhibition period.

Besides the uncertainty of the estimated inhibited oxidation rate due to curvature of the oxidation plot, there is uncertainty as to whether or not this plot simply represents the uptake of oxygen. The termination reaction may yield gaseous products, thereby lowering the apparent oxidation rate. Different types of inhibitors may give different stoichiometric amounts of gases upon terminating chains. This difference may occur because of differences in the chemistry of initiator units. The chemistry of initiator fragments may be important because chains are very short during inhibition. For example, a diamine might bring about termination and give twice as many moles of gas as a phenol:

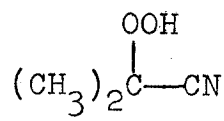
$$RO_2\cdot = (CH_3)_2\overset{\overset{OO\cdot}{|}}{C}-CN \qquad \text{(XVIII)}$$

(7) $2RO_2\cdot$ + 



(8) $2RO_2\cdot$ +   + 

(XIX)

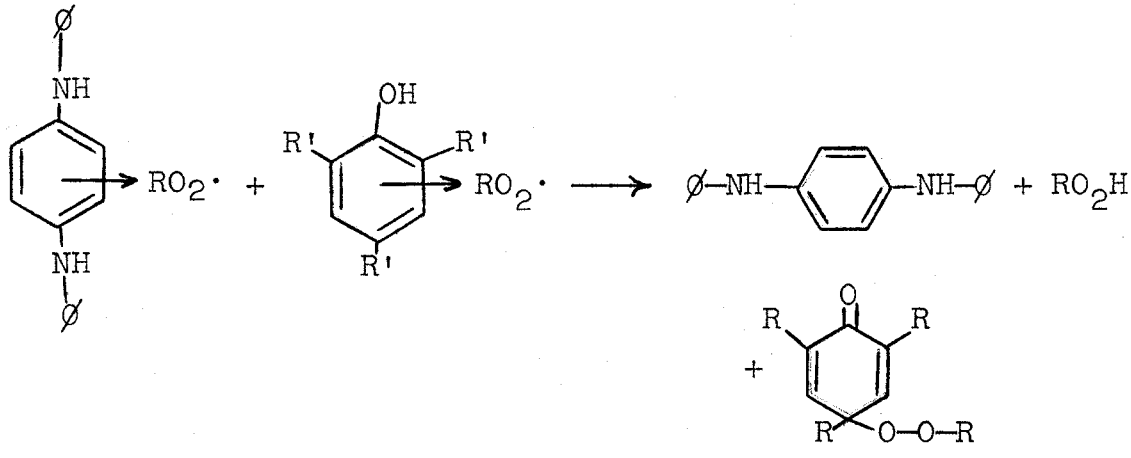
(9)  $\longrightarrow$ CH_3COCH_3 + HCN + other gaseous products

(XIX)

The diamine gives twice as many moles as does the phenol of a presumably unstable peroxide.

Relative efficiencies determined by the competitive technique show a decrease with time according to Table I. The relative efficiencies determined for 2,6-di-tert.-butyl-4-methoxyphenol at 6 minutes and 10 minutes are especially significant since their difference is obviously too large to be attributed to experimental error. One possible explanation of this variation of relative efficiency with time would be that the competing inhibitors interact in some

manner. For example, the complexes formed by the diamine inhibitor and the phenolic inhibitor after they had each reacted with one $RO_2\cdot$ could react in the following manner:



This would initially cause the diamine to disappear more slowly at first than if there were no interaction. The result would be an apparent decrease in the efficiency of the phenol later in the inhibition period.

Another possible explanation for the variation of relative efficiency of the phenolic inhibitors with time would be that the diamine inhibitor, the standard, is involved in some side reaction which has nothing to do with the competing inhibitor. This side reaction could consist of direct oxidation of the diamine by oxygen or initiation of radical chains by the diamine. Such side reactions for amine inhibitors have been suggested by others (39). This side reaction might occur to such a small extent that variations it might cause in the inhibition period would not be detectable. However, such side reactions of inhibitors, if considered detectable,

might be responsible for the deviation of their chain-stopping values (n values) from integral numbers (14). If the diamine, for example, has side reactions independent of the competing inhibitor, these side reactions would occur and affect the inhibition period even if the competing inhibitor were not present. Thus, when both inhibitors are present, their inhibition periods would still be additive providing that initial concentrations of the inhibitors in the competitive run were the same as they were in the non-competitive runs. This was the case in this study.

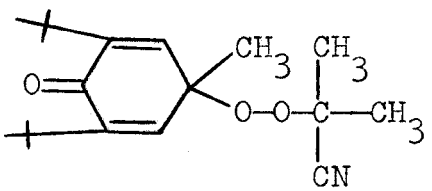
If the side reaction of the diamine also takes up a little oxygen, relative efficiencies determined by inhibited oxidation rates would be even somewhat less reliable than if the only trouble with them was production of differing quantities of gaseous products from breakdown of termination products. However, breakdown of termination products, if it occurs according to the equations on page 46, may not give much difference in the molar amounts of gaseous termination products for diamine and a phenol. If the phenol is not of nearly the same efficiency as the diamine, it will stop mostly alkylperoxy radicals. This means that both termination processes will yield almost the same molar quantity of XIX (for the phenol XIX would occur from initiation products). Therefore the large discrepancy in relative efficiencies obtained with the competitive and noncompetitive methods require either that there are other termination prod-

ucts that give gaseous products or that the inhibitors themselves are involved in side reactions which take up oxygen.

Small deviations from expected results obtained when initial concentrations of the inhibitors were varied can also be explained by assuming that the diamine inhibitor is involved in a side reaction. If the side reaction is first order or higher, an increase in the initial concentration of diamine should show some increase in the rate of appearance of diimine while, correspondingly, a lower initial concentration of diamine should show some decrease in the rate of appearance of diimine. The results of this study agree with this conclusion. Whether diamine is the only inhibitor present or not, an increase in initial diamine concentration gave a small increase in diimine concentration at a given time. A decrease in initial concentration of diamine gave a slightly decreased diimine concentration at a given time. Changing the initial concentration of the competing inhibitor had no effect on the rate of appearance of diimine. This result is expected if the competing inhibitor functions only as a chain terminator and the diamine alone is involved in side reactions. If both inhibitors in the competitive runs only stopped chains, then variation of the initial concentration of either inhibitor should not change the rate of appearance of diimine at all. Although some of the deviations obtained fall within the range of experimental error,

the larger ones do not (see Table IV for reproducibility data). The deviations are, therefore, small but real.

The results of this investigation apparently indicate that compound XVII had a trace of inhibitor (2,6-di-tert.-butyl-p-cresol) left in it. This is probably why XVII acted as if it were competing somewhat with the diamine in the runs with initiator, substrate, diamine, and XVII. If XVII and the diamine did react, the XVII would presumably oxidize the diamine to diimine, thus showing an increased rate of appearance of diimine instead of the decreased rate of appearance observed. If XVII did have a trace of inhibitor in it, the assumption that the products of the phenolic inhibitors do not affect the standard inhibitor is reasonable.



XVII

The most interesting result obtained from these studies is that hydroquinones apparently are capable of reducing diimines to diamines. In the competitive runs where a hydroquinone was the second or competing inhibitor, the hydroquinone appears to have been reducing diimine back to diamine and stopping chains at the same time. The diamine competed with the hydroquinone, but as soon as any diimine was produced due to chain stopping, it was reduced by the hydroquinone.

Thus by continually reducing diimine, the high kinetic reactivity of the diamine may be exploited in systems in which it is not feasible to use the diamine itself in high concentrations. Therefore the work with hydroquinones in this study yielded an interesting and valuable example of a type of synergism never before observed.

The relative strengths of the inhibitors compared in this study (Table I) do seem to vary with the electron-repelling abilities of the substituent groups on the aromatic ring of the inhibitor molecule. This fact verifies the concept that the strength of an inhibitor depends on the electron density of its aromatic nucleus. The results in Table I also show that steric hindrance at both ortho positions is much more effective than having a bulky group at just one ortho position. An inhibitor with only one bulky ortho group appears to be no more efficient than an inhibitor having the one bulky ortho group replaced by a methyl group. The strongest inhibitor is obtained by combining maximum steric hindrance with maximum electron density in the aromatic nucleus. Fulfilling only one of these two requirements considerably reduces the strength of the resultant inhibitor.

In summary, the assumption that the diamine standard inhibitor is involved in a side reaction of some sort may explain the decrease with time of the relative efficiencies of the competing inhibitors in this study. It may also help to explain why the relative efficiencies obtained from

inhibited oxidation rates do not agree with those obtained by the competitive technique, although the production of gaseous termination products may also contribute to the discrepancy. Small deviations from expected results upon varying initial inhibitor concentrations may also be explained in terms of a side reaction of the standard inhibitor. The fact that there was no deviation with a phenolic inhibitor but that there were deviations with diamine alone caused the exclusion from consideration of the possibility of side reactions for the phenols. This is compatible with previous findings (39).

Hydroquinones have been found to reduce diimine back to standard diamine while stopping autoxidation chains. This example of a synergism points the way to a possible exploitation of the high kinetic reactivity of diamine in systems where it may not be very soluble. The oxidation product of a phenol was also found not to affect the diamine standard used in this study. Increasing inhibitor potency was found to be related to increasing ortho steric hindrance and increasing electron density on the aromatic ring of the inhibitor molecule.

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