butyl radicals to ethylene and ethyl radicals is the dominant reaction. The large amount of ethane cannot be accounted for only by dimerization of methyl. Hydrogenation of ethylene and ethyl radicals by atomic and molecular hydrogen is indicated. The presence of methane, propane and propylene suggests the decomposition of about one-tenth the n-butyl radicals to propylene and methyl radicals. Carbon balances show less than 17% of the carbon content in the C_5–C_8 products.

Hydrogen balances on the gaseous products show an increase of 9–17% in hydrogen content.

Conclusion.—In the temperature range 200–450° azobutanes can be used as sources of free radicals. They decompose *via* first-order kinetics to give butyl radicals and nitrogen. However n-butyl, isobutyl and *sec*-butyl are unstable, easily decomposing to lower alkenes and alkyl radicals. If the isomeric butyl radicals as such are desired in a reaction, one must bear in mind this instability.

Oxidation Inhibition by Diphenylamine

BY J. R. THOMAS AND C. A. TOLMAN

A detailed study has been made of the inhibiting action of diphenylamine in the oxidation of cumene. Electron spin resonance has permitted the observation and identification of a relatively stable intermediate radical, diphenyl nitric oxide. Kinetic studies show that it is produced from a sequence of reactions between alkylperoxy radicals and diphenylamine which quantitatively follow the requirements of the Boozer–Hammond mechanism for oxidation inhibition. Critical rate constants are evaluated and limiting values are placed upon the equilibrium constant for the reversible reaction between cumylperoxy radical, diphenylamine and the complex species of the Boozer–Hammond mechanism.

The use of electron spin resonance has resulted in the observation and identification of the relatively stable intermediate radical, diphenylnitric oxide, when diphenylamine is used to inhibit the oxidation of hydrocarbons.[1,2,3] This paper presents the results of kinetic studies, made possible by e.s.r., which allow the inhibition mechanism to be specified in detail not previously possible.

Experimental

Diphenylnitric oxide was made by the method of Wieland.[4] It was purified by recrystallization from 50–50 ether and pentane. Tetraphenylhydrazine was prepared by the method of Wieland[5] or was material purchased from K and K Laboratories, Inc.

Oxidation Studies.—Oxidation studies were carried out in chlorobenzene solution at temperatures of 57.0 and 68.5°. The initiator used in all cases was azo-bis-isobutyronitrile (ABN). Oxygen absorption measurements were conducted in a stirred reactor in conjunction with a sensitive gasometer. The reactor, which also constituted the gas reservoir, was immersed in a carefully controlled water-bath. In cases where material was added to the reactor after the system was thermally equilibrated, a solution of the reagent was injected with a pipet through a controlled opening. All of the inhibitor studies were done this way, the inhibitor being added after the ABN-catalyzed oxidation rate had reached a steady value. Carefully done, this procedure caused very little upset to the system.

Electron spin resonance measurements were made with a Varian model 4500 spectrometer; 400 c.p.s. and 100 K.c.p.s. modulation were used at various times. The peak-to-peak height of the diphenylnitric oxide absorption band at low resolutions was used as a measure of concentration. The instrument was calibrated with samples of known concentration. All samples were thoroughly deoxygenated by alternate freezing and melting under vacuum. When diphenylnitric oxide reactions were studied in the absence of oxygen, they were sometimes done in sealed evacuated e.s.r. analysis tubes; at other times the reactions were conducted under nitrogen in conventional reactors from which samples were withdrawn at various times. If the samples, in e.s.r.

analysis tubes, were not measured immediately they were stored in liquid nitrogen until they were analyzed.

Use of Diphenylnitric Oxide as a Radical Trap.—Diphenylnitric oxide is an attractive material to use as a radical counting material in many situations. While in the pure crystalline form it is considerably less stable than the commonly used α,α'-diphenylpicryl hydrazyl, its solutions are stable for prolonged periods of time. Even in solvents containing reactive hydrogen, such as cumene, its half-life at 100° is in excess of 50 hours. In addition, as is discussed below, it can be used reliably in the presence of oxygen under some conditions. Its disadvantages are the lack of stability of the crystalline material at room temperature and its lack of the intense color change upon reaction which is characteristic of DPPH. This latter characteristic renders the use of e.s.r. equipment preferable for its analysis in most situations.

Materials.—Cumene and chlorobenzene were Eastman Kodak Co. white label products; the latter was used without further purification, the former was passed through an alumina column.

Azo-bis-isobutyronitrile (ABN) and the diphenylamine were Eastman Kodak Co. products. The former was purified by recrystallization from methanol while the latter was recrystallized from hexane.

Results and Discussion

The basic problem of interest is the detailed mechanism of oxidation inhibition by diphenylamine. Since the radical, diphenylnitric oxide, has been found as a reaction intermediate, it must be suitably incorporated into a comprehensive mechanism. Furthermore, one would like to utilize the unique features of the radical's chemistry to verify various features of proposed inhibition mechanisms which have been supported largely by kinetic studies of the oxygen absorption reaction itself.

With these goals in mind the following discussion concerns itself with the chemistry of diphenylnitric oxide, *i.e.*, its reactions with alkyl and alkylperoxy radicals, and its behavior as an inhibitor. Next, the concentration behavior of the radical during the inhibition period is considered, with discussion of some experiments involving the competitive reactions of diphenylamine and diphenylnitric oxide with the oxidation chain propagating alkylper-

(1) O. L. Harle and J. R. Thomas, J. Am. Chem. Soc., 79, 2973 (1957).

(2) J. R. Thomas, ibid., 82, 5955 (1960).

(3) J. C. Baird and J. R. Thomas, J. Chem. Phys., 35, 1507 (1961).

(4) H. Wieland and M. Offenbacker, Ber., 47, 2111 (1914).

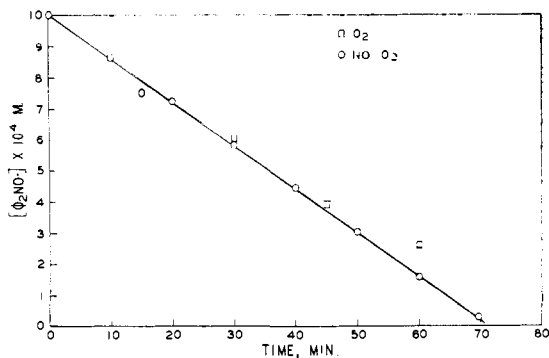(5) H. Wieland and S. Gambarjan, ibid., 39, 1500 (1906).

Fig. 1.—Consumption of $(C_6H_5)_2NO\cdot$ due to ABN decomposition 4 M cumene in chlorobenzene at 68.5°: 10^{-3} M $(C_6H_5)_2NO\cdot$, 4 × 10^{-3} M ABN.

oxy radical. As will be noted in detail, support develops from these experiments for the Boozer and Hammond[6] mechanism for the reaction between alkylperoxy radicals and amine. In light of this conclusion the reactions involved in the formation of diphenylnitric oxide and the characteristics which Boozer and Hammond's alkylperoxy radical-amine complex species must have are quantitatively discussed.

$(C_6H_5)_2NO\cdot$ + R·.—When azo-bis-isobutyronitrile (ABN) is decomposed in solutions free of oxygen in the presence of diphenylnitric oxide, the rate of disappearance of diphenylnitric oxide is constant and independent of its concentration over a wide range of concentration indicating that it functions as an effective radical trap for alkyl radicals. Table I gives detailed data under a variety of conditions while Fig. 1 shows a typical plot of $(C_6H_5)_2NO\cdot$ concentration *versus* time. These experiments yield a rate constant for ABN decomposition in chlorobenzene at 68.5° of 2.36 ± 0.15 × 10^{-5} sec.$^{-1}$, assuming that each ABN yields two effective radicals and that one radical destroys one diphenylnitric oxide. We find the rate constant by nitrogen evolution to be 3.5 × 10^{-5} sec.$^{-1}$ in agreement with extrapolated literature values for this temperature.[7] This difference, which is believed to arise from the solvent cage effect, gives an effective radical yield factor of 0.68 in reasonable agreement with the values determined by Hammond, Sen and Boozer.[7] The reaction $(C_6H_5)_2NO\cdot$ and R· may be reasonably written
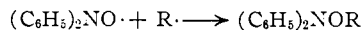
$$(C_6H_5)_2NO\cdot + R\cdot \longrightarrow (C_6H_5)_2NOR$$

$(C_6H_5)_2NO\cdot$ + RO_2·.—In cumene, diphenylnitric oxide also shows the behavior of an effective radial trap when ABN is decomposed in systems containing oxygen. The rate of radical production from ABN decomposition, as determined by $(C_6H_5)_2NO\cdot$ scavenging, is the same as that observed in the absence of oxygen as shown in Fig. 1. In chlorobenzene and tetralin, however, the apparent rate constant for ABN decomposition is reduced by nearly a factor of two. Table I lists the ratios of the apparent rate constants deter-

(6) C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).

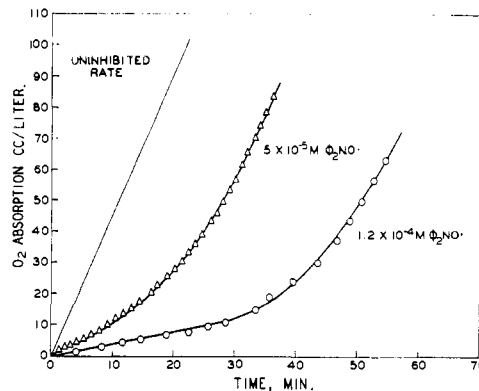(7) G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

Fig. 2.—Oxidation inhibition by $(C_6H_5)_2NO\cdot$ at 68.5°: 10^{-3} M ABN, 4 M cumene in chlorobenzene.
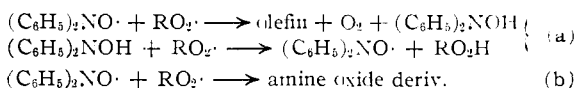
mined in the presence of oxygen to those determined in the absence of oxygen under various conditions for chlorobenzene solutions. Similar behavior is observed in tetralin. It can be shown by quantitative treatment of the data that the effect of oxygen cannot be accounted for by assuming that $(C_6H_5)_2$-$NO\cdot$ competes with oxygen for the alkyl radical and termination occurs only between alkylperoxy radicals. Similarly, it is possible to exclude, under all but the last two conditions listed in Table I, competing termination reactions between alkylperoxy radicals with $(C_6H_5)_2NO\cdot$ and with themselves. In the last two experiments listed in Table I this type of competitive termination is obviously coming into play.

TABLE I

DECOMPOSITION RATE CONSTANTS FOR
AZO-BIS-ISOBUTYRONITRILE IN CHLOROBENZENE, 68.5°

[ABN] × 10^3, moles/liter	$[(C_6H_5)_2NO\cdot]$ × 10^3, moles/liter	k × 10^5, sec.$^{-1}$	k_{0_2}/k
8	1	2.6	0.52
4	1	2.5	.52
2	1	2.5	.56
0.8	0.1	2.2	.49
.4	.1	2.2	.60
.4	.1	2.2	.58[a]
.2	.1	2.2	.56
.04	.01	2.3	.19
.04	.01	2.3	.19[a]

[a] Air atmosphere used rather than oxygen at 1 atm. as in others.

We have been unable to postulate any mechanism which could account for this oxygen effect except one in which two competing reactions between alkylperoxy radicals and $(C_6H_5)_2NO\cdot$ are involved. In one sequence the $(C_6H_5)_2NO\cdot$ is regenerated, serving essentially as a catalyst for the self-termination of alkylperoxy radicals, while the second results in a final addition product. One such scheme is outlined as

$(C_6H_5)_2NO\cdot + RO_2\cdot \longrightarrow$ olefin + O_2 + $(C_6H_5)_2NOH$ }

$(C_6H_5)_2NOH + RO_2\cdot \longrightarrow (C_6H_5)_2NO\cdot + RO_2H$ } (a)

$(C_6H_5)_2NO\cdot + RO_2\cdot \longrightarrow$ amine oxide deriv. (b)

Such a kinetic scheme fits the experimental data.

In cumene it must be assumed that a reaction such as b takes place to the exclusion of other paths.
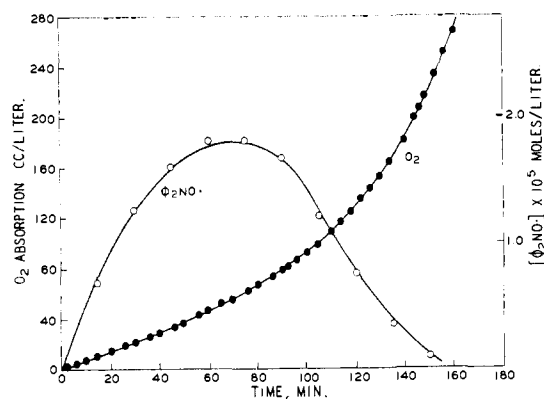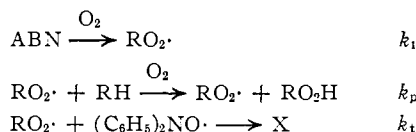
Fig. 3.—Oxygen absorption and $(C_6H_5)_2NO\cdot$ concentration versus time at 68.5°: $10^{-3}\ M$ ABN, $10^{-4}\ M$ $(C_6H_5)_2NH$, 4 M cumene in chlorobenzene.

$(C_6H_5)_2NO\cdot$ as an Oxidation Inhibitor.—The fact that $(C_6H_5)_2NO\cdot$ reacts with alkylperoxy radicals suggests that it should inhibit oxidation. As shown by the data given in Fig. 2, it is a good inhibitor for the oxidation of cumene. The number of chains terminated per $(C_6H_5)_2NO\cdot$ destroyed is found to be 1.1 ± 0.1 by the method of Boozer, Hammond, et al., at both 57° and 68.5°, in agreement with the discussion of the previous section. When $(C_6H_5)_2NO\cdot$ functions as an oxidation inhibitor and is exclusively responsible for chain termination, the mechanism

$$\text{ABN} \xrightarrow{\text{O}_2} \text{RO}_2\cdot \qquad\qquad k_1$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{\text{O}_2} \text{RO}_2\cdot + \text{RO}_2\text{H} \qquad k_p$$

$$\text{RO}_2\cdot + (C_6H_5)_2NO\cdot \longrightarrow X \qquad k_t$$

yields the oxidation rate expression

$$-\frac{d(\text{O}_2)}{dt} = \frac{k_1[\text{ABN}][\text{RH}]k_p}{[(C_6H_5)_2NO\cdot]k_t}$$

Using the previously determined values of k_1 and values of k_p = 0.45 (57.0°) and 0.64 (68.5°) for cumene,[8] k_t is found to be 2500 liters mole^{-1} sec.$^{-1}$ at 68.5° and 1750 liters mole^{-1} sec.$^{-1}$ at 57.0° from the initial rates of oxidation. One may compare this with a rate constant of about 3.4 × 10^4 liters mole^{-1} sec.$^{-1}$ for the self-termination of cumylperoxy radicals.[8]

Concentration Behavior of $(C_6H_5)_2NO\cdot$ During Inhibition by $(C_6H_5)_2NH\cdot$.—Figure 3 shows oxygen absorption data and $(C_6H_5)_2NO\cdot$ concentration as a function of time during the inhibited oxidation of cumene at 68.5°. Several points are of interest. First, the maximum concentration of $(C_6H_5)_2NO\cdot$ attained is about 20% of the starting diphenylamine concentration indicating that most, if not all, of the amine proceeds through this intermediate. Second, the end of the induction period corresponds to the disappearance of the $(C_6H_5)_2NO\cdot$ as expected in view of the inhibiting action of $(C_6H_5)_2NO\cdot$. Third, the $(C_6H_5)_2NO\cdot$ does not reach a steady state value early in the reaction as might be expected. This suggests that $(C_6H_5)_2NO\cdot$ and diphenylamine react with $\text{RO}_2\cdot$ radicals at comparable rates and excludes the use of steady

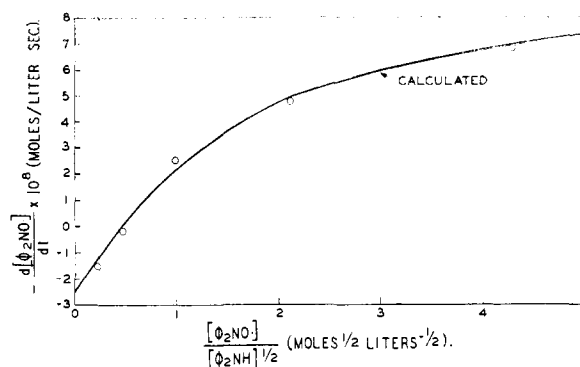(8) H. W. Melville and S. Richards, J. Chem. Soc., 944 (1954).

Fig. 4.—Rate of $(C_6H_5)_2NO\cdot$ disappearance versus $[(C_6H_5)_2NO\cdot]/[(C_6H_5)_2NH]^{1/2}$: $10^{-2}\ M$ ABN, 4 M cumene, 57.0°.
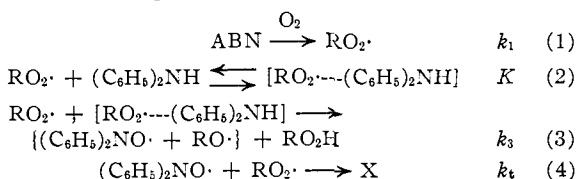
state kinetic treatments for the over-all reaction. Fourth, the data presented yield an over-all stoichiometry of 2.8 for chains stopped per $(C_6H_5)_2NH$ consumed.

Similar results were observed at 57.0° except that the stoichiometry drops to about 2.2. This is an important point which will be discussed later.

Competitive Reaction of $(C_6H_5)_2NO\cdot$ and $(C_6H_5)_2$-NH with $\text{RO}_2\cdot$.—Boozer and Hammond[6] made a major contribution to understanding the mechanism of oxidation inhibition when they found that there was no kinetic isotope effect with N-deuterated diphenylamine and showed that the inhibited oxidation rate was inversely proportional to the square root of the inhibitor concentration for N-methylaniline and phenol rather than the first power. On this basis they postulated that the critical reaction sequence involves a complex between inhibitor and $\text{RO}_2\cdot$ as

$$\text{RO}_2\cdot + \text{In} \rightleftharpoons [\text{RO}_2\cdots\text{In}]$$

$$[\text{RO}_2\cdots\text{In}] + \text{RO}_2\cdot \longrightarrow X$$
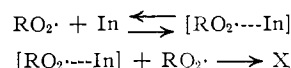
We have obtained confirmatory evidence for this reaction sequence by studying the competitive reaction of $(C_6H_5)_2NO\cdot$ and $(C_6H_5)_2NH$ with $\text{RO}_2\cdot$ radicals in oxidizing cumene. In Fig. 4 are plotted the initial rates of $(C_6H_5)_2NO\cdot$ disappearance as a function of $[(C_6H_5)_2NO\cdot]/[(C_6H_5)_2NH]^{1/2}$ in 4 M cumene catalyzed by ABN. The solid curve is a theoretical line calculated on the basis of the following mechanism which gives rise to rate eq. 5 below.

$$\text{ABN} \xrightarrow{\text{O}_2} \text{RO}_2\cdot \qquad\qquad k_1 \quad (1)$$

$$\text{RO}_2\cdot + (C_6H_5)_2NH \rightleftharpoons [\text{RO}_2\cdots(C_6H_5)_2NH] \qquad K \quad (2)$$

$$\text{RO}_2\cdot + [\text{RO}_2\cdots(C_6H_5)_2NH] \longrightarrow$$
$$\{(C_6H_5)_2NO\cdot + \text{RO}\cdot\} + \text{RO}_2\text{H} \qquad k_3 \quad (3)$$

$$(C_6H_5)_2NO\cdot + \text{RO}_2\cdot \longrightarrow X \qquad k_t \quad (4)$$

When the initial rate of $(C_6H_5)_2NO\cdot$ production is determined in systems containing only $(C_6H_5)_2NH$, it is found that the rate becomes independent of the amine concentration at high values and closely equal to one-half the rate of production of $\text{RO}_2\cdot$ radicals. These data are shown in Fig. 5. Thus, two alkylperoxy radicals are required per $(C_6H_5)_2NO\cdot$ formed rather than one as reaction 3 implies. We interpret this to mean that
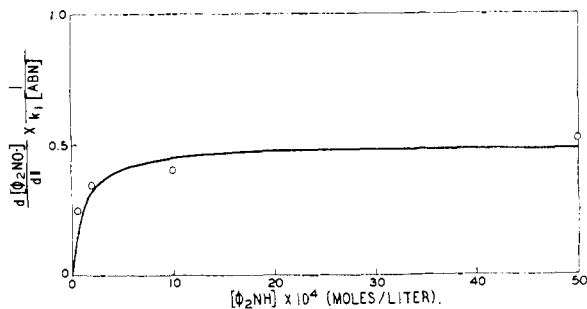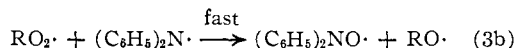
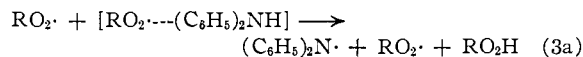Fig. 5.—Ratio of $(C_6H_5)_2NO\cdot$ formation rate to $RO_2\cdot$ formation rate *versus* concentration of diphenylamine: $10^{-2} M$ ABN, 3.8 M cumene, 57.0°.

reaction 3 suffers in yield by about the amount normally arising from the solvent cage effect, the brackets in eq. 3 indicating the "caged" radicals. On this basis it is seen, by the above mechanism, that the initial rate of $(C_6H_5)_2NO\cdot$ disappearance in competitive experiments with $(C_6H_5)_2NH$ is given by

$$-\frac{d[(C_6H_5)_2NO\cdot]}{dt} = \frac{2}{9}\frac{k^2_t[(C_6H_5)_2NO\cdot]^2}{k_3K[(C_6H_5)_2NH]}$$
$$\left[\left(1 + \frac{12k_3Kk_1[ABN][(C_6H_5)_2NH]}{k_t^2[(C_6H_5)_2NO\cdot]^2}\right)^{1/2} - 1\right] - \frac{k_1[ABN]}{3}$$

(5)

The solid curve in Fig. 4 is calculated in accordance with this expression using a value of the adjustable parameter, k_t^2/k_3K, of 10^{-3} sec.$^{-1}$ together with the experimentally determined value of $k_1[ABN]$. The agreement between the experimental data and the above mechanism is excellent and constitutes strong evidence in favor of Boozer and Hammond's mechanism. We have also confirmed the fact, previously reported by them, that the reaction between amine and $RO_2\cdot$ radicals does not involve a kinetic isotope effect by running competitive experiments with $(C_6H_5)_2ND$ and $(C_6H_5)_2NO\cdot$.

Production of $(C_6H_5)_2NO\cdot$ from $(C_6H_5)_2N\cdot$.—Reaction 3 can be written as (3a) and (3b) without altering the over-all kinetics.

$$RO_2\cdot + [RO_2\cdots(C_6H_5)_2NH] \longrightarrow$$
$$(C_6H_5)_2N\cdot + RO_2\cdot + RO_2H \quad (3a)$$
$$RO_2\cdot + (C_6H_5)_2N\cdot \xrightarrow{\text{fast}} (C_6H_5)_2NO\cdot + RO\cdot \quad (3b)$$

While the available data do not allow the two possibilities to be distinguished, it can be shown that reaction 3b occurs. Production of $(C_6H_5)_2NO\cdot$ from the diphenylnitrogen radical, $(C_6H_5)_2N\cdot$, is observed to occur readily when tetraphenylhydrazine is present in a system containing oxygen and ABN. Figure 6 gives a plot of $(C_6H_5)_2NO\cdot$ concentration *versus* time in a typical experiment. Lower concentrations of tetraphenylhydrazine exhibit similar behavior yielding stationary values of $(C_6H_5)_2NO\cdot$ which are proportional to the hydrazine concentration. In view of the relatively slow rate of dissociation of tetraphenylhydrazine reported for these conditions,[9] it must be concluded that the steady state values observed under many conditions result from some self-

(9) C. K. Cain and F. Y. Wiselogle, *J. Am. Chem. Soc.*, **62**, 1163 (1940).
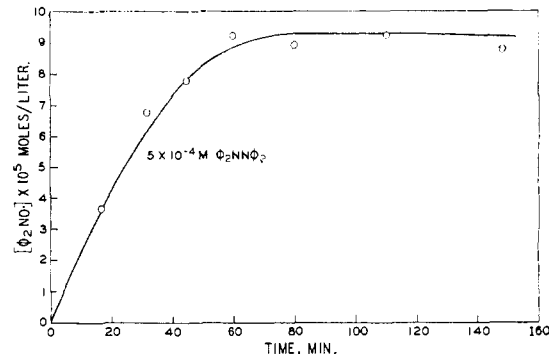

Fig. 6.—$(C_6H_5)_2NO\cdot$ concentration *versus* time due to oxidation of $(C_6H_5)_2NN(C_6H_5)_2$ at 68.5°: $10^{-3} M$ ABN, 4 M cumene in chlorobenzene.
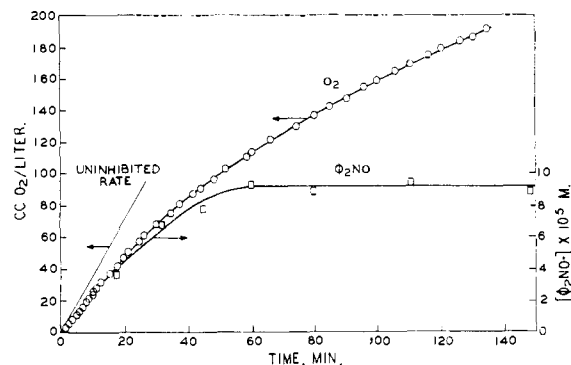

Fig. 7.—Oxidation inhibition by tetraphenylhydrazine: $10^{-3} M$ ABN, $5 \times 10^{-4} M$ $(C_6H_5)_2NN(C_6H_5)_2$, 4 M cumene in chlorobenzene.

termination by alkylperoxy radicals rather than implying complete dissociation of the hydrazine as suggested previously.[2a]

Diphenylnitric oxide is not produced by the reaction of atmospheric oxygen with $(C_6H_5)_2N\cdot$. Strong evidence that the reaction involved in the presence of ABN is that given in reaction 3b is obtained from the behavior of tetraphenylhydrazine as an oxidation inhibitor. In Fig. 7 is plotted the oxygen absorption in the oxidation of cumene and the $(C_6H_5)_2NO\cdot$ concentration *versus* time in the presence of tetraphenylhydrazine. As noted there, the oxidation rate decreases until the $(C_6H_5)_2NO\cdot$ reaches a stationary value. At this point, the oxidation rate is approximately that expected for the observed $(C_6H_5)_2NO\cdot$ concentration.

It may be concluded, therefore, that reaction 3b is reasonably fast and that $(C_6H_5)_2NO\cdot$ production from diphenylamine could proceed *via* the diphenylnitrogen radical.

The Over-all Stoichiometry.—Any proposed mechanism of inhibition must account for the over-all stoichiometry, that is, the number of chains terminated per inhibitor consumed. For cumene at 57°, we find values of 2.2 $\pm$ 0.1 for diphenylamine while at 68.5° the value is about 2.8. The method of Hammond and Boozer was used in making these estimates. At 62° they report 2.8 for cumene and 3.5 for tetralin.[10] The

(10) C. E. Boozer, G. S. Hammond, C. E. Hamilton and C. Peterson. *ibid.*, **77**, 3380 (1955).
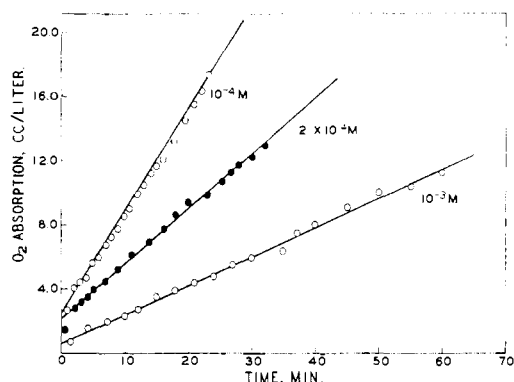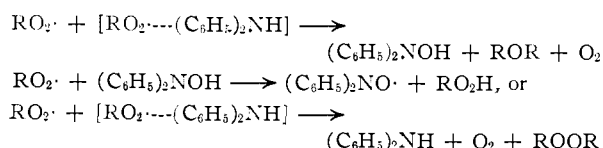
Fig. 8.—4 M cumene oxidation: oxygen absorption *versus* time for various concentrations of $(C_6H_5)_2NH$ 4×10^{-3} M ABN, 57.0°.

value of 2.2 which we observe at 57° was determined repeatedly using very carefully purified materials and is consistent with the mechanisms given above. The higher value for tetralin is readily explained by our observation that $(C_6H_5)_2NO\cdot$ terminates nearly two tetralylperoxy radicals but only one cumylperoxy radical as previously discussed. At higher temperatures, for cumene, the over-all stoichiometry is greater than two, a fact which might be explained by partial participation of one of the sequences

$RO_2\cdot + [RO_2\cdots(C_6H_5)_2NH] \longrightarrow$
$$(C_6H_5)_2NOH + ROR + O_2$$
$RO_2\cdot + (C_6H_5)_2NOH \longrightarrow (C_6H_5)_2NO\cdot + RO_2H,$ or
$RO_2\cdot + [RO_2\cdots(C_6H_5)_2NH] \longrightarrow$
$$(C_6H_5)_2NH + O_2 + ROOR$$

The Value of k_3K.—From the value of k_t, for the reaction of $(C_6H_5)_2NO\cdot$ and cumylperoxy radicals, and the value of k_t^2/k_3K determined from the data plotted in Fig. 4, the product k_3K, can be evaluated. This is found to be 2.9×10^9 liters^2 mole^{-2} sec.$^{-1}$ at 57°. This quantity can also be approximated from initial oxidation rate data for cumene, when inhibited by diphenylamine, from the reactions 1 through 3 and the normal propagation reaction by cumylperoxy radicals. This leads to the expression

$$\text{rate} = k_p[RH] \left(\frac{k_1[ABN]}{3k_3K[(C_6H_5)_2NH]} \right)^{1/2}$$

Figure 8 shows the oxygen absorption data *versus* time for several inhibitor levels. These experiments were run by injecting the inhibitor into the oxidizing system at time zero after the system was thoroughly equilibrated. The average value of k_3K deduced from these and similar data is $3.1 \pm 0.3 \times 10^9$ liters^2 mole^{-2} sec.$^{-1}$. This is in excellent agreement with the value deduced above from the experiments involving competitive reaction between diphenylamine and $(C_6H_5)_2NO\cdot$. It is also worthy of note that our inhibited rates of oxidation show, within experimental uncertainty, the inverse square root dependence upon diphenylamine concentration which Hammond and Boozer found for N-methylaniline and phenol.

It is informative to consider possible values which K might feasibly have. First, from the

known rate of initiation of 4×10^{-3} M ABN at 57° and the termination rate constant for cumylperoxy radicals, the uninhibited steady state cumylperoxy radical concentration can be reliably calculated to be 10^{-6} M. For an inhibited case, taking the specific example of 10^{-4} M diphenylamine inhibitor, and utilizing our value of k_3K, the steady state cumylperoxy radical concentration can be calculated to be 1.8×10^{-7} M. This assumes, as the mechanism implies, that the complex species does not propagate the chain.

One method of establishing an upper limit to K is to proceed as follows: As noted above, and as is seen from the data in Fig. 8, the new inhibited steady state is reached rapidly after the addition of inhibitor to the system. After five minutes, for example, at which time it was clear from Fig. 8 that the inhibited steady state had been reached, the maximum possible concentration of the complex species may be set equal to the amount of peroxy radical produced from the initiator during this period. This amounts to 9.2×10^{-6} M. From this, the above calculated steady state cumylperoxy radical concentration and the known concentration of inhibitor, a maximum value for K is seen to be 5×10^5. This implies a minimum value of k_3 equal to 6×10^3 liters mole^{-1} sec.$^{-1}$.

A second method is available to set an upper limit upon the value of K. This depends upon the fact that the existence of an equilibrium involving complex, alkylperoxy radical and inhibitor demands that the time required to achieve the inhibited steady state increase as the value of K increases. Thus one calculates, using the values of constants previously discussed, that the experiment at 10^{-3} M inhibitor in Fig. 8 will require 24 minutes to reach 90% of its new steady state value after inhibitor is added at time zero if $K = 5 \times 10^5$ liters mole^{-1}. The non-zero intercepts noted in Fig. 8 probably arise from time of mixing rather than representing the time required to reach the new steady state. The later effect would require non-zero intercepts on the x-axis rather than the y-axis. The data in Fig. 8 show that the new steady values are reached in five minutes or less implying a maximum value of 10^5 liters mole^{-1} for K.

At the other extreme k_3 cannot exceed its diffusion controlled value of approximately 10^9 liters mole^{-1} sec.$^{-1}$ implying a lower limit of about 3 liters mole^{-1} for K. This is in the range of the equilibrium constants for charge transfer complex formation between iodine atom–ethyl iodide[11] and that between iodine and various donor molecules.[12]

Recently, a radical–molecule complex mechanism, identical in kinetic form with that of our discussion, has been strongly supported by Porter and Smith[11,13] for the recombination of iodine atoms. Grover and Porter,[14] as well as Strong, Rand and Britt,[15,16] have observed these com-

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(12) P. A. D. deMaine. *J. Chem. Phys.*, **26,** 1192 (1957).

(13) G. Porter and J. A. Smith. *Nature*, **184,** 446 (1959).

(14) T. A. Grover and G. Porter, *Proc. Roy. Soc. (London)*, **262,** 476 (1961).

(15) S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82,** 5 (1960).

(16) R. L. Strong, S. J. Rand and J. A. Britt, *ibid.* **82,** 5053 (1960).

plexes in solution by absorption spectroscopy and have correlated the spectral characteristics with those expected of charge transfer complexes. Russell[17] has demonstrated solvent effects upon the chemistry of chlorine atoms and has attributed these effects to atom–molecule complexes. It appears that such radical–molecule complexes may play an important role in many areas of free radical chemistry.

Conclusion.—In summary, it seems worthwhile to re-emphasize that our results are entirely and quantitatively in agreement with the Boozer and

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Hammond postulate for the initial reaction sequence between alkylperoxy radicals and diphenylamine. The production of the radical, diphenylnitric oxide, as a product of that sequence is important since this material contributes significantly to the stoichiometry of the over-all process and to the rate of oxidation during the inhibition period. The effect of inhibitor structure upon the activity of the material as an antioxidant must, however, control this property largely through its influence upon the properties of the alkylperoxy–inhibitor complex rather than through its influence upon the properties of the product nitric oxide radical.

Nuclear Magnetic Resonance Spectroscopy. Long-Range H–F Spin–Spin Coupling in 1,1-Difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane[1]

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A 2 c.p.s. long-range H–F spin–spin coupling has been observed over five saturated bonds in 1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane, involving one of the fluorines at the 1-position and the protons of the 3-methyl group. Comparison of the spectrum with that of stereospecifically labeled 4-deuterio derivatives suggests that the fluorine involved in the long-range coupling is the one cis to the methyl group.

Several long-range H–F spin–spin couplings have been reported,[2,3] but couplings over five consecutive saturated single bonds appear to be previously unknown.

The fluorine n.m.r. spectrum of 1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane (I, from addition of 1,1-difluoro-2,2-dichloroethylene to α-methylstyrene)[4] shows the resonances of two

I
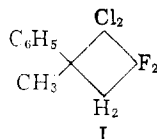
non-equivalent fluorines (F_1 and F_2) with a chemical shift difference of 435 c.p.s., each split by the F_1–F_2 coupling ($J_{12} = 187$ c.p.s.) and couplings with the two non-equivalent methylene protons attached to the 4-carbon ($J_{HF_1} = 1.9$ and 9.5 c.p.s.; $J_{HF_2} = 13.2$ and 20.3 c.p.s.) (Fig. 1A). In addition, the fluorine whose resonance comes at the higher field shows further splitting into 1:3:3:1 quartets with $J = 2.0$ c.p.s. (Fig. 1C). This strongly implies a coupling with three equivalent protons, presumably those of the methyl group at the 3-position and, indeed, the proton n.m.r.

(1) Supported in part by the Kureha Chemical Ind. Co. (Japan) and the Office of Naval Research.

(2) D. R. Davis. R. P. Lutz and J. D. Roberts. J. Am. Chem. Soc., **83**, 246 (1961).

(3) J. D. Roberts. "Nuclear Magnetic Resonance." McGraw-Hill Book Co., Inc.. New York. N. Y.. 1959. Chap. 3.

(4) Structure I for the adduct rather than 1,1-difluoro-2,2-dichloro-4-methyl-4-phenylcyclobutane is in good agreement with the magnitudes of the coupling constants between the methylene protons and the *gem*-fluorines. It is also supported by extensive analogy: J. D. Roberts and C. M. Sharts, in A. C. Cope, Ed., "Organic Reactions," Vol. XII (1962).

spectrum of I shows a doublet methyl resonance with $J_{F_2,CH_3} = 2.1$ c.p.s. (Fig. 2A).

The five-bond, H–F coupling is indicated to be a cis interaction by the following, rather involved, argument. We have designated the fluorines F_1 and F_2 and the protons H_3 and H_4, where F_2 and H_4 have been arbitrarily assigned as being at higher field than, respectively, F_1 and H_3.

From the spectrum of the methylene region (Fig. 2B) we can deduce the two coupling constants for H_3 (9.4 and 20.5 c.p.s.) and for H_4 (1.8 and 13.7 c.p.s.) and the mutual coupling constant $J_{34} = 13.1$ c.p.s. The eight peaks of the low-field H_3 are seen to be somewhat broadened, probably by long-range coupling with either the methyl or phenyl group, or both. This coupling was too small to be analyzed. The chemical shifts of H_3 and H_4 were determined by trial and error fitting of calculated[5] and observed spectra. The final calculated spectrum (Fig. 2C) is based on the above coupling constants, $v_3 = 194.3$ c.p.s. and $v_4 = 160.4$ c.p.s. Finally, comparison with the fluorine spectrum requires that we assign the coupling constants as follows: $J_{13} = 9.4$ c.p.s., $J_{14} = 1.8$ c.p.s., $J_{23} = 20.5$ c.p.s., $J_{24} = 13.7$ c.p.s. (and $J_{34} = 13.1$ c.p.s.).

The stereochemical relationships of H_3 and H_4 with respect to the phenyl group have been established by substitution of deuterium at the 4-position. Mixtures of I and trans-4-deuterio-1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane

(5) The calculations were set up for the two protons and two fluorines as an ABXY system using the program described by K. B. Wiberg and B. J. Nist. "Theoretical NMR Spectra." W. A. Benjamin. Inc.. New York. N. Y., in press. on an IBM 7090 computer at the Computing Center of the Jet Propulsion Laboratory. We are indebted to Mr. I. Sloan for his assistance with these calculations.