J. Am. Chem. Soc. **1981**, *103*, 7102-7106

Absolute Rate Constants for Hydrocarbon Autoxidation. 31. Autoxidation of Cumene in the Presence of Tertiary Amines[†]

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Abstract: Inhibition of cumene autoxidation by low concentrations of tertiary amines has been reinvestigated. The present work indicates that the reaction is a straightforward co-oxidation and that rates of co-oxidation can be predicted from the co-oxidation rate expression and the appropriate homo- and cross-propagation and -termination rate constants. Drastic reductions in rate occur because the tertiary amines are more reactive than cumene toward cumylperoxyl and because peroxyls derived from the tertiary amines have much larger mutual termination rate constants than cumylperoxyl. These conditions ensure a low steady-state peroxyl concentration and a low overall rate of co-oxidation for cumene containing low concentrations of the tertiary amine. It has also been demonstrated that the major rate-controlling chain-carrying peroxyl for autoxidation of some tertiary amines is hydroperoxyl. This radical is more reactive than an alkylperoxyl toward propagation and termination and its involvement in tertiary amine autoxidation is one of the reasons for the large homo-propagation and -termination rate constants found for these compounds.

A number of years ago Thomas[1] discovered that the tertiary amines triethylamine and tri-*n*-butylamine are reasonably active inhibitors of the liquid-phase autoxidation of cumene at 343 K. This unexpected result was attributed to the formation of a charge-transfer complex between the chain-carrying cumylperoxy radical and the amine followed by rapid reaction of the complex with a second peroxy radical to give inactive products (reactions 1 and 2); that is, it was concluded that the reaction mechanism was analogous to the mechanism that was in vogue at the time for inhibition of hydrocarbon autoxidation by phenols and aromatic amines.[2,3]

$$\mathrm{RO_2\cdot + R_3N \rightleftharpoons [RO_2^- \cdots\cdots R_3N^+]} \qquad (1)$$

$$\mathrm{[RO_2^- \cdots\cdots R_3N^+] + RO_2\cdot \rightarrow inactive\ products} \qquad (2)$$

The usual steady-state treatment of the transients involved in an autoxidation in which reactions 1 and 2 are the chain-termination reactions predicts that the initial inhibited rate of autoxidation, R_{inh}, is proportional to the square root of the rate of chain initiation, R_{i}, and inversely proportional to the square root of the amine concentration. Thomas, however, found that although $R_{\mathrm{inh}} \propto R_{\mathrm{i}}^{1/2}$, the inhibited rate was independent of $[\mathrm{R_3N}]$ at high amine concentrations. This led him to suggest that the charge-transfer complex could undergo a mutual termination reaction (reaction 3) and a propagation reaction (reaction 4) with a rate constant considerably larger than the rate constant for reaction of cumene with uncomplexed cumylperoxyls.

$$\mathrm{2[RO_2^- \cdots\cdots {}^+NR_3] \rightarrow inactive\ products} \qquad (3)$$

$$\mathrm{[RO_2^- \cdots\cdots {}^+NR_3] + RH \xrightarrow{O_2} inactive\ products + RO_2\cdot} \qquad (4)$$

It is, however, apparent from the recent work of Alexsandrov and co-workers in the Soviet Union[4-7] that homo-propagation and -termination rate constants for autoxidation of tertiary amines are unusually large. Thus they are significantly larger than rate constants for structurally analogous ethers, e.g., $k_{\mathrm{p}} = 370\ \mathrm{M^{-1}\ s^{-1}}$ and $2k_{\mathrm{t}} = 5 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$ at 303 K for autoxidation of 3-phenyl-1,3-oxazolidene while $k_{\mathrm{p}} = 3\ \mathrm{M^{-1}\ s^{-1}}$ and $2k_{\mathrm{t}} = (1.4\text{–}8) \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$ for autoxidation of dioxacyclanes. It, therefore, occurred to us that tertiary amines may inhibit cumene autoxidation by a mechanism analogous to the one proposed by Russell[8] for inhibition of cumene autoxidation by low concentrations of the more reactive tetralin. He proposed that relatively high concentrations of tetralylperoxyls are formed in solution containing mostly cumene. These radicals terminate much more readily than cumylperoxyls and a lower rate of oxidation is observed for the mixture than for pure cumene because of the lower overall steady-state concentration of alkylperoxyls.

In an attempt to test this theory we have made a thorough investigation of the influence of four tertiary amines on the oxidation of cumene. The results of this work, which are reported here, indicate that inhibition can be adequately explained by the Russell mechanism.

Experimental Section

Materials. The tertiary amines were all commercially available and were purified either by refluxing over activated charcoal and distillation under argon or by conversion to the hydrochloride or picrate, recrystallization, and regeneration of the amine with base. They were usually passed down a column of basic alumina prior to use. Cumene, chlorobenzene, α,α'-azobis(isobutyronitrile), and 2,6-di-*tert*-butyl-4-methylphenol were purified by standard procedures. *tert*-Butyl hyponitrite was prepared by the method of Kiefer and Traylor.[9] 2,6-Di-*tert*-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadien-1-one was prepared by the method of Kharasch and Joshi.[10] 4-(2-Cyanopropyl)peroxy, 4-*tert*-butylperoxy, and 4-(α-tetralyl)peroxy-2,6-di-*tert*-butyl-4-methyl-2,5-cyclohexadien-1-ones were gifts from Dr. K. U. Ingold. 2,6-Di-*tert*-butyl-4-methyl-4-(α-cumyl)peroxy-2,5-cyclohexadien-1-one was prepared by autoxidation of cumene in the presence of 2,6-di-*tert*-butyl-4-methylphenol at 303 K.

Procedure. Rates of autoxidation were determined on the apparatus described in a previous part of this series.[11]

Trapping the Chain-Carrying Peroxy Radical. The chain-carrying peroxy radicals involved in the autoxidation of triethylamine, dimethylaniline, diethylaniline, and triisopropylamine were identified by trapping experiments with 2,6-di-*tert*-butyl-4-methylphenol (BMP). In this technique the thermally initiated autoxidation of the tertiary amine was performed in the presence of a low concentration of BMP. During the inhibited reaction the chain-carrying peroxy radical abstracts the phenolic hydrogen from BMP to give 2,6-di-*tert*-butyl-4-methylphenoxyl (AO·) which is removed from the system by reaction with a second peroxy radical to give a 2,6-di-*tert*-butyl-4-methyl-4-alkylperoxy-2,5-cyclo-

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[†] Issued as NRCC No. 18932.

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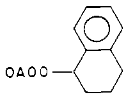
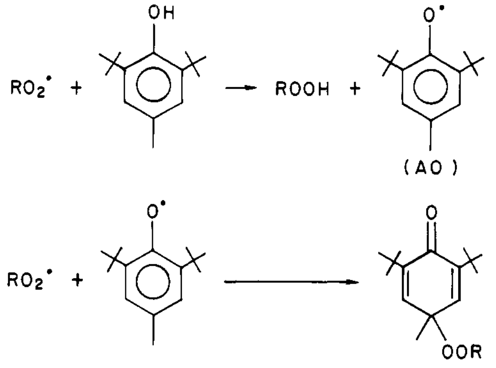
Table I. Elution Times (t_R) for Various 2,6-Di-*tert*-butyl-4-methyl-4-(alkylperoxy)-2,5-cyclohexadien-1-ones

compd	t_R/min[a] A	t_R/min[a] B
OAOOH	2.9	13.5
$OAOOC(CH_3)_2CN$	7.6	35.3
$OAOOC(CH_3)_3$	16.8	74.1
	20.0	91.8
$OAOOC(CH_3)_2Ph$	22.4	100.6
BMP	5.9	25.9

[a] A is 3.2 mL/min. B is 0.8 mL/min.

hexadien-1-one, ROOAO, as shown below, where R = H, if $HO_2\cdot$ is the chain carrier, or it is an alkyl radical derived from the substrate or initiator.



We have previously used this technique to demonstrate that $HO_2\cdot$ is the principal rate-controlling chain-carrying species for the liquid-phase autoxidation of cyclohexa-1,4-diene at 303 K[12] and that α-hydroxybenzylperoxyl is the principal rate-controlling chain carrier for the liquid-phase autoxidation of benzyl alcohol.[13] In the previous work a thin layer chromatographic method was used to separate HOOAO from ROOAO.[14,15] In the present work we have used reverse-phase high-performance liquid chromatography to determine the oxidation products of BMP. This method is very much more accurate than the TLC method for quantitative estimates of yields of ROOAO and HOOAO. Furthermore ROOAO's with different *R*'s are readily separated by HPLC (Table I). The chromatograph used for this work was a Spectra-Physics 3000 equipped with a Brownlee RP 8 column. Isochratic solvent elution was used and the eluting solvent was CH_3CN-H_2O, 70–30 (v/v), and the flow rate was either 0.8 or 3.2 mL/min. Typical retention times under these conditions are given in Table I.

Concentrations of ROOAO were determined by standard chromatographic procedures and yields were based on the number of peroxyls which reacted with AO·. This number was calculated from $R_it/2$ where t is the total reaction time and R_i is equal to $2ek_d[In_2]$ where $[In_2]$ is the concentration of the thermal initiator, k_d is the rate constant for unimolecular decomposition of In_2, and e is the efficiency with which In_2 gives free radicals. α,α'-Azobis(isobutyronitrile) and di-*tert*-butyl hyponitrite were used as thermal initiators.

In control experiments autoxidation of cyclohexa-1,4-diene containing AIBN (0.22 M) and BMP (2 mM) gave HOORO (~100%) and a very low yield of a product which, from its retention time, may have been 1,4-c-C_6H_7OOAO. Autoxidation of cumene (7.17 M) containing BMP (3.8 mM) and AIBN (0.1 M) gave $CNC(CH_3)_2OOAO$ (61%) and $PhCMe_2OOAO$ (13%), yields which are reasonably consistent with the relative reactivity of BMP and $PhCMe_2H$ toward $RO_2\cdot$.

Radical-trapping experiments with the tertiary amines were carried out in exactly the same manner except that in some experiments the amine was removed from the reaction mixture prior to analysis by distillation and the residue dissolved in CH_3CN.

Table II. Rates of Autoxidation of Cumene and Triethylamine at 303 K in the Presence of AIBN (0.06 M)[a]

[cumene]/ M	[triethylamine]/ M	$10^7(-d[O_2]/dt)$/ $M\ s^{-1}$
7.17	0	7.7
7.17	0.00049	1.2
7.17	0.001	0.46
7.17	0.0049	0.285
7.17	0.01	0.18
7.17	0.036	0.42
6.45	0.72	0.28
0	3.6[b]	7.1

[a] $R_i = 5.35 \times 10^{-9}$ M s^{-1}. [b] In chlorobenzene.

Products. Reaction products of tertiary amine autoxidation were identified by reverse-phase high-pressure liquid chromatography and by a combination of gas chromatography and mass spectrometry. Product yields were determined by standard chromatographic procedures. Total hydroperoxides were determined by iodometric titration. The fraction of H_2O_2 in the total hydroperoxide was determined by the water extraction procedure described previously.[12]

Results and Discussion

Triethylamine. Kinetic data for autoxidation of cumene in the presence of low concentrations of Et_3N are given in Table II and presented graphically in Figure 1a. These data confirm Thomas' findings[1] that low concentrations of Et_3N (<0.005 M) dramatically reduce the rate of autoxidation of cumene and that above a concentration of ~0.01 M the rate is almost independent of the amine concentration.

If it is assumed that the overall reaction is a co-oxidation, the elementary reactions given in Scheme I are needed to describe the reaction and to derive the overall rate expression, where AH and BH represent $PhCMe_2H$ and Et_3N, respectively and A·, B·, $AO_2\cdot$, and $BO_2\cdot$ represent the corresponding alkyl and alkylperoxy radicals.

Scheme I

initiation

$$\text{production of free radicals} \tag{5}$$

propagation

$$A\cdot + O_2 \rightarrow AO_2\cdot \tag{6}$$

$$B\cdot + O_2 \rightarrow BO_2\cdot \tag{7}$$

$$AO_2\cdot + AH \rightarrow AOOH + A\cdot \tag{8}$$

$$AO_2\cdot + BH \rightarrow AOOH + B\cdot \tag{9}$$

$$BO_2\cdot + BH \rightarrow BOOH + B\cdot \tag{10}$$

$$BO_2\cdot + AH \rightarrow BOOH + A\cdot \tag{11}$$

termination

$$\left.\begin{array}{l} AO_2\cdot + AO_2\cdot \\ AO_2\cdot + BO_2\cdot \\ BO_2\cdot + BO_2\cdot \end{array}\right\} \begin{array}{l} \rightarrow \\ \rightarrow \text{inactive products} \\ \rightarrow \end{array} \qquad \begin{array}{r} (12) \\ (13) \\ (14) \end{array}$$

By using the usual steady-state assumptions it is readily shown that the rate of co-oxidation is given by

$$\frac{-d[O_2]}{dt} = \frac{\{k_8k_{11}[AH]^2 + 2k_9k_{11}[AH][BH] + k_9k_{10}[BH]^2\}R_i^{1/2}}{\{k_{12}k_{11}^2[AH]^2 + k_{13}k_9k_{11}[AH][BH] + k_{14}k_9^2[BH]^2\}^{1/2}} \tag{15}$$

where k_8, k_9, etc., are the rate constants for reactions 8, 9, etc.

If this mechanism is correct it should be possible to simulate the shape of the plot of R_{inh} against $[Et_3N]$ from the data in Table I and absolute values of the rate constants k_8 to k_{14}. Of these seven rate constants two are known accurately, $k_8 = 0.18$ M^{-1} s^{-1} and $k_{12} = 1.5 \times 10^4$ M^{-1} s^{-1},[16] while we can reasonably assume

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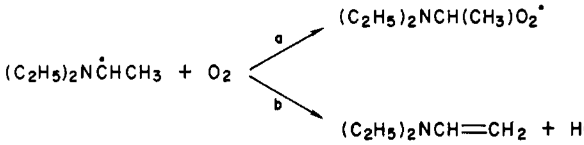
that $k_9 = 11.5$ M^{-1} s^{-1}, i.e., k_9 is equal to the overall rate constant for reaction of t-$BuO_2\cdot$ with Et_3N[17] divided by 2. Thus $PhCMe_2O_2\cdot$ and t-$BuO_2\cdot$ should have the same reactivity toward Et_3N and two peroxyls are almost certainly destroyed by each molecule of Et_3N under the conditions that the overall rate constant was measured. The value of $k_{10}/(k_{14})^{1/2} \sim 2.7 \times 10^{-3}$ $M^{-1/2}$ $s^{-1/2}$ was estimated from initial rates of AIBN-initiated oxidation of Et_3N in chlorobenzene. Autoxidation of Et_3N is very autoinhibiting and initial rates had to be used to estimate oxidizability. The value of $k_{10}/(k_{14})^{1/2}$ is, therefore, not too accurate but it does put a constraint in the values of k_{10} and k_{14} that can be chosen for the simulation.

Initially we assumed that the chain-carrying peroxyl for autoxidation of Et_3N was α-(diethylamino)ethylperoxyl, $(C_2H_5)_2NCH(CH_3)O_2\cdot$, and that its reactivity toward cross- and self-propagation and -termination was similar to the reactivity of secondary aralkylperoxyls.[13,18] It soon became apparent, however, that although plots of R_{inh} against $[R_3N]$ could be calculated from eq 15 to pass through most of the experimental data these calculations required unusually large values for the rate constants k_{10}, k_{13}, and k_{14}. Thus the solid line in Figure 1a was obtained with use of $k_{10} = 270$ M^{-1} s^{-1}, $k_{11} = 5.0$ M^{-1} s^{-1}, $k_{13} = 5 \times 10^9$ M^{-1} s^{-1}, and $k_{14} = 1 \times 10^{10}$ M^{-1} s^{-1}. This suggests that either $(C_2H_5)_2NCH(CH_3)O_2\cdot$ is extremely reactive toward propagation and termination or it is not the rate-controlling peroxyl. Radical trapping experiments were then performed and it was found that 2,6-di-*tert*-butyl-4-methylphenol was converted almost exclusively to 2,6-di-*tert*-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadien-1-one in oxidizing Et_3N. This indicates that HO_2 is the major chain-carrying peroxyl for this trialkylamine. This result is consistent with the high value of k_{14} estimated above because in nonpolar solvents $HO_2\cdot$ has homo-termination rate constants in the range (1–10) × 10^9 M^{-1} s^{-1}.[11]

It is somewhat surprising that oxygen reacts with α-(diethylamino)ethyl to give hydroperoxyl (reaction 16b) rather than a peroxyl (reaction 16a). Thus the disproportionation reaction only



$$(C_2H_5)_2N\dot{C}HCH_3 + O_2 \begin{cases} \xrightarrow{a} (C_2H_5)_2NCH(CH_3)O_2^{\bullet} \\ \xrightarrow{b} (C_2H_5)_2NCH{=}CH_2 + HO_2^{\bullet} \end{cases} \quad (16)$$

occurs if the unsaturated compound is particularly stable. For instance, cyclohexadienyl reacts with oxygen at ambient temperatures to give benzene and $HO_2\cdot$.[11] There are, however, several reports which indicate that α-(dialkylamino)alkyls readily lose an H atom. Thus diketones abstract an H atom from α-(dialkylamino)alkyls

$$RC(O)C(O)R + CH_3\dot{C}HN(C_2H_5)_2 \rightarrow RC(O)\dot{C}(OH)R + CH_2{=}CHN(C_2H_5)_2 \quad (17)$$

where R = CH_3 or C_6H_5, with rate constants 10^7–10^9 M^{-1} s^{-1}.[19-23] Furthermore paraquat (methylviologen) reacts with α-(diethylamino)ethyl in methanol at 300 K with a rate constant of 1.05 × 10^9 M^{-1} s^{-1}.[24]

The mechanism of the reaction of oxygen with α-(diethylamino)ethyl to give $HO_2\cdot$ may be an H-atom-transfer reaction or an electron-transfer reaction followed by protonation of the superoxide ion. Reaction 18 is quite feasible in low-polarity solvents because of the extremely low ionization potentials of α-(dialkylamino)alkyls.[25]

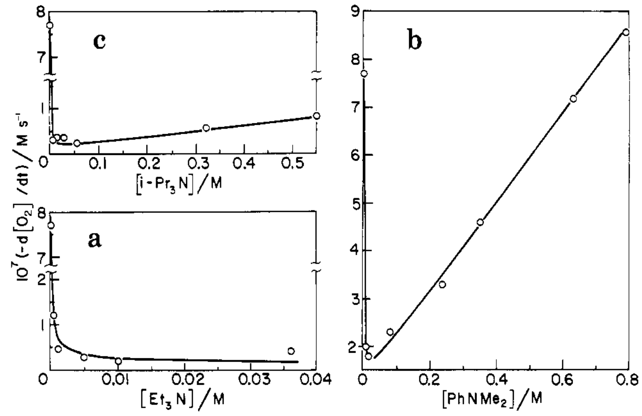


Figure 1. a. The rate of co-oxidation of cumene and Et_3N as a function of the amine concentration. b. The rate of co-oxidation of cumene and $PhNMe_2$ as a function of the amine concentration. c. The rate of cooxidation of cumene and i-Pr_3N as a function of the amine concentration.

Table III. Rates of Autoxidation of Cumene and Dimethylaniline at 303 K in the Presence of AIBN (0.061 M)

[cumene]/ M	[dimethylaniline]/ M	10^7-(−d[O_2]/dt)/ M s^{-1}
7.17	0	7.7
7.17	0.008	2.0
7.17	0.016	1.8
7.1	0.08	2.3
6.95	0.235	3.3
6.85	0.35	4.6
6.57	0.63	7.2
6.45	0.79	8.6
0	1.33[a]	11.7

[a] In chlorobenzene.

$$(C_2H_5)_2N\dot{C}HCH_3 + O_2 \rightarrow (C_2H_5)_2\overset{+}{N}CHCH_3 + O_2^- \rightarrow (C_2H_5)_2NCH{=}CH_2 + HO_2\cdot \quad (18)$$

***N,N*-Diethylaniline.** *N,N*-Diethylaniline is an efficient inhibitor of cumene autoxidation at 303 K and the shape of the plot of $-d[O_2]/dt$ against $[PhNEt_2]$ is similar to the one shown in Figure 1a. The effect of the two amines is, however, not exactly the same because below a concentration of ~0.1 M $PhNEt_2$ is slightly less efficient than Et_3N while above this concentration it is slightly more efficient. It seems reasonable to conclude that the mechanism for inhibition by $PhNEt_2$ is the same as the mechanism for inhibition by Et_3N, i.e., $PhNEt_2$ is more reactive than cumene to peroxyls and has a considerably larger mutual termination rate constant than the aralkane. This conclusion is supported by the fact that the overall rate constant for reaction of $PhNEt_2$ with t-$BuO_2\cdot$ at 303 K is 21 ± 3 M^{-1} s^{-1}.[17] Furthermore BMP is oxidized almost exclusively to HOOAO in $PhNEt_2$, indicating that $HO_2\cdot$ is the major chain-carrying peroxyl for this tertiary amine.

***N,N*-Dimethylaniline.** Autoxidation of cumene is inhibited by low concentrations of $PhNMe_2$ (Table III and Figure 1b). The minimum overall rate is, however, about 10 times faster than the minimum rate obtained with Et_3N and occurs at a higher amine concentration. Furthermore, the overall rate increases dramatically when the amine concentration is increased above about 0.02 M. The plot of $-d[O_2]/dt$ against $[PhNMe_2]$ has in fact the same shape as the curve obtained from oxidation of cumene containing low concentrations of tetralin.[8,26] A rate–composition curve of this shape indicates that k_p and $2k_t$ for $PhNMe_2$ are larger than

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the corresponding absolute rate constants for cumene. However, $2k_t$ cannot be as large as the values for Et_3N and $PhNEt_2$ because of the increase in rate at higher amine concentrations. This conclusion is consistent with the values of $k_p = 510\ M^{-1}\ s^{-1}$ and $2k_t = 2.4 \times 10^8\ M^{-1}\ s^{-1}$ for $PhNMe_2$ reported recently by Bakhturidge, Alexsandrov, and Edilashvili.[6]

An initial simulation of the rate–composition curve was made with use of Bakhturidge, Alexsandrov, and Edilashvili's rate constants and $k_8 = 0.18\ M^{-1}\ s^{-1}$, $k_{12} = 1.5 \times 10^4\ M^{-1}\ s^{-1}$, $k_9 = 24\ M^{-1}\ s^{-1}$ (i.e., one-half the overall rate constant for reaction of $t\text{-}BuO_2\cdot$ with $PhNMe_2$[17]), and $k_{13} = 1.2 \times 10^8\ M^{-1}\ s^{-1}$. We found, however, that most of the experimental rates at the higher dimethylaniline concentrations fell below this line. A much better simulation (the solid line in Figure 1b) was obtained if k_p for $PhNMe_2$, i.e., k_{10}, was reduced to $220\ M^{-1}\ s^{-1}$. This suggests that the oxidizability of $PhNMe_2$ may be lower than the value of $3.3 \times 10^{-2}\ M^{-1/2}\ s^{-1/2}$ reported by the Russian workers. In support of this conclusion our sample of $PhNMe_2$ gave $k_p/(2k_t)^{1/2} = (1.2 \pm 0.2) \times 10^{-2}\ M^{-1/2}\ s^{-1/2}$.

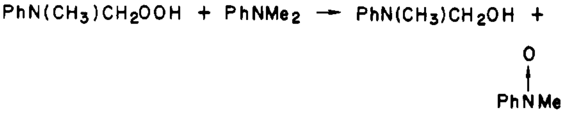
Bakhturidge, Alexsandrov, and Edilashvili reported that H_2O_2 was formed in a yield of ~24% from oxidation of $PhNMe_2$ which suggests that $HO_2\cdot$ might be an important chain-carrying species. We could, however, find no evidence for the production of HOOAO in BMP-inhibited oxidations of $PhNMe_2$ while there was a peak in the HPLC chromatogram which by analogy with other ROOAO's could have been $PhN(CH_3)CH_2OOAO$. This suggests that $PhN(CH_3)CH_2O_2\cdot$ and not $HO_2\cdot$ is the major chain-carrying peroxyl for autoxidation of $PhNMe_2$ which is consistent with the measured value of $2k_t$ because primary alkyl- and aralkylperoxyls have $2k_t$'s in the range $(0.5\text{–}3) \times 10^8\ M^{-1}\ s^{-1}$ while the value for $HO_2\cdot$ is about an order of magnitude larger.[16]

In support of this conclusion we found that a hydroperoxide, which was presumably $PhN(CH_3)CH_2OOH$, was formed in ~90% yield, based on the amount of O_2 absorbed. Extraction of oxidized $PhNMe_2$ with water did not give a water-soluble peroxidic product. If, however, oxidized $PhNMe_2$ was allowed to stand at room temperature under argon for several hours a product which liberated iodine from acidified KI was produced in substantial yields. This product turned out to be dimethylaniline *N*-oxide and not H_2O_2. We, therefore, conclude that $PhN(CH_3)CH_2O_2\cdot$ is the main chain-carrying peroxyl for autoxidation of $PhNMe_2$.

Bakhturidge, Alexsandrov, and Edilashvili[6] suggested reaction 19 for the formation of the major reaction products.

$$2PhN(CH_3)CH_2OOH \rightarrow H_2O_2 + PhN(CH_3)H + PhN(CH_3)CHO + CH_2O \quad (19)$$

It is, however, known that α-aminoalkyl hydroperoxides react rapidly with amines to give the *N*-oxide.[27] We, therefore, propose that the following reactions are consistent with the reaction products.



$$PhN(CH_3)CH_2OOH + PhNMe_2 \rightarrow PhN(CH_3)CH_2OH + PhN(\rightarrow O)Me_2 \quad (20)$$

$$PhN(CH_3)CH_2OH \longrightarrow PhNHCH_3 + CH_2O \quad (21)$$

$$PhN(CH_3)CH_2OOH + R^\bullet \rightarrow PhN(CH_3)CHO + RH \quad (22)$$

Thus dimethylaniline *N*-oxide, methylaniline, and *N*-methylformanilide are secondary reaction products and H_2O_2 is not formed in significant yields.

In experiments designed to confirm the extremely high value of the homo-propagation rate constant for autoxidation of $PhNMe_2$ we investigated the kinetics of inhibition of this substrate by BMP. Overall rates of oxidation in the presence of this hindered phenol usually obey the rate law

$$-d[O_2]/dt = k_p[RH]R_i/2k_{inh}[BMP] \quad (23)$$

where k_{inh} is the rate constant for reaction of $RO_2\cdot$ with BMP.[28,29] This is because hindered phenoxyls do not react with the substrate or accumulated hydroperoxide and are removed by reaction with a peroxyl. Absolute values of k_{inh} are known for a large number of alkylperoxyls and do not appear to depend to any great extent on the alkyl moiety in the radical.[30] Measurement of $-d[O_2]/dt$ at a known [RH] and R_i should therefore give a value for the rate constant ratio k_p/k_{inh} and some indication of the magnitude of k_p. Surprisingly we found that although BMP is an efficient inhibitor for autoxidation of $PhNMe_2$, inhibited rates were not proportional to the concentrations of BMP (Table IV). Inhibited rates which are independent of the inhibitor concentration are usually associated with inhibitors which give radicals that can propagate the chain and disappear by mutual reaction.[31] This should, however, not be the explanation in the present case because although hindered phenoxyls react with $PhNMe_2$ the rate is very slow, e.g., the rate constant for reaction of 2,4,6-tri-*tert*-butylphenoxyl with $PhNMe_2$ at 303 K is ~$0.001_2\ M^{-1}\ s^{-1}$ at 299 K. In addition the 2,6-di-*tert*-butyl-4-methylphenoxyl should not undergo mutual reaction but should disappear by reaction with a peroxyl. We have not yet made a thorough investigation of this reaction but we can conclude that eq 23 does not apply to the BMP-inhibited oxidation of $PhNMe_2$ and cannot be used to estimate k_p.

Table IV. Rates of Autoxidation of $PhNMe_2$ Containing AIBN (0.12 M) and 2,6-Di-*tert*-butyl-4-methylphenol at 303 K

10^3[BMP]/ M	$10^7(-d[O_2]/dt)$/ M s^{-1}	10^3[BMP]/ M	10^7-$(-d[O_2]/dt)$/ M s^{-1}
0	19 ± 2.8[a]	1.0	1.9
0.1	2.4	2.0	1.5
0.5	2.0	10	0.78

[a] 1.58 M in chlorobenzene.

Table V. Rates of Coautoxidation of Cumene and Triisopropylamine at 303 K in the Presence of AIBN (0.06 M)

[cumene]/ M	$[i\text{-}Pr_3N]$/ M	$10^7(-d[O_2]/dt)$/ M s^{-1}
7.17	0	7.7
7.17	0.005	0.3
7.17	0.011	0.36
7.17	0.026	0.36
7.18	0.053	0.22
6.76	0.32	0.55
6.47	0.53	0.8
0	2.6[a]	2.3

[a] In chlorobenzene.

Triisopropylamine. Triisopropylamine, which contains labile tertiary H atoms, inhibits the autoxidation of cumene (Table V and Figure 1c). Inhibition is, therefore, not confined to trialkylamines with primary and secondary hydrogens α to the nitrogen as might be expected from the Russell mechanism.

This trialkylamine oxidizes quite rapidly at 303 K and $k_p/(2k_t)^{1/2} = 1.2 \times 10^{-3}\ M^{-1/2}\ s^{-1/2}$ and the overall rate constant for reaction with $t\text{-}BuO_2\cdot$ is $29.7 \pm 3\ M^{-1}\ s^{-1}$. Product analyses indicated that $i\text{-}Pr_2NC(CH_3)_2OOH$ and H_2O_2 are formed in about equal yields in the uninhibited oxidation and that HOOAO is formed in about 30% yield in the BMP-inhibited oxidation. The principal rate-controlling chain-carrying peroxyl for autoxidation of $i\text{-}Pr_3N$ is, therefore, $HO_2\cdot$. This means that in the co-oxidation with cumene k_{14} must be ~$10^{10}\ M^{-1}\ s^{-1}$ and $k_{10} \sim 120\ M^{-1}\ s^{-1}$. Simulations of the rate–composition curve were made using this information and we found that an acceptable simulation (the solid curve in Figure 1c) was obtained with the following values for the unknown rate constants, $k_{11} = 5\ M^{-1}\ s^{-1}$, $k_{10} = 220\ M^{-1}\ s^{-1}$, $k_{13} = 5 \times 10^9\ M^{-1}\ s^{-1}$, and $k_{10} = 10^{10}\ M^{-1}\ s^{-1}$. In this simulation

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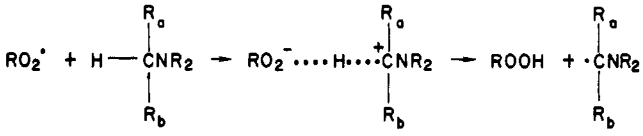
we have assumed that if $HO_2\cdot$ is the major rate-controlling peroxyl for Et_3N and $i\text{-}Pr_3N$ the values of k_{11}, k_{13}, and k_{14} should be the same for the two amines. The value of k_{10} is, therefore, a little larger than the value that can be calculated from $k_p/(2k_t)^{1/2}$.

Conclusions

Low concentrations of tertiary amines inhibit the liquid-phase autoxidation of cumene by a mechanism which is similar to the one proposed by Russell for inhibition of cumene by tetralin.[8] Thus they possess the two criteria, high reactivity toward propagation *and* termination, required by the Russell mechanism. They are extremely reactive in propagation because the transition state for abstraction of an α-hydrogen atom has substantial charge separation and because α-(dialkylamino)alkyls have remarkably high stabilization energies.[17,25]



$$RO_2^{\bullet} + H-\overset{R_a}{\underset{R_b}{C}}NR_2 \rightarrow RO_2^{-}\cdots H\cdots\overset{+R_a}{\underset{R_b}{C}}NR_2 \rightarrow ROOH + \cdot\overset{R_a}{\underset{R_b}{C}}NR_2$$

Furthermore the peroxyls derived from tertiary amines have very large overall termination rate constants. In some cases this is because $HO_2\cdot$ is the major rate-controlling chain-carrying radical.

Although homo- and cross-propagation and -termination rate constants can be derived from rates of co-oxidation by a curve-fitting procedure these rate constants should not be construed as absolute values but should only be taken as giving some indication of the magnitude of these rate constants.

Finally, a number of years ago Hammond, Boozer, Hamilton, and Sen[32] reported that *N*,*N*-dimethylaniline and *N*,*N'*-tetramethyl-*p*-phenylenediamine are inhibitors of hydrocarbon autoxidation "despite the absence of labile hydrogens". This was held as evidence for an inhibition mechanism in which the first step was the rate-controlling reversible formation of a loose molecular complex between inhibitor and $RO_2\cdot$. Clearly these tertiary amines do contain quite labile hydrogens and inhibition is adequately explained by the Russell mechanism.

Acknowledgment. The authors are grateful to Dr. K. F. Preston for writing the computer program to solve eq 15. We also thank Dr. D. Griller and Dr. J. C. Scaiano for helpful discussions.

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Electronic Control of Stereoselectivity. 8. The Stereochemical Course of Electrophilic Additions to Aryl-Substituted 9-Isopropylidenebenzonorbornenes[1]

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Received February 2, 1981

Abstract: A series of aryl-substituted 9-isopropylidenebenzonorbornenes (**1**–**4**) and the parent 7-isopropylidenenorbornene (**5**) have been synthesized, and the stereochemistry of addition of numerous electrophiles to their exocyclic double bond has been determined. For assistance in interpreting the results, photoelectron spectroscopic investigations and extensive ZDO and MINDO/3 calculations were also undertaken. When weak electrophilic reagents such as singlet oxygen, *m*-chloroperbenzoic acid, *N*-bromosuccinimide, *N*-methyltriazolinedione, and *tert*-butyl hypochlorite were studied, all gave product distributions which greatly favored anti addition when the aryl ring was unsubstituted or substituted by a pair of methoxyl groups. The placement of chlorine or fluorine groups on the aromatic ring was accompanied by a substantial enhancement in the relative amount of syn product. For strong electrophiles such as protonated *tert*-butyl hypochlorite, dichlorocarbene, the acetylium cation, and protonated formaldehyde, syn attack was greatly favored or dominated exclusively. These marked crossovers in syn/anti stereoselection, which serve as a convenient tool with which to assess relative electrophilicity, may be explained in terms of the involvement of bridged or open ion pathways. Where bridged ions develop (weak electrophiles), long-range homoaromatic charge delocalization to the aromatic ring develops, with the result that anti attack becomes kinetically dominant. When powerfully electrophilic species are involved, this phenomenon is not important and transient aryl complex formation appears controlling.

Numerous kinetic and product studies of electrophilic reactions have been carried out in an attempt to describe the structural features of transition states and activated complexes. Despite considerable success in this area,[3] essentially no attention has been paid to the possible control of electrophilic stereoselection by remote electronic influences. In our view, such electronic control of stereoselectivity is considered a potentially rich source of information concerning several important aspects of electrophilic processes. These include the following: (a) knowledge of pivotal transition-state orbital interactions which often go unappreciated, since they now will be determinative of product stereochemistry; (b) added reliability in gaining pertinent information concerning the nature of the transient species, in particular whether an open or bridged cation is involved; and (c) development of a stereochemical method for the qualitative assessment of relative electrophilicity.

It is widely recognized that linear free-energy relationships such as the Hammett and Taft correlations, as well as more recent multiple parameter versions, are of limited use because a single set of substituent steric and polar parameters is inadequate for

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