[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Air Oxidation of Hydrocarbons. III. Mechanism of Inhibitor Action in Benzene and Chlorobenzene Solutions

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

RECEIVED NOVEMBER 6, 1954

Most potent antioxidants possess one of the two structures, ArOH or ArNHR. The labile hydrogens have been viewed as a critical part of the structures and characterization of inhibition products shows that they are indeed removed during the course of the reactions. However, several lines of evidence indicate that hydrogen abstraction is not a discrete first step in the inhibition process. The key observations are: (1) there is no kinetic isotope effect noted if N-D-N-methylaniline and N-D-diphenylamine are compared with the corresponding undeuterated amine; (2) specifically designed compounds such as hydrazobenzene, do not prove to be as potent as inhibitors as their close relatives despite the fact that the former apparently should have a good aptitude for the hydrogen abstraction reaction; (3) the effects of substituents on the inhibitory efficiency of aromatic amines and phenols can be correlated with the Hammett equation in a manner which suggests that electron removal from the inhibitor is of paramount importance; (4) despite the absence of labile hydrogens dimethylaniline shows distinct, but weak, inhibitory action and N,N'-tetramethyl-*p*-phenylenediamine is a strong inhibitor; and (5) it has been found that the latter compound is converted to a complex which may be hydrolyzed to form a Würster dye. These data are held to be consistent with the view that the first step of the inhibition process is the reversible formation of a loose molecular complex between the inhibitor and $RO_2\cdot$. This complex then is destroyed by reaction with a second $RO_2\cdot$ radical.

The empirical generalization that most of the valuable commercial antioxidants are either phenols or aromatic amines which retain at least one hydrogen attached to nitrogen has led to the view that the first and rate-controlling step of the inhibition reaction is hydrogen abstraction from the hetero atom.[1]

$$ArOH + RO_2\cdot \longrightarrow ArO\cdot + RO_2H \quad (1)$$

$$ArNHR + RO_2\cdot \longrightarrow ArN\dot{R} + RO_2H \quad (2)$$

While these reactions are quite unlike the first steps involved in the inhibition of vinyl polymerization[2-5] it is evident that there must be mechanistic differences in the two reactions, since compounds which are potent polymerization inhibitors are ineffective as antioxidants. Furthermore, the hydrogen abstraction reactions would in general be exothermic with $RO_2\cdot$ as the attacking radical,[6] whereas the corresponding steps in vinyl polymerization would lead to the formation of C–H bonds and in some cases actually would be endothermic, which is in itself sufficient to eliminate such reactions from consideration as possible inhibitory processes. However, these facts merely serve to demonstrate that reactions 1 and 2 should be considered as possible termination steps. No evidence of a compelling nature ever has been presented to further sustain this view. As the result of the present investigation we have reached the conclusion that the simple hydrogen abstraction mechanism is inadequate to account for our experimental observations. A logical alternative mechanism involving prior addition of alkylperoxy radicals to the aromatic nucleus also has been found to give a poor account of the experimental observations. By a modest modification of the second mechanism it is possible to account for the experimental observations in a satisfactory manner. In this last mechanism it is assumed that $RO_2\cdot$ reacts reversibly with the inhibitor to give a complex which is then destroyed in an irreversible reaction with a second alkylperoxy radical.

Results

Deuterated Amines.—It is reasonable to expect that reaction 1 should show a kinetic isotope effect if the labile hydrogen is replaced by deuterium.[7,8] A normal isotope effect has been observed in the rate of oxidation of a heavily deuterated olefin[9] which can be attributed to a decrease in the rate of the chain-carrying step of the reaction, equation 3, when hydrogen is substituted for deuterium.[10] It also has been found[11] that the rate of the degradative chain transfer reaction of growing polyallylacetate radicals, equation 4, is decreased by a factor of 2.7 by deuteration of the monomer in the allylic position.

$$RO_2\cdot + -\overset{H(D)}{\underset{|}{C}}-C=C\!\!\rangle \longrightarrow RO_2H(D) + \rangle\dot{C}-C=C \quad (3)$$

$$R\cdot + CH_2{=}CHCHOAc \longrightarrow RH(D) + CH_2{-}\dot{C}HCHOAc \quad (4)$$

(with H(D) on the CH$_2$ group)

Figure 1 demonstrates that N-deuterated diphenylamine is not significantly different from the undeuterated amine in its antioxidant action. Similar results have been reported previously[11a] in the case of N-deuterated N-methylaniline.

Special Inhibitors.—Several compounds were studied because they possessed structures which lead to rather definite predictions as to their be-

(1) For key references see: (a) C. E. Boozer and G. S. Hammond, THIS JOURNAL, **76**, 3861 (1954); (b) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).

(2) P. D. Bartlett, G. S. Hammond and H. Kwart, *Disc. Faraday Soc.*, **2**, (1947).

(3) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

(4) S. G. Cohen, *J. Polymer Sci.*, **2**, 511 (1947); THIS JOURNAL, **67**, 17 (1945); **69**, 1057 (1950).

(5) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 162.

(6) Because of the resonance energy of the radicals ArO· and ArNCH$_3$.

(7) H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, **6**, 34 (1935).

(8) F. H. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949); O. Reitz, *Z. physik. Chem.*, **176**, 363 (1936); C. L. Wilson, *J. Chem. Soc.*, 1850 (1936).

(9) R. A. Max and F. E. Deatherage, *J. Am. Oil Chemists' Soc.*, **28**, 110 (1951).

(10) The alternative view that the decrease in the rate of oxidation is due to an increase in the rate of the chain-termination step is regarded as unlikely.

(11) P. D. Bartlett and F. A. Tate, THIS JOURNAL, **75**, 91 (1953).

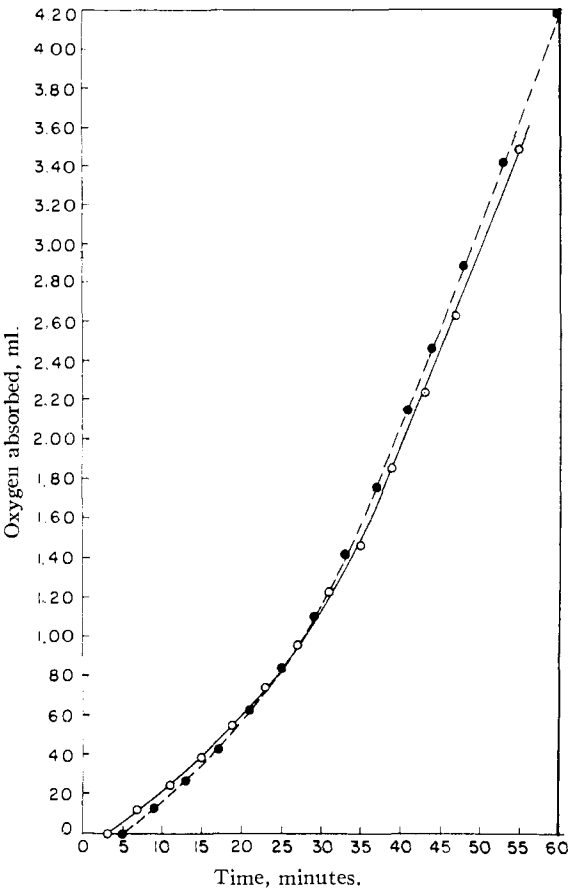
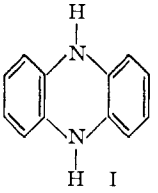
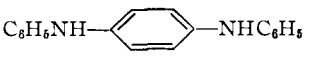


Fig. 1.—Oxidation of tetralin in chlorobenzene inhibited by $(C_6H_5)_2NH$ (O) and $(C_6H_5)_2ND$ (●): (1 × 10^{-5} mole of inhibitor and 6.09 × 10^{-4} mole AIBN in 4 ml. of solution).

havior based upon prior hydrogen abstraction as a rate-determining step in the inhibition process. It was observed that dihydrophenazine (I), hydrazobenzene and dimethylaniline were all very weak inhibitors. No definable induction periods could be observed in the presence of the compounds as the rates of oxidation of cumene and tetralin in their presence were considerable even at the start of a run and increased gradually toward the uninhibited rates. All three compounds were much less effective than N-methylaniline.[1] On the other hand, N,N′-diphenyl-*p*-phenylenediamine (II), which is known to undergo dehydrogenation quantitatively in oxidizing systems, is a very powerful antioxidant. Very sharply defined induction periods were observed in its presence and the rate of oxygen consumption was indistinguishable from that due to oxidation of the initiator.



I



II

Kinetics of Inhibited Oxidation.—With inhibitors with intermediate activity, such as N-methylaniline and phenol, it is feasible to carry out a study of the rate of oxidation of substrates under conditions such that the inhibitor is responsible for most of the chain termination. Both of the aforementioned inhibitors were studied in this manner with the surprising result that initial oxidation rates were found to be proportional to the square root of the initiator concentration and inversely proportional to *the square root of the inhibitor concentration.* The evidence in the case of N-methylaniline is presented graphically in Fig. 2.

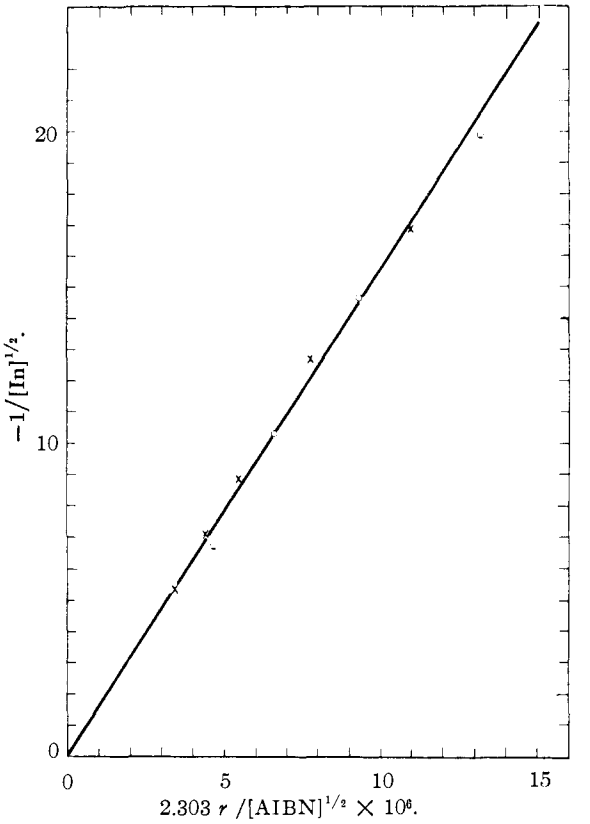


Fig. 2.—Rate of oxidation of tetralin in chlorobenzene at 62.5° with varying amounts of added N-methylaniline: X, [AIBN], 0.225 *M*; O, [AIBN], 0.390 *M*.

Substituent Effects.—In order to obtain a quantitative measure of the influence of substituents on the reactivity of inhibitors it is necessary to devise some method for the comparison of the oxidation rates of a common substrate in the presence of the inhibitors. Without doubt the most reliable procedure is the comparison of initial slopes of oxidation curves in the presence of known concentrations of inhibitors. The comparison is even then complicated unless it is known that the kinetics of inhibited oxidation are the same in all the cases included in a series. For compounds which show the behavior reported above the following analysis is appropriate.

$$\text{rate of initiation} = \text{rate of termination} \quad (5)$$

$$2ak_i[I] = 2k_{In}[RO_2\cdot]^2[In] \quad (6)$$

where

a = the efficiency of the initiator
k_i = the rate constant for initiator decomposition

[I] = initiator concentration
k_{In} = a rate constant which may be a product of a rate constant and an equilibrium constant
[In] = inhibitor concentration

$$r = \frac{-dO_2}{dt} - 2ak_i[I] = k_3[RH]\left\{\frac{ak_i[I]}{k_{In}[In]}\right\}^{1/2} \quad (7)$$

where

k_3 = rate constant for reaction of $RO_2\cdot$ with the substrate, RH
$2ak_i$ [I] = rate of oxygen uptake by the initiator

If rates r_1 and r_2 are measured in the presence of inhibitors In_1 and In_2

$$\frac{r_1}{r_2} = \frac{[RH]_1[In_2]^{1/2}[I]_1^{1/2}k_{In(2)}^{1/2}}{[RH]_2[In_1]^{1/2}[I]_2^{1/2}k_{In(1)}^{1/2}} \quad (8)$$

If the concentrations of initiator and substrate re held constant equation 8 becomes

$$\frac{r_1}{r_2} = \left(\frac{k_{In(2)}\ [In_2]}{k_{In(1)}\ [In_1]}\right)^{1/2} \quad (9)$$

Since the decomposition rate and initiator efficiency of azo-bis-isobutyronitrile are known[12] the values of $k_3/k_{In}^{1/2}$ were determined for inhibited oxidation in the presence of this initiator. In Table I we list values of $k_3/k_{In}^{1/2}$ determined from the oxidation of tetralin in chlorobenzene solution. Relative efficiencies, that is values of k_{In}/k_{In}°, also are shown with phenol as the reference compound. It is noteworthy that similar values for relative efficiencies were found when cumene was used as a substrate.

TABLE I

EVALUATION OF SEVERAL INHIBITORS IN CHLOROBENZENE WITH TETRALIN AS THE SUBSTRATE AT 62.5°

Inhibitor	$k_3/k_{In}^{1/2} \times 10^4$	Relative efficiency[a]
N-Methylaniline	5.27	0.67
Phenol	3.6	1.00
p-Cresol	1.07	3.30
o-Cresol	1.07	3.30
p-Methoxy-N-methylaniline	0.80	4.60
p-Methyl-N-methylaniline	2.5	1.42
p-Bromo-N-methylaniline	7.8	0.45
p-Nitro-N-methylaniline	1970	0.0018

[a] Referred to phenol as a standard.

Bolland and ten Haave[13] have compared the efficiencies of a series of polyhydric phenols as inhibitors in the benzoyl peroxide-initiated oxidation of ethyl linoleate. They established that in the presence of hydroquinone the rates were inversely proportional to inhibitor concentration and the relative efficiencies shown in Table II are calculated on that basis although it is conceivable that equation 7 would apply to some of the less efficient compounds.

TABLE II

RELATIVE EFFICIENCIES OF PHENOLS IN THE INHIBITION OF THE OXIDATION OF ETHYL LINOLEATE INITIATED BY BENZOYL PEROXIDE[20]

Inhibitor	Relative efficiency[a]	Inhibitor	Relative efficiency[a]
Resorcinol	0.50	Hydroquinone	31.2
β-Naphthol	2.4	Toluohydroquinone	46.8
p-Methoxyphenol	5.3	Pyrogallol	93.6
α-Naphthol	17.5	2,3,5-Trimethylhydroquinone	17.8
Catechol	19.7	Naphthohydroquinone	1250

[a] Referred to phenol as a standard.

So little oxidation of substrate occurs in the presence of powerful inhibitors that the differential method of measuring relative efficiencies is of little use. Various integral methods have been used as rough estimates of relative reactivities. We have measured the total amount of oxygen taken up during the inhibition period in presence of a standard concentration of inhibitor and have calculated the relative efficiencies reported in Table III on the assumption that these values are proportional to the values of k_{In}. Egloff and co-workers[14] measured efficiencies by comparing the time required to reach the rapid oxidation rate in the uninitiated oxidation of unsaturated oils.[15] Bickoff measured the time required for oxidation of 20% of the substrate in the presence of a standard concentration of inhibitor to compare the influence of a series of phenols on the rate of oxidation of carotene.[16] A particularly precise series of measurements of relative inhibitor efficiencies in gasoline oxidation was based upon the estimation of the concentration of inhibitor which permitted the uptake of a standard volume of oxygen during an arbitrarily fixed time interval.[17]

TABLE III

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

Inhibitor	Relative efficiency[a]
2,6-Di-*t*-butyl-*p*-cresol	3.3
2,5-Di-*t*-butylhydroquinone	1.3
Diphenylpicrylhydrazyl	1.6
4-*t*-Butylcatechol	14
N-Methylaniline	1.2
p-Methoxydiphenylamine	6.1
Diphenylpicrylhydrazine	1.00
Tetraphenylpyrrole	3.3
β-Naphthol	2.4
Diphenylamine	2.1
N,N'-Diphenyl-*p*-phenylenediamine	16
p,p'-Dihydroxyazobenzene	6.7
p-Hydroxydiphenylamine	5.6
2,2-Di-[*p*-hydroxyphenyl]-propane	1.7

[a] Referred to phenol as a standard.

In order to correlate the results of these various types of measurement by means of the Hammett equation[18] it is necessary to define parent systems for different series of inhibitors. The compounds

(12) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(13) J. L. Bolland and P. ten Haave, *Disc. Faraday Soc.*, **2**, 252 (1947).

(14) G. Egloff, J. C. Morrell, C. D. Lowry, Jr., and C. G. Dryer, *Ind. Eng. Chem.*, **24**, 1375 (1932); C. D. Lowry, J. C. Morrell and C. G. Dryer, *ibid.*, **25**, 804 (1933).

(15) This method, which does not appear to be very significant at first glance, is in actuality a reasonable method of correlation. The rapid oxidation is due to autocatalysis by RO_2H and the length of time required to achieve a rapid rate is, therefore, related to the rate of accumulation of RO_2H during the induction period.

(16) E. M. Bickoff, *J. Am. Oil Chemists' Soc.*, **28**, 65 (1951).

(17) R. H. Rosenwald, J. R. Hoatsen and J. A. Chenicek, *Ind. Eng. Chem.*, **42**, 162 (1950).

(18) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Co., Inc., New York, N. Y., 1940, Chapt. VII.

chosen as reference points were phenol, diphenylamine and N-methylaniline. The values of *log relative efficiency*, as compared to the appropriate parent, for the different compounds were then plotted against the values of the Hammett σ-constants. For polysubstituted compounds the values of the σ-constants were added and *para*-σ-constants were used for *ortho* substituents. All primary and secondary alkyl groups were treated as equivalent and were assigned the same σ-constant as *n*-butyl. An effective σ-constant for the benzo substituent was determined from the efficiency of α-naphthol relative to that of phenol and this value was then used in placing naphthoquinone. The results are shown in Fig. 3. The method chosen for presentation of the data place the three parent compounds at the same point on the plot. If values are plotted with a single reference compound, three parallel straight lines can be drawn through the points with no more scattering of the points than is observed in the Fig. 3. The semi-quantitative data of reference 14 have not been included, but they seem to be consistent with the general trend. The ρ-value corresponding to the line drawn through the points is -3.7.

Dielectric Effects on Inhibitor Efficiency.—The oxidation of tetralin in the presence of N-methylaniline was studied in a series of six solvents. The values of $k_3/k_{In}^{1/2}$ are summarized in Table IV.

TABLE IV

EFFECT OF SOLVENT ON THE EFFICIENCY OF N-METHYLANILINE ON THE INHIBITION OF OXIDATION OF TETRALIN AT 62.5°

Solvent	$k_3/k_{In}^{1/2} \times 10^4$	Dielectric constant
Benzene	4.8	2.27
o-Dichlorobenzene	6.0	10.36
Chlorobenzene	5.27	5.62
Nitrobenzene	5.15	34.82
Nitromethane	1.92	35.86
Carbon tetrachloride	0.63	2.23

Detection of an Intermediate.—N,N,N′,N′-Tetramethyl-*p*-phenylenediamine was found to be a fairly potent inhibitor despite the absence of a labile N–H function in its structure. Figure 4 demonstrates that it gives rise to a well defined induction period in oxidations. The lengths of the induction periods led to the assignment of stoichiometric factors of 1.75–1.90 which implies that the substance is capable of terminating two chains per molecule. When the kinetic runs were carried out in nitromethane solution it was noted that a distinct purple color was developed and later dissipated during the inhibition period. No such phenomenon was observed when the oxidation was carried out in chlorobenzene. However, if an oxidation in chlorobenzene was interrupted before the end of the inhibition period it was found that the purple color could be developed by adding nitromethane to the solution. The color faded again upon addition of more chlorobenzene. If water was added to such a chlorobenzene solution a purple color appeared in the aqueous phase which was shown by measurement of the visible absorption spectrum to

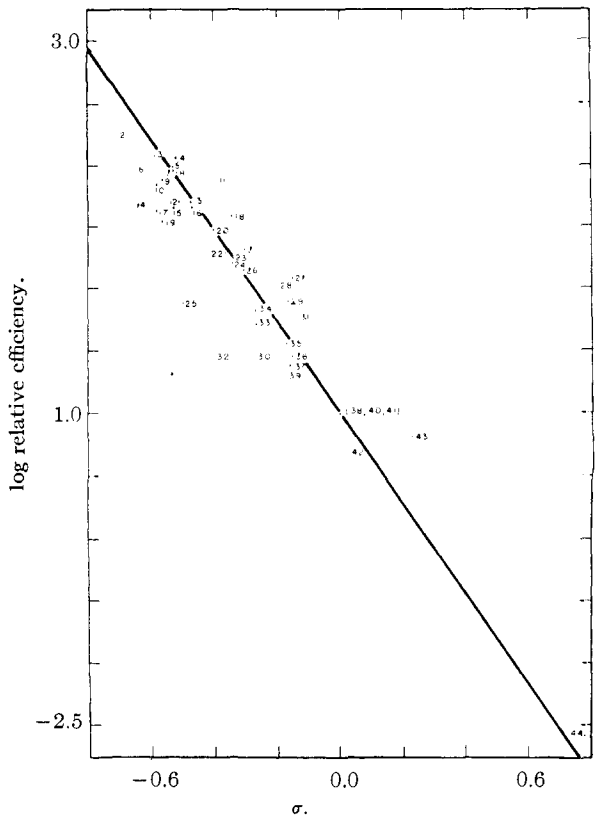


Fig. 3.—Correlation of relative inhibitor efficiencies with the Hammett relationship: 1, 1,4-naphthohydroquinone; 2, 2,3,5-trimethylhydroquinone; 3, N-(2-butyl)-4-aminophenol; 4, 3-*n*-dodecylcatechol; 5, 2,4-dimethyl-6-*t*-butylphenol; 6, 2-amino-4-phenylphenol; 7, pyrrogallol; 8, 4-*t*-butylcatechol; 9, 2,6-di-*t*-butyl-4-methylphenol; 10, 2-*t*-butyl-4-methoxyphenol; 11, 2-phenylhydroquinone; 12, 2,4,6-trimethylphenol; 13, 2,4-dimethyl-6-alkylphenol; 14, 1- and 4-aminophenols; 15, 2,6-dimethoxyphenol; 16, toluohydroquinone; 17, 2,4,6-tri-*t*-butylphenol; 18, 2-*t*-butyl-4-alkylphenol; 19, 2,4-di-*t*-6-methylphenol; 20, hydroquinone; 21, 2-alkyl-4-methylphenols; 22, catechol; 23, α-naphthol; 24, 2,6- and 2,4-dimethylphenols; 25, N,N′-diphenyl-*p*-phenylenediamine; 26, 2-methyl-6-alkylphenols; 27, 2-methyl-4-alkylphenols; 28, 2-*t*-butylphenol; 29, 3-aminophenol; 30, 4-methoxydiphenolamine; 31, 2-alkylphenols; 32, 4-hydroxydiphenylamine; 33, 4-methoxyphenol; 34, 4-methoxy-N-methylaniline; 35, 2- and 4-methylphenol; 36, 4-alkylphenols; 37, β-naphthol; 38, diphenylamine; 39, 4-methyl-N-methylaniline; 40, phenol; 41, N-methylaniline; 42, resorcinol; 43, 4-bromo-N-methylaniline; 44, 4-nitro-N-methylaniline.

be due to the presence of the Würster cation, III.[19] If water was included as a second phase during the oxidation the purple color was developed in the water phase during the reaction. Quantitative absorption measurements showed that as much as 5% of the original charge of inhibitor appeared in the form of the water-soluble dye. The induction period was not shortened by the presence of the water and at the end of the reaction the dye color had disappeared. The hydrolysis of an intermediate therefore is shown to be completely reversible. Appropri-

(19) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940, p. 282.

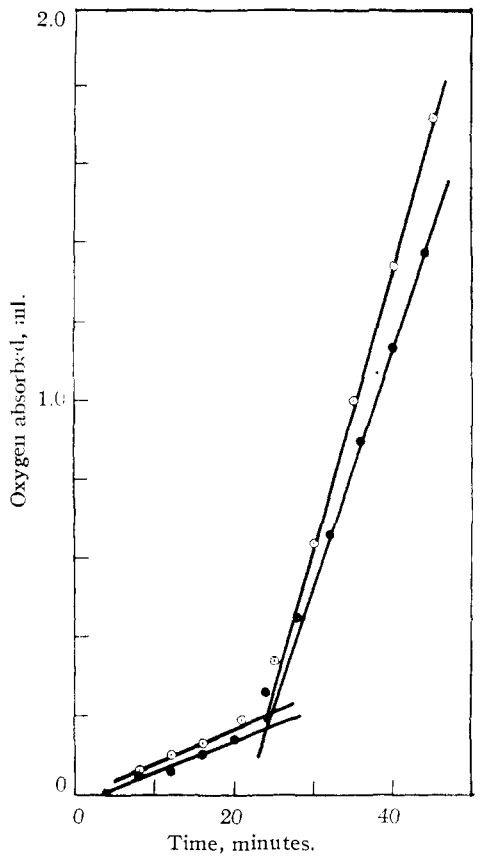


Fig. 4.—Oxidation of cumene in chlorobenzene containing N,N,N′,N′-tetramethyl-*p*-phenylenediamine (6.3 × 10^{-6} mole; 3.05 × 10^{-4} mole of AIBN): O, anhydrous; ●, water added as a second phase.

ate controls were carried out to show that the observed phenomena were dependent upon the coexistence of oxygen and the decomposing initiator in the system. In the absence of initiator the diamine is oxidized by oxygen to give the dye, but the rate of the process is relatively slow.

Discussion

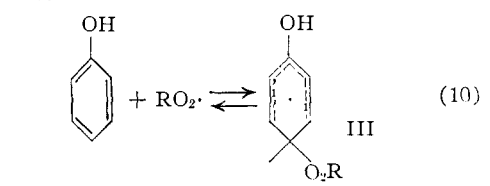
Several lines of evidence argue against reaction 1 as the rate-controlling step in the inhibition reactions. Most directly it is difficult to see any reason for the failure of such a reaction to be slower by a factor of at least two with deutero compound. An effect of this order of magnitude would be very easily measurable with N-methylaniline and diphenylamine since their efficiencies are low enough to permit appreciable oxidation in their presence. In general our data are sufficiently accurate and reproducible to lead us to expect that changes of 20% in the value of $k_3/k_{In}^{1/2}$ would be readily detectable.

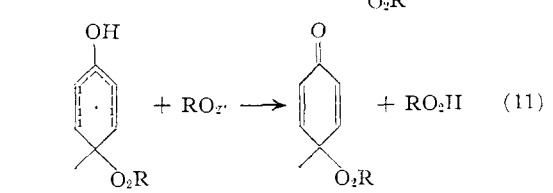
Substituent effects are likewise difficult to comprehend if hydrogen abstraction is a common first step in inhibition. Dimethylaniline and tetramethyl-*p*-phenylenediamine both have measurable inhibitory activity despite the fact that neither has a labile hydrogen. Since methylaniline is a distinctly more potent inhibitor than dimethylaniline, one could maintain that the tertiary amines react by a mechanism which has nothing in common with the behavior of primary and secondary amines. If one adopts this view it becomes quite difficult to account for the behavior of hydrazobenzene and dihydrophenazine. On hydrogen abstraction these compounds should yield radicals of greater stability than that from methylaniline. Similarly it is difficult to see why the presence of a *p*-nitro group should inhibit very strongly the removal of hydrogen from methylaniline.

The general effect of nuclear substituents is to lead one to feel that electron accession from the substituent to the ring or to the functional group is of great importance in determining the substituent effects. The large negative value of ρ is a quantitative expression of this trend. While side-chain radical reactions have been found to fit the Hammett equation[20,21] the ρ-values associated with such reactions are usually very small.

A final argument against prior hydrogen abstraction can be raised on the basis of the kinetic studies with methylaniline and phenol. The observation of half-order dependence of the inhibited oxidation rate on initiator concentration demands that chain termination must be bimolecular in $RO_2\cdot$ even when chains are terminated by the antioxidant. This requires that reaction 1, if it occurs, must be a reversible step with these two inhibitors. While no rigorous argument can be raised against this view it does not seem to be a likely possibility.

It is known that cyclohexadienones are formed by the attack of alkyl peroxy radicals on trisubstituted phenols, and it can be inferred from stoichiometric relationships that similar behavior may occur with other phenols and aromatic amines. Since hydrogen abstraction does not seem to be a likely first step, a logical alternative is the supposition that the first peroxy radical adds to the aromatic nucleus and that hydrogen is lost in a second step as in equations 10 and 11.





Equation 10 is written as reversible in order to account for the kinetics discussed above. There are two chief objections to this formulation. First, it would be expected that bulky groups such as *t*-butyl would inhibit attack at the position to which they are attached. However, it is observed that the effect of *t*-butyl groups is essentially cumulative if they are substituted in positions *ortho* and *para* to a phenolic hydroxyl. Furthermore, the near equivalence of *ortho* and *para* substituents implies that these positions remain nearly equivalent in the

(20) F. R. Mayo, F. M. Lewis and C. Walling, THIS JOURNAL, **70**, 1529 (1948).

(21) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

transition states of the rate-controlling reactions. This is inconsistent with the view that a new bond is formed to such a position before the rate-determining step. The second argument involves consideration of N,N'-diphenyl-*p*-phenylenediamine. It has been found that this compound undergoes nearly quantitative dehydrogenation to IV when it functions as an antioxidant.

IV

If equations 10 and 11 were accepted as representing the mechanism of the reaction of secondary amines and phenols, one would be required to assume that the diamine functions by an entirely different mechanism. The position of the diamine in Fig. 3 indicates that it is, if anything, less reactive than would be expected. The view that it reacts by a fundamentally different mechanism from other compounds would require that it be unusually reactive in order to allow the new mechanism to supersede the common mechanism.

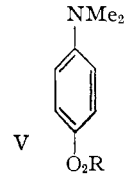
A modification of the above mechanism gives a much better account of the data. If it is assumed that the product of association of $RO_2\cdot$ with the inhibitor is a loose complex rather than an adduct such as III, the substituent effects become much more comprehensible. The stability of molecular compounds is believed to be a function the π-electron densities in the aromatic nuclei[22] and the separation between the partners is probably large enough to make complexing rather insensitive to steric effects. The mechanism then would be represented by equations 12 and 13.

$$RO_2\cdot + In \underset{}{\overset{K_c}{\rightleftharpoons}} [RO_2\cdot \longrightarrow In] \qquad (12)$$

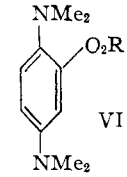
$$[RO_2\cdot \longrightarrow In] + RO_2\cdot \xrightarrow{k'_{In}} \text{products} \qquad (13)$$

The relative values of k_{In}, which would be the product of K_c and k'_{In}, might very well be largely determined by variations in K_c since reaction 13 would probably be a very rapid, unactivated process. It may even be diffusion controlled in many cases. This also accounts for the failure of the deuterated amines to show kinetic isotope effects. However, since the first $RO_2\cdot$ is not rigidly oriented in the complex it is quite possible for reaction 13 to take different paths with different compounds. If two labile hydrogens are available, both of the alkoxy radicals can be converted to hydroperoxide. If only one is present it can be removed while the rest of the structure collapses to form a dienone or dienamine. When there is no labile hydrogen present the reactions of the complex with another radical become relatively slow so that complexing stability is no longer alone responsible for inhibitor potency. Since dimethylaniline and tetramethyl-*p*-phenylenediamine do inhibit oxidation, it is quite possible that they form complexes which react with a second radical to form aromatic substitution products such as V and VI. Since aryl peroxides are unknown and may be highly unstable this proposal can be considered only as tentative.

(22) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).



V



VI

The experiments with tetramethyl-*p*-phenylenediamine indicate that this substance forms something which can accumulate to appreciable concentration and which reacts reversibly with water and nitromethane to form the Würster cation. This does not establish the nature of the intermediate unequivocally but the hydrolysis of the complex seems reasonable.

$$[RO_2\cdot \longrightarrow In] + H_2O \longrightarrow RO_2H + In\cdot^+ + OH^- \qquad (14)$$

Detailed description of the complex is not feasible. The lack of any obvious correlation of inhibitory efficiencies with the dielectric constants of the solvents listed in Table IV discourages the view that structures such as (RO_2^- $In\cdot^+$) make an important contribution to their structure.

Experimental

Materials.—Many of the materials are described in another place.[1] Tetralin was washed with concentrated sulfuric acid until the acid layer showed no more coloration, washed with water, dried and distilled under nitrogen through a 4-foot Oldershaw column, b.p. 204.5–205.0°, $n^{25}D$ 1.5444. Carbon tetrachloride was dried over calcium chloride and distilled. Nitromethane and nitrobenzene were fractionated carefully through an efficient column. The *o*-dichlorobenzene was washed with concentrated sulfuric acid and distilled.

The 9,10-dihydrophenazine was prepared by the method of Rise[23] and recrystallized from chlorobenzene, m.p. 305–306°, in a sealed tube under nitrogen, 270° in an open tube. Some phenazine prepared from the dihydro compound melted at 169°.

N,N,N',N'-Tetramethyl-*p*-phenylenediamine, Eastman Kodak Co., was obtained as the dihydrochloride. The free base was precipitated and recrystallized from aqueous ethanol.

The N-deutero-N-methylaniline and N-deuterodiphenylamine were prepared by exchange in acid solution of the amine with 99.8% deuterium oxide. Each exchange was effected by refluxing the mixture about 30 minutes, removing the water layer and adding fresh deuterium oxide. Five exchanges with a 400% excess deuterium oxide were carried out on 1-g. samples of the amines. Infrared spectra of the amines indicated that at least 60% of the available hydrogens had been replaced by deuterium.

Experiments with the Deuterated Amines.—Both the deuterated diphenylamine and the deuterated N-methylaniline gave oxidation rate curves identical with those observed with the corresponding protonated compounds when they were used to inhibit the oxidation of cumene and tetralin in chlorobenzene at 62.5° (Figs. 1 and 2). The N-methylaniline is not a very good inhibitor, so the result is not due to the inhibitor being so good that it is insensitive to moderate changes.

Inhibition Periods and Oxidation Rates.—The procedures used were the same as those described before.[1]

Observations Concerning N,N,N',N'-Tetramethyl-*p*-phenylenediamine.—This inhibitor proved to be very susceptible to air oxidation and was therefore difficult to obtain in a pure state. Furthermore, the standard solutions of this inhibitor were found to change appreciably in less than a day. For these reasons the inhibition periods in Fig. 3 correspond to a stoichiometry of less than two. During the course of the inhibition period in the experiments in nitromethane the solution took on the characteristic purple color of the Würster cation, but the color had disappeared by the end of the inhibition period. This color also could be developed by addition of water to a chlorobenzene solution of

(23) C. Rise, *Ber.*, **19**, 2206 (1886).

the partially oxidized inhibitor. The visible absorption spectrum of one such solution was measured and the characteristic absorption maxima at 565 and 615 mμ were used to estimate the concentration of the ion. The intensity of the absorption was about 5% of what it would have been if all of the inhibitor were present as the Würster cation. Identical observations were made in an experiment in which water was added before the reaction was started. Blank experiments were run without initiator to determine that the formation of the Würster cation was not due to air oxidation. The cation was formed but only to a barely perceptible extent during the time involved in these experiments.

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

AMES, IOWA

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Efficiency of Radical Production from Azo-bis-isobutyronitrile

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

RECEIVED NOVEMBER 6, 1954

Radicals are produced in pairs by the thermal decomposition of azo-bis-isobutyronitrile (AIBN). It is shown that an appreciable fraction of these radicals react with each other before they diffuse apart. The evidence consists of the demonstration that various radical scavengers such as butyl mercaptan, α,α-diphenyl-β-picrylhydrazyl (DPPH), iodine and oxygen do not capture the decomposition products quantitatively. Quantitative efficiency measurements have been carried out with the last three scavengers. It is shown that DPPH does not give an accurate count of the radicals produced but leads to variable underestimation of the rate of radical production. However, efficiencies measured by iodine scavenging and by a method involving the use of oxidation inhibitors give quantitative agreement in five different solvents.

There are various indications that the efficiency of production of free radicals in thermal decomposition reactions may not reach 100%. Arnett and Peterson[1] have reported that the efficiency of initiation of styrene polymerization by AIBN is only about 60% and that the efficiency of initiation of other monomers by the same initiator varies upward from this figure reaching 100% with acrylonitrile. Bateman and Morris[2] found evidence that the initiation of oxidation of butyl acetate, tetralin and digeranyl by AIBN and benzoyl peroxide was measurably inefficient. Inefficiency in radical production from benzoyl peroxide has been observed frequently but is, at least in part, interpretable as being due to the wastage of the initiator by chain decomposition.[3] However, it has been shown repeatedly that the decomposition of azonitriles is free of such complications.[4,5] A reasonable explanation of the inefficiency is found in the observation that the recombination and disproportionation of the radicals produced from the initiator may be diffusion controlled reactions. If this is the case some of the radical pairs produced in the primary decomposition process may destroy each other before they diffuse apart. It has previously been suggested on the basis of a study of the fate of benzoyloxy radicals produced in the decomposition of benzoyl peroxide that such "cage effects" may account for some of the anomalous behavior exhibited by these radicals.[6]

It was the purpose of the present study to carry out a careful investigation of the efficiency of radical production from AIBN by carrying out the decomposition in the presence of efficient radical scavengers. Efficiencies can be studied either by comparing the rate of disappearance of the scavenger with the rate of decomposition of AIBN or by studying the products formed from the azo compound.

Experimental

Azo-bis-isobutyronitrile was recrystallized twice from aqueous alcohol. The substance melted at 102° with decomposition. Infrared spectra as well as nitrogen evolution experiments showed the absence of tetramethylsuccinonitrile.

***n*-Butyl Mercaptan.**—Eastman Kodak white label material was dried over Drierite and fractionated twice in nitrogen atmosphere. The concentrations of mercaptan in each of the mixtures were determined accurately by the iodine method.[7]

α,α-Diphenyl-β-picrylhydrazyl was prepared by the method of Goldschmidt and Renn,[8] and was purified by recrystallizing from chloroform (m.p. 140°). Solutions of DPPH in the various solvents used showed an absorption maximum at 5200 Å. and obeyed Beer's law throughout and beyond the range of concentrations used in the present work.

Baker and Adamson reagent quality resublimed iodine was used. Solutions of iodine in carbon tetrachloride, benzene, toluene, chlorobenzene and nitromethane showed absorption maximum at 5200, 5000, 5100 and 4800 Å., respectively. Optical density measurement in the various solvents were carried out at the respective wave length of maximum absorption as cited above. A slit width of 0.02 mm. has been used in every case.

Solvents.—Toluene, carbon tetrachloride, chlorobenzene, nitromethane and benzene were purified, dried and fractionated by usual methods.

Studies with *n*-Butyl Mercaptan.—AIBN (8.20 g., 0.05 mole) was dissolved in 250 ml. of solvent containing known amounts of *n*-butyl mercaptan. The mixture, contained in a liter flask, was frozen in a Dry Ice-acetone-bath, evacuated and sealed under vacuum. The sealed flask was immersed in an oil-bath maintained at 80 ± 0.1°. Reaction was allowed to take place for about 20 hours which equals 16 half-life periods for the decomposition of AIBN at 80°. The flask was cooled, opened, and the solvent and mercaptan were removed by evaporation under reduced pressure at room temperature. The residue, usually a mixture of yellowish oil and white crystals, was filtered carefully,

(1) L. M. Arnett and J. H. Peterson, THIS JOURNAL, **74**, 2031 (1952); L. M. Arnett, *ibid.*, **74**, 2027 (1952).

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

(3) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); **69**, 2299 (1947).

(4) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

(5) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

(6) G. S. Hammond, J. T. Rudesil and F. J. Modic, *ibid.* **73**, 3929 (1951).

(7) Sidney Siggia, "Quantitative Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 85–86.

(8) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).