Detection of Thiyl Radicals by Spin Trapping in the Radiolysis of Liquids

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Summary The e.s.r. spectra of thiyl nitroxides have been identified following the low-temperature radiolysis of alkanethiols containing $\mathrm{Bu^tNO}$ as a radical trap. Thiyl radicals are also generated in the radiolysis of dimethyl sulphide and dimethyl disulphide.

ALTHOUGH thiyl (RS·) radicals are thought to be important intermediates in mechanisms of radioprotection involving thiol compounds,[1] their unequivocal e.s.r. detection in radiolysis does not appear to have been achieved for two reasons. Firstly, direct e.s.r. detection in the liquid state is considered highly improbable on account of the π-orbital degeneracy of these radicals,[2] and secondly, it was pointed out recently[3] that many of the solid-state e.s.r. spectra previously attributed to RS· radicals can be more reasonably assigned on the basis of their g tensors to adduct radicals of the type $\mathrm{RS\dot{-}SR_2}$. However, these limitations can be circumvented by the spin-trapping technique,[4] and we now report convincing e.s.r. evidence for the intermediacy of thiyl radicals in the liquid-phase radiolysis of compounds containing thiol, sulphide, and disulphide groups.

As in the previous study of methanol,[5] 2-methyl-2-nitrosopropane ($\mathrm{Bu^tNO}$) was used as the diamagnetic scavenger to produce long-lived nitroxide radicals at low temperatures. Solutions (*ca.* 10^{-1} M) prepared by high-vacuum techniques were kept at room temperature before irradiation to allow for dissociation of the inactive $\mathrm{Bu^tNO}$ dimer, the γ irradiations and subsequent e.s.r. observations being carried out in the range between -50 and -110 °C depending on the thermal stability of the derived nitroxides. N.m.r. studies[6] have shown that when $\mathrm{Bu^tNO}$ solutions are cooled below room temperature, the monomer–dimer equilibrium is not rapidly attained and a high monomer concentration persists for much longer than the typical irradiation time (*ca.* 10 min) in these experiments.

TABLE Isotropic e.s.r. parameters for thiyl nitroxides  $\mathrm{(RS)(Bu^t)N{-}O\cdot}$ generated by the radiolysis of the corresponding thiols (RSH) in the presence of $\mathrm{Bu^tNO}$

Trapped radical RS·	Temp/°C	Hyperfine couplings/G a_N	$a_H(3)$	g
MeS·	-103	18·9	1·2	2·0064
EtS·	-92	17·4		2·0063
$\mathrm{Pr^nS\cdot}$	-85	17·8		2·0063
$\mathrm{Pr^iS\cdot}$	-97	16·7		2·0062
$\mathrm{Bu^nS\cdot}$	-73	17·8		2·0063

The e.s.r. spectrum obtained after γ radiolysis of a methanethiol solution at -110 °C is dominated by a ^{14}N triplet of well-resolved 1:3:3:1 quartets indicating clearly that the trapped radical possesses three equivalent hydrogens. Assignment of this pattern to the methanethiyl t-butyl nitroxide, $\mathrm{MeS(Bu^t)NO\cdot}$ is supported by the similarity of the e.s.r. parameters ($a_N = 18·9$ G, $g = 2·0064$) to those of the simple triplet spectrum generated by the u.v. photolysis of butane-1-thiol solutions and ascribed to butane-1-thiyl t-butyl nitroxide ($a_N = 18{\cdot}5$ G, $g = 2{\cdot}0071$).[7] The observation of the ^{1}H coupling for the methanethiyl spin adduct, a_H (3) = 1·2 G, provides conclusive evidence for the identification. This coupling is comparable to the corresponding value of 1·4 G for the methoxyl radical adduct,[5] although the ^{14}N couplings and g factors for these *S*- and *O*- nitroxides differ appreciably, as expected.

In the radiolysis of several other alkanethiols at −110 °C the corresponding thiyl nitroxide was produced almost exclusively in every case. However, irradiation at − 70 °C gave additional weaker signals from mercaptoalkyl nitroxides suggesting the onset of secondary radical reactions at the higher temperature. The radiolysis of dimethyl sulphide and of dimethyl disulphide solutions resulted similarly in the trapping of methanethiyl radicals but in these systems there was also a signal of comparable intensity from the spin adduct of the methyl radical. The e.s.r. parameters for the thiyl nitroxides are summarized in the Table.

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[1] 'Radiation Damage and Sulphydryl Compounds,' International Atomic Energy Agency, Vienna, 1969.
[2] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.
[3] M. C. R. Symons, *J.C.S. Perkin II*, 1974, 1618.
[4] M. J. Perkins in 'Essays on Free Radical Chemistry,' ed. R. O. C. Norman, *Chem. Soc. Special Publ. No.* **24**, 1970, ch. 5; E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.
[5] J. A. Wargon and F. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 7917.
[6] B. M. Benjamin, J. A. Wargon, and F. Williams, unpublished work.
[7] I. H. Leaver, G. C. Ramsay, and E. Suzuki, *Austral. J. Chem.*, 1969, **22**, 1891.