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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 31. Rate Constants for Spin Trapping. 1. Primary Alkyl Radicals¹

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Abstract: Rate constants for the addition of primary alkyl radicals to most of the commonly employed spin traps have been determined at 40 °C using the [1-¹³C]-5-hexenyl radical as the primary standard. In the presence of a spin trap there is a competition between direct addition of this radical to give a ¹³C labeled spin adduct and its cyclization to the cyclopentylmethyl radical which, when it adds to the trap, gives an unlabeled spin adduct. The results obtained with this radical have been extended by means of competitive experiments using pairs of spin traps and the 1-hexyl radical. Additional rate data has been obtained by measurement of spin adduct concentrations under steady-state conditions.

In the EPR spectroscopic technique of "spin trapping", a transient radical, R·, is "visualized" by allowing it to add to a spin trap, T, and so form a persistent spin adduct, RT·.³

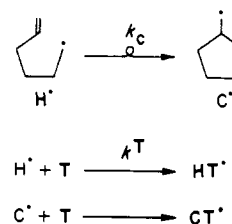


This technique has been used qualitatively to detect and identify reactive free radicals for several years.³ However, the fact that a spin adduct is observed when a trap is added to some particular reaction system is not of as much help in deducing the reaction mechanism as might be supposed. This is partly because EPR spectroscopy is such an extremely sensitive probe for radicals that a spin trapping experiment may yield a "positive" result on a minor side reaction, while the main reaction is overlooked if it is nonradical, or even when it does involve radicals if they are not readily trapped or yield non-persistent spin adducts. The ambiguity of a positive result can be largely avoided if kinetic data are available regarding the rates of spin trapping of the radicals in question *and* the rates at which the spin adducts so formed are themselves destroyed. There are relatively few rate data available for spin trapping,⁴⁻¹¹ and there is even less information available concerning the rates at which spin adducts are destroyed. In view of the great potential of spin trapping, we have begun a program to determine accurate rate constants for the trapping of some of the more commonly encountered radicals. This, the first paper,¹ is devoted to the trapping of primary alkyl radicals in benzene.

The 5-hexenyl radical, H·, provides the mainstay for the present work. This radical isomerizes irreversibly to yield the cyclopentylmethyl radical, C·.¹² The rate constant for this cyclization, k_c , was initially estimated at ambient temperatures by combining some product studies of Walling et al.¹³ with a rotating-sector kinetic study of our own on the trialkyltin hydride-alkyl halide reaction.¹⁴ We subsequently investigated this cyclization by kinetic EPR spectroscopy and obtained Arrhenius parameters which confirmed the earlier results.¹⁵

Since both H· and C· are primary alkyls, the spin adducts that they form with any particular spin trap will have similar properties, i.e., similar kinetic and thermodynamic stabilities, which is an advantage, and similar EPR spectra, which is a handicap. However, a nice distinction between the spectra of the two spin adducts, HT· and CT·, can be obtained by labeling the 5-hexenyl radical with carbon-13 ($I = 1/2$) in the 1 position. In most cases, hyperfine splitting (hfs) by this ¹³C atom should be detectable in the EPR spectrum of HT· because of the proximity of the ¹³C to the orbital containing the unpaired electron in this adduct. However, in CT· the ¹³C will be too remote from the unpaired electron to produce any appreciable hyperfine splitting. The reaction system depicted in Scheme I allows the rate constant for the spin trapping of H· to be

Scheme I



calculated from the trap concentration and the measured ratio of the initial rates of formation of the two spin adducts, i.e.,

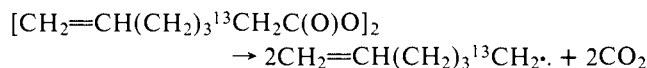
$$k_T = \frac{k_c (d[\text{HT} \cdot]/dt)_{t \rightarrow 0}}{[\text{T}] (d[\text{CT} \cdot]/dt)_{t \rightarrow 0}} \quad (1a)$$

Implicit in this equation is the assumption that *all* of the alkyl radicals formed are captured by the spin trap (vide infra). As long as the total concentration of the adducts does not approach the steady-state level, this equation is equivalent to

$$k_T = \frac{k_c[\text{HT} \cdot]}{[\text{T}][\text{CT} \cdot]} \quad (1b)$$

Thus, the spin trapping rate constant can be evaluated from the spin adduct ratio during the early stages of the reaction. The ratio must be extrapolated back to zero time if it shows any variation. This could occur if the spin trapping were reversible (in which case, the $[HT\cdot]/[CT\cdot]$ ratio would decrease with time) or if the rate constants for the various processes which lead to the destruction of $HT\cdot$ and $CT\cdot$ were not exactly equal.

As our source of ^{13}C labeled $H\cdot$ we have used di($[2-^{13}C]$ -6-heptenyl) peroxide (90 at. % ^{13}C) which can be decomposed thermally or photochemically.



The spin trapping rate constants obtained in the way outlined above have been augmented using the 1-hexyl radical (generated from di-*n*-heptanoyl peroxide) by competitive experiments in which this radical was formed in the presence of two spin traps that gave readily distinguishable EPR spectra. The spin traps that we have studied (or endeavored to study) can conveniently be divided into three categories. (1) **Nitroso Compounds:** 2-methyl-2-nitrosopropane (NtB), $(CH_3)_3CNO$;¹⁶ nitrosobenzene (NB), C_6H_5NO ;¹⁷ nitrosodurene (ND), 2,3,5,6- $(CH_3)_4C_6HNO$;¹⁸ and 2,4,6-tri-*tert*-butylnitrosobenzene (Bu'_3NB), 2,4,6- $[(CH_3)_3C]_3C_6H_2NO$.¹⁹ (2) **Nitrones:**²⁰ 5,5-dimethylpyrroline 1-oxide (DMPO), $(CH_3)_2C\overline{C}H_2CH_2CH=N\rightarrow O$;⁶ methylene-*N-tert*-butyl nitron (MBN), $CH_2=N(O)C(CH_3)_3$;²⁴ phenyl-*N-tert*-butyl nitron (PBN), $C_6H_5CH=N(O)C(CH_3)_3$;^{22,25} phenyl-*N-tert*-per-*deuterio*butyl nitron (PBN-*d*₉);²⁶ and the following ring substituted PBNs, 4-methoxy-PBN (4-MeO-PBN),^{5,6} 4-methyl-PBN (4-Me-PBN),^{5,6} 4-cyano-PBN (4-CN-PBN), 4-nitro-PBN (4-NO₂-PBN),^{5,6} 2,4,6-trimethoxy-PBN (2,4,6-(MeO)₃-PBN),²⁷ and 2,4,6-trimethyl-PBN (2,4,6-Me₃-PBN).²⁷ (3) **Miscellaneous Compounds:** 1,1-di-*tert*-butylethylene, $[(CH_3)_3C]_2C=CH_2$;²⁸ di-*tert*-butyl thioketone, $[(CH_3)_3C]_2C=S$;²⁹ di-*tert*-butyl selenoketone, $[(CH_3)_3C]_2C=Se$;³⁰ 4-chlorobenzonitrile oxide, $C_6H_4ClC\equiv NO$;³¹ 2,4,6-trimethoxybenzonitrile oxide, $(CH_3O)_3C_6H_2C\equiv NO$;³² and 3-phenyl-2-*tert*-butyloxazirane, $C_6H_5CHONC(CH_3)_3$.³²

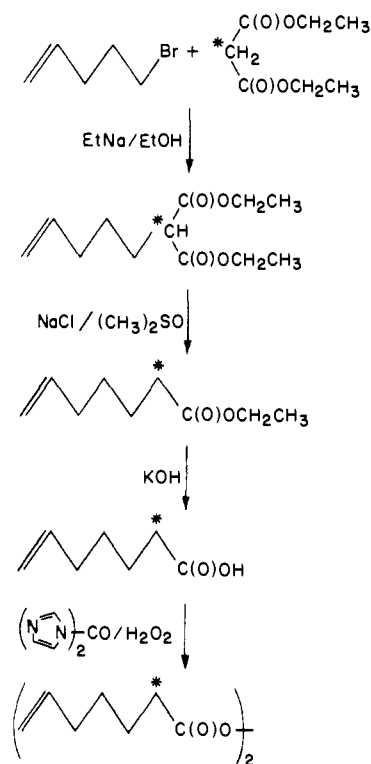
Experimental Section

Materials. Diacyl Peroxides. Di($[2-^{13}C]$ -6-heptenyl) peroxide was prepared by the series of reactions shown in Scheme II. Into 6.2 mL of a 1.02 N solution of sodium ethoxide in dry ethanol³⁵ was added 1 g (6.24 mmol) of diethyl $[2-^{13}C]$ malonate (90 at. % ^{13}C , Merck Sharp & Dohme) and 1 g (6.7 mmol) of 5-bromopent-1-ene (Chemical Samples). The mixture was refluxed for 2 h and cooled, and 30 mL of H₂O was added. Extraction with ether, drying of the organic phase, and removal of the solvent yielded crude diethyl $[2-^{13}C]$ -4-pentenylmalonate. After purification by trap to trap distillation the yield was 1.08 g (4.7 mmol, 75%); ¹H NMR (CDCl₃, δ values in parts per million downfield from TMS) 1.10–2.16 (t + m, 12 H, CH₃ and CCH₂C), 3.14 (t, 1 H, *z*-CH), 4.08 (q, 4 H, OCH₂), 4.79–5.04 (m, 2 H, H₂C=C), 5.48–5.89 (m, 1 H, C=CH).

The malonic ester was decarboxylated by the procedure of Krapcho and Lovey.³⁴ A solution of 1.08 g of diethyl $[2-^{13}C]$ -4-pentenylmalonate, 0.8 g of NaCl, and 0.4 mL of H₂O, in 11 mL of dimethyl sulfoxide was refluxed for 4 h. After cooling, 60 mL of H₂O was added and the mixture was extracted with ether (3 × 50 mL). The organic phase was dried over sodium sulfate, the solvent was removed, and the crude ethyl $[2-^{13}C]$ -6-heptenoate was purified to 96% (VPC) by trap to trap distillation: yield, 0.50 g (3.2 mmol, 68%); ¹H NMR (CDCl₃) δ 1.20–2.42 (t + m, 11 H, CH₃ and CCH₂C), 4.18 (q, 2 H, OCH₂), 4.90–5.16 (m, 2 H, H₂C=C), 5.62–6.04 (m, 1 H, C=CH).

The ethyl $[2-^{13}C]$ -6-heptenoate, 0.48 g, was hydrolyzed by heating to 120 °C for 8 h in a well-stirred vessel with 4 g of KOH in 8 mL of H₂O. The clear, basic, solution was cooled and extracted twice with ether. The aqueous phase was acidified with 2 N HCl and extracted

Scheme II



with ether (3 × 50 mL). The ethereal solution was dried (Na_2SO_4), the solvent removed, and the crude $[2-^{13}C]$ -6-heptenoic acid purified by trap to trap distillation: yield, 0.32 g (2.5 mmol, 81%); ¹H NMR (CDCl₃) δ 1.31–2.43 (m, 8 H, CCH₂C), 4.76–5.06 (m, 2 H, H₂C=C), 5.50–5.93 (m, 1 H, C=CH), 9.00 (s, 1 H, OH).

The acid was converted to the diacyl peroxide by Staab's carbonyldiimidazole route³⁵ because the previously used acid chloride route to this peroxide^{36,37} was found to be unsatisfactory when starting with small quantities of the acid. To a solution of 346 mg (2.13 mmol) of *N,N*-carbonyldiimidazole (Aldrich) in 5 mL of tetrahydrofuran was added a solution of 278 mg (2.16 mmol) of $[2-^{13}C]$ -6-heptenoic acid in 2 mL of tetrahydrofuran. The solution was stirred for 30 min at room temperature and then cooled in an ice bath, 121 mg (1.07 mmol) of H₂O₂ (in a 30% solution) was added, and the mixture was stirred for a further 2 h in the cold. Thereafter, 30 mL of a saturated solution of NaCl was added and the reaction solution was extracted with ether (3 × 40 mL). The organic layer was washed with a saturated salt solution (3 × 30 mL) and dried over Na_2SO_4 . Removal of the solvent under vacuum yielded 300 mg of material which, to judge from its NMR spectrum, appeared to be reasonably pure di($[2-^{13}C]$ -6-heptenyl) peroxide, the only apparent contaminants being traces of imidazole and tetrahydrofuran. Titration³⁸ of samples of unlabeled peroxide prepared in an identical manner showed a peroxide content of 80–90% in all instances. ¹H NMR (CDCl₃) showed δ 1.30–2.50 (m, 16 H, CCH₂C), 4.75–5.10 (m, 4 H, H₂C=C), 5.40–6.10 (m, 2 H, C=CH).

Di-*n*-heptanoyl peroxide was also prepared by Staab's route³⁵ from *n*-heptanoic acid.

Di($[2-^{13}C]$ -acetyl) peroxide was synthesized by the reaction of $[2-^{13}C]$ acetic anhydride (90 at. % ^{13}C ; Merck Sharp & Dohme) with sodium peroxide.³⁹

Spin Traps. 2-Methyl-2-nitrosopropane was prepared by the method of Stowell.⁴⁰ Solutions of this compound were always handled in the dark. **Nitrosobenzene** (Aldrich) was recrystallized from methanol. **Nitrosodurene** was prepared by the procedure of Smith and Taylor.⁴¹ 2,4,6-Tri-*tert*-butylnitrosobenzene was a gift from Professor L. R. C. Barclay.

5,5-Dimethylpyrroline 1-oxide and the following ring substituted phenyl-*N-tert*-butyl nitrones, 4-MeO-PBN, 4-Me-PBN, 4-CN-PBN, and 4-NO₂-PBN, were gifts from Professor E. G. Janzen. **Methylene-*N-tert*-butyl nitron** was prepared as a solution in benzene from NtB and diazomethane⁴² by the method of Baldwin et al.⁴³ and was immediately used. **Phenyl-*N-tert*-butyl nitron** (Eastman) was used without purification. **2,4,6-Trimethoxy-PBN**, **2,4,6-trimethyl-PBN**,

and phenyl-*N-tert-perdeuteriobutyl* nitron were gifts from Dr. K. Sommermeyer.

1,1-Di-*tert-butylethylene*,²⁸ di-*tert-butyl* thioketone,²⁹ and di-*tert-butyl* selenoketone³⁰ were available from earlier work. 4-Chlorobenzonitrile oxide was prepared by treating the corresponding hydroxamic acid chloride (obtained by chlorination of 4-chlorobenzal-doxime⁴⁴) with triethylamine.⁴⁵ 2,4,6-Trimethoxybenzonitrile oxide⁴⁶ and 3-phenyl-2-*tert-butyl*oxaziridine⁴⁷ were prepared by literature methods.

N-n-Hexyl-N-tert-butylhydroxylamine was prepared by reaction of *n*-hexylmagnesium bromide with NtB in an argon atmosphere.⁴⁸ The reaction mixture was treated with an ammonium chloride solution and extracted with ether. The organic phase was dried (Na₂SO₄) and transferred to a vacuum line, and the solvent was removed under vacuum. The hydroxylamine was isolated by trap to trap distillation. Attempts to purify this material by recrystallization of the hydrogen oxalate⁴⁹ were not successful, the product obtained being the salt of di-*tert-butyl* hydroxylamine. Attempts to purify the *N-n-hexyl-N-tert-butyl* hydroxylamine by HPLC (Waters μCN column, 3% 2-propanol in *n*-hexane (v/v) as eluent) were somewhat more successful, but a small amount of di-*tert-butyl* nitroxide was always present as an impurity, no matter how carefully light and air were excluded during the chromatography.

General Procedure. Samples were prepared in quartz EPR tubes by adding aliquots of stock solutions of the spin traps to known quantities of the diacyl peroxide. The solutions were degassed by the freeze-thaw procedure and were sealed under 550 Torr of argon. The samples were stored in liquid nitrogen until required. All spectra were recorded on a Varian E-4 EPR spectrometer.

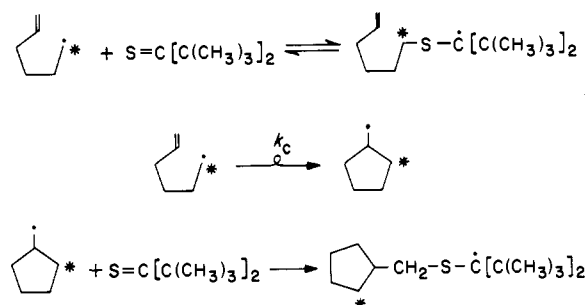
Thermal Generation of Radicals. The frozen samples were transferred to the preheated cavity of the spectrometer and spectra were recorded as a function of time. The ratios of the concentrations of the two spin adducts were determined by double integration of nonoverlapping lines (of known degeneracy) in the first derivative EPR spectra. With the ¹³C labeled 5-hexenyl radical and any single spin trap the lines due to the ¹³C labeled adduct and to the normal adduct were of identical width. The ratio of [uncyclized adduct]/[cyclized adduct] could therefore be determined from the ratio of the heights of (corresponding) peaks of [labeled adduct]/[unlabeled adduct] after correction for (i) the fact that the 5-hexenyl radical was enriched to only 90 at. % ¹³C, and (ii) the fact that the cyclopentylmethyl adduct will have natural abundance (1.1%) ¹³C satellite lines.

Absolute concentrations of the spin adduct, which were required for the steady-state measurements (see below), were determined by calibration against DPPH in the usual manner.⁵⁰

Rate of Peroxide Decomposition. The rate of decomposition of the peroxide was determined by monitoring the initial rate of formation of spin adducts.⁵ With NtB, MBN, ND, and PBN, at low and intermediate concentrations (see Table VI) the decay rate was first order in peroxide and independent of the trap and of its concentration. In benzene at 40 °C the rate constant for decomposition of di-*n*-heptanoyl peroxide to free radicals, *k*_i, was found to be 1.5 × 10⁻⁷ s⁻¹, in good agreement with other data.⁵¹ These facts provide strong evidence that the spin traps are able to trap *all* of the radicals produced from the peroxide under the conditions used in this work. At the highest trap concentrations employed (see Table VI) values of *k*_i increased by a factor of ~2 for all traps, which implies that the traps themselves can induce peroxide decomposition. This phenomenon does not, of course, influence competitive kinetic data.

Photochemical Generation of Radicals. UV photolysis of acyl peroxides is an excellent method for generating alkyl radicals,³⁷ but this technique is not usually suited to quantitative work on spin trapping because the majority of traps are photolabile.³ However, several potential traps which were known to us to be fairly resistant to direct photolysis did not give adducts in appreciable yield under thermal conditions (presumably because adduct formation is slow relative to adduct destruction). Since the rate of radical production by photolysis is much higher than the rate by thermolysis (at ~40 °C) the di([2-¹³C]-6-heptenoyl) peroxide was photolyzed in the presence of these traps. This did not prove particularly helpful in the case of 1,1-di-*tert-butylethylene*, nor in the case of di-*tert-butyl* selenoketone (see Results), but useful information was obtained with di-*tert-butyl* thioketone. With this last compound the trapping reaction must be readily reversible because the [HT·]/[CT·] ratio decreased rapidly with time. That is, the spectrum due to HT· could be detected immediately after the start of irradiation, but it was rapidly swamped by

Scheme III



the spectrum due to CT·, the ¹³C satellite lines being reduced after a few minutes to their natural abundance intensity (2 × 0.55% of the ¹²C lines). The overall result is represented in Scheme III. The correct [HT·]/[CT·] ratio was obtained as follows. The sample was subjected to short light pulses of a fixed duration of 0.52 s which was obtained during each rotation of a "rotating sector" disk through the light path. The magnetic field was set to coincide first with the maximum of the ¹³C peak and then, after an interval long enough for all the signals to die away, with the maximum of the ¹²C peak. The ¹³C and ¹²C peak heights were recorded as a function of time and extrapolation of their ratio back to the start of irradiation yielded the true [HT·]/[CT·] ratio. The accessible range in temperature and in trap concentration were severely limited by the need to obtain reasonable [HT·]/[CT·] ratios and by light absorption by the thione when it was present in high concentration.

Decay of *n*-Hexyl-*tert-butyl* Nitroxide. These radicals were generated by H atom abstraction from the parent hydroxylamine with photochemically generated *tert*-butoxy radicals.⁵⁰ The rate constant for decay was determined by monitoring the decrease in the nitroxide concentration when the light was cut off. The experimental procedure has been described previously.⁵⁰

Dimerization of Nitrosodurene. In solution, nitrosodurene is known to be largely dimerized.¹⁸ Since only the monomer will be active as a spin trap it was necessary to determine the equilibrium for dimerization, $K = [\text{dimer}]/[\text{monomer}]^2$. This was done by monitoring the optical density of solutions of nitrosodurene in benzene at 22 °C over a concentration range from 8 × 10⁻⁴ M to a nearly saturated 1.6 × 10⁻² M on a Cary 15 spectrophotometer at a wavelength of 750 nm. This wavelength is somewhat below the absorption maximum of the monomer, but this was necessitated by the fact that the maximum occurs near 800 nm, which is too close to the operating limit of the spectrophotometer for accurate measurements to be made. Assuming that there is just a simple monomer-dimer equilibrium, that light is absorbed only by the monomer, and that Beer's law applies, then *K* can be calculated from the relation⁵²

$$\frac{D_{750}}{lc} = \epsilon_{750} - \frac{D_{750}^2}{\epsilon_{750}^2 c} \cdot 2K$$

where *c* is the molar concentration of nitrosodurene (calculated as monomer), *l* is the cell length in centimeters, and *D*₇₅₀ and ϵ_{750} are the optical density and molar extinction coefficient per centimeter of the monomer at 750 nm, respectively. As implied by this equation, a plot of *D*₇₅₀/*lc* against *D*₇₅₀²/*l*²*c* did give a straight line from which ϵ_{750} (= intercept) was found to be 16⁵³ and *K* (= slope × intercept/2) was found to be 286 M⁻¹.⁵⁵ At 40 °C under spin trapping conditions, *K* is estimated to be 250 ± 25 M⁻¹. The rather large error in *K* arises from three factors: (i) the instrumental problem referred to above, (ii) the low solubility of nitrosodurene, and (iii) the small extinction coefficient of the monomer. Fortunately, the nitrosodurene concentrations that had to be used for spin trapping were quite low, and so the uncertainty in *K* proved to be of small consequence.

Results

Competition between Spin Trapping and Cyclization of the [1-¹³C]-5-Hexenyl Radical. This competition was studied in benzene using the thermally generated radical with 2-methyl-2-nitrosopropane (NtB), tri-*tert-butyl*nitrosobenzene, phenyl-*tert-butyl* nitron (PBN), and its *tert-butyl* *d*₉ analogue. Figure 1 shows part of the spectrum obtained with NtB at 40 °C. The approximate magnitude to be expected for the

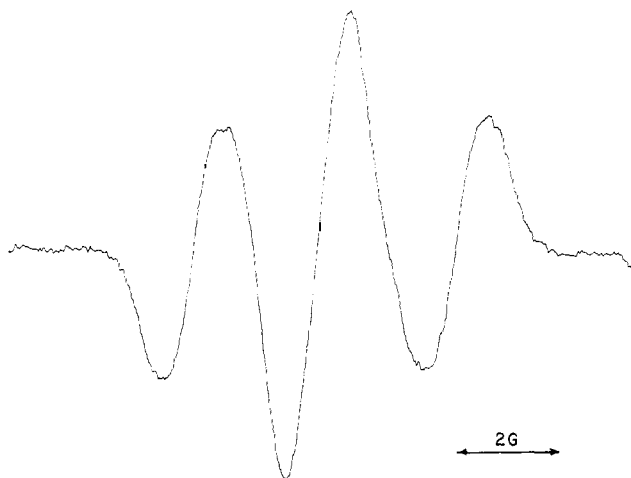
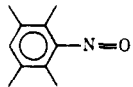
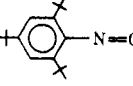


Figure 1. Lowest field lines, corresponding to $1/12$ of the total signal intensity, in the spectrum obtained by heating a benzene solution of di($[2-^{13}\text{C}]$ -6-heptenyl) peroxide, 0.066 M, and 2-methyl-2-nitrosopropane, 0.032 M, to 40 °C. The center line is due to $\text{CT}\cdot$ and the side lines to $\text{HT}\cdot$.

Table I. ^{13}C Hyperfine Splittings (in Gauss) for Some Spin Adducts Produced by Trapping the $[1-^{13}\text{C}]$ -5-Hexenyl Radical and the $[^{13}\text{C}]$ Methyl Radical at 40 °C

Spin trap	$a^{13\text{C}}(\text{HT}\cdot)$	$a^{13\text{C}}(\text{CH}_3\text{T}\cdot)$	
NtB	$(\text{CH}_3)_3\text{CN}=\text{O}$	5.0	5.1 ^a
ND			6.95 ^a
Bu ₃ 'NB		6.8	7.7
PBN	$\text{C}_6\text{H}_5\text{CH}=\text{N}(\text{O})\text{C}(\text{CH}_3)_3$	3.1	3.2 ^b
	$[(\text{CH}_3)_3\text{C}]_2\text{C}=\text{S}$	21.0	23.5 ^c

^a For comparison, $a^{13\text{C}}$ in $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{N}(\text{O})\cdot^{13}\text{CH}_3$ is 6.1 G, in $[(\text{CH}_3)_3^{13}\text{C}]_2\text{NO}\cdot$ it is 4.38 G, and in $\text{C}_6\text{D}_5\text{N}(\text{O})\cdot^{13}\text{CH}_3$ it is 6.0 G; see R. Briere, H. Lemaire, and A. Rassat, *J. Chem. Phys.*, **48**, 1429 (1968). ^b $a^{13\text{C}} = 3.15$ G.²⁶ ^c Reference 29.

^{13}C hfs were determined prior to the kinetic runs by using ^{13}C labeled methyl radicals generated by thermal decomposition of ^{13}C labeled acetyl peroxide. The ^{13}C hfs obtained are listed in Table I.

The ratio of the $\text{HT}\cdot$ and $\text{CT}\cdot$ peak heights yields the ratio of the concentrations of these two radicals (see Experimental Section) and hence, via eq 1b, the rate constant ratio, $k^{\text{T}}/k_{\text{c}}$. Values of $k^{\text{T}}/k_{\text{c}}$ are compiled in Table II together with values of k^{T} , which are based upon k_{c} obtained from the relation¹⁵

$$\log(k_{\text{c}}/\text{s}^{-1}) = 10.7 - 7.8/\theta$$

where $\theta = 2.3RT$ kcal/mol. The range of spin trap concentrations that could be covered was severely limited by the need to obtain comparable concentrations of $\text{HT}\cdot$ and $\text{CT}\cdot$. The temperature range was also somewhat restricted, the lower limit being determined by the need for an adequate rate of peroxide decomposition and the upper by the boiling point of benzene. Except for NtB the $[\text{HT}\cdot]/[\text{CT}\cdot]$ ratios did not change during an experiment. However, with NtB this ratio tended to decrease with time (e.g., by ~20% in 30 min at 40 °C). It was therefore necessary to extrapolate the NtB $[\text{HT}\cdot]/[\text{CT}\cdot]$ ratios back to zero time.

Thermal decomposition of the labeled diacyl peroxide did not produce any substantial yield of the spin adducts with 1,1-di-*tert*-butylethylene, di-*tert*-butyl thioketone, or di-

Table II. Rate Constants Derived from the Competition between Spin Trapping and Cyclization of the $[1-^{13}\text{C}]$ -5-Hexenyl Radical in Benzene

Spin trap,	M	T, °C	$k^{\text{T}}/k_{\text{c}}$, M ⁻¹	$k^{\text{T}} \times 10^{-5}$, M ⁻¹ s ⁻¹
NtB,	0.026	40	50.4	89.7
NtB,	0.032	40	50.9	90.6
NtB,	0.033	55	34.8	110
NtB,	0.033	71	20.3	112
Bu ₃ 'NB,	0.30	56	1.20	3.94
Bu ₃ 'NB,	0.30	73	1.03	6.08
PBN,	0.44	23	1.11	0.963
PBN,	0.44	40	0.75	1.34
PBN,	0.295	40	0.75	1.34
PBN,	0.89	55	0.48	1.52
PBN,	0.89	71	0.38	2.10
PBN- <i>d</i> ₉ ,	0.45	40	0.69	1.23

Table III. Competition between Spin Trapping and Cyclization of the $[1-^{13}\text{C}]$ -5-Hexenyl Radical and Di-*tert*-butyl Thioketone (0.5 M) in Toluene^a

T, °C	$k^{\text{T}}/k_{\text{c}}$, M ⁻¹	T, °C	$k^{\text{T}}/k_{\text{c}}$, M ⁻¹
-82	1.92		
-42	0.69	-38	0.81
-95	2.79	-94	2.34
-57	0.74	-45	0.79
-73	1.59	-84	1.87

^a $[\text{Di}([2-^{13}\text{C}]$ -6-heptenyl) peroxide] = 0.07 M. Experiments were carried out in a random order, as indicated.

Table IV. Summary of Kinetic Data for Spin Trapping of the 5-Hexenyl Radical by Di-*tert*-butyl Thioketone^a

Solvent	Toluene ^b	Isopentane ^c
Temp range, K	178–235	134–210
E^{T} , kcal/mol	$5.8 \pm 1.1^{\text{d}}$	$6.8 \pm 1.1^{\text{d}}$
$\log(A^{\text{T}}/\text{M}^{-1} \text{s}^{-1})$	$8.7 \pm 1.1^{\text{d}}$	$9.8 \pm 1.1^{\text{d}}$
k^{T} at 25 °C, M ⁻¹ s ⁻¹	$3 \times 10^4^{\text{e}}$	$7 \times 10^4^{\text{e}}$

^a [Peroxide] = 0.07 M. ^b Data from Table III. ^c Combination of data obtained with thioketone concentrations of 0.25 and 0.5 M. ^d Error limits are standard deviations. ^e Extrapolated value.

tert-butyl selenoketone. However, photolysis of the peroxide in the presence of the thioketone (using short light flashes because of the reversibility of trapping; see Experimental Section) did yield signals from both $\text{HT}\cdot$ and $\text{CT}\cdot$ from which the $k^{\text{T}}/k_{\text{c}}$ ratio could be determined. Data from a representative experiment are given in Table III and the kinetic data obtained with this trap are summarized in Table IV.

The ^{13}C labeled peroxide was photolyzed in neat di-*tert*-butylethylene (6 M) over a temperature range from -40 to +60 °C, but at no temperature did the heights of the ^{13}C satellite lines exceed those expected from naturally abundant ^{13}C in the $\text{CT}\cdot$ adduct (i.e., $2 \times 0.55\%$ of the ^{12}C lines). It seems certain that 5% $\text{HT}\cdot$ could have been detected and, therefore, at 25 °C, $k^{\text{T}}/k_{\text{c}} < 8 \times 10^{-3}$ and $k^{\text{T}} < 850$ M⁻¹ s⁻¹.

Photolysis of the labeled peroxide with the selenoketone gave two radicals, the unlabeled alkyl spin adduct and a second, more persistent, radical which unfortunately obscured the ^{13}C satellite lines of any labeled adduct. This prevented the spin trapping rate constant from being determined.

Competition between Two Spin Traps. The data obtained with the $[1-^{13}\text{C}]$ -5-hexenyl radical were extended by competitive experiments using pairs of spin traps that gave adducts with the 1-hexyl radical which had easily distinguished EPR spectra. That is

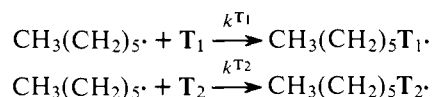


Table V. Competitive Spin Trapping of 1-Hexyl in Benzene at 40 °C

T ₁ , M × 10 ³	T ₂ , M × 10 ³	[T ₂]/[T ₁]	k ^T ₁ /k ^T ₂
NtB, 3.8	PBN, 290	76	75.5
NtB, 4.7	PBN, 260	55	83.6
NtB, 3.5	PBN, 111	32	60.8
NtB, 4.0	PBN, 96	24	64.8
NtB, 9.3	PBN, 21	2.3	60.0
NtB, 4.5	PBN-d ₉ , 256	57	64.9
NtB, 3.8	4-MeO-PBN, 250	66	77.0
NtB, 4.2	4-MeO-PBN, 250	60	78.5
NtB, 3.8	4-Me-PBN, 280	74	67.1
NtB, 3.8	4-Me-PBN, 280	74	78.9
NtB, 3.8	4-CN-PBN, 98	26	52.4
NtB, 3.8	4-CN-PBN, 98	26	55.0
NtB, 4.2	4-NO ₂ -PBN, 130	31	29.5
NtB, 4.2	4-NO ₂ -PBN, 130	31	33.5
NtB, 15	Bu ₃ 'NB, 139	9.3	21.0
NtB, 18	Bu ₃ 'NB, 84	4.7	20.2
NtB, 20	Bu ₃ 'NB, 62	3.1	16.0
PBN, 203	ND, 1.77 ^a	0.0087	0.00341
PBN, 203	ND, 0.90 ^a	0.0044	0.00344
PBN, 407	ND, 1.77 ^a	0.0043	0.00327
PBN, 230	ND, 0.90 ^a	0.0039	0.00305
PBN, 203	ND, 0.52 ^a	0.0026	0.00413
PBN, 203	ND, 0.29 ^a	0.0014	0.00317
PBN, 350	DMPO, 44	0.126	0.0503
PBN, 519	DMPO, 44	0.085	0.0529
PBN, 164	MBN, 26	0.158	0.0459
PBN, 218	MBN, 17	0.078	0.0435
PBN, 273	MBN, 8.5	0.031	0.0391
PBN, 59	(MeO) ₃ -PBN, 145	2.5	6.8
PBN, 54	(MeO) ₃ -PBN, 88	1.6	6.4
PBN, 130	(MeO) ₃ -PBN, 120	0.9	8.7

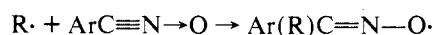
^a Concentration of nitrosodurene monomer calculated from the total concentration of nitrosodurene and the measured (see Experimental Section) dimer-monomer equilibrium constant (250 M⁻¹).

and hence

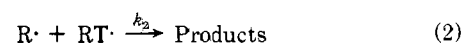
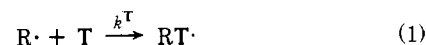
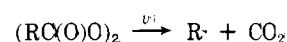
$$k^{T_1} = k^{T_2} \left(\frac{[T_2](d[\text{CH}_3(\text{CH}_2)_5\text{T}_1\cdot]/dt)_{t \rightarrow 0}}{[T_1](d[\text{CH}_3(\text{CH}_2)_5\text{T}_2\cdot]/dt)_{t \rightarrow 0}} \right) \quad (\text{II})$$

The 1-hexyl radicals were generated thermally from di-*n*-heptanoyl peroxide (0.06 M) in benzene at 40 °C. A non-competitive experiment was carried out first with all traps for which the EPR spectrum of the 1-hexyl adduct (if it were formed) was not known. In the competitions the range of spin trap concentration ratios was limited by the need to obtain comparable concentrations of the two spin adducts. The experimental results are given in Table V.

A number of potential spin traps proved unsatisfactory for quantitative work for one reason or another. Thus, 2,4,6-trimethyl-PBN gave only a weak and short-lived EPR signal. Presumably the alkyl spin adduct is formed relatively slowly but decomposes rapidly, probably by an intra- or intermolecular hydrogen atom transfer from a mesityl methyl group to the nitroxide oxygen.⁵⁸ Nitrosobenzene was found to be thermally (as well as photochemically) unstable at 40 °C, the only EPR spectrum ever obtained being that due to diphenyl nitroxide. 4-Chlorobenzonitrile oxide (which is thermally unstable⁴⁵) and 2,4,6-trimethoxybenzonitrile oxide are both rather insoluble in benzene (maximum concentration <0.05 M) and the iminoxy radicals which are formed by trapping



are not very persistent. Some nitroxide radicals are also formed from both nitrile oxides. 3-Phenyl-2-*tert*-butyloxaziridine, which is an isomer of PBN, did not trap primary alkyl radicals under our conditions.

Scheme IV

Steady-State Experiments. Additional rate constants can be obtained by measuring the steady-state concentration of the spin adduct⁵⁹ at different concentrations of spin trap. Thus, nitroxide radicals are known to trap alkyl radicals and to undergo bimolecular self-reactions. The overall situation for a nitroso or nitrone spin trap can therefore be represented by reaction Scheme IV. Applying the usual steady-state treatment to these reactions yields eq III.

$$\frac{k^T[\text{T}] - k_2[\text{RT}\cdot]_{\text{ss}}}{k^T[\text{T}] + k_2[\text{RT}\cdot]_{\text{ss}}} = \frac{2k_3}{v_i} [\text{RT}\cdot]_{\text{ss}}^2 \quad (\text{III})$$

The rate of radical formation, v_i , can be determined by measuring the initial rate of formation of the spin adduct.⁵ There is some induced decomposition of the peroxide at high concentrations of spin trap (see Experimental Section). For the calculation of $2k_3$ according to eq V we used the average of the v_i values measured at the highest concentrations of the various traps, viz., $2 \times 10^{-8} \text{ M s}^{-1}$ (which corresponds to $k_i = 3 \times 10^{-7} \text{ s}^{-1}$). Since k^T , v_i , and $[\text{T}]$, are all known quantities the rate constants for the two remaining reactions in Scheme IV can be readily evaluated. This is most simply accomplished by plotting $[\text{RT}\cdot]_{\text{ss}}$ against $[\text{T}]$. The initial slope of such a plot yields k_2 via eq IV, and the limiting value of $[\text{RT}\cdot]_{\text{ss}}$ at high $[\text{T}]$ yields $2k_3$ via eq V.⁶⁰ Once these two rate constants have been determined the theoretical curve for $[\text{RT}\cdot]_{\text{ss}} = f[\text{T}]$ can be calculated via eq III.⁶¹

$$\left(\frac{d[\text{RT}\cdot]_{\text{ss}}}{d[\text{T}]} \right)_{T \rightarrow 0} = \frac{k^T}{k_2} \quad (\text{IV})$$

$$([\text{RT}\cdot]_{\text{ss}})_{T \rightarrow \infty} = (v_i/2k_3)^{1/2} \quad (\text{V})$$

The results of our steady-state measurements with four spin traps in benzene at 40 °C are listed in Table VI, together with the calculated values of $[\text{RT}\cdot]_{\text{ss}}$ at each experimental trap concentration. The rate constants used for the theoretical calculations are summarized in Table VII. It should be noted that with the NtB and MNB we have deliberately utilized identical (averaged) values for k_2 and $2k_3$. This is because it seems highly probable that the spin adducts from these two traps will exhibit almost identical kinetic properties since they differ by only a single CH₂ unit in the *n*-alkyl chain. Plots of $[\text{RT}\cdot]_{\text{ss}} v[\text{T}]$ for these two traps are shown in Figure 2. For all four traps there is reasonable agreement between experiment and theory (see Table VI and Figure 2)—which is extremely gratifying.

Bimolecular Self-Reaction of *n*-Hexyl-*tert*-butyl Nitroxide.

In order to check at least one of the $2k_3$ values found by the foregoing steady-state method, we attempted a direct measurement of the rate of the bimolecular self-reaction of *n*-hexyl-*tert*-butyl nitroxide. The radical was generated photochemically from the parent hydroxylamine (see Experimental Section) but the exact value of $2k_3$ could not be determined because we were unable to prepare this hydroxylamine uncontaminated by traces of *N,N*-di-*tert*-butylhydroxylamine and di-*tert*-butyl nitroxide.⁶³ The effect of these impurities was to accelerate the decay of the *n*-hexyl-*tert*-butyl nitroxide. Under conditions of minimum impurities we were able to establish that *n*-hexyl-*tert*-butyl nitroxide decayed with second order kinetics and that $2k_3 < 246 \pm 47 \text{ M}^{-1} \text{ s}^{-1}$ at 40 °C in

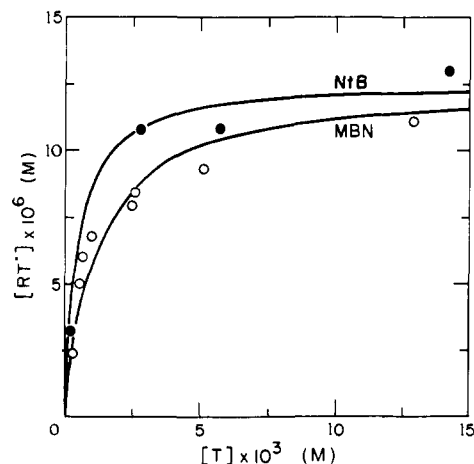


Figure 2. Steady-state concentrations of *n*-hexyl-NtB (filled circles) and *n*-hexyl-MBN (open circles) as a function of trap concentration.

Table VI. Spin Adduct Steady-State Concentrations at Different Trap Concentrations in Benzene at 40 °C^a

Trap	[T] × 10 ³ , M	[RT•] _{ss} × 10 ⁶ , M	
		Obsd	Calcd ^b
NtB	28.4	11.6	12.4
NtB	14.2	13.0	12.2
NtB	5.7	10.8	11.7
NtB	2.8	10.8	10.9
NtB	0.28	3.2	5.2
MBN	64.4	9.6	12.4
MBN	12.9	11.3	11.4
MBN	5.1	9.3	10.1
MBN	2.6	8.4	8.6
MBN	2.5	7.9	8.5
MBN	1.0	6.8	5.9
MBN	0.64	6.0	4.5
MBN	0.51	5.0	3.8
MBN	0.26	2.4	2.2
ND	2.79 ^c	18.8	18.6
ND	1.53 ^c	18.1	17.7
ND	0.90 ^c	14.4	16.4
ND	0.24 ^c	9.2	11.5
ND	0.12	4.5	8.2
PBN	813	105	106
PBN	407	92	85
PBN	163	55	54
PBN	98	32	37
PBN	81	27	32
PBN	16	6.7	7.1
PBN	8.1	3.5	3.5

^a [Di-*n*-heptanoyl peroxide] = 0.066 M. ^b From data in Table VII; see text. ^c Concentration of monomer.

Table VII. Kinetic Data Used to Calculate Spin Adduct Steady-State via Eq III for Table VI

Trap	$k^T \times 10^{-6}$, M ⁻¹ s ⁻¹	$k_2 \times 10^{-8}$, M ⁻¹ s ⁻¹	$2k_3$, M ⁻¹ s ⁻¹	$v_1 \times 10^8$, M s ⁻¹
NtB	9.0	3.5	125	2
MBN	3.1	3.5	125	2
ND	39	4.2	50	2
PBN	0.13	3.0	1	2

benzene. This is in not unreasonable agreement with the value of 125 M⁻¹ s⁻¹ found by the steady-state method.

Discussion

The rate constants for the spin trapping of primary alkyl radicals were determined by two independent methods for the

Table VIII. Summary of the Rate Constants for Spin Trapping of Primary Alkyls in Benzene at 40 °C

Spin trap	Method ^a	$k^T \times 10^{-5}$, M ⁻¹ s ⁻¹
2-Methyl-2-nitrosopropane (NtB)	A, B	90.2
Nitrosodurene (ND)	B	394
Tri- <i>tert</i> -butylnitrosobenzene (Bu ₃ NB)	B	4.7
Dimethylpyrrolone 1-oxide (DMPO)	B	25.8
Methylene- <i>tert</i> -butyl nitron (MBN)	B	31.3
Phenyl- <i>tert</i> -butyl nitron (PBN)	A, B	1.33
PBN- <i>d</i> ₉	A, B	1.31
4-MeO-PBN	B	1.16
4-Me-PBN	B	1.24
4-CN-PBN	B	1.68
4-NO ₂ -PBN	B	2.86
(MeO) ₃ -PBN	B	0.182
1,1-Di- <i>tert</i> -butylethylene	A	<0.015 ^b
Di- <i>tert</i> -butyl thioketone	A	0.445 ^c

^a A, competition with 5-hexenyl cyclization; B, competition between spin traps. ^b Neat material. ^c In toluene, extrapolated value.

Table IX. Relative Rates of Spin Trapping for Some Different Radicals^a

Spin Trap	C ₆ H ₅ C-(O)O ^b	(CH ₃) ₃ CO ^{c,d}	(CH ₃) ₃ CO ^e	<i>n</i> -Alkyl ^f
NtB		0.27 ^g	~1.0	68
DMPO		91		19
MBN		55-91		24
PBN	(1) ^h	(1) ^h	(1) ^h	(1) ^h
4-MeO-PBN	2.3	1.0		0.87
4-Me-PBN	1.6	0.62		0.93
4-NO ₂ -PBN	0.45	1.6		2.2
(k^T) _{PBN} × 10 ⁻⁶ ⁱ	~40 ^j	~5.5 ^k	1.1-5.5 ^l	0.13

^a At 40 °C unless otherwise noted. ^b Reference 5. ^c Reference 6. ^d At 25 °C. ^e Reference 8. ^f This work. ^g This particular value may be too low by as much as a factor of 100; see ref 11. ^h Assumed. ⁱ M⁻¹ s⁻¹ units. ^j See ref 7. ^k Estimated to be ≥60 × 10⁶ M⁻¹ s⁻¹ for CH₃O-trapping; see ref 10. ^l See ref 9.

two most commonly employed traps, viz., 2-methyl-2-nitrosopropane (NtB) and phenyl-*tert*-butyl nitron (PBN). The ratio, (k^T)_{NtB}/ (k^T) _{PBN}, of the averaged rate constants determined by way of the 5-hexenyl cyclization is 67.3, while direct competition between the traps for the 1-hexyl radical gave a mean ratio of 68.9. The excellent agreement between these numbers implies that our experimental procedures are fairly reliable. We believe that the *relative* k^T values are probably accurate to ca. ±30% in most cases. The error is rather large because it is difficult to measure initial rates of spin adduct formation. At the start of the reaction the signal to noise ratio is unfavorable while, as the reaction progresses and the signals increase in strength, the extrapolation back to zero time becomes less and less reliable. The *absolute* values of k^T at 40 °C, which are summarized in Table VIII, are probably reliable to no more than about a factor of 2 because of uncertainty in the precise value of the rate constant for the 5-hexenyl cyclization.¹⁵

Examination of the rate constants listed in Table VIII, and comparison with the limited data available for other radicals (Table IX), reveals the following facts about the spin trapping of primary alkyls.

(1) Nitroso compounds would, in general, appear to be better, i.e., faster, traps for *n*-alkyls than nitrones. This behavior contrasts with that reported⁸ for *tert*-butoxycarbonyl which is rather indiscriminating and with that reported⁶ for *tert*-butoxy radicals. However, in the case of alkoxy adducts

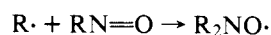
there would appear to be some doubt as to the reliability of the data.^{11,64} Differences in trapping abilities are clearly a factor to be considered when selecting a spin trap for a particular task.

(2) Aromatic nitroso compounds trap *n*-alkyls faster than nitrosoalkanes (ND > NtB) unless steric hindrance is very pronounced (Bu₃'NB). In fact, nitrosodurene has the highest *k*^T of any trap examined, but this does *not* necessarily imply that it will be the best trap to use on all (alkyl radical) occasions since the utility of a trap depends also on many other factors. (For example, the ease with which the trapped radical can be identified, the persistence of the spin adduct (i.e. *k*₂, 2*k*₃, etc.), the thermal and photo-stability of the trap, and so on.) The great reactivity of moderately hindered nitrosoaromatics can probably be attributed to stabilization⁶⁵ of the spin adducts by delocalization of the unpaired electron into the aromatic ring. That is, alkylaromatic nitroxides must be stabilized to a greater extent than dialkyl nitroxides (but this does *not* imply that they will necessarily be more persistent).⁶⁵

(3) Aliphatic nitrones trap *n*-alkyls faster than aromatic nitrones. The same is true for their trapping of the *tert*-butoxy radical.⁶ Two factors are probably responsible for the greater reactivity of the aliphatic nitrones. In the first place, both aliphatic nitrones are sterically less crowded than any of the aromatic nitrones examined. The fact that steric hindrance can play an important role in these reactions is made obvious by the *k*^T values for PBN and (MeO)₃-PBN. In this connection, it is interesting to note that the two aliphatic nitrones are of similar effectiveness in trapping both *n*-alkyl and *tert*-butoxy radicals. Secondly, adduct formation by the aromatic nitrones will be disfavored because conjugation between the C=N double bond and the aromatic ring must be disrupted.

(4) Electron-withdrawing groups enhance and electron-donating groups reduce the rate of *n*-alkyl addition to substituted PBNs, though the effect is not large ($\rho = 0.2 \pm 0.1$ with σ_{para}^- values). This is just the opposite to the polar effect observed by Janzen et al.⁵ with benzoyloxy radicals ($\rho = -0.47$ with σ_{para}^+ values). However, it is interesting to note that these workers predicted "one might anticipate a less negative slope (maybe positive) for a nucleophilic radical". It would appear that *n*-alkyl radicals are sufficiently nucleophilic to bear out this prediction, it being well known that alkyl are more nucleophilic than the majority of reactive free radicals.⁶⁶ We presume that the polar effects we observe are due mainly to the influence of the substituents on the stabilities of the PBNs in their ground states. That is, the ground states will be stabilized (i.e., made less reactive) by electron-donating substituents (because these stabilize the ⁺N→O⁻ bond) and will be destabilized (i.e., made more reactive) by electron-withdrawing substituents. The more commonly observed effect of substituents in stabilizing/destabilizing charge separated transition states⁶⁹⁻⁷¹ is probably of much less significance.

(5) Effective spin traps have high *k*^T values. The absolute rate constants obtained in the present work are in the general range found for the trapping of other radicals (see Table IX; other *k*^T values include C₆H₅· + PBN, $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ⁷ and (Me₃CO)₂CH· + NtB, $0.9-4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ⁹). Some *k*^T values for the reaction



in the gas phase are also in this general range,⁷² e.g., $4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for R = CD₃ at 25 °C.

Because primary alkyls are trapped rapidly, the activation energies for spin trapping must be small. This was confirmed for four spin traps (see Tables IV and X). The pre-exponential factors for trapping by di-*tert*-butyl thioetone, NtB, and PBN are (within their accuracy) in the general range to be expected for radical additions to double bonds.⁷³ However, the pre-

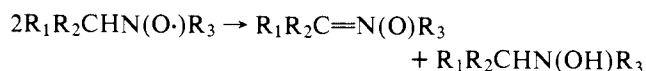
Table X. Arrhenius Parameters for Spin Trapping *n*-Alkyl Radicals in Benzene

Spin trap	Temp range, K	<i>E</i> ^T , kcal/mol ^a	log (<i>A</i> ^T /M ⁻¹ s ⁻¹) ^a
NtB	313-344	2.0	8.4
Bu ₃ 'NB	313-346	1.0	6.5
PBN	300-344	3.2	7.3

^a Error limits have not been computed because they would not be justified in view of the small temperature ranges covered and the limited number of experimental points.

exponential factor for tri-*tert*-butylnitrosobenzene appears to be well below this range which implies that the steric effect of the two ortho *tert*-butyl groups manifests itself more in the entropy, than in the enthalpy, of activation. That is, although there is only a small potential energy barrier to be surmounted, the reaction is slow because adduct formation requires a fairly exact configuration of the reactants.

There is satisfactory agreement between the measured and calculated values of the steady-state spin adduct concentrations at different trap concentrations (see Table VI and Figure 2). For these four traps (NtB, MBN, ND, and PBN,) therefore the overall system is adequately described by the reactions shown in Scheme IV and some reliance can be placed on the rate constants derived from these measurements, i.e., the *k*₂ and 2*k*₃ values given in Table VII. Thus, the rate constants for reaction of the nitroxide spin adducts with the *n*-hexyl radical all lie in the range $3-5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. They are therefore in excellent agreement with rate constants that have been found for the addition of various other alkyl radicals to sterically hindered dialkyl nitroxides,⁷⁴⁻⁷⁷ e.g., $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the addition of cyclopentyl to 2,2,6,6-tetramethyl-4-oxopiperidine-*N*-oxyl.⁷⁷ Similarly, the rate constants for the bimolecular self-reactions of these spin adducts are all well within the very wide range of values⁷⁸ that have been encountered with other nitroxides.^{50,79} These reactions involve an irreversible disproportionation to form the nitrone and the corresponding hydroxylamine,⁵⁰ i.e.,



The rate constants are greatly reduced by steric protection of the hydrogen atom(s) available for transfer,⁷⁸ and it must be this factor that is responsible for the decrease in 2*k*₃ from 125 M⁻¹ s⁻¹ for the NtB and MBN adducts, through 50 M⁻¹ s⁻¹ for the ND adduct, to 1 M⁻¹ s⁻¹ for PBN adduct. A direct attempt to measure 2*k*₃ for *n*-hexyl-*tert*-butyl nitroxide (the NtB adduct) was not very successful (it gave 2*k*₃ ≤ 246 M⁻¹ s⁻¹; see Results), but it did serve to confirm that the indirect value of 125 M⁻¹ s⁻¹ is not seriously in error.

Acknowledgment. We are deeply indebted to Professor L. R. C. Barclay (Mount Allison), Professor E. G. Janzen (Guelph), and Dr. K. Sommermeyer (Freiburg) who provided us with generous samples of spin traps that they had prepared for their own work. Without these chemicals our own investigations would have taken longer and been less comprehensive. We should also like to thank Professor Janzen for some extremely helpful suggestions.

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