and again to the twisted form in the liquid-crystalline state. By taking into account the low-energy barrier of the torsional potential, the biphenyl group is considered to experience a thermal motion, such as flip-flop motion of the benzene rings, in the high-temperature liquid-crystalline phase. The details of the molecular conformational change and the vibrational assignments will be reported in a separate paper.

Acknowledgment. The authors thank the Laboratory of X-ray Analysis in the Research Center for Protein Engineering, Osaka University, Japan for their kind permission to utilize the X-ray diffraction and structure analysis systems.

Supplementary Material Available: Tables of the fractional coordinates and temperature factors of the constituent atoms (4 pages); tables of the observed and calculated structure factors for the crystal forms α and β (17 pages). Ordering information is given on any current masthead page.

Detection of Alkyl, Alkoxyl, and Alkyperoxyl Radicals from the Thermolysis of Azobis(isobutyronitrile) by ESR/Spin Trapping. Evidence for Double Spin Adducts from Liquid-Phase Chromatography and Mass Spectroscopy

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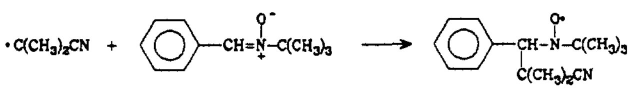
Abstract: The thermolysis of azobis(isobutyronitrile) (AIBN) in the presence of oxygen has been investigated by spin trapping by using α-phenyl *N-tert*-butyl nitrone (PBN) and 5,5-dimethylpyrroline *N*-oxide (DMPO). The aminoxyl products identified by ESR and mass spectroscopy (MS) are the result of trapping 2-cyano-2-propyl radicals (CP$^•$) in the presence of oxygen. By low-temperature ESR the 2-cyano-2-propylperoxyl adduct of PBN-*nitronyl*-^{13}C is detectable in the presence of oxygen. The mass spectrum of the alkoxyl adduct is detectable only by the use of liquid chromatography/mass spectroscopy (LC/MS). The alkoxylamines, the *C*-(2-cyano-2-propyloxyl), *O*-(2-cyano-2-propyl) mixed double adducts of PBN (CPO-PBN-CP) and DMPO (CPO-DMPO-CP), have been observed for the first time. The normal double adducts, CP-PBN-CP or CP-DMPO-CP, are not detected.

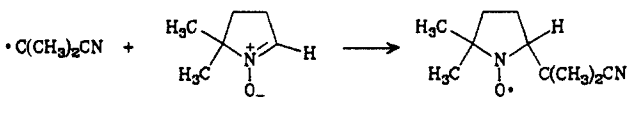
Introduction

Some of the first nitrone spin trapping experiments published[1,2] involved the thermolysis of azobis(isobutyronitrile)[3] (AIBN), in the presence of α-phenyl *N-tert*-butyl nitrone (PBN) or 5,5-dimethylpyrroline *N*-oxide (DMPO). The ESR spectra obtained after thermolysis at 110 °C were consistent with the addition of the 2-cyano-2-propyl radical (CP$^•$), to the nitrone to yield the corresponding aminoxyl spin adducts. Also reported[4,5] was the radical 1,3-addition to nitrones VII–IX, similar in structure to PBN, to produce the corresponding N,N,O-trisubstituted hydroxylamines (or alkoxylamines) when AIBN or other azo initiators were decomposed in xylene 90–110 °C. However no "double trapping" was reported for PBN or DMPO. It was therefore apparent that some nitrones react with certain radicals to give single adducts which are stable aminoxyls, while others give 1,3-addition products. CIDNP studies[6,7] of reacting systems later confirmed that 1,3-addition to the nitrone function proceeds with initial radical addition to the nitronyl carbon atom followed by a second radical–radical coupling at the oxygen atom of the aminoxyl intermediate.

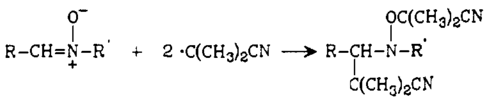
$$\underset{\text{I}}{CN(CH_3)_2C{-}N{=}N{-}C(CH_3)_2CN} \xrightarrow{\Delta} \underset{\text{II}}{2\,{\bullet}C(CH_3)_2CN} + N_2 \qquad (1)$$


(2)

III IV


(3)

V VI


(4)

$$R{-}CH{=}\overset{O^-}{\underset{+}{N}}{-}R' + 2\,{\bullet}C(CH_3)_2CN \longrightarrow R{-}\underset{C(CH_3)_2CN}{CH}{-}\overset{OC(CH_3)_2CN}{N}{-}R'$$

VII R,R' = C_6H_5

VIII R = C_6H_5, R' = $C_6H_5CH_2$

IX R = $C_6H_5{-}\overset{O^-}{\underset{+}{N}}{=}CH$, R' = C_6H_5

Since the initial work by Iwamura and Inamoto,[1,2] spin trapping studies using PBN with AIBN as the radical source have subsequently described two different ESR spectra which have *both* been assigned to the 2-cyano-2-propyl radical adduct, (CP-PBN$^•$)!

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† National Research Council of Canada.

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Thus Ohto et al.[8] obtained a triplet of doublets with $a_N = 13.87$ and $a_H^\beta = 2.09$ G in benzene, while Bevington and co-workers reported[9] $a_N = 14.05$ and $a_H^\beta = 3.10$ G also in benzene. It occurred to us that the presence of oxygen, the temperature of thermolysis, and the duration of heating might make the difference in this experiment since both 2-cyano-2-propylperoxyl (CPOO•) and 2-cyano-2-propyloxyl (CPO•) radicals should be formed[10-14] when AIBN is thermolized in the presence of oxygen. In a previous

$$\cdot C(CH_3)_2CN + O_2 \rightarrow \underset{\textbf{X}}{\cdot OOC(CH_3)_2CN} \qquad (5)$$

$$2\cdot OOC(CH_3)_2CN \rightarrow \underset{\textbf{XI}}{2\cdot OC(CH_3)_2CN} + O_2 \qquad (6)$$

publication we reported[15] that the 2-cyano-2-propyloxyl adduct of PBN (CPO-PBN•), has the hyperfine splitting constants (hfsc's) of $a_N = 13.93$ and $a_H^\beta = 2.16$ G and thus corresponds to the adduct reported by Ohto et al.[8] This assignment was based on the magnitude of the α-^{13}C hfsc obtained from spin trapping experiments with PBN-*nitronyl*-^{13}*C*, namely $a_\alpha^{13C} = 4.70$ G (benzene). The magnitude of this hfsc is characteristic of oxyl adducts of PBN.[15]

In this publication we report on a study by ESR/spin trapping as well as by NMR and mass spectroscopy on the spin trapping thermolysis reaction of AIBN in the presence of PBN or DMPO. LC/MS is demonstrated in this paper to be particularly useful for the identification of fragile spin adducts. From this work we have ESR/spin trapping evidence for CP•, CPO•, and CPOO• radicals produced in systems containing a variable amount of oxygen. Two stable alkoxylamines, the result of 1,3-mixed-radical addition to nitrones (CPO-PBN-CP and CPO-DMPO-CP), are produced in the presence of oxygen. Several accounts have previously appeared on the use of probe MS[16-19] and GC/MS[20-25] for structural studies of spin adducts, but this is the first report describing the use of LC/MS in spin trapping.

Experimental Section

Commercially available AIBN (Eastman) was purified by repeated recrystallization from methanol at 4 °C and was stored at -20 °C. PBN is available from Aldrich, and PBN-d_9 was available[26,27] in these laboratories synthesized from deuterated precursors. Both were purified by vacuum sublimation prior to use. DMPO is available from Aldrich and was also purified by vacuum distillation prior to use.

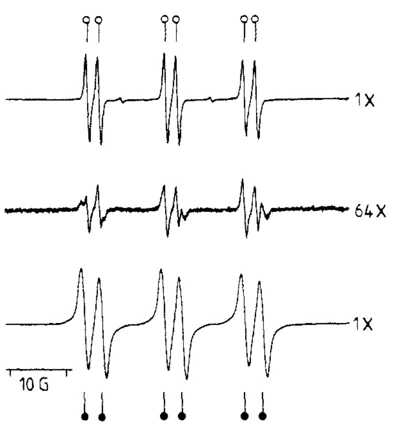

Figure 1. ESR spectra of spin trapping products obtained during AIBN thermolysis with PBN: (○) ≡ CPO-PBN• and (●) ≡ CP-PBN•; (a) Exposed to atmospheric oxygen and heated at 65 °C for 10 min; (b) oxygen depleted by degassing with N_2 heated at 65 °C for 10 min (64× vertical scale); (c) oxygen depleted by degassing with argon heated at 95 °C for ~150 min.

Thermolysis experiments were carried out with ~60 mM AIBN, 50 mM spin trap in benzene or xylene at 65–70 °C or 95 °C in a temperature regulated oil bath. The presence of oxygen was varied by (a) exposing the solutions to atmospheric oxygen, (b) bubbling with O_2, or (c) bubbling with argon or nitrogen through a vented rubber septum system.

The detection of a thermally labile peroxyl adduct of PBN was accomplished by irradiating for 5 min a partially O_2 depleted solution of AIBN and PBN at 205 K with a 75-W Xenon lamp. ESR spectra were recorded during and after photolysis under low ambient light conditions (laboratory lights off).

ESR spectra were recorded by the use of a Bruker ER-200D spectrometer by using a X-band ST ESR cavity with 100-KHz field modulation, modulation amplitude of 0.125 G, and microwave power at 10 dB. For low-temperature work, the cavity was fitted with a variable-temperature dewar, and the temperature was controlled by a Bruker ER 4111VT unit. Spectrometer settings were 6-KHz field modulation, modulation amplitude of 0.25 G, and microwave power 10 dB. Spectral accumulation and averaging was done by using a Bruker ER-140 (Aspect 2000) data system. The g value for CPO-PBN• was determined by comparison with Fremy's salt in saturated sodium bicarbonate solution (g value = 2.005 50 ± 0.000 005[28]) in a capillary tube taped to the ESR cell. The g values for the remaining spin adducts were determined from computer simulations of overlapping spectra resulting from a mixture containing the particular spin adduct and CPO-PBN• using the g value of CPO-PBN• as a comparison. The estimated error in the computer simulations was ±0.000 003.

^{1}H-NMR spectra were obtained by use of a Bruker WP-400 spectrometer in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as internal standard.

Analytical HPLC of the thermolysis products was accomplished with a reverse-phase C-18 column and a mobile phase consisting of 7:3 acetonitrile–water, 0.02 M potassium phosphate buffer, pH 5.8, pumped isocratically at 1.0 mL/min. The HPLC system, as described previously,[29] employed electrochemical detection (EC) at +0.7 V vs Ag/AgCl as reference electrode in series with UV detection at 214 nm. Semipreparative HPLC purification of PBN adducts was accomplished with a Spherisorb 5 μm ODS 2 column, 10 mm i.d. × 25 cm (HPLC technology).

HPLC purified spin adducts and double adducts of PBN were analyzed by GC/MS with electron ionization (EI) at 70 eV or by chemical ionization (CI) with isobutane as a reagent gas. The equipment consisted of a Hewlett-Packard 5790 gas chromatograph interfaced directly to a VG 12000 quadrupole mass spectrometer. Chromatography was carried out with a J&W 0.25 mm i.d. × 15 m DB5 fused silica capillary column,

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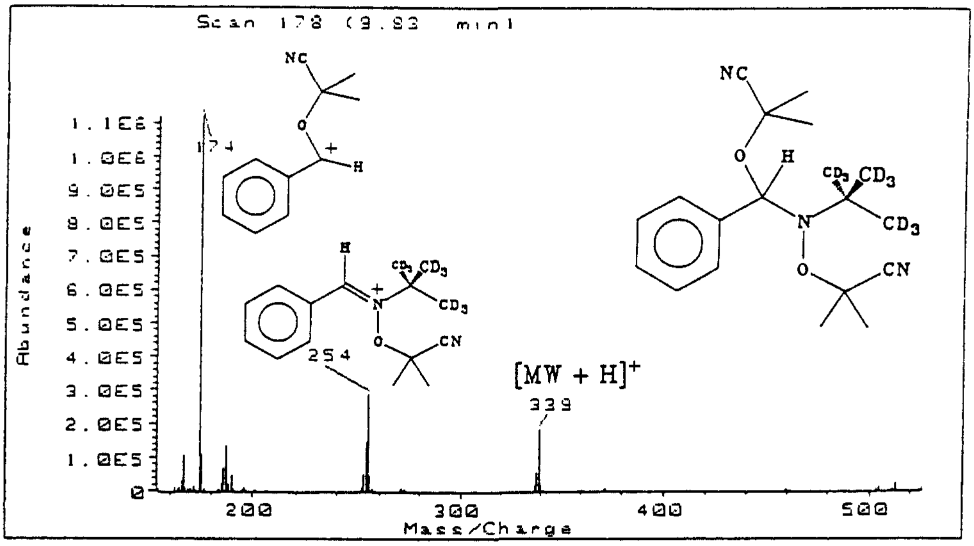


Figure 2. Thermospray LC/MS spectrum of the HPLC-purified nonparamagnetic product formed during AIBN thermolysis in the presence of atmospheric O_2 and PBN-d_9 (chromatographic peak, t_R = 9.84 min.).

by using helium as a carrier gas, and a temperature program from 100 °C to 320 °C at 10 °C/min.

Thermospray LC/MS of whole sample reaction products and of purified adducts of PBN was accomplished by the use of a Hewlett-Packard 1090 HPLC system fitted with a 200 mm × 2.1 mm 5 μm hypersil ODS Hewlett-Packard column maintained at 45 °C, a Hewlett-Packard 5988 mass spectrometer with a thermospray LC to MS interface, and a HP Chem Station data system. The mobile phase was 7:3 methanol-water and was pumped at 1.0 mL/min. Ionization of solute molecules was accomplished in the absence of an organic ammonium buffer by operating with the "filament-on". Mass spectroscopic results reported in numerical summary use the following format: retention time, *m/z*, relative abundance, ion identity, or fragment loss from the parent ion (P).

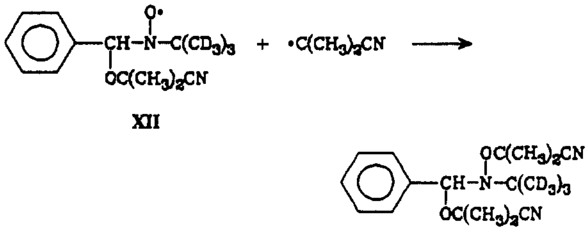
Results

PBN. ESR of Thermolyzed Samples. The ESR-detectable products formed during AIBN thermolysis in the presence of PBN show a marked dependence on the presence of oxygen, the thermolysis temperature, and duration of heating. When the sample is open to air during thermolysis at ~65 °C for 5 min to several hours, only one spin adduct is detected (Figure 1a). The hfsc's obtained, a_N = 13.87 and a^{β}_H = 2.06 G, are typical of an oxygen-centered adduct of PBN and are similar to those previously reported and assigned to CPO-PBN$^{\bullet}$, by using the α-^{13}C hfsc from PBN-*nitronyl*-^{13}*C* as evidence.[15] The carbon-centered spin adduct CP-PBN$^{\bullet}$ is not observed. The amount of oxygen-centered adduct of PBN is increased only slightly (double integration of the ESR signal gives an increase of 3%) when the experiment is repeated with an enriched oxygen atmosphere. When the experiment is carried out under O_2-depleted conditions, the signal intensity is drastically reduced, and two components are evident (Figure 1b). ESR parameters of the addition product were determined by computer simulation of a spectrum accumulated and averaged at a higher receiver gain. The hfsc's of the new spin adduct, a_N = 14.30 and a^{β}_H = 3.22 G, are consistent with the carbon-centered spin adduct, CP-PBN$^{\bullet}$. With time (e.g., 2 days) and in the absence of additional oxygen, the ESR spectrum due to the oxyl adduct disappears, and only the spectrum assigned to the carbon-centered adduct remains. When AIBN thermolysis is carried out at a higher temperature (95 °C in xylene) under oxygen-depleted conditions (by argon bubbling for 15 minutes in a capped reaction container), heating for 2.5 h in the presence of PBN produces only CP-PBN$^{\bullet}$ (a_N = 14.17 and a^{β}_H = 3.13 G, Figure 1c). The small amount of CPO-PBN$^{\bullet}$, produced in O_2-depleted samples at 65 °C likely results from residual O_2 reacting with CP$^{\bullet}$ or perhaps from the peroxide impurity in crystalline AIBN. Upon extended reaction in a sealed container or thermolysis at higher temperatures CP-PBN$^{\bullet}$ is the only spin adduct detected.

In the case of the small triplet which appears during thermolysis of AIBN in the presence of O_2 at 65 °C (Figure 1a), the hfsc, a_N = 7.95 G, is consistent with an aminoxyl of the type RCO-(N-O$^{\bullet}$)R'. Such acyl aminoxyls are common ESR detected products of peroxyl radical reactions with nitrones.[30,31]

Chromatography and Mass Spectroscopy. The HPLC profile of the reaction products for the AIBN sample thermolyzed at 65 °C in the presence of PBN-d_9 and atmospheric oxygen gave only one peak (t_R = 5.52 min) by using the EC detector which was identified by ESR as CPO-PBN$^{\bullet}$. A nonparamagnetic product which is detected by UV-HPLC (t_R = 12.30 min) but which is not electrochemically active accumulates with longer duration of heating. These two products were isolated by semipreparative HPLC and subjected to mass spectroscopic analysis. However the paramagnetic compound could not be identified by GC/MS. On-column decomposition at the GC temperature or decomposition in the GC injector port was suspected. The same sample, when subjected to heating in the ESR cavity, was found to decompose completely at 110 °C. Signal decay occurred gradually over the 60–110 °C range.

The HPLC purified nonparamagnetic product detected by UV was found to be detectable by GC/MS and could be collected in sufficient quantities for ^{1}H NMR (see next section). Both chemical ionization GC/MS and LC/MS methods confirmed the molecular weight and structure to be the product of 1,3-mixed-radical addition to PBN namely CPO-PBN-CP. The mass spectrum for CPO-PBN-CP from thermospray LC/MS (t_R = 9.84 min) is shown in Figure 2. The protonated parent ion [M + H]$^+$ (*m/z* = 339) is detected with good intensity in the LC/MS spectrum (16% of the base peak). Major fragment ions present are consistent with the assigned structure: *m/z* = 254 corresponds to the loss of $(CH_3)_2(CN)OH$, and *m/z* = 174 corresponds to loss of $(CD_3)_3CNHOC(CH_3)_2CN$ from the protonated parent ion. Ions containing the partially deuterated *tert*-butyl group, e.g., *m/z*



$$C_6H_5\text{-}\underset{\displaystyle OC(CH_3)_2CN}{CH}\text{-}\overset{\displaystyle O^{\bullet}}{N}\text{-}C(CD_3)_3 + {}^{\bullet}C(CH_3)_2CN \longrightarrow C_6H_5\text{-}\underset{\displaystyle OC(CH_3)_2CN}{CH}\text{-}\overset{\displaystyle OC(CH_3)_2CN}{N}\text{-}C(CD_3)_3 \quad (7)$$

XII

XIII

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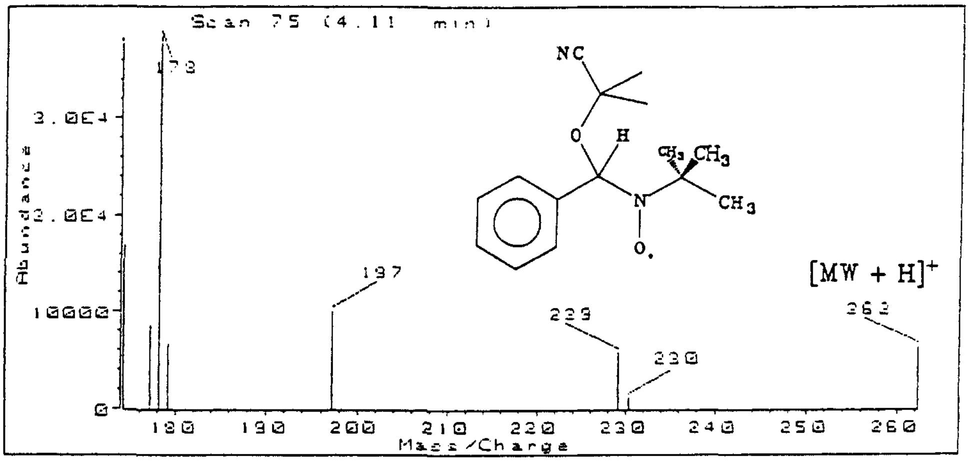

Figure 3. Thermospray LC/MS spectrum of the paramagnetic reaction product after thermolysis of AIBN in the presence of O_2 and PBN for 30 h at 21 °C (chromatographic peak, t_R = 4.10 min.).

= 339 and 254, are evident from the intensity of the M−1 and M−2 peaks which arise from incomplete deuteration of PBN-d_9 (~93% deuterated). The CI-GC/MS results were t_R = 7.3 min and m/z = 339 (2.6%, $[M + H]^+$. Fragmentation was also consistent for the structure of XIII. When analyzed by EI-GC/MS, the molecular ion of CPO-PBN-CP is not present in the mass spectrum. However, the deuterated *tert*-butyl group of PBN-d_9 results in the $C_4D_9^+$ ion (m/z = 66, 36%)[25] which assists in identifying the compound as a PBN-d_9 adduct.

The mass spectrum of the paramagnetic compound detected by analytical HPLC was successfully obtained by the use of thermospray LC/MS. A benzene solution of PBN and AIBN exposed to atmospheric O_2 was left at room temperature (~21 °C) for 30 h. The sample was found to contain unreacted AIBN and PBN as well as CPO-PBN• (t_R = 4.10 min, mass spectrum shown in Figure 3). The highest mass ion (m/z = 262) corresponds to $[M + H]^+$ and results from transfer of a proton to the parent molecule, most likely from the HPLC solvent (7:3 methanol–water) since no buffer was used. The appearance of $[M + H]^+$ is common in "thermospray-MS"[32] and is the primary mode of ionization of all aminoxyl spin adducts of PBN studied by LC/MS thus far.[33] Structurally significant fragment ions include m/z = 230 (loss of CH_3OH from $[M + H]^+$), m/z = 229 (loss of H• from m/z = 230), m/z = 178 (loss of initially trapped radical, $•OC(CH_3)_2CN$, from $[M + H]^+$), and m/z = 174 ($C_6H_5CHOC(CH_3)_2CN$). The m/z = 197 peak could not be assigned.

A compound tentatively assigned to 2-cyano-2-propyl peroxide coeluted with AIBN: t_R = 2.63 min, m/z = 233 (12.9, $[M + CH_3OH_2•CH_3OH]^+$), 201 (100, $[M + CH_3OH_2]^+$), 169 (43.5, $[M + H]^+$.

$$\underset{\text{XI}}{2•OC(CH_3)_2CN} \rightarrow \underset{\text{XIV}}{NC(CH_3)_2COOC(CH_3)_2CN} \quad (8)$$

The products of AIBN thermolysis at 95 °C in the absence of O_2 were analyzed by LC/MS to confirm the assignment of the ESR spectrum (Figure 1c) to CP-PBN•. After heating for 1.5 h, the sample was found to contain only CP-PBN•: t_R = 4.16 min; m/z = 246 (100, $[M + H]^+ \equiv P$), 245 (56.7, M^+), 17.7, P − OCH_3), 189 (8.0, P − C_4H_9), 178 (9.2, P − $C(CH_3)_2CN$).

NMR. The 400-MHz ^{1}H-NMR spectrum (in $CDCl_3$) provided further evidence for CPO-PBN-CP: δ = 1.254 ppm (s, *tert*-butyl H); 1.625, 1.785, 1.800, and 1.823 ppm (4s × 3 H, four methyl groups); 6.219 ppm (s, 1 H, benzylic); 7.320–7.620 ppm (m, 5 H, aromatic). The methyl proton resonances of the 2-cyano-2-propyl groups occur in the region of ~1.62–1.82 ppm but were not individually assigned. Each methyl in the 2-cyano-2-propyl groups is magnetically nonequivalent because of the chiral benzylic carbon atom. It is apparent from these results that inversion at the nonplanar nitrogen atom and also rotation about the α-C–N bond must be rapid on the NMR time scale, otherwise eight methyl resonances as in the 2-cyano-2-propyl radical double adduct (1,3-addition product) of nitrone VIII reported by Iwamura and Iwamura[34] would have been observed.

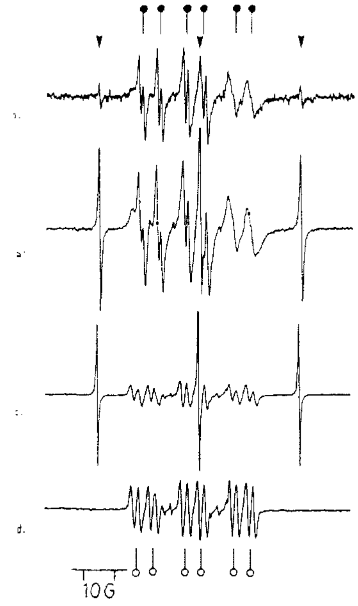

Figure 4. Photolysis of AIBN in the presence of O_2 and PBN-*nitronyl*-^{13}C at reduced temperature in toluene. ESR spectra were obtained during a brief photolysis with a 75-W Xenon lamp at 205 K and after photolysis as the temperature was raised: (●) ≡ CPOO-PBN•; (○) ≡ CPO-PBN, and (▼) ≡ CPO-MNP; (a) 205 K; (b) 230 K; (c) 250 K; and (d) 270 K.

In Situ ESR at Reduced Temperature. A solution of AIBN and PBN-*nitronyl*-^{13}C in toluene was partially oxygen depleted and photolyzed for 5 min at 205 K. A new ESR spectrum is observed under these conditions: a_N = 12.84, a_H^β = 1.23, $a^{\alpha}{}_{^{13}C}$ = 5.05 G (Figure 4a,b). These parameters are consistent with a peroxyl radical adduct of PBN,[8,31,35-40] CPOO-PBN•, since peroxyl spin

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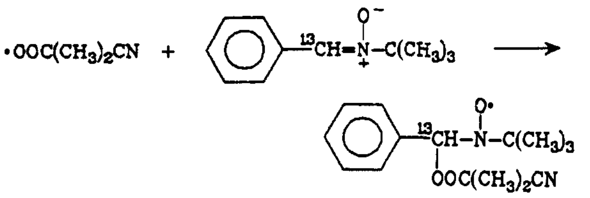
Table I. Hyperfine Splitting Constants (hfsc's) of Selected Spin Adducts

spin trap	radical addend	a_N	a_H	a_{other}	g value	solvent	ref
PBN	$^{\bullet}C(CH_3)_2CN$	14.6	3.07			tetrahydrofuran	1, 2
PBN	$^{\bullet}C(CH_3)_2CN$	14.05	3.10			benzene	9
PBN-*nitronyl*-^{13}C	$^{\bullet}C(CH_3)_2CN$	14.28	3.29	$\alpha^{13}C = 5.78$		benzene	15
PBN	$^{\bullet}C(CH_3)_2CN$	14.17	3.13			xylene	this work
PBN	$^{\bullet}C(CH_3)_2CN$	14.30	3.22		2.00599	benzene	this work
PBN-*nitronyl*-^{13}C	$^{\bullet}OC(CH_3)_2CN$	13.93	2.16	$\alpha^{13}C = 4.70$		benzene	15
PBN-d_9	$^{\bullet}OC(CH_3)_2CN$	13.87	2.06		2.00610	benzene	this work
PBN-*nitronyl*-^{13}C	$^{\bullet}OOC(CH_3)_2CN$	12.84	1.23	$\alpha^{13}C = 5.05$		toluene	this work
PBN	$^{\bullet}OOC(CH_3)_2CN$	12.94	1.25			toluene	this work
PBN	$^{\bullet}OOC(CH_3)_3$	13.42	0.95	$\beta^{17}O = 2.9$		toluene	39
PBN-*nitronyl*-^{13}C	$^{\bullet}OOC(CH_3)_3$	13.25	1.15	$\alpha^{13}C = 4.65$		benzene	15
PBN	$^{\bullet}OOC(CH_3)_3$	13.25	1.38			benzene	31
DMPO	$^{\bullet}OC(CH_3)_2CN$	12.66	8.37	$^1H = 1.89$ ^{H} 0.62		benzene	this work
DMPO	$^{\bullet}C(CH_3)_2CN$	14.6	20.4			xylene	1, 2
MNP	$^{\bullet}OC(CH_3)_2CN$	28.48			2.00529	toluene	this work

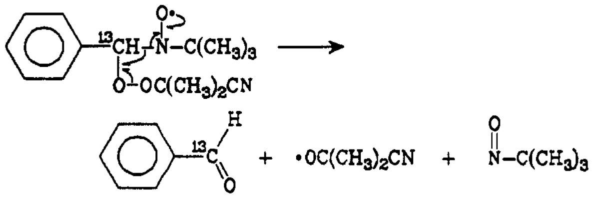
adducts are characterized by unusually small ^{14}N and β-H hfs's[41] (see Table I for comparisons).



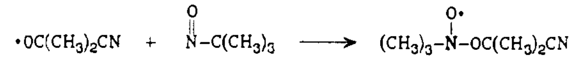
(9)

XV

The spectrum assigned to CPOO-PBN$^{\bullet}$ is temperature sensitive. As the temperature is increased from 205 K through 250 K the intensity decreases and a triplet, a_N = 28.48 G, g = 2.00529 (toluene), which was present in small amounts immediately after photolysis, becomes much more intense. At 230 K the spectrum due to CPOO-PBN$^{\bullet}$ disappears entirely leaving an intense triplet and a weaker spectrum due to CPO-PBN$^{\bullet}$ (Figure 4c). These components are stable at 250 K but when the temperature is increased to 270 K, the sharp triplet also disappears, leaving only the spectrum due to CPO-PBN$^{\bullet}$ (Figure 4d). The sharp triplet with relatively large ^{14}N hfsc (28.48 G) may be the result of decomposition of the peroxyl spin adduct of PBN and formation of the CPO$^{\bullet}$ spin adduct of 2-methyl-2-nitrosopropane. Aminoxyls of this type are known to have very large ^{14}N hfsc's, namely 20–30 G.[36,42,43] This mechanism also accounts for the loss of the nitronyl α-^{13}C coupling in the ESR spectrum of XVI. It is unclear whether CPO-PBN$^{\bullet}$ arises from decomposition of the CPOO-PBN$^{\bullet}$ or from decomposition of some non-paramagnetic product as the temperature is raised.



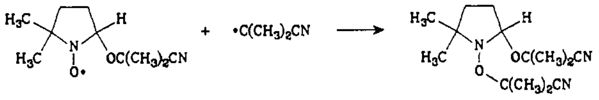
(10)



$$\cdot OC(CH_3)_2CN + \overset{O}{\overset{\|}{N}}-C(CH_3)_3 \longrightarrow (CH_3)_3-\overset{O\cdot}{\overset{|}{N}}-OC(CH_3)_2CN \quad (11)$$

XVI

DMPO. The thermolysis of AIBN in a benzene solution of DMPO exposed to atmospheric O_2 produced a paramagnetic compound detected by ESR. The hfsc's are consistent with the oxyl adduct, CPO-DMPO$^{\bullet}$ (a_N = 12.63, a_H^{β} = 8.4, a_H^{γ} = 1.85, a_H^{γ} $\simeq$ 0.62 G). After extended thermolysis at 75 °C, an aliquot of the total sample was analyzed by LC/MS. This experiment revealed the presence of the mixed double adduct of DMPO (CPO-DMPO-CP): t_R = 3.31 min; m/z = 266 (80.1, $[M + H]^+ \equiv P$), 213 (18.3, P − CH_2CHCN), 199 (4.1, P − $C_4H_5N_5$), 197 (2.8, P − $CH(CH_3)_2CN$), 181 (100, P − $HOC(CH_3)_2CN$).



(12)

XVII XVIII

Discussion

The rate constant for spin trapping CP$^{\bullet}$ radicals by PBN is not known but expected to be relatively slow because of steric hindrance to addition.[44] Both *tert*-butyl and CP$^{\bullet}$ radicals give relatively weak signals when detected with PBN. In the presence of oxygen CPOO$^{\bullet}$ and CPO$^{\bullet}$ radicals are obtained as expected if 2-cyano-2-propyl radicals behave like *tert*-butyl radicals. *Tert*-butoxyl radicals are known to undergo β-cleavage to methyl radicals and acetone at a rate which increases with polarity of solvent.[45] However, a comparable reaction of CPO$^{\bullet}$ radicals has not been observed to date at the temperatures used. When both CPO$^{\bullet}$ and CP$^{\bullet}$ radicals are produced in the same solution, the trapping of CPO$^{\bullet}$ predominates probably because of a faster rate constant of addition (for *tert*-butyl and *tert*-butoxyl radicals the rate constants of spin trapping are 1×10^4 M^{-1} s^{-1} [46] and 5.5×10^6 M^{-1} s^{-1},[47] respectively). Thus the CPO-PBN$^{\bullet}$ signal is always stronger than that of CP-PBN$^{\bullet}$. However, the trapping of alkyl radicals by aminoxyls to produce alkoxylamines is very fast (10^8–10^9 M^{-1} s^{-1} [48]), while oxygen-centered radicals do not add to the nitroxyl function of aminoxyls.[49] Thus it is perhaps not

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[43] It should be noted that Adamic et al.[12] reported a triplet with splittings of about 30.0 G in CF_2Cl_2 when solutions of AIBN or azobiscyclohexylnitrite were irradiated in the presence of O_2. The signal appeared at −110 °C was modestly stable up to about −90 °C but disappeared rapidly at −60 °C. Although it is difficult to compare the hfsc's in the two solvents, the difference in thermal stability suggests that these radicals may not be the same.

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surprising that mixed double adducts are formed in the thermolysis of AIBN in the presence of oxygen with the sequence of 1,3-addition determined by the rate constants of addition, i.e., CPO• radicals add first to the carbon atom of the nitronyl function followed by CP• addition to the oxygen atom of the nitroxyl function. With respect to the trapping of 2-cyanopropylperoxyl radicals, it is assumed that combination to produce 2-cyanopropyloxyl radicals should be much faster than spin trapping peroxyl radicals, but this point has not been established. The decomposition products of the peroxyl spin adduct have also not been ascertained, and whether 2-cyanopropyloxyl radicals are formed in this process is not known.

The combination of mild chromatographic conditions of HPLC and the soft ionization of thermospray LC/MS permits the mass spectrum of spin adducts and double adducts of PBN and DMPO to be obtained. However, the ionization technique appears to be less sensitive than electron impact, and the mass spectra can be complicated by a variety of ion source reactions. Although in the case of the spin adducts of PBN the highest mass ion results from proton addition to the nitroxyl function, for the nitrones PBN and DMPO, the highest mass ion corresponds to a dimer of the nitrone plus a proton, $[2M + H]^+$. It is clear from the HPLC retention times that the nitrone does not exist as a dimer in solution. Instead, the mass spectroscopic results indicate quasi-dimer formation in the ion source.[50] Addition of $CH_3OH_2^+$ formed from the HPLC solvent in the ion source occurs to a minor degree in the ionization of the alkoxylamine CPO-PBN-CP but constitutes the base peak in the mass spectrum of AIBN. The mass spectrum of AIBN is further complicated by the addition of two molecules of methanol and a proton to give $[M{\cdot}CH_3OH - CH_3OH_2]^+$. A compound which coelutes with AIBN showed the same ionization behavior. These characteristics combined with the magnitude of the mass (m/z = 169, $[M + H]^+$) has led us to the tentative assignment of this compound to 2-cyano-2-propyl peroxide, a previously unreported compound (XIV).

Summary

Spin trapping studies must in the future also account for double adducts if a measure of quantitation is to be expected. In addition to the products of the so-called 1,3-addition reaction, R-ST-R (where R is the radical and ST is the spin trap), mixed double adducts are also possible, R′-ST-R. In the case of 2-cyano-2-propyl radicals from AIBN, we have presented evidence for four monospin adducts CP-PBN•, CPO-PBN•, CPOO-PBN•, and CPO-DMPO• as well as two mixed double adducts CPO-PBN-CP and CPO-DMPO-CP. Other possible mixed double adducts of PBN and DMPO, e.g., CPOO-ST-CP, remain to be detected.

Acknowledgment. This work has been supported by the Natural Sciences and Engineering Research Council of Canada. Grateful acknowledgment is hereby made.

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