

## Study of Autoxidation by Spin Trapping. Spin Trapping of Peroxyl Radicals by Phenyl *N*-*t*-Butyl Nitron

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The autoxidation of several organic compounds has been studied by the spin trapping technique. The chain-carrying peroxy radicals were trapped by phenyl *N*-*t*-butyl nitron (PBN) under the conditions of oxidation and hyperfine splitting constants were measured for several peroxy radicals. Peroxy radicals generated from other sources such as induced decomposition of hydroperoxides and thermal decomposition of azo-compounds under oxygen also gave similar results. The rate constants for the reaction of cumyl- and tetralinyl-peroxy radicals with PBN were found to be much lower than those for the reactions of corresponding alkyl radicals with PBN. The hyperfine splitting constants of the spin adduct obtained in the oxidation of propan-2-ol in the presence of PBN were found to agree well with those observed in the oxidation of cyclohexa-1,4-diene, suggesting that the chain-carrying radical in the oxidation of propan-2-ol is not 1-hydroxy-1-methylethylperoxy radical but hydroperoxy radical.

OXIDATION of organic compounds by molecular oxygen is an important chemical and biochemical process where oxyl radicals play an important role as chain-carrying species. Although peroxy radicals have been observed by e.s.r. and u.v. absorption spectra using flow methods<sup>1</sup> and pulse radiolysis<sup>2,3</sup> respectively, it is difficult to observe them directly during oxidation due to their low concentration. Recently, the spin trapping technique, trapping of reactive and short-lived radicals by conversion into stable radicals detectable by e.s.r., has been

developed and much interesting information has been obtained on the mechanism of free radical reactions. Harbour *et al.*<sup>4</sup> studied the spin trapping of the hydroperoxy radical formed by the photochemical decomposition of hydrogen peroxide in aqueous solution. However, this spin trapping technique has been but little applied to the autoxidation of organic compounds and, to our knowledge, no data have been presented for the spin adducts of organic peroxy radicals in organic solvents. The primary objective of the present work was to study the

<sup>1</sup> M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 959.

<sup>2</sup> J. Rabani and S. O. Nielsen, *J. Phys. Chem.*, 1969, **73**, 3736.

<sup>3</sup> G. Czapski, *Ann. Rev. Phys. Chem.*, 1971, 171.

<sup>4</sup> J. R. Harbour, V. Chow, and J. R. Bolton, *Canad. J. Chem.*, 1974, **52**, 3549.

trapping of peroxy radicals and to elucidate the chain-carrying radical in the autoxidation of propan-2-ol. Phenyl *N*-*t*-butyl nitron was used as spin trapping reagent.

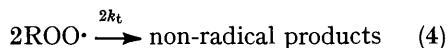
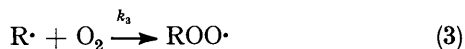
#### EXPERIMENTAL

**Materials.**—Cumene, tetralin, ethylbenzene, and chlorobenzene were washed successively with 90% sulphuric acid, water, a 5% aqueous solution of sodium hydroxide, and water, and after drying (CuCl<sub>2</sub>) were distilled under reduced pressure of nitrogen. Cyclohexa-1,4-diene, benzene, *t*-butyl alcohol, and acetic acid were of the best quality commercially available. Azobisisobutyronitrile (AIBN) was used after repeated recrystallization from methanol. Azobis- $\alpha$ -phenylethane (APE) was kindly supplied by Dr. Okuma. Tetralinyl hydroperoxide (THP) was prepared by the autoxidation of tetralin followed by repeated recrystallization from hexane. *t*-Butyl hydroperoxide (BHP) was distilled prior to use. Phenyl *N*-*t*-butyl nitron (PBN), phenylazotriphenylmethane (PAT), and cumyl hydroperoxide (CHP) were commercially available. Di-*t*-butyl peroxyoxalate (DBPO) was prepared and purified by the method of Bartlett *et al.*<sup>5</sup>

**Procedures.**—Oxidation was carried out in an ampoule immersed in a silicone oil-bath and the rate of oxidation was measured either by following the pressure change using a pressure transducer or by following the volume of oxygen absorbed by a manometer using a constant pressure closed system. After the reaction was over, the solution was transferred quickly into an e.s.r. sample tube and the e.s.r. spectra were measured after degassing under vacuum. Oxidation was carried out at 60 °C and the e.s.r. spectra were measured at room temperature. The rate of initiation by AIBN was calculated from the induction period observed by the addition of the antioxidant, 4-methyl-2,6-di-*t*-butylphenol.<sup>6</sup>

#### RESULTS AND DISCUSSION

(a) *Effect of Addition of PBN on the Rate of Oxidation.*—It is now generally agreed that the AIBN-initiated autoxidation of hydrocarbons with sufficient oxygen proceeds by the mechanism (1)–(4). Under these circumstances,

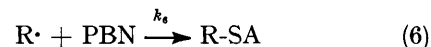


$$R_o = k_p(R_i/2k_t)^{1/2}[\text{RH}] \quad (5)$$

the rate of oxidation,  $R_o$ , is given by equation (5) where  $R_i (= 2ek_i[\text{AIBN}])$  is the rate of initiation, the constants  $e$  and  $k_i$  being the efficiency of radical production and the rate constant, for unimolecular decomposition of AIBN respectively.

If PBN traps radicals and the spin adducts formed do

not decompose to give radicals, then oxidation must be inhibited by the addition of PBN. If the inhibition occurs by trapping of alkyl radicals by PBN [reaction (6)]



and the alkyl radical spin adduct, R-SA, is stable, then the rate of inhibited oxidation,  $R_p$ , can be expressed as equation (7), where equation (8) applies. On the other

$$R_p = (k_p[\text{RH}]/4k_t)((f^2k_p^2[\text{RH}]^2 + 8k_tR_i)^{1/2} - fk_p[\text{RH}]) \quad (7)$$

$$f = k_6[\text{PBN}]/(k_3[\text{O}_2] + k_6[\text{PBN}]) \quad (8)$$

hand, if inhibition occurs by trapping of peroxy radicals by PBN, reaction (6) is replaced by (9) and the rate of inhibited oxidation is given by equation (10). When



$$R_p = (k_p[\text{RH}]/4k_t)((k_9^2[\text{PBN}]^2 + 8k_tR_i)^{1/2} - k_9[\text{PBN}]) \quad (10)$$

PBN traps both alkyl and peroxy radicals, the rate of inhibited oxidation is given by equation (11) where (12) applies.

$$R_p = (k_p[\text{RH}]/4k_t)[(F^2 + 8k_tR_i)^{1/2} - F] \quad (11)$$

$$F = k_9[\text{PBN}] + fk_p[\text{RH}] \quad (12)$$

The effect of addition of PBN on the rate of AIBN-initiated oxidations of several hydrocarbons at 60 °C has been measured and Figure 1 shows plots of the ratio

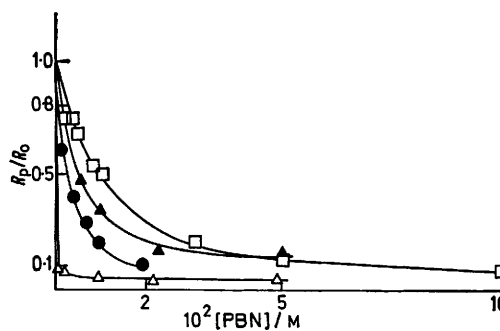


FIGURE 1 Effect of addition of PBN on the rate of autoxidation of hydrocarbons at 60 °C. [AIBN]  $2.00 \times 10^{-2}$  M. ●, Neat cumene; □, neat tetralin; ▲, neat ethylbenzene; △, cyclohexa-1,4-diene in benzene

of inhibited to uninhibited rates of oxidation,  $R_p/R_o$ , as a function of PBN concentration. The observed rate of oxygen absorption was corrected for nitrogen evolution and oxygen absorption and evolution associated with initiation and termination reactions. Figure 1 shows that the addition of PBN decreased the rate of oxidation of all the substrates studied. Table 1 shows the effect of substrate concentration on the inhibited rate of oxidation of cumene in chlorobenzene in the presence of 2 ×

<sup>5</sup> P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **80**, 1762.

<sup>6</sup> C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, 1955, **77**, 3233.

$10^{-3}\text{M}$ -PBN and it shows that the rate of inhibited oxidation is directly proportional to the substrate concentration, suggesting that equation (10) holds and that  $k_9[\text{PBN}] \gg fk_p[\text{RH}]$  in equation (12). When equation (7) holds, the plots of inhibited rate of oxidation against

TABLE I

Effect of cumene concentration on the inhibited rate of oxidation in chlorobenzene at 60 °C.  $[\text{AIBN}] = 2.00 \times 10^{-2}\text{M}$ ,  $[\text{PBN}] = 2.0 \times 10^{-3}\text{M}$

$[\text{RH}]/\text{M}$	$10^5 R_p/\text{mol l}^{-1} \text{ s}^{-1}$	$R_p/R_i$	$10^6 R_p/[\text{RH}]^{-1}/\text{s}^{-1}$
1.44	1.42	4.4	0.99
2.16	2.23	7.0	1.03
3.60	5.20	16.2	1.44
5.04	7.40	23.0	1.47
7.20	10.4	32.5	1.44

substrate concentration should give upward convex curvature. These results suggest that alkyl radicals react exclusively with oxygen before they are trapped by PBN and the suppression of oxidation is attributed mainly to the trapping of peroxy radicals by PBN. Table I also shows that there is a long kinetic chain length, suggesting that the radical trapped by PBN is cumylperoxyl rather than 1-cyano-1-methylethylperoxyl formed from the initiator.

The rate constants  $k_9$  for the reactions of cumyl- and tetralinyl-peroxy radicals with PBN were calculated from equation (10) using the rate of oxidation and other rate constants,  $k_p$  19.3,  $2k_t$   $1.29 \times 10^7$  for tetralin<sup>8</sup> and  $k_p$  0.72,  $2k_t$   $4.68 \times 10^4$   $\text{l mol}^{-1} \text{ s}^{-1}$  for cumene.<sup>9</sup> Thus, the rate constant  $k_9$  was obtained as 200 and 40  $\text{l mol}^{-1} \text{ s}^{-1}$  for tetralinyl- and cumyl-peroxy radicals respectively. The rate constant  $k_8$  was then calculated from equation (11) as  $10^6$   $\text{l mol}^{-1} \text{ s}^{-1}$  for both tetralinyl and cumyl radicals. Janzen and Evans<sup>10</sup> observed the rate constants for the reactions of alkyl radicals with PBN as  $10^6$ – $10^8$   $\text{l mol}^{-1} \text{ s}^{-1}$ . Therefore alkyl radicals are much more reactive than peroxy radicals toward PBN as observed toward olefins.<sup>11</sup> The rate constants for the addition of tetralinyl- and cumyl-peroxy radicals to styrene have been previously obtained as 64 and 27  $\text{l mol}^{-1} \text{ s}^{-1}$  respectively.<sup>12</sup> These data suggest that PBN is a few times more reactive than styrene toward these peroxy radicals and that tetralinylperoxy radical is several times more reactive than cumylperoxy radical in addition reactions as observed from hydrogen atom abstraction.<sup>13</sup> Figure 3 illustrates the effect of PBN on the rates of several important elementary reactions in the oxidation of cumene at 60 °C. It clearly shows how the relative importance of each elementary reaction varies with the amount of PBN added. When PBN is  $>10^{-2}\text{M}$ , the oxidation of cumene proceeds substantially by reactions (1)–(3) and (9). At higher concentration of PBN, trapping of alkyl radicals and 1-cyano-1-methylethylperoxy radical may also become important.

<sup>7</sup> K. U. Ingold, *Accounts Chem. Res.*, 1969, **2**, 1.

<sup>8</sup> J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1966, **44**, 1119.

<sup>9</sup> D. G. Hendry, *J. Amer. Chem. Soc.*, 1967, **89**, 5433.

<sup>10</sup> E. G. Janzen and C. A. Evans, *J. Amer. Chem. Soc.*, 1975, **97**, 205.

Figure 1 shows that the effect of addition of PBN on the rate of oxidation is dependent on the substrate. This may be ascribed to the different relative importance of the two competing reactions (2) and (9) for each hydrocarbon.

The absolute propagation rate constants are calculated as 19.3 and 0.72  $\text{l mol}^{-1} \text{ s}^{-1}$  for tetralin<sup>8</sup> and cumene,<sup>9</sup> respectively, and that for ethylbenzene is between the two. Thus, the smaller the propagation rate constant, the larger the rate of decrease in the rate of oxidation by the addition of PBN. The more significant effect of addition of PBN observed for cyclohexa-1,4-diene must be ascribed to a larger rate of addition of hydroperoxyl

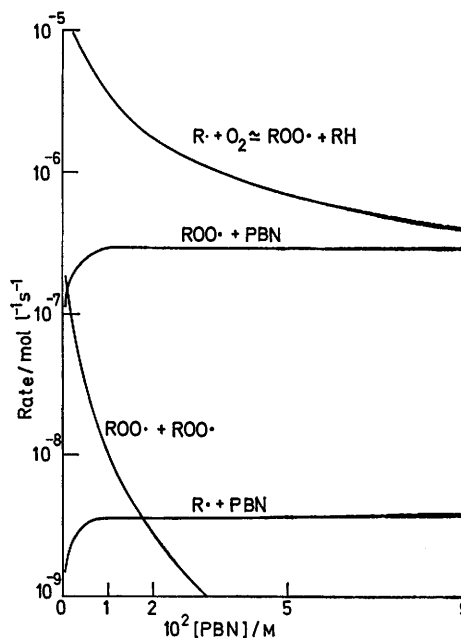


FIGURE 2 Effect of addition of PBN on the elementary reactions in the oxidation of cumene at 60 °C.  $[\text{AIBN}] 2.00 \times 10^{-2}$ ,  $[\text{cumene}] 7.20\text{M}$ ;  $k_8 10^6$ ,  $k_4 40$   $\text{l mol}^{-1} \text{ s}^{-1}$

radical, the chain carrying peroxy radical in the oxidation of cyclohexa-1,4-diene, to PBN than for alkylperoxy radicals.

(b) *Spin Adducts of Peroxy Radicals with PBN.*—The e.s.r. spectra of the spin adducts of peroxy radicals with PBN were studied under several conditions with different peroxy radical sources.

Cumene was oxidized in benzene at 60° in the presence of AIBN and PBN and the mixture was then subjected to e.s.r. analysis. Two spin adducts were observed, one a triplet with hyperfine splitting constant  $a_N$  7.92 G and the other a triplet of doublets with  $a_N$  13.55 and  $a_H$  1.82 G. The oxidation of tetralin, ethylbenzene, and cyclohexa-1,4-diene was carried out similarly and in each case similar e.s.r. spectra were observed and the formation of

<sup>11</sup> J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1965, **43**, 2729; 1966, **44**, 1113.

<sup>12</sup> E. Niki, Y. Kamiya, and N. Ohta, *Bull. Chem. Soc. Japan*, 1969, **42**, 2312.

<sup>13</sup> J. A. Howard, *Adv. Free-radical Chem.*, 1972, **4**, 49.

the-former spin adduct with triplet spectrum was always <1% of total spin adducts. The triplet spectrum with  $a_N$  7.92 G may be assigned to *N*-benzoyl-*N*-*t*-butyl nitroxide. The mechanism of this nitroxide formation in the oxidation of hydrocarbons is not clear at present. It may be worth noting that this nitroxide was also observed in the decomposition of DBPO in the presence of PBN under oxygen but not under nitrogen. The formation of this nitroxide has been observed in different systems by other investigators<sup>14,15</sup> and the splitting constant observed in the present study agrees well with the reported values.

Peroxy radicals were also generated by the induced decomposition of hydroperoxide. Figure 3 shows the

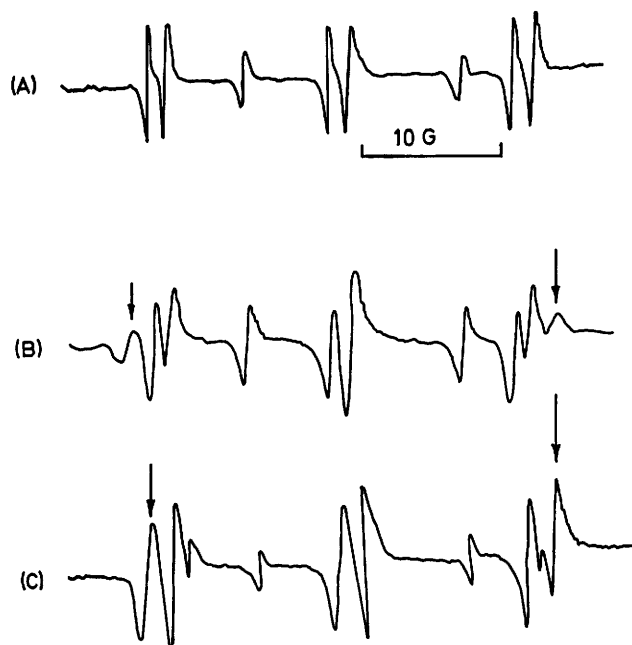


FIGURE 3 E.s.r. spectra of spin adducts observed in DBPO and *t*-butyl hydroperoxide at room temperature in benzene. [DBPO], [*t*-butyl hydroperoxide], [PBN]: (A)  $1.06 \times 10^{-2}$ , 0.90,  $8.42 \times 10^{-2}$ ; (B)  $1.86 \times 10^{-2}$ ,  $1.76 \times 10^{-2}$ , 0.102; (C)  $1.28 \times 10^{-2}$ ,  $1.6 \times 10^{-3}$ ,  $9.42 \times 9.45 \times 10^2 M$

e.s.r. spectra obtained in the decomposition of *t*-butyl hydroperoxide at room temperature in the presence of DBPO and PBN. At high *t*-butyl hydroperoxide concentrations [Figure 3(A)], two spin adducts were obtained with  $a_N$  7.92 G (triplet) and  $a_N$  13.40 and  $a_H$  1.57 G (triplet of doublets) as observed in the autoxidation of cumene in the presence of a high concentration of *t*-butyl hydroperoxide. On the other hand, as the concentration of *t*-butyl hydroperoxide decreased, the spin adduct with the triplet of doublets decreased and the new spin adduct increased [arrows in Figure 3(B) and (C)], which agreed well with observations for the decomposition of DBPO in the presence of PBN. Therefore, this new adduct must

<sup>14</sup> E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481; E. G. Janzen, 'Creation and Detection of the Excited State,' ed. W. R. Ware, Marcel Dekker, New York, 1976, vol. 4, p. 97.

be assigned to the *t*-butoxyl radical spin adduct.  $\alpha$ -Methylbenzylperoxy radical was generated by the photochemical decomposition of APE under oxygen.<sup>16</sup>

In order to make comparisons with peroxy radicals, the spin adducts of alkyl radicals were also studied. The alkyl radicals were generated by the hydrogen atom abstraction from the parent hydrocarbon by *t*-butoxyl or phenyl radical formed by the thermal decomposition of DBPO and PAT respectively. 1-Cyano-1-methylethyl radical was generated by the decomposition of AIBN under nitrogen. The results are summarized in Table 2

TABLE 2

Peroxy and alkyl radical spin adducts by PBN in benzene

	Autoxidation <sup>a</sup>		Other source	
	$a_N/G$	$a_H/G$	$a_N/G$	$a_H/G$
Cumylperoxy	13.55	1.82	13.54	1.71 <sup>b</sup>
Tetralinylperoxy	13.66	1.84	13.68	1.78 <sup>b</sup>
$\alpha$ -Methylbenzylperoxy	13.57	1.74	13.54	1.82 <sup>c</sup>
<i>t</i> -Butylperoxy	13.40	1.57	13.34	1.25 <sup>b</sup>
Hydroperoxy	14.28	2.25		
<i>t</i> -Butoxyl			14.21	1.83 <sup>d</sup>
Cumyl			14.25	2.19 <sup>e</sup>
Tetralinyl			14.30	2.26 <sup>e</sup>
1-Cyano-1-methylethyl			13.87	2.09 <sup>f</sup>
Phenyl			14.41	2.21 <sup>g</sup>

<sup>a</sup> Peroxy radicals were trapped by PBN during autoxidation of parent hydrocarbons except for *t*-butylperoxy radical, which was generated by the oxidation of cumene in the presence of 1*M*-*t*-butyl hydroperoxide. Under these circumstances, the chain-carrying radical is *t*-butylperoxy radical (J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Adv. Chem. Series*, 1968, **75**, 6). The e.s.r. analysis was performed *in vacuo*. <sup>b</sup> Peroxy radicals were generated by the *t*-butoxyl radical induced decomposition of corresponding hydroperoxides. <sup>c</sup>  $\alpha$ -Methylbenzylperoxy radical was generated by the photolysis of APE under oxygen. <sup>d</sup> DBPO was thermally decomposed in benzene in the presence of PBN *in vacuo*. <sup>e</sup> Cumyl, tetralinyl, and  $\alpha$ -methylbenzyl radicals were generated from cumene, tetralin, and ethylbenzene respectively by hydrogen atom abstraction by *t*-butoxyl and phenyl radicals. <sup>f</sup> AIBN was decomposed in benzene under nitrogen in the presence of PBN. <sup>g</sup> PAT was thermally decomposed in benzene in the presence of PBN.

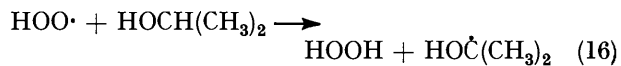
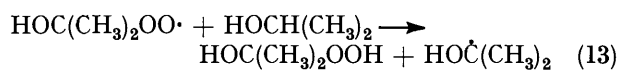
which shows that the spin adducts obtained in the oxidation agree reasonably well with those generated from hydroperoxide and azo-compound under oxygen. Thus, it may be concluded that peroxy radicals are trapped by PBN to give stable spin adducts which have triplet of doublets e.s.r. spectra with splitting constants  $a_N$  13.3–13.7 and  $a_H$  1.2–1.8 G. Hydroperoxy radical spin adduct gives considerably different splitting constants from organic peroxy radicals.

(c) *Identification of the Chain-carrying Radical in the Oxidation of Propan-2-ol.*—Oxidation of alcohol has been extensively studied and the oxidation of propan-2-ol is well known to give hydrogen peroxide and acetone. Hydrogen peroxide and acetone may be formed either by the homolysis of 1-hydroxy-1-methylethyl hydroperoxide [reactions (13) and (14)] or by reactions (15) and

<sup>15</sup> A. L. Bluhm and J. Weinstein, *J. Amer. Chem. Soc.*, 1970, **92**, 1444.

<sup>16</sup> K. Okuma, E. Niki, and K. Kamiya, *J.C.S. Perkin II*, 1977, 59.

(16). In the former case, the chain-carrying radical is



1-hydroxy-1-methylethylperoxyl, while in the latter case it is hydroperoxyl radical. We examined the e.s.r.

spectra for the oxidation of propan-2-ol. Oxidation was carried out in neat propan-2-ol with added AIBN and PBN, and after oxidation propan-2-ol was evacuated and then benzene was vacuum transferred into the sample tube and subjected to e.s.r. analysis in order to minimize the solvent effect. The hyperfine splitting constants were found to be  $a_{\text{H}}$  14.25 and  $a_{\text{H}}$  2.23 G, which agreed well with those of the spin adduct observed in the oxidation of cyclohexa-1,4-diene. This implies that the chain-carrying radical in the oxidation of propan-2-ol is hydroperoxyl rather than 1-hydroxy-1-methylethylperoxyl.

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