Hyperfine Interactions with Remote δ-Protons in the ESR Spectra of Thiyl Spin Adducts of 5,5-Dimethyl-3,4-dihydropyrrole *N*-Oxide (DMPO)

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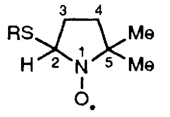
Small proton hyperfine interactions (*ca.* 0.1 mT) are observed from the δ-protons of the alkyl group of the parent thiyl radical in spin adducts from 5,5-dimethyl-3,4-dihydropyrrole *N*-oxide.

Thiyl radicals are important mediators in the reactions of sulfur antioxidants in hydrocarbons[1] and in many biological systems where sulfur compounds reduce free radical-induced tissue injury.[2,3] They may also be the cause of arteriosclerosis in homocysteinuria.[4] Unfortunately their large *g*-factor anisotropy, arising from the near-degeneracy of two π-type orbitals at the sulfur centre, causes such extensive line broadening as to make the radicals unobservable directly by electron spin resonnance (ESR) spectroscopy in the liquid state.[5] Recourse has to be made to spin traps which convert the thiyl radicals to 'stable' *N*-oxide spin adducts which are readily detected by ESR.[6] However, there is the disadvantage that only primary radical types rather than specific radical structures can usually be determined for most spin adducts, especially those from nitrone spin traps, since no hyperfine interactions with magnetic nuclei in the primary radical are observed. Here we show that the thiyl spin adducts of the nitrone spin trap 5,5-dimethyl-3,4-dihydropyrrole *N*-oxide (DMPO) are exceptional in that they do show resolvable coupling to δ-protons of the alkyl group attached to the sulfur and hence allow more definitive primary radical assignment to be made.

Previous ESR studies of the spin adducts (**X**) of DMPO with thiyls have also reported proton hyperfine interactions in addition to those from the nitrogen and the single β-proton nuclei.[7-9] However, it was not possible to decide whether these additional interactions arose from δ-protons of the thiyl group or from γ-protons in the ring of the DMPO itself. Additional proton interactions in other DMPO spin adducts with heteroatoms such as nitrogen and oxygen bonded at the C-2 position have been assigned to γ-protons at the C-3 and C-4 ring positions and taken to indicate non-planarity at the *N*-oxyl function.[10,11] A firm assignment can be made by selective deuteration of the reactants or by studying a series of thiyls with different numbers of δ-protons, which is the approach we have taken.



X

Table 1 Hyperfine interactions in DMPO spin adducts of thiyl radicals in toluene

Thiyl	a_N^{a}	$a_{\beta\text{-H}}$	$a_{\delta\text{-H}}$	*T*/K
MeS·	1.318 (1.533)^b	1.07 (1.80)^b	0.10 (3H)	216
EtS·	1.31 (1.533)^b (1.34)^c	1.03 (1.77)^b	0.11 (2H)	220
$C_{12}H_{25}S$·	1.31	1.056	0.10 (2H)	246
$C_{16}H_{33}S$·	1.31	1.061	0.10 (2H)	258
$PhCH_2S$·	1.34 (1.36)^c	1.125 (1.17)^c	0.11 (2H)	258
Pr^{i}S·	1.31 (1.35)^c	1.035 (1.12)^c	0.10 (1H)	221
Bu^{t}S·	1.325 (1.34)^c	1.0375 (1.12)^c		258
PhS·	1.29	1.415		223

[a] Hyperfine interactions in mT. [b] Values in water (ref. 7). [c] Values in benzene (ref. 11).

The thiyl radicals, RS·, were generated by photolysing toluene solutions of the corresponding disulfides, RSSR with unfiltered light from a 1 kW Kratos xenon arc lamp. This leads to homolytic scission of the S–S bond.[7,12,13] Deoxygenated solutions of the parent disulfide (10^{-4} mol dm^{-3}) and DMPO (0.009 mol dm^{-3}) were photolysed in the variable-temperature cavity of a Varian E109 X band spectrometer with 100 kHz modulation. *g*-Values were determined by using diphenylpicrylhydrazyl (DPPH) as a reference. The temperature was varied to obtain the best resolved spectra. Excellent simulations of the observed spectra were obtained using our isotropic simulation program or that available with a JEOL Espirit unit. The parameters listed in Table 1 are those obtained from the best simulations. No spin adduct spectra were observed in the absence of the disulfides.

Representative spectra of the DMPO spin adducts from the photolysis of the series of disulfides are shown in Fig. 1 and the derived ESR parameters are listed in Table 1. All the spin adducts had a *g*-value of 2.006 ± 0.0005. The most significant

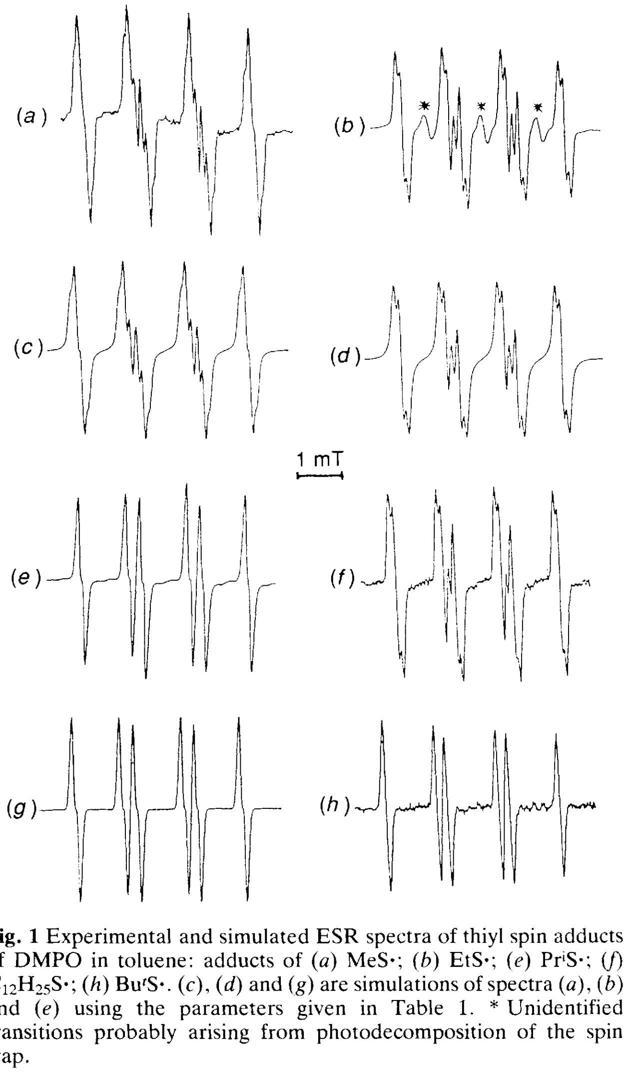


Fig. 1 Experimental and simulated ESR spectra of thiyl spin adducts of DMPO in toluene: adducts of (*a*) MeS·; (*b*) EtS·; (*e*) Pr^{i}S·; (*f*) $C_{12}H_{25}S$·; (*h*) Bu^{t}S·. (*c*), (*d*) and (*g*) are simulations of spectra (*a*), (*b*) and (*e*) using the parameters given in Table 1. * Unidentified transitions probably arising from photodecomposition of the spin trap.

observation in the present context is that of the different additional multiplets as the number of δ-protons is varied: singlets from $Bu^tS\cdot$ and $PhS\cdot$; doublets from $Pr^iS\cdot$; triplets from $EtS\cdot$, $C_{12}H_{25}S\cdot$, $C_{16}H_{33}S\cdot$ and $PhCH_2S\cdot$; and quartets from $MeS\cdot$. These provide convincing evidence that the additional interactions arise from the δ-protons of the thiyl group. It is highly unlikely that different alkyl groups in the thiyl component would change the conformation of the ring to produce an accidental coincidence of interactions with different numbers of ring γ-protons to match exactly the pattern expected from the thiyl protons. For the corresponding adducts from the alkoxyl radicals, a large hyperfine interaction with one unique γ-proton at C-3 has been reported (0.206 and 0.23 mT respectively for the DMPO adducts of $Bu^nO\cdot$ and $Bu^tO\cdot$) and interpreted to indicate a ring puckering at C-2.[10] No such interactions are observed for the thiyl radicals. The differences between alkoxyl and thiyl adducts probably arise from the lower electronegativity of the sulfur which lowers γ-proton interactions and the availability of empty low-lying d-orbitals on sulfur which leads to significant δ-proton interaction.

The nitrogen and β-proton hyperfine interactions reported here are close to those found for the same adducts in benzene[7] and lower than those in water[7] in accordance with the known increase in interaction constants with increase in the relative permittivity (dielectric constant) of the solvent.[6]

There is an interesting reversal in the relative magnitudes of the nitrogen and β-proton hyperfine interactions in the phenyl thiyl adduct where $a_N < a_{\beta\text{-H}}$. A similar reversal has been reported for chlorophenylthiyl and triphenylmethylthiyl spin adducts of DMPO.[9] This may indicate electron withdrawal from the *N*-oxyl function towards the aromatic π-systems of the phenyl groups again through the mediation of sulfur d-orbitals.

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