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 $^1/_2(a_\alpha + a_\beta)$. The value of the coupling constant of the methylene protons of biradical **1** is close to the value predicted from the coupling constants of nitronyl nitroxide monoradicals.

The nmr spectra of triradical **3** and tetraradical **4** were almost identical with the spectrum observed from the 2,2,6,6-tetramethyl-4-hydroxypiperidine 1-oxide monoradical[16] (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

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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, $(CH_3)_3CO\cdot$, 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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[1] J. Q. Adams, *J. Amer. Chem. Soc.*, 90, 5363 (1968).

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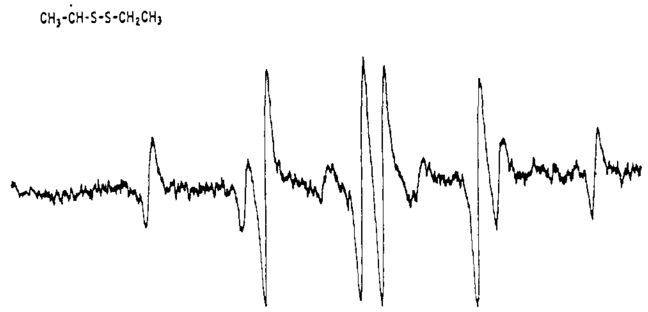

Figure 1. Epr spectrum of the free radical from photolysis of *t*-butyl peroxide, diethyl disulfide, and isooctane.

Table I. Comparison of Hyperfine Coupling Constants in Alcohol, Ether, Sulfide, and Disulfide Radicals

Radical[a]	Hyperfine coupling constants, G a_α^H	a_β^H	a_δ^H
$\dot{C}H_2-O-H$	16.9[b]		
$\dot{C}H_2-O-CH_3$	16.6[c]		
$CH_3\dot{C}H-O-H$	15.1[b]	21.9	
$CH_3\dot{C}H-O-CH_2CH_3$	13.8[c]	21.5	1.5
$CH_3\dot{C}H-S-CH_2CH_3$	16.8	19.8	1.6
$CH_3\dot{C}H-S-S-CH_2CH_3$	16.8	20.6	
$CH_3CH_2CH_2\dot{C}H-O-H$	15.0[b]	19.8	
$CH_3CH_2\dot{C}H-O-CH_2CH_2CH_3$	13.3[c]	19.7	1.5
$CH_3CH_2CH_2\dot{C}H-S-CH_2CH_2CH_2CH_3$	16.9	17.2	0.7
$CH_3CH_2CH_2\dot{C}H-S-S-CH_2CH_2CH_2CH_3$	17.3	18.3	

[a] Proton labeling convention: $-\underset{\beta}{CH_2}-\underset{\alpha}{\dot{C}H}-X-\underset{\gamma}{CH_2}$. [b] Reference 1. [c] Reference 2.

mixtures. As will be shown, the radicals detected by epr in the reactions have the general structure

$$R-\underset{\beta}{CH_2}-\underset{\alpha}{\dot{C}H}-X-\underset{\delta}{CH_2}-R'$$

$$X = -S \text{ or } -S-S$$

Ethyl Disulfide. The epr spectrum of a reacting solution with ethyl disulfide consists of eight lines which can be viewed as two quartets with intensity ratios of 1:3:3:1 (Figure 1). The radical is very probably $CH_3\dot{C}HSSCH_2CH_3$. No radical of the form $\dot{C}H_2CH_2SSCH_2CH_3$ was observed. No δ-hydrogen splitting was observed in this case, indicating that the effect of the unpaired electron was not transmitted across the sulfur–sulfur bond.

Ethyl Sulfide. A reacting solution with ethyl sulfide gave the epr spectrum of Figure 2. The more complex spectrum of Figure 2 can be seen to result from splitting each of the lines of Figure 1 into a triplet. Since some of the lines of Figure 1 fall close together, splitting each of them into three lines causes overlap, resulting in a complex shape. When the spectrum was synthesized by computer, the splitting constants necessary for the proper fit fortunately produced striking changes in the shape of the computed spectrum, even when the trial splitting constants were changed only slightly. Agreement between the experimental (Figure 2A) and computed (Figure 2B) spectra is excellent in this case. The radical is very probably $CH_3\dot{C}HSCH_2CH_3$, where the small triplet splitting comes from the methylene across the sulfur from the carbon atom which lost the hydrogen atom. The ether radicals also showed this small methylene coupling.[2]

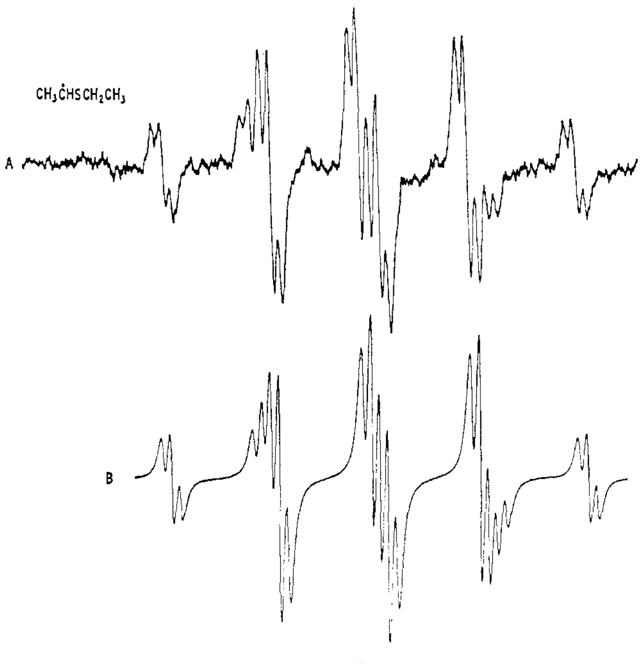

Figure 2. (A) Epr spectrum of the free radical from photolysis of *t*-butyl peroxide, diethyl sulfide, and isooctane. (B) Computer synthesis of the free-radical epr spectrum from proposed coupling constants.

***n*-Butyl Disulfide.** The epr spectrum of a reacting solution with *n*-butyl disulfide consisted of four lines (Figure 3). The distortion of the two center lines in the spectrum is believed to result from imperfect overlap of two sets of triplets of intensity ratio 1:2:1. The radical is very probably $CH_3CH_2CH_2\dot{C}HSSCH_2CH_2CH_2CH_3$, showing unexpected behavior. No serious overlap of this sort occurred in the ethyl disulfide radical or in the ether radicals.[2] Computer syntheses of the spectrum, assuming the structure given, indicated that the spectrum resulted from two hydrogen atoms of 18.3-G splitting and one hydrogen atom of 17.3-G splitting. As in the ethyl disulfide, there was no hyperfine splitting of the unpaired electron by the methylene across the disulfide group.

***n*-Butyl Sulfide.** A reacting solution with *n*-butyl sulfide gave the epr spectrum of Figure 4. This spectrum has the same problem with overlapping lines as the ethyl sulfide spectrum of Figure 2. To good approximation, the spectrum is that of Figure 3 with each line, including the overlapping lines, of Figure 3 split into a triplet by the interaction of the unpaired electron with the δ-hydrogen atoms. The radical is very probably $CH_3CH_2CH_2\dot{C}HSCH_2CH_2CH_2CH_3$.

Computer synthesis of the spectrum was necessary to unravel the complex overlap in Figure 4. The little wiggles in the two center lines in Figure 4 proved to be a real part of the spectrum, as can be seen by comparing the experimental spectrum, Figure 4A, with the computed spectrum, Figure 4B. It was very easy to analyze the spectrum using the computer, since even small changes in the trial splitting constants produced profound changes in the line shapes of the computer spectrum.

Other Sulfides and Disulfides. The reactions of $(CH_3)_3CO\cdot$ with methyl, propyl, and isobutyl sulfides and disulfides were examined with epr, but no free radicals were found. No satisfactory reason for this

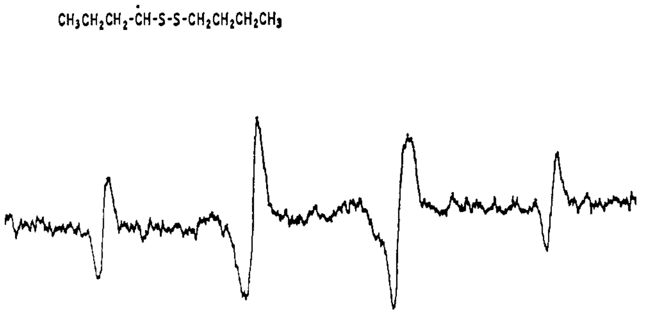

Figure 3. Epr spectrum of the free radical from photolysis of *t*-butyl peroxide, di-*n*-butyl disulfide, and isooctane.

has been uncovered. Extraordinary care in peroxide purification did not help. Although a particular effort was made to obtain spectra from the isobutyl species, which should exaggerate the unusual β-hydrogen effect discussed later, no radical species of any sort were detected.

Discussion

Several interesting comparisons can be made from the hyperfine coupling constants of the alcohol, ether, sulfide, and disulfide radicals listed in Table I, where the radicals have been segregated into groups characterized by having methyl substituents, ethyl substituents, and longer alkyl substituents. Changes in the α-hydrogen coupling constant reflect changes in the electron spin density on the α-carbon atom.[3] Changes in the β-hydrogen coupling constant which are not proportional to changes in the α-hydrogen coupling constant have been interpreted in terms of hindered internal rotation about the bond between the α- and β-carbon atoms of the radical.[4] In the alcohol, ether, sulfide, and disulfide radicals, the α-hydrogen coupling constant is much less than that found in the methyl radical, 23 G. There is apparently a significant amount of electron delocalization from the α-carbon atom. In the group with ethyl substituents, replacement of the ether oxygen by a sulfide or disulfide group significantly changes the electron delocalization in the radical. The electron spin density on the α-carbon atom appears to be considerably greater in the sulfide and disulfide radicals than in the ether or alcohol radicals. It would be very satisfying if a radical could be obtained from methyl sulfide or disulfide, so that a comparison of spin density could be obtained without the complicating presence of a β-carbon atom. In the radicals with alkyl groups longer than ethyl, the α-hydrogen coupling constants appear to be little changed from the radicals with ethyl substituents. This is not true for the β-hydrogen coupling constants.

The radicals from the molecules with ethyl substituents show a significant difference in β-hydrogen coupling constant between the species containing oxygen and those containing sulfur. In the sulfur-containing radicals the α-hydrogen coupling constant is greater, but the β-hydrogen coupling constant is less. It is difficult to explain these opposing trends by changes in electron delocalization alone. An additional hindered internal rotation effect can rationalize qualitatively such strange β-hydrogen coupling constant behavior.

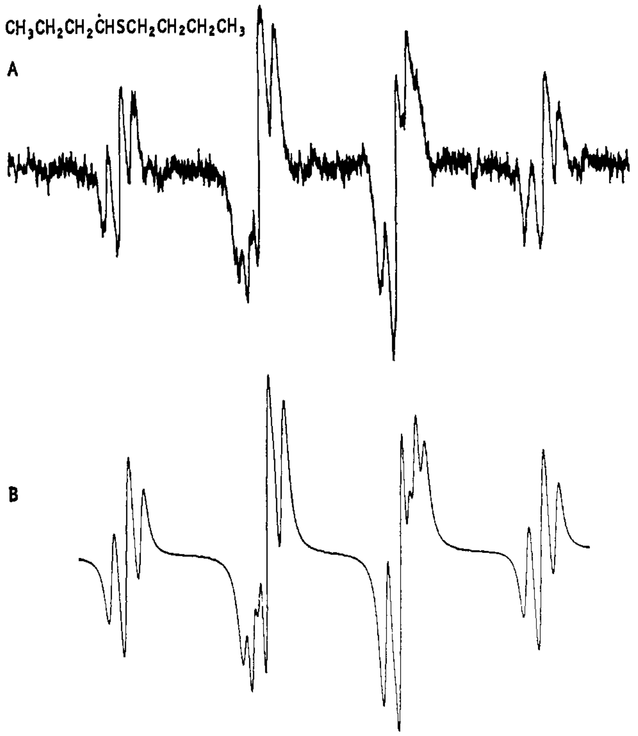

Figure 4. (A) Epr spectrum of the free radical from photolysis of *t*-butyl peroxide, di-*n*-butyl sulfide, and isooctane. (B) Computer synthesis of the free-radical epr spectrum from proposed coupling constants.

The opposite trends in the α- and β-hydrogen coupling constants are even more pronounced in the radicals from molecules with alkyl groups larger than ethyl. Increasing the length of the alkyl group appears to have very little effect on the δ-hydrogen coupling constant in the ether radicals; however, in the sulfur radicals the δ-hydrogen coupling constant is reduced by one-half when the alkyl substituent is changed from ethyl to *n*-butyl.

The anomaly of the sulfides and disulfides may have to await rationalization by electronic structure calculations. The recently introduced INDO–SCF techniques appear promising for radicals such as these.[5] The appropriate calculations are now underway in our laboratory.

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