

six-membered rings.¹⁸ Holzman refers to the fact that inversion is found to be slower than 10^4 sec^{-1} in three- and four-membered ring systems and concludes the ease with which the nitrogen can assume a planar transition state is the dominant factor in determining the rate of inversion. Although there is some difficulty in comparing cyclic and acyclic amines, one could argue that highly substituted acyclic amines should have a more favorable planar transition state than six-membered cyclic amines.³ Therefore, an inversion rate constant of 10^8 – 10^9 sec^{-1} for the compounds studied here is not unreasonable.

Leyden and Whidby have shown a plot of the rate of inversion of methyliminodiacetic acid *vs.* the reciprocal of the Hammett acidity function in sulfuric acid–water

solvent.¹⁹ Although the kinetics of this system are complicated by direct proton extraction by the HSO_4^- ion, the shape of the plot is that predicted by eq 10 in the limit of high acidity.

The mechanism by which the second-order proton exchange process stimulates inversion is not completely understood. However, one can postulate that during this process, the salt transfers a hydronium ion to the adjacent free base in the transition complex. If the newly formed free base then inverts during the dissociation of the complex, it may be immediately hydrated (or protonated) leading to one inversion during the protolysis reaction. The possible stimulation of inversion by substituents on the amine, such as the case of ethanolamines, also requires further investigation.

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Magnetic Resonance Studies of Polyradicals. II.¹ Nitronyl Nitroxide Biradicals, Nitroxide Tri- and Tetradicals

Peter W. Kopf,² Robert Kreilick,³ D. G. B. Boocock,^{4a} and Edwin F. Ullman^{4b}

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627, and Synvar Research Institute, Palo Alto, California 94304. Received January 19, 1970

Abstract: We have examined the nmr and esr spectra of two nonconjugated nitronyl nitroxide biradicals and a tri- and tetranitroxide radical. Magnetic susceptibility measurements were made on each of these compounds. Zero-field splittings were observed from the two biradicals, and D and E values were calculated. The nmr spectra were used to determine electron–proton coupling constants. The temperature dependence of the contact shifts was monitored. These results were used to obtain estimates of the magnitudes of the exchange integrals, J .

The esr spectrum of a solution of a biradical with a relatively large electron–electron dipole–dipole interaction generally consists of a single broadened line.⁵ When this is the case, one is unable to obtain electron–nuclei coupling constants from the esr spectrum. The spectra of solutions of biradicals with smaller dipole–dipole interactions may be well resolved, and in some cases one is able to use these spectra to estimate the magnitude of the electron–electron exchange integral (J).⁶ Conjugated biradicals have generally been characterized by relatively large dipolar interactions, while the nonconjugated nitroxide biradicals have been observed to have smaller dipolar interactions and resolved esr spectra.

The sign and magnitude of the electron–nuclei coupling constants can be determined from the nmr spectra of the biradicals in some instances.¹ The

equation relating nmr shifts (ΔH) to coupling constants (a_i) and molar susceptibilities (χ_m) is given by

$$\left(\frac{\Delta H}{H}\right) = -a_i \chi_m / N g_n \beta_n \quad (1)$$

If the molar susceptibility of the biradical is given by⁷

$$\chi_m = \frac{S(S+1)g^2\beta^2N}{3kT} \left[\frac{1}{1 + \exp \frac{J}{RT} \exp \frac{-\Delta S}{R}} \right] \quad (2)$$

then the equation for the contact shift is

$$\left(\frac{\Delta H}{H}\right) = \frac{-a_i g \beta S(S+1)}{3kT} \left(\frac{\gamma_e}{\gamma_N} \right) \left[\frac{1}{1 + \exp \frac{J}{RT} \exp \frac{-\Delta S}{R}} \right] \quad (3)$$

In this equation, J is the energy separation of the singlet and triplet states and ΔS is the entropy difference between the singlet and triplet states. If one makes independent measurements of the contact shifts and the susceptibility, one can determine the

(1) Part I: P. W. Kopf and R. W. Kreilick, *J. Amer. Chem. Soc.*, **91**, 6569 (1969).

(2) NSF Graduate Trainee, 1966–1968; NDEA Graduate Fellow, 1968–1969; University of Rochester.

(3) Alfred P. Sloan Foundation Fellow; University of Rochester.

(4) (a) Synvar Postdoctoral Fellow, 1967–1969; (b) Contribution No. 15 from Synvar Research Institute.

(5) S. I. Weissman, *J. Chem. Phys.*, **29**, 1189 (1958).

(6) C. P. Slichter, *Phys. Rev.*, **99**, 479 (1955); D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, **33**, 700 (1960).

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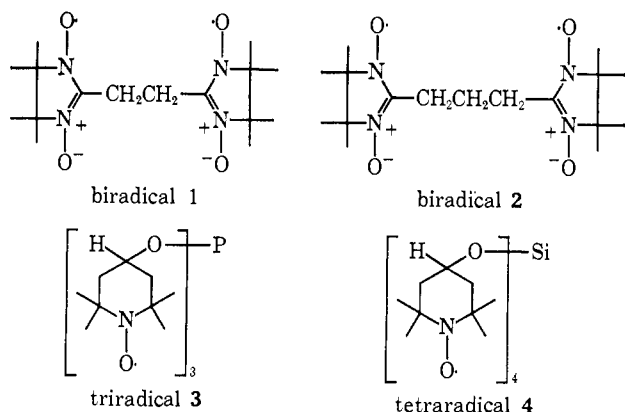


Figure 1. Polyradicals studied.

sign and magnitude of the a_i 's and J 's in some instances. In the limiting case in which $RT > J$ and the entropy change is associated solely with differences in electronic degeneracies, eq 3 reduces to

$$\left(\frac{\Delta H}{H}\right) = \frac{-a_i g \beta S(S+1)}{4kT} \left(\frac{\gamma_e}{\gamma_N}\right) \quad (4)$$

The magnitude of the coupling constants depends on the rate of spin exchange ($2J/h$) between the two halves of a given biradical.⁸ If one considers a symmetric biradical with n_i equivalent nuclei on each side, the esr spectrum will contain $2n_i I + 1$ lines separated by a_i in cases in which $a_i > J$, and $4n_i I + 1$ lines separated by $a_i/2$ in cases in which $J > a_i$. One cannot use nmr spectra to distinguish these two cases in instances in which $RT > J$ (eq 4). When this is the case, one predicts the same shifts for biradicals with $a_i > J$ and those with $J > a_i$.

The equations for the contact shifts of molecules with three or four unpaired spins can be derived by introducing the correct expressions for the susceptibilities into eq 1. In instances in which the separation between the quartet and doublet level of the three-electron species or the quintet, triplet, and singlet levels of the four-electron species is less than RT , one predicts the same shifts for the three- and four-electron species as are observed for a structurally similar monoradical.

We have investigated the nmr and esr spectra of the two nitronyl nitroxide biradicals and the tri- and tetranitroxide radicals which are shown in Figure 1. The susceptibility of each of these compounds was measured by monitoring the shift of the line from tetramethylsilane (TMS) as a function of the concentration of the paramagnetic species.⁸ The temperature dependence of the contact shifts was also measured. We were able to determine the sign and magnitude of the electron-proton coupling constants from these measurements. In some cases we were also able to estimate the value of J .

Experimental Section

(1) **Preparation of the Biradicals.** (a) **Biradical 1, 1,2-Bis[4,4,5,5-tetramethyl-1-oxyl-2-imidazolin-2-yl-3-oxide]ethane.** A solution of succinaldioxime⁹ (5.8 g, 0.05 mol) in 54 ml of 10% sulfuric

acid was cooled to 0°. Sodium nitrite (7.0 g) was added in small portions with vigorous stirring at such a rate as to avoid visible evolution of nitrogen dioxide. The temperature was maintained between -5 and 0° throughout the addition. The solution was then allowed to warm to 20°, and the lemon-colored solution was neutralized with small portions of calcium carbonate. The precipitated calcium sulfate was removed by filtration, and the filtrate was added dropwise over a period of 1 hr to a solution of N,N'-dihydroxy-2,3-diamino-2,3-dimethylbutane (13.5 g, 0.090 mol) in 200 ml of saturated aqueous sodium acetate. After being stirred for an additional hour, the mixture was filtered and the residue washed with a little cold water. It was then suspended in water (800 ml), and sodium periodate (37 g) was added in small portions with vigorous stirring. The solution turned dark red and almost all the suspended solid disappeared. The solution was quickly filtered through glass wool and extracted several times with methylene chloride. The combined extracts yielded a crystalline product which was triturated and washed several times with petroleum ether to give 7.0-8.1 g (45-52% based on the bishydroxylamine) of the biradical. A sample recrystallized from benzene-petroleum ether (30-60°) melted at 160-161°; $\lambda_{\text{max}}^{\text{KBr}}$ 875 (w), 1145, 1210, 1255, 1375, 1420 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 317 $\text{m}\mu$ (ϵ 29,000), 522 (3130), 552 (3235).

Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{N}_4\text{O}_4$: C, 56.45; H, 8.29; N, 16.46; mol wt, 340. Found: C, 56.27; H, 8.09; N, 16.46; m/e , 340 (M).

(b) **Biradical 2, 1,3-Bis[4,4,5,5-tetramethyl-1-oxyl-2-imidazolin-2-yl-3-oxide]propane.** N,N'-Dihydroxy-2,3-diamino-2,3-dimethylbutane (13 g, 0.148 mol) was dissolved in 300 ml of saturated aqueous sodium acetate. A 25% aqueous glutaric dialdehyde solution (17.5 ml) was diluted to 50 ml with water and added dropwise with vigorous stirring to the bishydroxylamine solution over a period of 1 hr. After an additional hour at room temperature, the mixture was filtered and the precipitate washed with a little cold water. Oxidation with sodium periodate as described in the previous experiment yielded the crystalline biradical (5 g, 32%) which melted at 145° after recrystallization from benzene-petroleum ether; $\nu_{\text{max}}^{\text{KBr}}$ 880, 1140, 1170, 1205, 1253, 1370, 1410 cm^{-1} .

Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_4$: C, 57.60; H, 8.53; N, 15.81; mol wt, 354. Found: C, 57.36; H, 8.75; N, 15.75; m/e , 354 (M).

(2) **Preparation of the Tri- and Tetranitroxide Radicals.** Compound 3 was synthesized by the technique of Neiman.¹⁰ Compound 4 was synthesized by Rozantsev's technique.¹¹

(3) **Nmr and Esr Measurements.** The two biradicals were very soluble in CDCl_3 , and we were able to observe lines from each set of equivalent nuclei when nmr spectra were taken of solutions of the biradicals dissolved in this solvent. Spectra were also taken of samples dissolved in a mixture of CDCl_3 and di-*n*-butyl nitroxide (DBNO). The nmr spectrum of the triradical 3 was taken with a mixture of CDCl_3 and DBNO as the solvent, and the spectrum of tetradical 4 was taken with a mixture of acetone- d_6 and DBNO as the solvent. The susceptibilities were measured by monitoring the shift of the line from TMS as a function of radical concentration.⁸ The purity of the various paramagnetic compounds was determined by comparing the integrals of peaks (nmr) from the paramagnetic compounds with the integrals of lines from diamagnetic impurities. We are confident in the results obtained for the biradicals, as the various lines in the nmr spectra were well separated and we were able to obtain accurate integrals. The lines from the tri- and tetradicals were overlapped with peaks from diamagnetic impurities, and our results for these compounds are not as accurate. All of the nmr spectra were taken on a Jeolco 4H-100 100-MHz nmr spectrometer. The spectra of the paramagnetic compounds were obtained either with a special base-line stabilization unit employing 10-KHz modulation or with a broad-line unit employing 35-Hz field modulation.

The esr spectra were taken on a Jeolco 3BSX esr spectrometer. Samples were made in sealed, degassed apparatus. The solvent for the two biradicals was a mixture of toluene and methylcyclohexane. The solvent for the tri- and tetradical was benzene. The zero-field splitting parameters were obtained from spectra of samples which had been cooled to about -150°.

Results and Discussion

The esr spectra of solutions of biradical 1 and biradical 2 consisted of single broadened lines. Spectra

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(9) L. C. Keagle and W. H. Hartung, *J. Amer. Chem. Soc.*, 68, 1609 (1946).

Table I. Shifts, Coupling Constants, Dipolar Splittings, and Singlet-Triplet Energy Separations at 297°K

Compd	Group	Shift, kHz	a , G	$\chi_m \times 10^3$	D , cal	E , cal	J , cal	ΔS , eu
1	CH ₃	1.51	-0.112	2.30	0.0614 (223 G)	0.0066 (25 G)	+409	+2.84
	CH ₂	13.0	-0.956					
2	CH ₃	1.53	-0.103	2.48	0.0558 (212 G)	0.0032 (12 G)	<200	
	α -CH ₂	15.2	-1.01					
	β -CH ₂	0.83	+0.056					
3	CH ₃ (α_1)	3.14	-0.14	3.72			>0.004 (15 G)	
	CH ₃ (α_2)	~ 0	~ 0					
	CH ₂ (β_1)	2.22	-0.098					
	CH ₂ (β_2)	3.56	-0.159					
	CH (γ)	0.55	+0.025					
	N		5.14					
4	CH ₃ (α_1)	3.06	-0.102	4.96			>0.004 (15 G)	
	CH ₃ (α_2)	~ 0	~ 0					
	CH ₂ (β_1)	2.15	-0.072					
	CH ₂ (β_2)	3.46	-0.116					
	CH (γ)	0.56	+0.019					
	N		3.89					

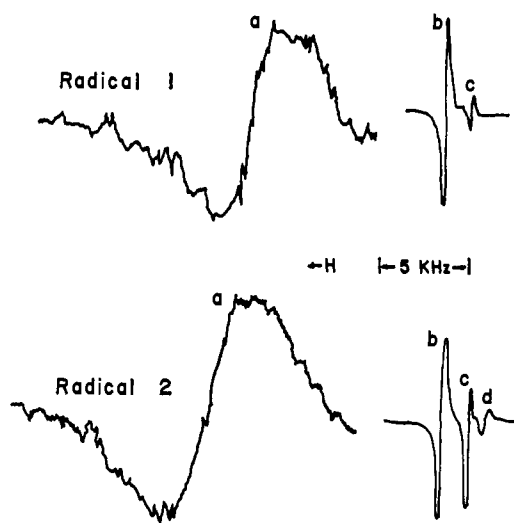


Figure 2. Nmr spectra of biradicals 1 and 2 in CDCl₃: biradical 1, (a) methylene protons; (b) methyl protons; (c) diamagnetic methyl protons; biradical 2, (a) α -methylene protons; (b) methyl protons; (c) diamagnetic methyl protons; (d) β -methylene protons.

taken from samples frozen in rigid glasses showed the normal six-line pattern which is expected for biradicals with nonvanishing E values. Half-field resonances were also observed. The D and E values obtained from these spectra are listed in Table I. The large D values which are observed indicate that the two heterocyclic rings must be relatively close to one another. These two rings are probably folded on top of one another in the favored conformation. The D values are comparable to those observed from conjugated nitronyl nitroxide biradicals¹² and much larger than those observed from nonconjugated nitroxide biradicals.¹³

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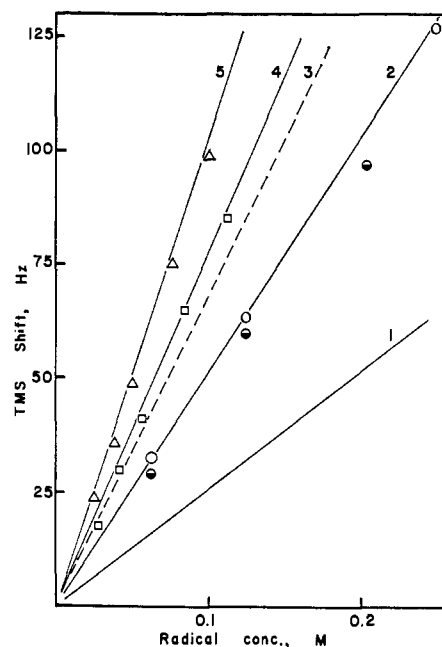


Figure 3. Susceptibility shifts for polyradicals at 297°K: (1) theoretical line for doublet, (2) theoretical line for biradical with $RT > J$, (3) theoretical line for triplet, (4) theoretical line for triradical with $RT > J$, (5) theoretical line for tetradical with $RT > J$; \circ , biradical 2; \bullet , biradical 1; \square , triradical 3; Δ , tetradical 4.

The esr spectrum of triradical 3 shows a coupling to three equivalent nitrogens,¹⁰ while the spectrum of tetradical 4 shows a splitting from four equivalent nitrogens.¹¹ These spectra indicate that $J > a_N$ for these compounds. The electron-electron dipole-dipole interaction is very small and one cannot observe zero-field splittings from samples of compounds 3 or 4 which have been frozen in rigid glasses.

The nmr spectra of the nitronyl nitroxide biradicals contained lines from the methyl and methylene protons. The peaks from the methyl and α -methylene protons were shifted to high field, while the line from the β -methylene protons was shifted to low field. The spectra of the biradicals are shown in Figure 2, and shifts are listed in Table I. The shifts are close to what one

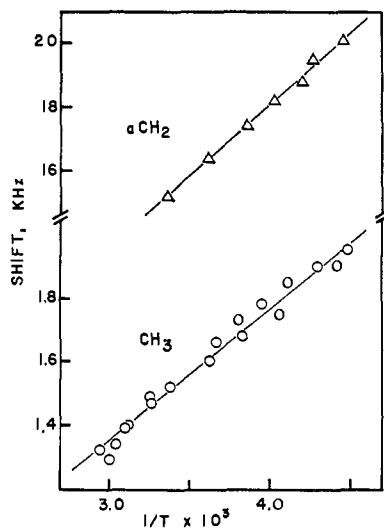


Figure 4. Contact shift temperature dependence for biradical 2: Δ , α -methylene protons; O, methyl protons. The lines represent the predicted behavior when $RT \gg J$.

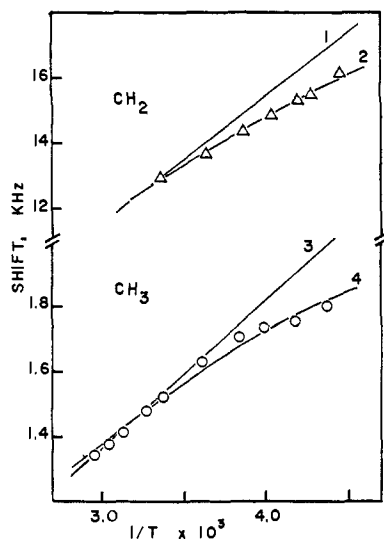


Figure 5. Contact shift temperature dependence for biradical 1: Δ , methylene protons; O, methyl protons; (1) and (3) predicted behavior when $RT \gg J$; (2) line predicted when $a(\text{CH}_2) = -0.956 \text{ G}$, $J = +340 \text{ cal/mol}$, and $\Delta S = +2.62 \text{ eu}$; (4) line predicted when $a(\text{CH}_2) = -0.112 \text{ G}$, $J = +409 \text{ cal/ml}$, and $\Delta S = +2.84 \text{ eu}$.

would predict for nitronyl nitroxide monoradicals with aliphatic substituents.¹⁴

The molar susceptibilities of the biradicals were determined, and these results were combined with the contact shifts to obtain coupling constants. The susceptibilities and coupling constants are listed in Table I. The susceptibility of biradical 2 was identical with the susceptibility predicted for cases in which $RT > J$. The susceptibility determined for biradical 1 was lower than the value predicted when $RT > J$. A plot of susceptibility shifts vs. concentration is shown in Figure 3. These results indicate that biradical 1 is a ground-state singlet with a thermally accessible triplet state.

(14) R. W. Krelick, J. Becher, and E. F. Ullman, *J. Amer. Chem. Soc.*, **91**, 5121 (1969); D. G. B. Boocock, R. Darcy, and E. F. Ullman, *ibid.*, **90**, 5945 (1968).

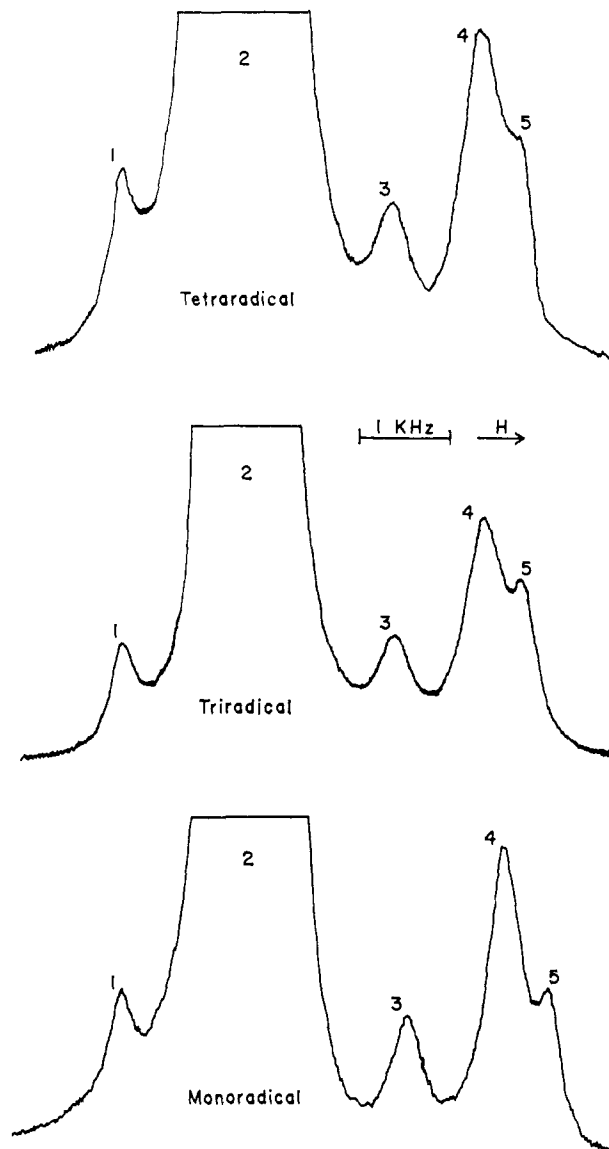


Figure 6. Nmr spectra of tetraradical 4, triradical 3, and the 2,2,6,6-tetramethyl-4-hydroxypiperidine 1-oxide monoradical: (1) $\text{CH}(\gamma)$ protons, (2) DBNO solvent, (3) $\text{CH}_2(\beta_1)$ protons, (4) $\text{CH}_2(\alpha_1)$ protons, (5) $\text{CH}_2(\beta_2)$ protons.

The temperature dependence of the contact shifts was monitored to obtain estimates of the energy and entropy separation of the singlet and triplet states. The shifts of the lines from the methyl and α -methylene protons were monitored as a function of temperature. The shifts of the lines from biradical 2 followed the behavior predicted for compounds in which $RT > J$ (Figure 4). The shifts of the peaks from biradical 1 did not follow the behavior predicted for cases in which $RT > J$ (Figure 5). These lines were shifted less than the predicted amount at lower temperatures, indicating an increase in the population of the singlet state. The experimental data from biradical 1 were fitted with a nonlinear least-squares program to obtain values for J and ΔS (Table I). The relatively large value of J again indicates that the two heterocyclic rings must be close to one another in the favored conformation. The entropy change is slightly larger than the value associated with differences in electronic degeneracies, indicating a change in geometry in going from the singlet to the triplet state.

The coupling constant of the α -methylene protons of biradical **1** is smaller than the coupling constant of the same protons in biradical **2**. It is also less than one-half the coupling from the α protons of nitronyl nitroxide monoradicals. The lower value may be explained by a difference in the twist angle between the heterocyclic ring and the methylene group.¹⁵ An alternative explanation involves the coupling one would predict from the two halves of the biradical. The methylene protons of biradical **1** are α to one of the heterocyclic rings but β to the other ring. The molecular orbitals of the biradical may be taken as a linear combination of the monoradical's wave functions. If the coupling constants of the monoradical are a_α and a_β , then one predicts that the biradical will have a coupling equal to $\frac{1}{2}(a_\alpha + a_\beta)$. The value of the coupling constant of the methylene protons of biradical **1** is close to the value

(15) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

predicted from the coupling constants of nitronyl nitroxide monoradicals.

The nmr spectra of triradical **3** and tetradical **4** were almost identical with the spectrum observed from the 2,2,6,6-tetramethyl-4-hydroxypiperidine 1-oxide monoradical¹⁶ (Figure 6). One predicts identical spectra for cases in which the separation among the various energy levels is less than RT . The susceptibility shifts (Figure 3) and the temperature dependence of the contact shifts also indicate that RT was greater than the energy level separations. The esr spectra showed that $J > a_N$, and the coupling constants listed in Table I were calculated with the assumption that $J > a_H$.

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Electron Paramagnetic Resonance of *t*-Butoxy Radical Reactions with Sulfides and Disulfides

J. Q. Adams

Contribution from the Chevron Research Company,
Richmond, California 94802. Received November 8, 1969

Abstract: Epr spectra were used to characterize what appear to be the first-formed free radicals in the reactions of alkyl sulfides and disulfides with the *t*-butoxy radical, produced in a flow system by photolysis of di-*t*-butyl peroxide in 2,2,4-trimethylpentane at room temperature. In each case, the radical resulted from removal of a hydrogen atom from the carbon atom bonded to a sulfur atom. The *t*-butoxy radical was not detected. A comparison of similar alcohol, ether, sulfide, and disulfide radicals shows striking changes in hydrogen hyperfine coupling which are as yet unexplained. Severely hindered internal rotations may be present in the sulfides and disulfides.

Transient free-radical reaction intermediates, characterized by epr, in the reactions of a presumed *t*-butoxy radical, $(\text{CH}_3)_3\text{CO}\cdot$, with various alcohols and ethers have been studied.^{1,2} In the work described here, mixtures of di-*t*-butyl peroxide and an alkyl sulfide or disulfide in 2,2,4-trimethylpentane were photolyzed within the microwave cavity of an epr spectrometer used to follow directly the reactions of the *t*-butoxy radical from the cleaved peroxide. The sulfide and disulfide radicals probably resulted from the primary reaction of the *t*-butoxy radical with the sulfide or disulfide.

Experimental Section

The experimental apparatus and techniques have been discussed in detail.¹ Only a minimal description of the experiment will be given here.

Materials. The di-*t*-butyl peroxide was obtained in 97% purity from the U. S. Peroxygen Corp. The isooctane was Phillips 2,2,4-trimethylpentane (99 mol % minimum). The sulfides and disulfides were Eastman White-Label reagents.

Apparatus and Methods. The *t*-butoxy radical was generated by photolysis of a di-*t*-butyl peroxide solution in a one-stream flow system constructed of Teflon and glass. While flowing through a

fused silica cell placed in the microwave cavity of a conventional Varian X-band epr spectrometer, the solution was irradiated by an unfiltered, focused 500-W mercury short-arc lamp.

The epr spectra were described adequately by the high-field spin Hamiltonian. No g -value measurements were made since the identity of the chemical species could be determined by the hyperfine splitting pattern. The optimization of resolution and signal-to-noise ratio were the dominant experimental problems.

Results

The hydrogen hyperfine coupling constants of the alkyl sulfide and disulfide radicals are summarized in Table I. Free radicals could be obtained from only ethyl sulfide, ethyl disulfide, *n*-butyl sulfide, and *n*-butyl disulfide, although prolonged attempts were made to detect radicals from a family of sulfide and disulfide molecules similar to those used in the ether reaction studies. The experimental procedures were identical with those used in the alcohol studies.¹ Under these conditions, the signal-to-noise ratio of the epr spectra for both sulfides and disulfides was less than one-tenth that of the corresponding ether radicals.

No alkoxy radicals were detected in this study. The inability to detect an alkoxy radical epr signal suggests the possibility that other free-radical intermediates, also invisible to epr, may be present in the reaction

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(2) J. Q. Adams, submitted for publication.