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ELECTRON SPIN RESONANCE OF ALKYLSULFINYL AND ALKYLSULFONYL RADICALS

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Aryl and alkylsulfinyl radicals RSO· have been commonly postulated as thermodynamically rather stable and somewhat unreactive intermediates in the reactions of sulfoxides, thiolsulfinates and other oxygen derivatives of sulfur compounds.[3] Despite their general occurrence, however, the direct observation of sulfinyl radicals in solution by electron spin resonance (esr) is unreported.

We wish to present novel methods for the generation of sulfinyl radicals for esr study and to compare their spectra with the related sulfonyl $RSO_2\cdot$ and thiyl RS· radicals. Upon ultraviolet irradiation of a solution of t-butyl methanesulfenate[4a] in cyclopropane solution, an intense esr spectrum appears immediately which consists of a 1:3:3:1 quartet [A(H) = 6.57 G, <g> = 2.00965 ± 0.00003]. There is no evidence for any other species by esr, including the t-butyl radical.[4b] Analysis of the photolysate indicates a high yield of isobutylene and we propose that the spectrum is due to the methylsulfinyl radical formed in the following manner:

$$CH_3SOC(CH_3)_3 \xrightarrow{h\nu} CH_3\dot{S} + (CH_3)_3C\dot{O}$$

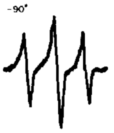
$$(CH_3)_3C\dot{O} + CH_3SOC(CH_3)_3 \longrightarrow (CH_3)_3COH + CH_3SOC(CH_3)_2\dot{C}H_2$$

$$CH_3SO(CH_3)_2\dot{C}H_2 \longrightarrow CH_3SO\cdot + CH_2{=}C(CH_3)_2$$

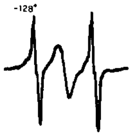
The same esr spectrum is observed during photolysis of (a) a solution of dimethyl disulfide, isopropyl alcohol and di-t-butyl peroxide (DTBP) or (b) a mixture of methanethiol, DTBP and ethylene. In the latter experiments the spectrum of $CH_3SO\cdot$ appears only after the mixtures are irradiated for a few minutes, and the signal slowly grows in intensity with continued irradiation. It suggests that a precursor (probably the same t-butyl methanesulfenate) is accumulating during the induction period.

The esr spectra of a variety of other alkylsulfinyl radicals listed in Table I can also be obtained by photolysis of solutions containing the corresponding alkyl disulfide, isopropyl alcohol and DTBP. The esr spectrum of each of these sulfinyl radicals is characterized by somewhat broad lines ($\Delta H_{mls} \gtrsim 0.5G$) and rather small hyperfine splittings (hfs) by the α-protons (shown in I for the n-propylsulfinyl radical at -127° C). Application of the Walsh rules predicts a bent structure for the sulfinyl radicals similar to that of alkylperoxy radicals,[5] and the odd electron would be largely localized in a S-O π orbital. If a hyperconjugative mechanism is assumed, the splitting by the α-protons should follow a $\cos^2\theta$ dependence (θ is the dihedral angle between H_α and the π orbital).

I



II



III

The esr spectrum of the methylsulfinyl radical is unchanged over a wide range of temperatures. On the other hand, the triplet splitting due to α-protons in other primary alkylsulfinyl radicals (see Table I) decreases as the temperature is lowered. This temperature dependence of α-proton hfs constants as well as the fact that α-proton hfs constants are smaller than that of $CH_3SO\cdot$ suggest that the stable conformations of these $R'CH_2SO\cdot$ radicals have the R'-C bond essentially eclipsed with the odd electron π orbital on the sulfur atom.[6] Furthermore, the esr spectrum of isobutyl derivative undergoes a pronounced alternating linewidth behavior (illustrated in II and III), in which the two α-protons are exchanging between inequivalent positions. This selective broadening of lines in the spectra as well as the somewhat larger α-proton hfs constant of the isobutylsulfinyl radical compared to those of n-alkyl derivatives suggest that the R'-C bond of this radical at the stable conformations is less eclipsed with the odd electron π orbital and that the linewidth alternation originates from the hindered rotation around the C-S bond. The significantly smaller value of the splitting by the lone α-proton in secondary alkylsulfinyl radicals indicate that it lies close to the nodal plane.[6] Additional studies involving ^{17}O and ^{33}S splittings would help to further clarify the structural and conformational properties of alkylsulfinyl radicals.

Table I. α-Proton Hyperfine Coupling Constants of Alkylsulfinyl Radicals.[a]

$CH_3SO\cdot$	6.57 (q, -95°)
$CH_3CH_2SO\cdot$	3.25 (t, -102°) 3.17 (t, -112°) 3.08 (t, -121°)
$CH_3CH_2CH_2SO\cdot$	3.51 (t, -96°) 3.29 (t, -117°)[b]
$(CH_3)_2CHCH_2SO\cdot$	4.24 (t, -90°) 4.14 (t, -120°)[c]
$CH_2{=}CHCH_2SO\cdot$	3.40 (t, -121°)[d]
$(CH_3)_2CHSO\cdot$	0.86 (d, -105°)
$CH_3CH_2CH(CH_3)SO\cdot$	~0.9[f] (d, -110°)[e]

[a] Coupling in gauss. Letters in parenthesis denote splitting pattern: d = doublet, t = triplet, q = quartet, and temperature in °C. $\Delta H_{mls} \approx 0.5$ G unless otherwise noted. [b] $A(H_\beta) = 0.35$ G (t). [c] $A(H_\beta) = 0.44$ G (d). [d] $\Delta H_{mls} = 0.91$ G. [e] $\Delta H_{mls} = 1.8$ G. [f] Unresolved.

For comparison we have also investigated the esr spectra of alkyl<u>sulfonyl</u> radicals by independent methods. Photolysis of a mixture of diacetyl peroxide and sulfur dioxide in cyclopropane solutions at -111°C afforded a spectrum consisting of a 1:3:3:1 quartet [A(H) = 0.76 G, <g> = 2.00501]. The same spectrum was obtained from methanesulfonyl chloride and photochemically generated silyl radicals.[7] These esr parameters for methylsulfonyl

$$CH_3\cdot + SO_2 \longrightarrow CH_3SO_2\cdot \xleftarrow{-Et_3SiCl} CH_3SO_2Cl + Et_3Si\cdot$$

radicals are similar to those obtained by other methods,[8] but differ significantly from the results in Table I.

Finally, we were unable to obtain any esr evidence for methylthiyl and related radicals in solution.[9] Although we have not yet rigorously eliminated the possibility that the species we have observed are not thiyl radicals, we consider it highly unlikely since the observed g-factors are significantly smaller than those of thiyl radicals reported in solids (g_{av} = 2.02 - 2.03).[10] Furthermore, the orbitally degenerate ground state of thiyl radicals will lead to line broadening by the same reasoning[12] applied to alkoxy radical and render these radicals unobservable in solution by esr techniques.

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