OXIDATION OF N,N-DIMETHYLANILINE

II. THE REACTION WITH OXYGEN CATALYZED BY BENZOYL PEROXIDE1

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ABSTRACT

When benzoyl peroxide was used to initiate the reaction of oxygen with *N*,*N*-dimethylaniline, a chain reaction was shown to occur, resulting in an almost quantitative yield of hydrogen peroxide. The reaction was inhibited by mercaptan and benzoquinone, but not by hydroquinone, and was shown to be autoinhibited as well. The rate of oxidation was observed to be much greater in polar solvents, such as acetonitrile or methanol, than in non-polar solvents such as toluene and benzene. Diethyl- and dipropyl-aniline exhibited no chain characteristics under similar conditions, whereas dimethylbenzylamine and dimethyldodecylamine did not react at all.

A mechanism has been postulated involving both semiquinone and peroxide chain carriers which is consistent with all of these observations. From an analysis of the oxidation rates in the presence and absence of mercaptan inhibition, the appropriate rate constants have been determined.

INTRODUCTION

The research described in this series of papers was originally undertaken in an attempt to clear up some of the confusion concerning the mechanism by which tertiary aromatic amines act as inhibitors in hydrocarbon oxidation. In studying the inhibition of cumene autoxidation by dimethylaniline, it became apparent that the amine was being rapidly and preferentially oxidized in the initial stages of the reaction. As the reaction progressed, the amount of retardation increased, indicating that the autoxidation products of the amine are very effective antioxidants. Accordingly, it was realized that in order to understand the antioxidant action of tertiary amines, it was first necessary to investigate the mechanism of their autoxidation.

It was found that highly purified dimethylaniline autoxidized extremely rapidly at 60° C. The highest maximum rate observed for freshly purified dimethylaniline was 2×10^{-4} mole/l. per sec; the corresponding rate measured for pure tetralin was 5×10^{-6} mole/l. per sec. The reaction was initially autocatalytic, and appeared to be also auto-inhibited. The maximum degree of oxidation that could be obtained before the rate began to approach zero was about 2 mole%.

Unfortunately, in all cases the measured rates were irreproducible within an order of magnitude and there appeared little prospect of obtaining useful information under such conditions. It therefore appeared desirable to work at lower temperatures using benzoyl peroxide as an initiator in the hope of minimizing side reactions. Some time after the inception of this work, Horner and Junkermann (2) published some semiquantitative results on this system; however, their postulated mechanism was based primarily on the products isolated in the presence of oxygen and of nitric oxide, and differs in detail from that indicated by the results presented in this paper.

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EXPERIMENTAL

Dimethylaniline, benzoyl peroxide, toluene, acetonitrile, and tetramethylbenzidine were purified as in Part I (1). Hydroquinone (Eastman) was recrystallized from benzene under nitrogen. Benzoquinone (Eastman) was recrystallized from methanol. 1-Dodecanethiol (Humphrey-Wilkinson) was fractionally distilled; a middle cut boiling at 126° C and 6 mm (of nitrogen) was used. Diethyl-, Dipropyl-, methylethyl-, and methylaniline were Eastman White Label grade, and were purified by fractional distillation under vacuum, in a nitrogen atmosphere.

Oxygen Absorption Measurements

Oxygen absorption was measured with an apparatus of the constant pressure type, slightly modified from that described by Cooper and Melville (3). The reaction flask was first cleaned with alcoholic sodium hydroxide, concentrated nitric acid, rinsed five times with distilled water, and flamed while under a pressure of less than 10^{-5} mm. The amine to be studied was transferred to the reaction flask using an all-glass apparatus in the absence of oxygen. Benzoyl peroxide and the inhibitors were added to the flask immersed in liquid nitrogen as solutions in the solvent to be used. The flask was then evacuated and filled with oxygen. It was then placed in a thermostat and shaken at a rate of 200 strokes per minute; zero time was taken as the time at which the pressure stopped increasing (usually 2–3 minutes).

Measurements at different oxygen pressures indicated that the initial rate was independent of the oxygen pressure above about 150 mm; accordingly, most of the results reported were made at an oxygen pressure of 750 mm in order to minimize the possibility of oxygen diffusion controlled kinetics.

RESULTS

Rate Measurements

Highly purified dimethylaniline exhibited no measurable autoxidation at 0° C; however, the addition of a small amount of benzoyl peroxide caused an extremely rapid uptake of oxygen. On oxidation, the solution changed from light yellow to deep red; at very high concentrations of peroxide and amine, a green solid was observed to precipitate. The catalyzed reaction was much less sensitive to the purity of the dimethylaniline than was the high temperature autoxidation reaction. For example, the catalyzed rate of oxidation of a sample taken from a freshly opened bottle was 5.02×10^{-5} mole/l. per sec, while for the highly purified material, the rate was 6.15×10^{-5} mole/l. per sec; the corresponding autoxidation rates were 0 and 2×10^{-4} mole/l. per sec respectively, at 60° C.

The data are summarized in Table I, and some representative oxygen absorption curves are shown in Fig. 1. No induction period was detected; although if it were less than 2–3 minutes, the time required for the reaction mixture to warm to 0° C, it would not have been observable.

The order dependence of the initial rate on peroxide concentration was between 0.5 and 1.0, and increased with increasing amine concentration. With respect to amine concentration, it was between 1.0 and 1.5, and decreased with increasing peroxide concentration. It was found by plotting $(-d[O_2]/dt)_0/[A]_0[P]_0$ vs. $([A]_0/[P]_0)^{1/2}$, where $(-d[O_2]/dt)_0$ is the initial rate of oxygen uptake, and $[A]_0$ and $[P]_0$ are the initial concentrations of amine and peroxide respectively, that the data are closely fitted by an equation of the form:

$$(-d[O_2]/dt)_0 = k_c[A]_0[P]_0 + k_d[A]_0^{3/2}[P]^{1/2}.$$
[1]

The values obtained for k_c and k_d at 0° C and 25° C from least square plots are given in the second and fifth columns of Table VI.

It was also observed that when acetonitrile is used as a solvent, the rate is increased about sevenfold with no apparent change in the order dependence of the rate on peroxide. This is further substantiated by the fact that, for solvent mixtures of acetonitrile and toluene, the ratios of the rates in the mixed solvents to that in the pure toluene (plus amine), when plotted against solvent composition, all fell on a smooth curve, irrespective of the initial concentrations of reactants (Fig. 2). No difference was noted between the

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Reagents

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	(D)	$(-d[\mathrm{O}_2]/dt)_0$, mole/l. sec $ imes 10^6$		[O ₂] _T	[O ₂] _T , mmole/l.		
[A] ₀ , mole/l.	[P] ₀ , mmole/l.	Obs.	Calc.*	Obs.	Calc.†	- [P] _T , mmole/l.	
			At 0° C				
0.213	129	2.99	3.08				
0.371	196	8.11	8.31				
0.479	129	9.21	8.69				
0.500	177	12.0	11.4				
0.631	177	15.5	15.5				
0.631	129	12.4	12.5				
0.631	98.8	9.87	10.5				
0.631	54.0	6.87	7.07				
0.835	36.0	8.14	8.01				
0.972	129	23.0	22.4				
0.982	24.0	7.66	7.94	62	65.5	54	
0.982	24.0	7.72	7.94	63	65.5	48	
1.14	121	27.1	26.3				
1.50	24.0	14.2	14.7	73	79.0	54	
1.97	24.0	21.8	21.8	88	89.4		
2.54	24.0	31.3	31.6	98	100		
2.80	98.8	90.9	82.7	160	230		
2.80	61.0	61.5	61.2	136	175		
2.80	24.0	37.3	36.2	106	105		
2.80	12.0	25.8	25.0	67	72.6		
2.80	8.83	20.4	21.1	64	61.7	5 5	
3.38	24.0	48.5	48.0	117	115		
3.38	12.0	30.8	32.8				
3 38	8.83	28.3	27.9	65	67.7	10	
3.38	4.40	18.5	19.4	51	47.2	43	
4.58	24.0	75.1	74.4				
4.58	- 12.0	49.6	51.9	09	70.0		
4.58	8.80	45.5	43.7	93 .	78.2		
4.58	4.40	31.5	30.5	54	54.8		
0 596	0 1E	11.0	At 25° C				
0.520	8.40 22.1	$\frac{11.4}{204.7}$. 24	23 -	-	
0.520	33.1 54 7	24.7	20.0	00	. 51		
0.020	04.7 01 1	04.U 51 1	30.3	07	09		
0.520	91.1	76 5	49.0	90 191	90 191		
0.020	2 15	10.0	11.4	131	131		
1 15	0.40 9.45	25 4	26 6	28	21		
1.10	0.40 9.45	51 G	50.U	40	20		
1 07	8 45	76 0	75-6	40	00 11		
2.31	8 45	194	195	40	44 59		

TABLE I

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NOTE: [A]₉, [P]₉, [O₂]_T, [P]_T are, respectively, the initial amine concentration, the initial benzoyl peroxide concentration, the total oxygen absorbed, and the concentration of the peroxide produced. *From equation [1]. †From equation [7].

rate in benzene and that in toluene at 25° C, but an increase in rate was observed in a mixture of methanol (55 mole%) and toluene at 0° C, and this increase is almost exactly equivalent to that which would be observed in the corresponding acetonitrile-toluene mixture.

The rate of oxidation was shown to be autoinhibited by an inhibitor formed in the reaction with oxygen; whereas the reaction of benzoyl peroxide in the absence of oxygen appeared to produce a compound which accelerates the rate. This is apparent from the following two sets of experiments. Solutions of amine (1-2 mole/l.) and peroxide (24 mmole/l.) were allowed to react to completion in the presence of oxygen; a known concentration of peroxide was then added and the rate of oxygen uptake measured. The



FIG. 1. Benzoyl peroxide initiated oxidation of dimethylaniline in toluene at 0° C; initial amine concentration, 2.80 mole/l.; initial peroxide concentrations, \bigcirc 98.8, \bigcirc 24.0, \bigcirc 8.8 mmole/l. FIG. 2. Dependence of the initial rate of oxidation on solvent composition for toluene-acetonitrile mixtures. Initial amine (mole/l.) and peroxide (mmole/l.) concentrations, respectively: \bigcirc 0.835, 36.0; \bigcirc 1.50, 24.0; \bigcirc 1.94, 12.0; \bigcirc 2.80, 8.75; \bigcirc 2.80, 24.0.

observed rate was in all cases about one-half that estimated from equation [1] after allowing for the decrease in amine concentration by the initial reaction. These experiments were repeated; however, in this case the solutions were degassed before mixing and the preliminary reaction was carried out in the absence of oxygen. The reacted mixture was then placed in an oxygen atmosphere. No oxygen uptake was observed until more peroxide was added; and then the rate of oxidation was about 1.5 times that estimated from equation [1].

Stoichiometry

The total amount of oxygen that reacted, $[O_2]_T$, in any given run appeared to approach a maximum which was dependent on the initial concentrations of reactants. In fact when $[O_2]_T/[P]_0$ was plotted against $([A]_0/[P]_0)^{1/2}$ linear relations were obtained.

It would be particularly desirable to supplement the oxidation uptake measurements with simultaneous measurements of the total peroxide content of the reacting mixture. Unfortunately, due to the extreme lability of the system, the results obtained varied so widely as to be meaningless. It was possible though, to determine the peroxide present at the end of the reaction, $[P]_T$, and to obtain reproducible results; these are given in Table II. Thus, most of the oxygen which is absorbed is in the form of peroxide at the completion of the reaction.

Inhibition

In contrast to its ability to inhibit completely the rate of autoxidation of dimethylaniline, hydroquinone was found to have no effect on the peroxide-catalyzed reaction. Also, although it has been stated (2) that benzoic acid, "by virtue of its acidic function",

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Peroxide production [A]₀, mole/l. [O₂]_T, mmole/l. [P]_T, mmole/l. [P]₀, mmole/l. $[P]_T/[O_2]_T$ 0.98224.00.87 24.063 0.982480.7624.00.741.507354 $\frac{2.80}{3.38}$ 8.83 64 550.784.4051 43 0.84

retards the decomposition of benzoyl peroxide in dimethylaniline, its presence produced no diminution in rate, nor did the presence of a much stronger acid, toluenesulphonic acid.

Dodecanethiol-1 (RSH) and benzoquinone (Q) were found to retard the reaction considerably, and both proved quite useful in elucidating the reaction mechanism. With both inhibitors the rate was retarded, but no induction period was observed; in addition, the total oxygen absorbed appeared to be decreased.

The results obtained in the presence of benzoquinone are given in Table III. It is

TABLE III Inhibition by benzoquinone

[A] ₀ , mole/l.	[P]₀, mmole/l.	[Q] ₀ , mmole/1.	Oxygen press., mm Hg	$(-d[O_2]/dt)_0,$ mole/l. sec $\times 10^6$	[O ₂] _T , mmole/l.	$(-d[O_2]/dt)_0[Q]_0/[A]_0[P]_0,$ sec ⁻¹ ×10 ⁶
2.80	99.2	59.0	729	2.8	8.7	59
$^{2.80}_{2.80}$	$98.6 \\ 98.8$	11.4 9.14	719 730	$\begin{array}{c} 8.29\\ 12.7\end{array}$	$\frac{27}{37}$	$\begin{array}{c} 34.2 \\ 42.0 \end{array}$
$\frac{2.80}{2.80}$	98.6 98.7	5.68 3.04	$\begin{array}{c} 731 \\ 730 \end{array}$	$\begin{array}{c} 20.0\\ 35.2 \end{array}$	$\begin{array}{c} 62 \\ 110 \end{array}$	$\begin{array}{c} 41.2\\ 38.7 \end{array}$
2.80	102	2.27	$720 \\ 721$	49.1	132	39.1
$1.17 \\ 2.80$	36.0	9.03 9.10	728	4.43		$\begin{array}{c} 43.2\\ 39.9\end{array}$
$3.82 \\ 2.80$	$98.8 \\ 98.6$	9.14 9.10	728 579	$\begin{array}{c} 17.4\\10.7\end{array}$	29	42.2
2.80 2.80	98.8 98.6	9.10 9.10	313 220	$\begin{array}{c} 7.32 \\ 3.80 \end{array}$		
$2.80 \\ 2.80$	98.8	9.11	134	1.81		

apparent from the last column that the initial inhibited rate is proportional to the product of the initial concentrations of amine and peroxide, and is inversely proportional to the initial quinone concentration. This rate is also a function of the oxygen pressure; however, the direct proportionality suggested by the results cannot be assumed, since no correction has been made for the vapor pressure of the solution, and the rate might well be diffusioncontrolled at low pressures. The initial rate of oxidation, in the presence of quinone, is therefore given by the relation: $(-d[O_2]/dt)_0 = 4.01 \times 10^{-7}[A]_0[P]_0/[Q]_0$, at 726 mm, 0° C, in toluene.

In contrast to inhibition by benzoquinone where the rate approaches zero as the inhibitor concentration is increased, in the presence of mercaptan the rate appears to approach a limiting minimum value as the concentration of inhibitor is increased. This minimum rate is proportional to both the initial amine and peroxide concentrations. These results are given in Table IV. Another striking thing about the values obtained for the inhibited rate is that, when they are divided by the product $[A]_0[P]_0$ the result

[A] ₀ , mole/l.	[P] ₀ , mmole/l.	[RSH]₀, mole/l.	$(-d[O_2]/dt)_{0},$ mole/l. sec $\times 10^6$	$(-d[O_2]/dt)_0/[A]_0[P]_{0_1}$ 1./mole sec $\times 10^6$
·		In tolu	iene at 0° C	
$\begin{array}{c} 0.482 \\ 0.478 \\ 1.50 \\ 1.50 \\ 1.50 \\ 2.80 \\ 2.80 \end{array}$	129 129 98.8 98.8 98.8 98.8 98.8 98.0	$\begin{array}{c} 0.78 \\ 0.18 \\ 0.20 \\ 1.7 \\ 0.86 \\ 0.98 \\ 0.01 \end{array}$	$\begin{array}{c} 6.64 \\ 6.14 \\ 16.2 \\ 15.4 \\ 15.5 \\ 30.0 \\ 54.3 \end{array}$	$ 107 \\ 99.5 \\ 109 \\ 106 \\ 105 \\ 108 \\ 198 $
2.00	0010	In tolu	ene at 25° C	
$\begin{array}{c}2.80\\1.50\end{array}$	$\begin{array}{c} 8.45\\ 8.45\end{array}$	$\begin{array}{c} 1.1 \\ 1.0 \end{array}$	$\begin{array}{c} 18.7 \\ 9.80 \end{array}$	792 774
		In aceto	nitrile at 0° C	
$\begin{array}{c} 0.835 \\ 0.835 \\ 1.50 \end{array}$	$124 \\ 61.0 \\ 98.8$	$\begin{array}{c} 0.72 \\ 0.79 \\ 0.98 \end{array}$	$12.8 \\ 6.40 \\ 19.6$	$124 \\ 126 \\ 132$

TABLE IV Inhibition by mercaptan

is almost exactly equal to twice the rate constant k_c . As will be seen later, k_c is the initiation rate constant, k_0 , and this equality can be predicted from the postulated mechanism. The values of k_0 in the third column of Table VI are $(-d[O_2]/dt)_0/2[A]_0[P]_0$ and are equal to the corresponding values in the second column, within experimental error. This makes it possible to determine the rate constants k_c and k_d from two initial rate measurements, one in the presence of mercaptan and one in its absence. The rate constants for the four other temperatures given in Table VI were obtained in this way from the data in Table V.

Temp.,	[A] ₀ ,	[P] ₀ ,	[RSH] ₀ ,	$(-d[O_2]/dt)_0,$	$(-d[O_2]/dt)_0/[A]_0[P]_0,$
<u> </u>	11010/1.	11111010/1.	11010/1.		
10	2.80	8.45	1.0	5.37	227
10	1.50	8.45	1.0	2.74	216
10	2.80	8.45		44.8	
10	1.50	8.45		13.6	
15	2.80	8.45	1.0	7.44	314
15	1.50	8.45	1.0	4.18	330
15	2.80	8.45		66.7	
15	1.50	8.45		24.5	
20	2.80	8.45	1.0	13.6	574
20	1.50	8.45	1.0	7.45	588
20	2.80	8.41		97.0	
20	1.50	8.41		36.3	

TABLE V Determination of rate constants by the inhibitor method

DISCUSSION

In determining a mechanism for this reaction, it is necessary to account for the chain character of the oxidation (which is evident from the kinetics and from the stoichiometry), and for the products formed. The former is readily explained in terms of the mechanism used to describe hydrocarbon oxidation (4); this mechanism is, however, not compatible with the products isolated, nor can it easily explain quinone inhibition. Hence, a reaction

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Mechanism

sequence has been suggested which is superficially similar to the hydrocarbon mechanism, but which can account for these other observations. The following mechanism is necessarily an oversimplification of the entire process, but is, at least, consistent with the information presently available concerning the initial stages of the reaction. The separate steps have been numbered in such a fashion so as to emphasize the similarities between this chain mechanism and that postulated for hydrocarbon oxidation.

 $[6] \qquad \qquad 2\dot{O}_2^- \qquad \rightarrow O_2 + O_2^-$

The symbols used have been defined in Part I (1).

Reactions [0] and $[1_{a-c}]$ have been discussed in Part I. The following considerations are important in the choice of the remaining three reactions.

Reaction [2]

There is no direct evidence available concerning the step involving the reaction of molecular oxygen. Isolation of formaldehyde, hydrogen peroxide, and methylaniline led Horner and Junkermann (2) to postulate the formation of a peroxide which hydrolyzed to these products on contact with water. All attempts to synthesize this peroxide failed, although a peroxidic solid was obtained from dimethylmesidine with performic acid as an oxidizing agent. The existence of this peroxide is therefore questionable, and an alternative mechanism would seem desirable.

One of the distinguishing features of hydroquinone oxidation, as contrasted with the oxidation of hydrocarbons, is the nature of the peroxides formed; in the former case, hydrogen peroxide is exclusively produced, while, in the latter, hydroperoxides and diperoxides are the main products. This difference undoubtedly arises because of the ability of non-hydrocarbon compounds to enter into electron transfer reactions. Hence, as the results reported here seem to indicate, it is likely that the peroxide formed in this reaction is hydrogen peroxide, probably existing in equilibrium with $[C_6H_5N(CH_3)_2OH^+]OH^-$.

Since it was observed that highly purified *N*-methylaniline is a very effective retarder for both the benzoyl peroxide catalyzed oxidation and the high temperature autoxidation reactions, it appears likely that this compound is responsible, at least in part, for the observed autoinhibition. The results indicate that it is formed only in the reaction sequence involving oxygen and not in the reactions with benzoyl peroxide. Thus, methylaniline and formaldehyde are likely produced mainly in the later stages of the reaction, possibly by rearrangement of dimethylaniline oxide (5–7) or its hydrate, or, by a similar mechanism, from hydrolysis of the unstable diimine of tetramethylbenzidine* (8).

The kinetics of benzoquinone inhibition also favors a semiquinone oxidation mechanism. Benzoquinone is a very poor inhibitor of hydrocarbon oxidation (10), where its action is presumably due to free radical addition. Here, though, it was found to be an extremely efficient inhibitor, and the inhibited rate of oxidation is dependent on the oxygen as well

*It is probably due to this instability that quinone catalysis (9) does not play an important part in the reaction mechanism.

as on the inhibitor concentration. This immediately suggests that the inhibitor is competing with oxygen for some reactive intermediate. The fact that hydroquinone is formed quantitatively from the quinone that reacts (11) is analogous to the formation of hydrogen peroxide from oxygen, and further suggests the similarity of action of these two oxidizing agents here.

It seems probable, therefore, that benzoquinone, and hence oxygen, are acting, in a sense, as electron acceptors. Also, since no low temperature oxidation of dimethylaniline in the absence of benzoyl peroxide was detected, and because of the known susceptibility of the semiquinones of diamines to reaction with oxygen, reaction [2] has been postulated to explain the absorption of oxygen.

Reaction [3]

This reaction is analogous to reaction [1a] and involves electron transfer between the peroxide radical \dot{O}_2^- and dimethylaniline.

Reaction [6]

Chain termination occurs by electron transfer between two peroxide radicals to a diperoxide and oxygen. This reaction follows from the independence of the rate with respect to oxygen pressure, and it is equivalent to disproportionation of two $R\dot{O}_2$ radicals, which appears to be the main mode of termination in the oxidation of many hydrocarbons at high oxygen pressures (12).

Assuming the applicability of the steady state approximation, this mechanism leads to the following expression for the rate of oxidation at high pressures:

$$-d[O_2]/dt = nk_0[A][P] + k_3(k_0/k_6)^{1/2}[A]^{3/2}[P]^{1/2}$$
^[2]

If, as written in reaction [6], oxygen is produced in the termination reaction, then n = 1, otherwise n = 2, assuming 100% initiation efficiency.

There are three main ways in which reaction with inhibitor might occur:

$$\dot{O}_2^- + I \rightarrow \text{products}$$

 $-d[O_2]/dt = 2k_0[A][P] + 2k_0k_3[A]^2[P]/k_7[I]$ [3]

At high inhibitor concentrations,

$$-d[O_2]/dt = 2k_0[A][P]$$
[4]

If Bz \dot{O} reacts with inhibitor as well, the inhibited rate will be 1/2 this.

$$\dot{\mathrm{T}}^+ + \mathrm{I} \rightarrow \mathrm{products}$$

$$-d[O_2]/dt = 2k_0[A][P]k_2[O_2]/k_8[I]$$
[5]

[9]

[8]

$$T + I \rightarrow \text{products}$$
$$-d[O_2]/dt = k_0[A][P]k_{1c}[P]/k_9[I]$$
[6]

In deriving the expression for the rate, in each case the assumption has been that termination occurs predominantly by reaction with inhibitor, that oxygen is not one of the products of the inhibition reaction, and that the primary radical, BzÖ, does not react with inhibitor as rapidly as with amine.

It is apparent from the data given in Table IV that mercaptan inhibition occurs, in this case, by reaction [7]. The initial rate is proportional to the initial peroxide and amine concentrations. In addition, the ratio $-d[O_2]/dt[A]_0[P]_0$ is, within experimental error, equal to twice the rate constant obtained from the intercept of the rate plot. Therefore, oxygen is released in the termination step (i.e., n = 1), and the rate constants can be evaluated from equations [2] and [4], and are reported in Table VI.

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		Rate co	nstants		
		$10^{5}k_{c} = 10^{5}k_{0}^{*}$			
Temp., °C	From equation [2]	From mercaptan inhibition	From peroxide decom- position (1)	$10^{5}k_{d}^{*}$	$10^3k_3/k_6^{1/2}$ †
		Dimethylanili	ne in toluene		
$\begin{array}{c} 0 \\ 10 \\ 15 \\ 20 \\ 25 \\ 10^{-6} \mathrm{A} \\ E (\mathrm{kcal}) \end{array}$	5.3 ± 0.2 	$5.35 \pm 0.15 \\ 11 \pm 3 \\ 16 \pm 2 \\ 29 \pm 2 \\ 39 \pm 3 \\ 1.3 \pm 0.1 \\ 13.0 \pm 0.3$	5.0 12 27 53 37 14.8	$\begin{array}{c} 4.51 \pm 0.02 \\ 9 \pm 3 \\ 14 \pm 4 \\ 20 \pm 5 \\ 26.9 \pm 0.2 \\ 11.5 \pm 0.3 \end{array}$	$\begin{array}{c} 6.2 {\pm} 0.1 \\ 9 {\pm} 3 \\ 11 {\pm} 3 \\ 12 {\pm} 3 \\ 13.6 {\pm} 0.7 \\ 5.0 {\pm} 0.3 {\ddagger} \end{array}$
		Dimethylaniline	e in acetonitrile		
0 25 E (kcal)	$11 \pm 12 \\ 90 \pm 60$	6.4 ± 0.2		$\begin{array}{c} 36\pm1\\ 247\pm7\end{array}$	${}^{45\pm2}_{82\pm40}_{7\ddagger}$
		Methylethylan	iline in toluene		
0	· ·	4.5	-	4.0	6.0
		Diethyl- and diprop	yl-aniline in tolu	iene	
0	·	3		0(?)	0(?)

TABLE VI

	and the second se
*L/mole sec.	
$\pm (1 / mole coo$	1/2
I (1./ IIIOIC SEC	• • • • •

 $E_3 - \frac{1}{2}E_6$. NOTE: All precision indices are 90% confidence limits (t test).

The k_0 values are surprisingly close to those obtained from peroxide decomposition in the absence of oxygen, with the exception of the 25° C value. The difference in the E_0 results are due to this discrepancy. This may reflect either the poorer precision that is obtainable from the peroxide decomposition results, or a real decrease in initiation efficiency with increasing temperature. The latter could be due to the instability of one of the intermediates involved in reactions [1] to [4].

There is very little useful information that can be inferred from the ratio $k_3/k_6^{1/2}$ without knowing the magnitude of one of the constants. Since the activation energy, E_6 , is usually close to zero, the value obtained for the energy difference, $E_3 - \frac{1}{2}E_6$, places dimethylaniline between the highly susceptible aldehydes and the less readily oxidizable hydrocarbons with respect to "dehydrogenation".

On comparing equation [5] and the relation obtained for the rate of oxidation in the presence of benzoquinone, it appears likely that quinone inhibition occurs by reaction [8]. This reaction is readily understood either in terms of a semiquinone-quinone complex, or in terms of electron transfer. Both would lead to the formation of hydroquinone from the inhibitor. Unfortunately, since the solubility of oxygen in mixtures of dimethylaniline and toluene is not known, the rate constants involved in inhibition can not be determined.

The observed stoichiometry can also be explained by this mechanism. If equation [2] describes the entire reaction, the ratio of total oxygen absorbed to peroxide initially present will be given by the relation:

$$\frac{[O_2]_{\mathrm{T}}}{[P]_0} = \frac{n}{3} + \frac{6-2n}{9} \frac{k_3^2}{k_0 k_6} \frac{[A]_0}{[P]_0}.$$
^[7]

Values of $[O_2]_T$ calculated from this relation and the measured rate constants are given in Table I and agree quite well with the observed results. This agreement does not necessarily conflict with the observation that the reaction is autoretarded, since it might be expected that the stoichiometry would be much less sensitive than the rate to this type of inhibition.

The increase in rate observed in going from toluene to acetonitrile (or methanol) is likely a result of the increase in dielectric constant. Such an effect should be very small in purely free radical reactions, and it was for this reason that a mechanism involving charged species seems most likely, particularly since the increase appears to occur mainly in the second term of the rate equation, i.e. in k_3 or k_6 . This may mean that the sensitive reaction is the termination reaction, since reactions [0] and [3] are similar, and reaction [6] involves the reaction of two anions, or, at least, two strongly polarized radicals. The order of magnitude of the effect is only explainable in terms of the reaction of two likecharged species. The fact that there are probably other reactions involved in polar solvents than those considered in deriving equation [7] is apparent from the $[O_2]_T$ values obtained in acetonitrile. These are much larger than the corresponding values observed in toluene, but much less than would be predicted on the basis of equation [7]. It may be that the apparent continuity of mechanism is fortuitous.

Oxidation of Related Compounds

Tetramethylbenzidine is of particular interest since it is apparently an intermediate in the oxidation of dimethylaniline. It proved impossible to obtain any accurate kinetic data, since at 0° C the reaction is much too fast to follow, and only a rough estimate of its relative overall reactivity could be made. It was found that, for a toluene solution of tetramethylbenzidine (53.2 mmole/l.) and benzoyl peroxide (99.6 mmole/l.), the initial rate was at least 7×10^{-5} mole/l. per sec; the corresponding rate for dimethylaniline would be 4.0×10^{-7} mole/l. per sec. Hence, tetramethylbenzidine oxidizes at least 200 times as fast as dimethylaniline. The reaction may be retarded by mercaptan, but not sufficiently to allow accurate rate measurements.

Results obtained for several other compounds are given in Table VII. Methylethylaniline

TADLE VII

Oxidation rates of related compounds						
Compound $ \begin{array}{ccc} [\mathrm{RSH}]_0, & (-d[\mathrm{O}_2]/dt)_{\mathrm{max}}, & [\mathrm{O}_2]_{\mathrm{T}}, \\ \mathrm{mole}/\mathrm{l}. & \mathrm{mole}/\mathrm{l}. \; \mathrm{sec} \times 10^6 & \mathrm{mmole}/\mathrm{l}. \end{array} $						
Dimethylaniline Methylethylaniline	—	$57.0 \\ 50.4 \\ 12.4$	$\begin{array}{c} 164 \\ 100 \end{array}$			
Diethylaniline		$\begin{array}{c}13.5\\4.48\\5.06\end{array}$	20			
Dipropylaniline	1.0	4.65 4.87	30 30 30			
Dimethylbenzylamine Dimethyldodecylamine		0.0085 0.015	0			

Note: The initial amine and peroxide concentrations were, respectively, 2.80 mole/l., and 54.4 mmole/l. The reactions were carried out at 0° C, in toluene.

appears to oxidize by the same mechanism as dimethylaniline; the estimated rate constants are given in Table VI. *Diethylaniline* and *dipropylaniline*, however, do not exhibit a corresponding similarity. Their oxidation rates are much less than for dimethylaniline, and the reaction is not inhibited by mercaptan; if anything, it is slightly accelerated. In

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addition, although it was difficult to estimate accurately the total oxygen absorbed, because of the low rates, it appeared to be equal to about 0.3 to 0.5 times the initial peroxide concentration.

These results would seem to indicate the almost complete absence of a chain reaction, with the initial rate of oxidation being approximately equal to $2k_0[A]_0[P]_0$. The values of k_0 reported in Table VI are based on this assumption.

If oxidation occurred by the N-alkyl dehydrogenation mechanism of Horner and Junkermann (2), a diminution in rate might be expected as the size of the alkyl group is increased, although, perhaps not as great as observed here. On the other hand, increasing the size of the alkyl group will undoubtedly sterically hinder the formation of the complex which precedes electron transfer in reaction [3]. In addition, there might be expected to be a limit, beyond which, increasing the size of the alkyl group would not further influence the reaction, as was observed with diethyl- and dipropyl-aniline. If this is the case, the rate of reaction [3] should be greater in solvents of high dielectric constant, where the separation of the cationic quinone and anionic oxygen should be greater.

The other two amines listed in Table VII showed no tendency to react, and the rate limits are those imposed by the experimental conditions.

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