trolled should exhibit curvature at concentrations above about 0.01 M. The curvature is caused by the bimolecular lifetime effect which leads to a quencher dependent correlation length. The extent of curvature, however, depends strongly on the unimolecular lifetime and the diffusion constant of the fluorophore. This is readily apparent in Figure 3. While both perylene and 9-vinylanthracene have the same value of k^{obsd} at low oxygen concentration, the curvature in the Stern–Volmer plot is significantly greater for the longer lived 9-vinylanthracene.

The second general feature demonstrated by the calculations is the diminution of curvature for reactions which are not diffusion controlled. Slower reactions reduce the effect of the bimolecular lifetime on k^{obsd} with a subsequent loss of sensitivity to increased quencher concentration. While we have speculated that this is the cause of the negligible curvature for oxygen quenching of tryptophan in water, the effect itself is quite general.

The quality of agreement between experiments and the calculations based on eq 15 or 17 is good. Further tests of the theory, however, suggest themselves. For example, it would be useful to have data on quenching rates and diffusion constants in a variable solvent system like glycerol–water to test the effect of changing viscosity on the low quencher concentration value of k^{obsd}. The only data we have seen of this sort are two data points for the aniline quenching of uranin.[24] Although a calculation based on eq 17 is in agreement with these data, it would be nice to have a full range of weight percent mixtures with which to compare the theory. We are hopeful that such experiments will be forthcoming. While charge effects have not been included in the present calculations, they can in principle be added. Experimental data involving the effect of ionic strength would be particularly useful for charged systems.

The effects discussed in this paper have been confined to fluorophores which do not engage in molecular association with quencher molecules. If molecular complexes are formed which do not fluoresce, then the Bowen–Metcalfe result in eq 6 combined

with the definition of the lifetime of A*, i.e., $\tau = (\tau_0^{-1} + k^{obsd}\cdot[Q])^{-1}$, shows that

$$I_0/I = (1 + K[Q])\tau_0/\tau \qquad (19)$$

Thus in the absence of this type of molecular association

$$I_0/I = \tau_0/\tau \qquad (20)$$

which is one of the criteria for the absence of quenching via molecular association and has been verified, for example, for the oxygen quenching of tryptophan.[7] As we have shown, the purely dynamic effects described in this paper lead to positive curvature in Stern–Volmer plots even when molecular association is absent. If static quenching via molecular association also occurs, then eq 19 shows that I_0/I will be greater than τ_0/τ. Furthermore, the molecular association constant can be obtained as the slope of a plot of $I_0\tau/I\tau_0$ vs. [Q]. An interesting limiting case occurs when the lifetime τ_0 is short enough or the quenching rate constant is small enough that $k^{obsd}[Q]\tau_0 \ll 1$. This implies that dynamic quenching is negligible and that $\tau/\tau_0 \approx 1$. In this case only static quenching will be observed and

$$I_0/I \approx (1 + K[Q])$$

Quenching through this sort of purely static mechanism has been observed for several flavin compounds in aqueous solution.[28]

Registry No. Anthracene, 120-12-7; quinine sulfate, 804-63-7; uranin, 518-47-8; 9-vinylanthracene, 2444-68-0; perylene, 198-55-0; tryptophan, 73-22-3.

(28) G. Weber in "Flavins and Flavoproteins", E. C. Slater, Ed., Elsevier, Amsterdam, 1966, pp 15–21, Table II.

Spin Trapping of Peroxy Radicals by Phenyl-*N*-(*tert*-butyl)nitrone and Methyl-*N*-durylnitrone

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Abstract: The spin trapping of *tert*-butylperoxy and tetralylperoxy radicals by phenyl-*N*-(*tert*-butyl)nitrone (PBN) and methyl-*N*-durylnitrone (MDN) has been investigated. The peroxy radicals were generated by the alkoxy radical induced decomposition of hydroperoxides, hydrogen atom abstraction from hydrocarbon in the presence of oxygen, and decomposition of hydroperoxides by cobaltous ion and lead tetraacetate. The spin adducts of peroxy radicals were observed by ESR and their hyperfine splitting constants were determined. The spin adduct of peroxy radicals by MDN could be clearly distinguished from that of alkoxy radical. The nitrone spin adducts of oxygen radicals were found to be reasonably stable at room temperature in the dark, but they decayed readily in the ordinary laboratory light.

A process commonly referred to as "spin trapping" has been applied in the studies of free-radical chemistry and biology.[1-4] The transient radicals are scavenged by spin traps and converted to longer lived spin adducts, whose ESR spectra provide valuable information concerning the structure of the intermediate radicals

and the mechanisms of the reactions in which they are involved. At the same time, however, it has been pointed out that cautions have to be observed especially in the stability of the spin adducts and interpretation of ESR spectra.[2,5,6] The trapping of oxygen radicals has received considerable attention.[2,3,6,7] We have previously reported[8] the spin trapping of peroxy radicals by

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(3) Perkins, M. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 1–64, and references cited therein.

(4) Janzen, E. G.; Evans, C. A.; Davis, E. R. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; pp 433–446; *ACS Symp. Ser.* No. 69.

(5) Coxon, J. M.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 379–381.

(6) Rosen, G. M.; Rauckman, E. J. In "Oxygen and Oxy-Radicals in Chemistry and Biology"; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; pp 97–108.

(7) Harbour, J. R.; Bolton, J. R. *Photochem. Photobiol.* **1978**, *28*, 231–238.

Table I. Hyperfine Splitting Constants of Peroxy and Alkoxy Radical Spin Adducts by PBN[a]

radical	source	temp[b]/°C	solvent	a_N/G	a_H/G	ref
BOO	BOOH–DBPO	r.t.	PhH	13.35	1.38	this work
BOO	BOOH–Co²⁺	r.t.	PhH	13.53	1.39	this work
BOO	BOOH–DBPO	r.t.	PhH	13.34	1.25	8
BOO	BOOH–Pb(OAc)₄	−80	PhH	13.39	1.19	9
BOO	BC(=O)B–$h\nu$–O₂	−80	PhCH₃	13.42	0.95	10
TOO	TOOH–CO²⁺	r.t.	PhH	13.79	1.98	this work
TOO	TOOH–DBPO	r.t.	PhH	13.96	1.94	this work
TOO	TOOH–Pb(OAc)₄	r.t.	PhH	13.86	1.83	this work
TOO	TH–DBPO–O₂	r.t.	PhH	13.81	1.88	this work
TOO	TOOH–DBPO	r.t.	PhH	13.68	1.78	8
BO	DBPO	r.t.	PhH	14.11	1.83	this work
BO	BOOH–Co²⁺	r.t.	PhH	14.48	1.86	this work
BO	c	r.t.	PhH	14.34	1.84	this work
BO	DBPO	r.t.	PhH	14.21	1.83	8
BO		r.t.	PhH + t-BuOH	14.61	1.99	13
TO	TOOH–Co²⁺	r.t.	PhH	14.18	2.28	this work

[a] B = *tert*-butyl, T = 1-tetralyl. [b] r.t. = room temperature. [c] DBPO was decomposed in benzene containing benzyl *tert*-butyl ether and NtB (see text).

phenyl-*N*-(*tert*-butyl)nitrone (PBN). At about the same time, Merritt,[9] Howard,[10] and Zubarev[11] also reported on the spin trapping of peroxy radicals by PBN. The peroxy radicals were generated either by the oxidation of hydrocarbons by molecular oxygen in the presence of radical initiator,[8] induced decomposition of hydroperoxides,[8] thermal decomposition of azo compounds in the presence of oxygen,[8] interaction of superoxide anion radical with alkyl halide,[9] decomposition of hydroperoxides by lead tetraacetate,[9] photolysis of dialkyl ketones in oxygen-saturated solution,[10] or X-ray irradiation of hydrocarbons in the presence of oxygen.[11] Although peroxy radicals could be trapped by PBN and ESR spectral parameters of the peroxy radical spin adducts have been measured, it has been argued that these spin adducts are unstable and can be replaced by the alkoxy radical spin adduct.

Although it was referred to only briefly in the previous papers,[8,12] we found that the peroxy radical spin adducts were unstable toward light. We first realized this phenomenon by the troublesome, poor reproducibility of the experiments in spin trapping. Light was found to be responsible, and reproducible and reliable data could be obtained when the experiments were carried out under quite low levels of light or in the dark. The effect of light on the stability of spin adducts of hydroxyalkyl radicals has been recently reported by Gilbert and co-workers.[5]

Considering the importance of peroxy radical as a chain carrier in the oxidation of various systems, we have undertaken the reinvestigation of the spin trapping of peroxy radicals by PBN. One

PBN   MDN
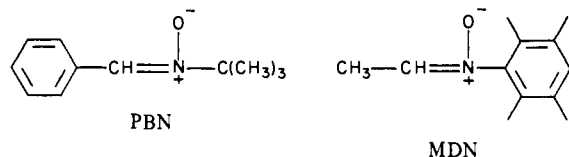
of the difficulties was that the spin adducts of peroxy and alkoxy radicals by PBN have similar coupling constants. It was possible to overcome this difficulty by using a novel spin trap, methyl-*N*-durylnitrone (MDN), which was found by Konaka[13] to give spin adducts of peroxy and alkoxy radicals that could be distinguished clearly from each other.

Experimental Section

Materials. The spin trap MDN was kindly provided by Dr. Konaka at Shionogi Research Laboratories. PBN and nitroso-*tert*-butane (NtB)

were used as received from Aldrich.

Commercial *tert*-butyl hydroperoxide (BOOH) was distilled under reduced pressure prior to use, 42 °C (24 torr). 1-Tetralyl hydroperoxide (TOOH) was prepared by the air oxidation of tetralin in the presence of azobisisobutyronitrile, followed by recrystallization from heptane. Di-*tert*-butyl diperoxyoxalate (DBPO)[14] and benzyl *tert*-butyl peroxide[15] were synthesized by the methods described in the literature. Commercial benzoyl peroxide (BPO) and phenylazotriphenylmethane (PAT) were also used as a radical source.

Procedure. In general, the radical initiator and spin trap were placed into an ESR tube, and hydroperoxide and solvent were contained in a side arm of the ESR tube. The solvent was frozen, evacuated, and then vacuum transferred into the ESR tube. ESR spectra were recorded on an X-band JEOL FE1X spectrometer at room temperature, in benzene, under vacuum and in the dark or under quite low level of light unless otherwise noted.

Results and Discussion

The hyperfine coupling constants of the spin adducts of the oxygen radicals by PBN observed in this study and in the literature are summarized in Table I.[16]

The spin trapping of peroxy radical generated by the DBPO-induced decomposition of hydroperoxide was first studied. Upon thermal decomposition, DBPO gives *tert*-butoxy radicals and carbon dioxide (reaction 1). The *tert*-butoxy radical abstracts
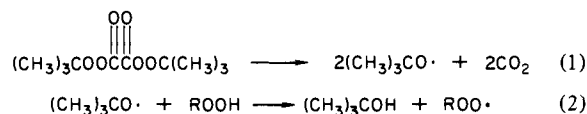
the hydroperoxidic hydrogen quite rapidly to give peroxy radical (reaction 2), which is scavenged by the spin trap PBN (reaction 3). Some *tert*-butoxy radical may possibly be scavenged by the
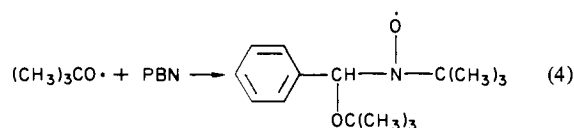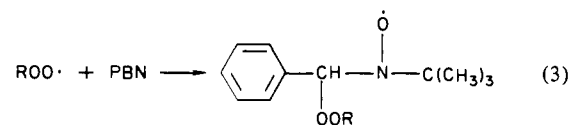
(8) Ohto, N.; Niki, E.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1770–1774.

(9) Merritt, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713–3719.

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(11) Zubarev, V. E.; Beleveskii, V. N.; Yakarav, S. P. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1392–1396.

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(13) Konaka, R.; Terabe, S.; Mizuta, T.; Sakata, S. *Can. J. Chem.* **1982**, *60*, 1532–1541.

(14) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762–1768.

(15) Korublum, N.; DeLaMare, H. E. *J. Am. Chem. Soc.* **1952**, *74*, 3079–3083.

(16) (a) Recently, Pryor[16b] found that the decomposition of triphenyl phosphite ozonide at or above −30 °C in the presence of PBN led to a peroxy radical spin adduct, a_N = 13.25 G and a_H = 1.25 G. (b) Pryor, W. A.; Govindan, C. K. *J. Org. Chem.*, **1981**, *46*, 4679–4682.

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	[DBPO]/ mM	[BOOH]/ mM	[PBN]/ mM	[BOOH]/ [PBN]
a	19.7	440	56.5	7.79
b	23.3	88.8	58.8	1.51
c	18.7	8.88	62.1	0.14
d	17.9	0	58.2	0

Figure 1. ESR spectra observed in the DBPO-induced decomposition of BOOH in benzene in the presence of PBN at room temperature in the dark.

spin trap (reaction 4). The ratio of reactions 2 to 4 depends on the ratio of [ROOH]/[PBN].

Figure 1 shows the results of decomposition of DBPO in benzene containing different concentrations of BOOH and PBN. These results agree well with those observed previously.[8] Decomposition of DBPO in the presence of PBN but in the absence of BO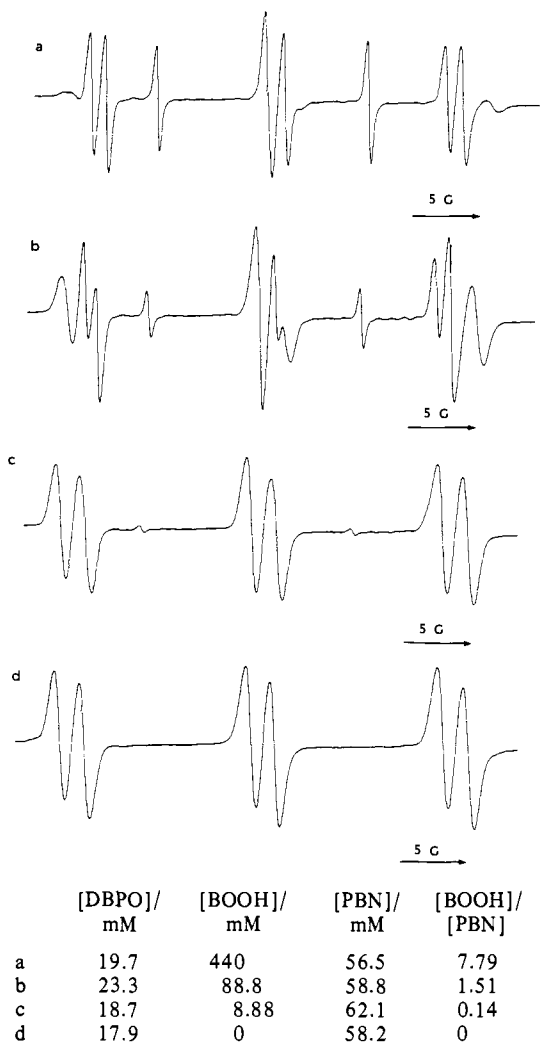OH yields triplet of doublets ESR spectrum (Figure 1d) with the coupling constants $a_N = 14.11$ G and $a_H = 1.83$ G. This spectrum is assigned to the spin adduct of *tert*-butoxy radical of PBN. The coupling constants observed in this study are in good agreement with those previously observed,[8] $a_N = 14.21$ G and $a_H = 1.83$ G. Figure 1 shows that, as the ratio [BOOH]/[PBN] increased from 0 to 7.79, the spin adduct of *tert*-butoxy radical decreased and instead a new adduct appeared with $a_N = 13.35$ G and $a_H = 1.38$ G.[17] This new spin adduct may well be assigned to that of *tert*-butylperoxy radical. Apparently, reaction 2 is favored over reaction 4 with increasing ratio of [BOOH]/[PBN], and the peroxy radical spin adduct is observed exclusively.

It is noteworthy that benzoyl *tert*-butyl nitroxide having $a_N = 7.98$ G, which is often called PBN-OX,[18] increased in yield with increasing [BOOH]/[PBN].

tert-Butylperoxy radical was also generated by the cobalt-catalyzed decomposition of *tert*-butyl hydroperoxide. Figure 2

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(17) It is known[3] that the hyperfine splitting constants increase with increasing polarity of the solvent. The addition of *tert*-butyl hydroperoxide increases the polarity of the medium, but the coupling constants become smaller.

(18) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481–4490.

	[Co(acac)$_2$]/ mM	[BOOH]/ mM	[PBN]/ mM	[BOOH]/ [PBN]
a	13.7	585	38.0	15.35
b	9.38	117	248	0.472
c	23.9	108	820	0.132

Figure 2. ESR spectra observed in the Co-catalyzed decomposition of BOOH in benzene in the presence of PBN at room temperature in the dark.

shows the ESR spectra observed when *t*-butyl hydroperoxide was decomposed in benzene at room temperature by cobaltous acetylacetonate in the presence of PBN. Substantially the same results were obtained as in Figure 1; that is, the *tert*-butoxy radical spin adduct decreased while the *tert*-butylperoxy radical spin adduct and PBN-OX increased with increasing [BOOH]/[PBN].

$$BOOH + Co^{2+} \rightarrow BO\cdot + OH^- + Co^{3+} \qquad (5)$$

$$BOOH + Co^{3+} \rightarrow BOO\cdot + H^+ + Co^{2+} \qquad (6)$$
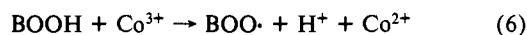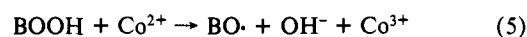
The spin adducts of *tert*-butoxy and *tert*-butylperoxy radicals by PBN were examined by a different approach. When DBPO was decomposed in benzene containing benzyl *tert*-butyl ether and NtB, three spin adducts were observed; they were *tert*-butoxy radical spin adduct by NtB and PBN-OX, and *tert*-butoxybenzyl radical spin adduct by NtB. *tert*-Butoxy radical formed from DBPO either reacts with NtB or abstracts benzylic hydrogen from benzyl *tert*-butyl ether to give *tert*-butoxybenzyl radical, which is scavenged by NtB to give the spin adduct. This spin adduct is identical with the *tert*-butoxy radical spin adduct by PBN. The coupling constants of this spin adduct, $a_N = 14.34$ G and $a_H = 1.84$ G, are in good agreement with those obtained in the decomposition of DBPO in the presence of PBN, $a_N = 14.11$ G and $a_H = 1.83$ G. PBN-OX must have been formed by the reactions 11, 12, and 13; *tert*-butoxybenzyl radical readily undergoes β-scission to give *tert*-butyl radical and benzaldehyde, whose acyl hydrogen is abstracted and resulting benzoyl radical is scavenged by NtB.

DBPO was also decomposed in benzene containing benzyl *tert*-butyl peroxide and NtB. The ESR spectrum was complicated. PBN-OX was observed as major product and only a small amount of *tert*-butylperoxybenzyl radical spin adduct by NtB was found. This must be ascribed to the rapid β-scission of *tert*-butylper-

$(CH_3)_3CO\cdot + PhCH_2OC(CH_3)_3 \longrightarrow$

$$(CH_3)_3COH + Ph\overset{\cdot}{C}HOC(CH_3)_3 \quad (7)$$

$$(CH_3)_3CO\cdot + (CH_3)_3CNO \longrightarrow (CH_3)_3O\overset{|}{\underset{\underset{O}{|}}{N}}C(CH_3)_3 \quad (8)$$

$$Ph\overset{\cdot}{C}HOC(CH_3)_3 + (CH_3)_3CNO \quad (9)$$

$$PhCH-\overset{\overset{\overset{\cdot}{O}}{|}}{N}-C(CH_3)_3$$

$$(CH_3)_3CO\cdot + PhCH=\overset{\underset{O}{|}}{N}-C(CH_3)_3 \qquad OC(CH_3)_3 \quad (10)$$

$$Ph\overset{\cdot}{C}HOC(CH_3)_3 \longrightarrow PhCHO + (CH_3)_3C\cdot \quad (11)$$

$$(CH_3)_3CO\cdot + PhCHO \longrightarrow (CH_3)_3COH + Ph\overset{\cdot}{C}O \quad (12)$$

$$Ph\overset{\cdot}{C}O + (CH_3)_3CNO \longrightarrow Ph-\overset{\underset{\underset{O}{||}}{}}{C}-\overset{\underset{\underset{O}{|}}{}}{N}-C(CH_3)_3 \quad (13)$$
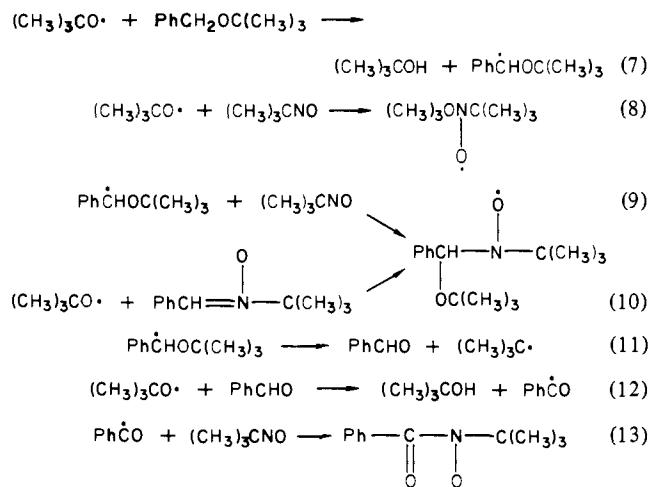
oxybenzyl radical to benzaldehyde and *tert*-butoxy radical (reaction 17).

$$(CH_3)_3CO\cdot + PhCH_2OOC(CH_3)_3 \longrightarrow (CH_3)_3COH +$$

$$Ph\overset{\cdot}{C}HOOC(CH_3)_3 \quad (14)$$

$$Ph\overset{\cdot}{C}HOOC(CH_3)_3 + (CH_3)_3CNO \quad (15)$$

$$PhCH-\overset{\overset{\overset{\cdot}{O}}{|}}{N}-C(CH_3)_3 \quad (15)$$

$$(CH_3)_3COO\cdot + PhCH=\overset{}{N}-C(CH_3)_3 \qquad \overset{|}{OOC(CH_3)_3} \quad (16)$$

$$Ph\overset{\cdot}{C}HOOC(CH_3)_3 \longrightarrow PhCHO + (CH_3)_3CO\cdot \quad (17)$$

The spin trapping of tetralylperoxy radical was studied similarly. Tetralylperoxy radical was generated by (1) the induced decomposition of tetralyl hydroperoxide by *tert*-butoxy radical generated by the thermal decomposition of DBPO, (2) redox decomposition of tetralyl hydroperoxide by cobaltous acetylacetonate (Figure 3), and (3) decomposition of DBPO in the presence of tetralin and oxygen. The spin adduct of tetralylperoxy radical was obtained in every case, and it was found to be reasonably stable at room temperature in the dark. However, the stability was such that the ESR spectrum of the peroxy radical spin adduct disappeared when it stood overnight in the dark at room temperature. The coupling constants of tetralylperoxy radical spin adduct are also included in Table I. The smaller difference between the hydrogen and nitrogen hyperfine splitting constants of the alkoxy and peroxy radical adducts in the tetralin system compared to the *tert*-butyl system may possibly reflect a mixture of peroxyl and alkoxyl adducts.[9]

The results given above are in good agreement with those reported previously,[8] and they suggest that the peroxy radicals can be trapped by PBN and the resulting spin adducts are relatively stable at room temperature in the dark. The coupling constants a_N and a_H of the peroxy radical spin adduct by PBN are smaller than those of the alkoxy radical, but the difference is not large enough to distinguish them unequivocally.

Konaka and his co-workers[13] recently found that methyl-*N*-durylnitrone (MDN) gave peroxy radical spin adducts that could be clearly distinguished from those of the alkoxy radical. It has been previously found that ESR spectra of alkyl duryl nitroxides show a wide variation of the β-hydrogen splitting constants depending on the structure of the radical trapped.[19]

We have also studied the spin trapping of peroxy radicals using MDN as a spin trap. The results are summarized in Table II. Figure 4 shows the ESR spectrum observed when DBPO was decomposed in benzene containing MDN. This is ascribed to the spin adduct of *tert*-butoxy radical by MDN and the coupling constants were obtained as $a_N = 14.10$ G and $a_H = 7.47$ G.

Figure 5 shows the variation of the ESR spectra observed when DBPO was decomposed in benzene containing MDN and varying

(19) Terabe, S.; Kumura, K.; Konaka, R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1252–1258.

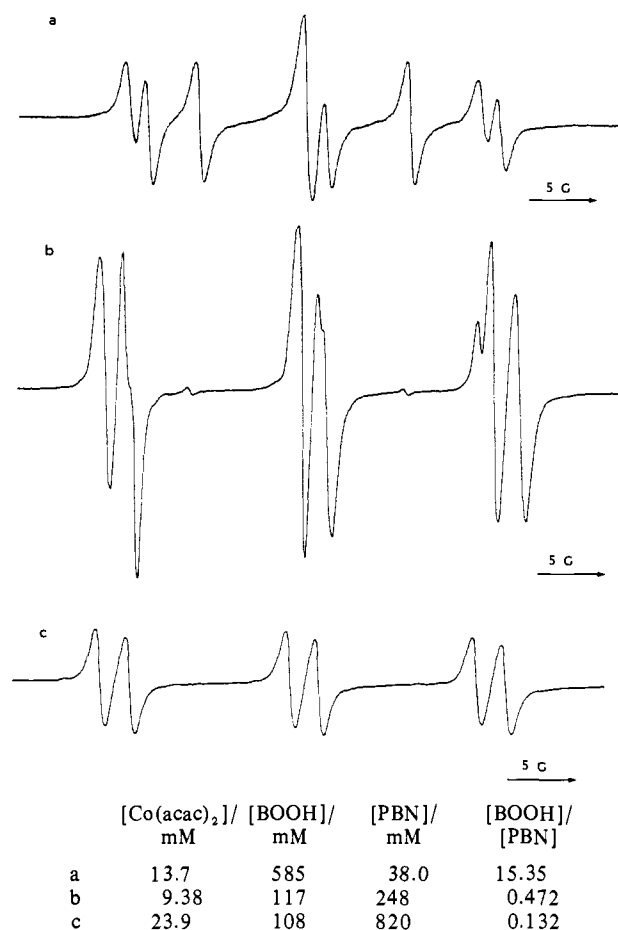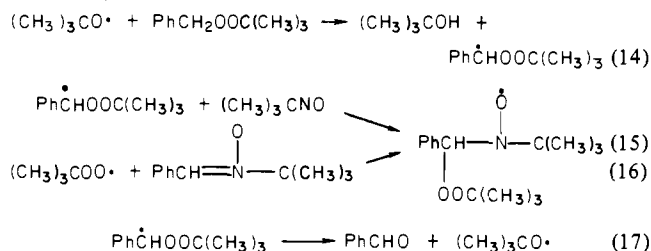|	[Co(acac)₂]/ mM	[TOOH]/ mM	[PBN]/ mM	[TOOH]/ [PBN]
a	20.5	668	38.0	17.53
b	14.5	165	36.8	4.50
c	27.3	9.15	73.3	0.125
d	17.9	9.15	179	0.051
e	20.5	1.53	458	0.003
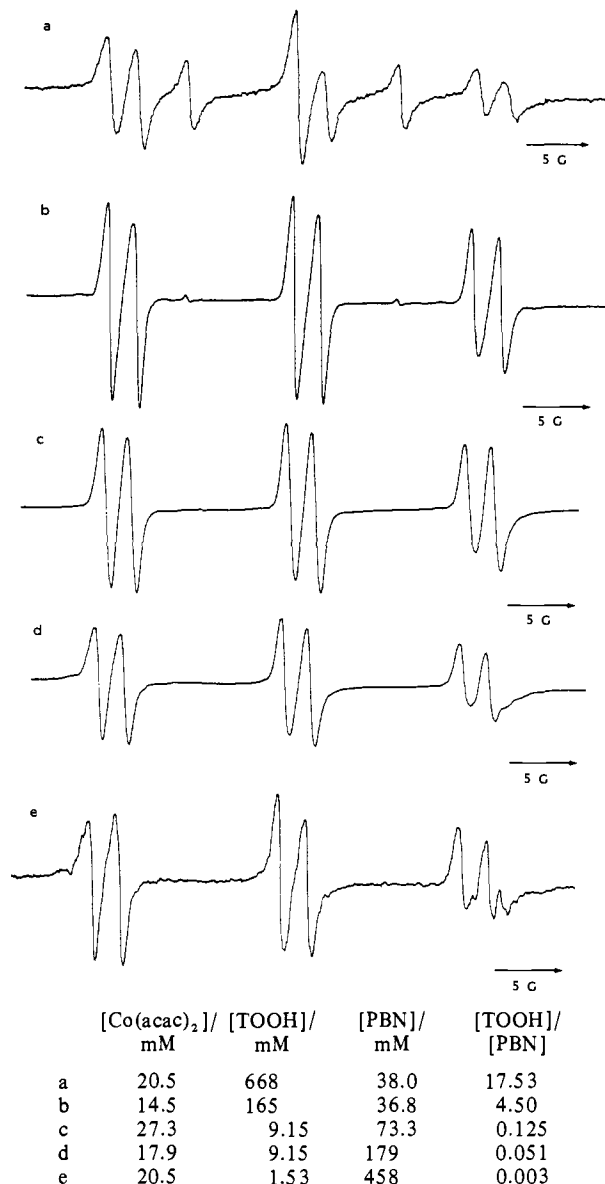
Figure 3. ESR spectra observed in the Co-catalyzed decomposition of TOOH in benzene in the presence of PBN at room temperature in the dark.

Table II. Hyperfine Splitting Constants of Oxygen Radical Spin Adduct by MDN[a]

radical	source	temp[b]/ °C	solvent	a_N/G	a_H/G	ref
BOO	BOOH + DBPO	r.t.	PhH	12.80	4.61	this work
BOO	BOOH		PhH + *t*-BuOH	12.82	4.76	13
TOO	TOOH + DBPO	r.t.	PhH	12.63	4.55	this work
BO	DBPO	r.t.	PhH	14.10	7.47	this work
BO	c		PhH + *t*-BuOH	13.26	8.47	13
BO	DBPO		PhH + *t*-BuOH	13.45	8.40	13
TO	TOOH + Co²⁺	r.t.	PhH	13.08	5.95	this work

[a] B = *tert*-butyl, T = tetralyl. [b] r.t. = room temperature.
[c] DBPO was decomposed in the presence of *tert*-butyl ethyl ether and nitrosodurene.

concentrations of *tert*-butyl hydroperoxide. By comparing Figures 4 and 5, it may well be said that the spin adduct observed at high

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Figure 4. ESR spectrum observed when DBPO was decomposed in benzene in the presence of MDN at room temperature in the dark: [DBPO] = 66.0 mM, [MDN] = 55.8 mM.
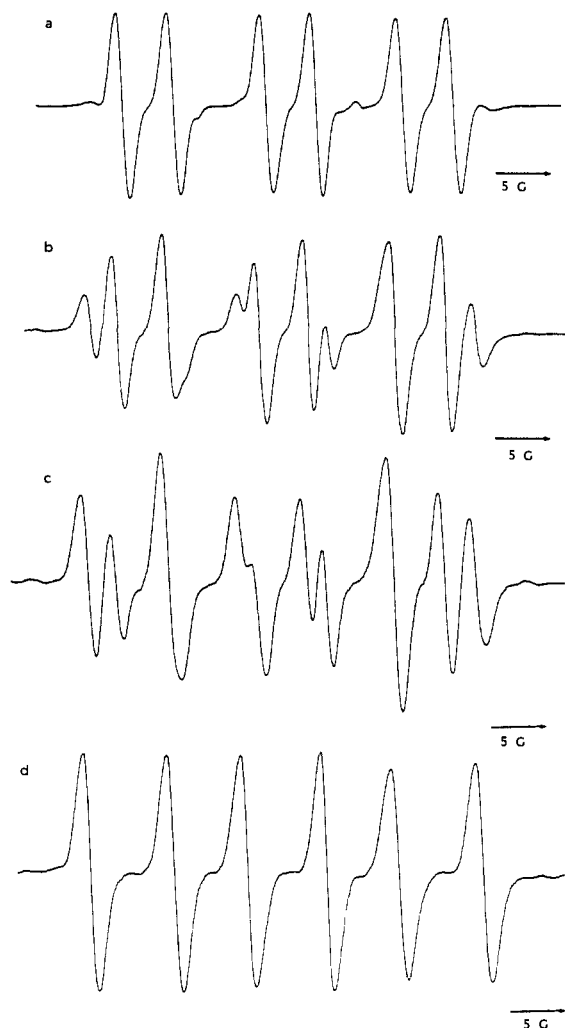
	[DBPO]/ mM	[BOOH]/ mM	[MDN]/ mM	[BOOH]/ [MDN]
a	66.3	438	17.1	25.6
b	79.0	24.2	17.1	1.41
c	57.8	9.05	17.1	0.53
d	32.0	2.53	11.8	0.21

Figure 5. ESR spectra observed in the DBPO-induced decomposition of BOOH in benzene in the presence of MDN at room temperature.
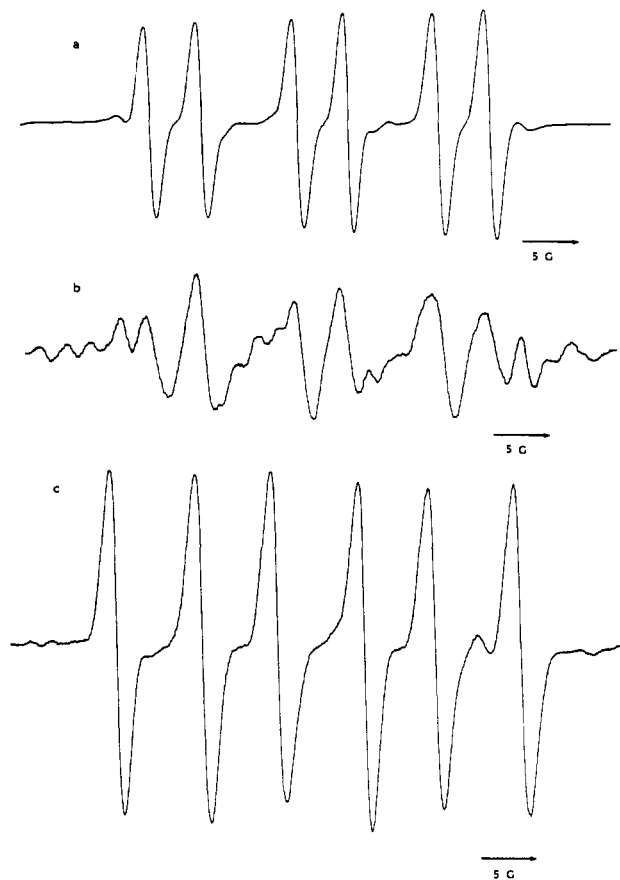
	[DBPO]/ mM	[TOOH]/ mM	[MDN]/ mM	[TOOH]/ [MDN]
a	65.3	48.8	21.0	2.32
b	65.3	13.7	26.3	0.52
c	66.3	7.63	27.5	0.28

Figure 6. ESR spectra observed in the DBPO-induced decomposition of TOOH in benzene in the presence of MDN at room temperature.

ratio of [BOOH]/[MDN] is that of peroxy radical.

Figure 6 shows the change in ESR spectra observed when DBPO was decomposed similarly in the presence of varying ratios of tetralyl hydroperoxide to MDN.

Table II shows that the coupling constants, especially a_H, for alkoxy and peroxy radicals can be clearly distinguished from each other.

As mentioned already, these experiments were carried out at room temperature in the dark or under quite low levels of light. The alkoxy radical and peroxy radical spin adducts by MDN and PBN were reasonably stable under these conditions. However, the spin adducts decayed much faster when the ESR tube was taken out of the ESR cavity and exposed to ordinary laboratory light (diffuse daylight and fluorescent light).

It must be mentioned that in our system the tert-butoxy radical is generated continuously from DBPO. The rate constant for unimolecular decomposition of DBPO is 1.6×10^{-5} s^{-1} at 25 °C and its half-life is 12 h.[14] When DBPO was decomposed in benzene in the presence of PBN, the tert-butoxy radical spin adduct increased linearly for 2 h. On the other hand, when DBPO was decomposed in benzene in the presence of tert-butyl hydroperoxide as well as PBN, a different result was obtained. For example, when the ratio of [BOOH]/[PBN] was 19.5, which was high enough to convert tert-butoxy radical to tert-butylperoxy radical (see Figure 1), the spin adduct of tert-butylperoxy radical and PBN-OX increased linearly with time for the first 30 min, but then became almost constant. The tert-butoxy radical spin adduct remained quite small. The ESR tube was kept in the cavity in the dark for 84 min; then it was taken out of the cavity and exposed to laboratory light for 60 min. tert-Butylperoxy radical

Figure 7. Formation of spin adducts in the decomposition of DBPO in benzene at room temperature in the presence of *tert*-butyl hydroperoxide and PBN. The experiment was carried out in the dark until 90 min; then the ESR tube was taken out of the ESR cavity and exposed to laboratory light for 60 min: [DBPO] = 17.9 mM, [BOOH] = 440 mM, [PBN] = 226 mM, [BOOH]/[PBN] = 1.95. ■, peroxyl spin adduct; ▲, alkoxyl spin adduct; ●, PBN-OX.

spin adduct decreased markedly, but the *tert*-butoxy radical spin adduct did not increase.

Figure 7 shows the results of similar experiment but with lower ratio of [BOOH]/[PBN]. At the initial stage, more peroxy radical spin adduct was formed than alkoxy radical spin adduct, but soon *tert*-butoxy radical spin adduct became predominant as the *tert*-butyl hydroperoxide was consumed. After the ESR tube stood in the cavity for 90 min in the dark, it was taken out of the cavity and exposed to laboratory light for 60 min; the amount of peroxy radical spin adduct decreased whereas that of the alkoxy radical spin adduct and PBN-OX increased.

Similar results were obtained with MDN. When 66.3 mM DBPO was decomposed in benzene containing 438 mM *tert*-butyl hydroperoxide and 17.0 mM MDN, only the peroxy radical spin adduct was observed. Then the ESR tube was taken out of the cavity and placed under ordinary laboratory light; it was found that the *tert*-butylperoxy radical spin adduct decayed at an appreciable rate and it was replaced completely in 1 h by a new ESR spectrum. It is a simple triplet with coupling constant a_N = 7.25 G. This may be ascribed to acetyl-*N*-durylnitroxide or MDN-OX by analogy with PBN-OX.

It was also found that the tetralylperoxy radical spin adduct of MDN gave the same MDN-OX when exposed to laboratory light.

MDN-OX

The stability of the peroxyl adducts of PBN and MDN toward light was not compared in detail. Qualitatively, the peroxyl ad-

ducts of MDN decayed similarly but at a somewhat faster rate than those of PBN.

It is not clearly established why peroxy radical spin adduct is photolabile, nor is it known how it decomposes. It has been pointed out that nitrones and their spin adducts are often photolabile.[5] Ingold[21] has shown that bimolecular self-reactions of dialkyl nitroxide radicals give hydroxylamine and nitrone by a mechanism which involves the reversible formation of a diamagnetic nitroxide dimer. It is known[22] that oxygen and nitrogen atoms adjacent to the carbon from which a hydrogen atom is abstracted have an accelerating effect in reactivity. Thus, the α hydrogens of alcohols, ethers, and, probably, peroxides have higher reactivity than corresponding hydrocarbons, especially toward oxygen radicals.[23]

These previous observations and the present results given above indicate that the tertiary hydrogen of the spin adducts of PBN and MDN must be quite reactive toward oxygen radicals, and the removal of this hydrogen atom may possibly give PBN-OX and MDN-OX. The alkoxy radical formed in the reactions 18

(18)

(19)

and 19 may react with either hydroperoxide or the spin trap. When the ratio of hydroperoxide to spin trap is high, the alkoxy radical should react predominantly with hydroperoxide and the alkoxy radical spin adduct is not observed.

In conclusion, peroxy radicals are trapped by nitrones to give spin adducts which are stable at room temperature in the dark. MDN is a better spin trap than PBN to distinguish peroxy radical from alkoxy radical. The spin adducts of peroxy radicals by PBN and MDN are photolabile, their decomposition giving primarily PBN-OX or MDN-OX and alkoxy radicals.

(20) It is not clear why *tert*-butylperoxyl and tetralylperoxyl adducts give different coupling constants nor why the difference between peroxyl and alkoxyl adducts is smaller for tetralyl than for *tert*-butyl.

(21) Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 6555–6561.

(22) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, pp 37–112.

(23) Niki, E.; Kawakami, A.; Kamiya, Y., unpublished work. We found that alkoxy and peroxy radicals attack both α and β hydrogens of 2-phenylethanol, although phenyl radical attacks benzylic hydrogen exclusively.