

## Photolysis of Dialkyl Sulphoxylates: Formation of Alkoxy and Trialkoxysulphuranyl Radicals

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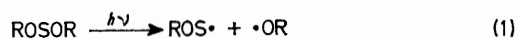
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*Summary* Using e.s.r. spectroscopy it is shown that u.v. irradiation of dialkyl sulphoxylates generates alkoxy radicals which add to the sulphoxylate to produce trialkoxysulphuranyl radicals.

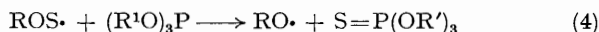
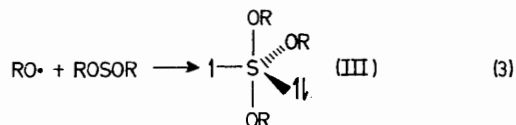
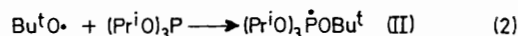
ALKOXYL radicals add rapidly to trialkyl phosphites to form tetra-alkoxyphosphoranyl radicals,  $(RO)_4\dot{P}$ .<sup>1</sup> In the hope of generating the analogous sulphuranyl radicals,  $(RO)_3\dot{S}$ ., we initiated a study of the reactions of alkoxy radicals with dialkyl sulphoxylates  $[(RO)_2S]$ . During the course of this work we have also found that u.v.-photolysis of dialkyl sulphoxylates provides a novel photochemical source of alkoxy radicals.

When a cyclopropane solution containing di-*t*-butyl sulphoxylate† (2.0 M) and tri-*i*-propyl phosphite (0.15 M) was irradiated with high-intensity u.v. light, whilst the sample was in the cavity of an e.s.r. spectrometer, an intense spectrum of the phosphoranyl radical (II) was detected at 170 K.‡ At higher temperatures the spectrum of the *t*-butyl radical, produced by  $\beta$ -scission of (II),<sup>1</sup> was observed. In addition, a strong singlet was detected which we assign to the tri-*t*-butoxysulphuranyl radical (III; R = Bu<sup>t</sup>).

It seems reasonable<sup>1,2</sup> to assume that the radical ROS· [equation (1)] will be rapidly desulphurised by trialkyl phosphites, thus providing a further source of alkoxy radicals.



(I)



Photolysis of di-*t*-butyl sulphoxylate in cyclopropane in the absence of trialkyl phosphite gave rise initially only to the spectrum of (III; R = Bu<sup>t</sup>) and no signal assignable to Bu<sup>t</sup>OS· could be detected;§ however as the photolysis progressed the spectra of other sulphur-centred radicals, probably derived from Bu<sup>t</sup>OS· or its reaction products, became apparent. In cyclopentane solvent, photolysis afforded the spectra of the cyclopentyl radical, the radical (III; R = Bu<sup>t</sup>), and the cyclopentanesulphinyl radical<sup>3</sup> [c-C<sub>5</sub>H<sub>9</sub>S=O; *a*(H) 1.1 G (1H), *g* 2.0093 at 180 K]. The sulphinyl radical is probably derived from the reaction of cyclopentyl radicals with Bu<sup>t</sup>OS· or its dimer (Bu<sup>t</sup>OS)<sub>2</sub>.

The intensities of the spectra obtained for transient alkyl radicals (cyclopentyl or *t*-butyl) demonstrate that the quantum yields of *t*-butoxyl radicals from photolysis of (Bu<sup>t</sup>O)<sub>2</sub>S or Bu<sup>t</sup>OOBu<sup>t</sup> are similar.

TABLE. E.s.r. parameters for trialkoxysulphuranyl radicals in cyclopropane solution.

Radical <sup>a</sup>	Temp./K	<i>g</i> -Factor <sup>b</sup>	Hyperfine splittings/G
(MeO) <sub>3</sub> S· <sup>c,d</sup>	190	2.0067	1.7 (6H)
(EtO) <sub>3</sub> S·	163	2.0068	1.6 (4H)
(Pr <sup>i</sup> O) <sub>3</sub> S·	163	2.0068	e
(Bu <sup>t</sup> O) <sub>3</sub> S·	153	2.0069	—
(V; R = Bu <sup>t</sup> )	163	2.0067	47.0 (1 <sup>33</sup> S)
(V; R = Et)	153	2.0069	1.5 (2H)

<sup>a</sup> Acyclic radicals were generated by photolysis of solutions containing (RO)<sub>2</sub>S and (EtO)<sub>3</sub>P (R = Me, Et, Pr<sup>i</sup>) or (Pr<sup>i</sup>O)<sub>3</sub>P (R = Bu<sup>t</sup>). E.s.r. spectra of the appropriate phosphoranyl radical or of the alkyl radicals produced by its β-scission (at higher temperatures) were also detected. <sup>b</sup> These *g*-factors are all similar to that (2.0060) reported (ref. 4) for (CF<sub>3</sub>O)<sub>3</sub>S·, generated by photolysis of CF<sub>3</sub>OCF<sub>3</sub> in the presence of OCS. <sup>c</sup> Some confusion appears to exist in the literature regarding dimethyl sulphoxylate. We prepared this material (b.p. 65–66 °C at 755 mm Hg) from methanol and di-1-imidazolyl sulphide, following the procedure employed previously for higher homologues (L. Birkofer and H. Niedrig, *Chem. Ber.*, 1966, **99**, 2070). <sup>d</sup> Still detectable at 250 K; *a*(H) 1.9 G (6H). <sup>e</sup> The expected splitting from two equivalent protons was not resolved; peak to peak line-width was 1 G at 170 K.

Other dialkyl sulphoxylates (I; R = Me, Et, Pr<sup>i</sup>) undergo photolytic cleavage to give alkoxy radicals which are

† The u.v. absorption spectrum above 250 nm of (Bu<sup>t</sup>O)<sub>2</sub>S in iso-octane shows λ<sub>max</sub> 341 nm (ε 0.7) with a shoulder at 260 nm (ε 50).

‡ N.m.r. studies (<sup>1</sup>H and <sup>31</sup>P) showed that there was no thermal reaction between (Bu<sup>t</sup>O)<sub>2</sub>S and (EtO)<sub>3</sub>P, even after 1 h at 340 K.

§ The solution e.s.r. signal from such a radical would probably be very broad.

¶ The electronic structures of (III) and (V) have been drawn to emphasise the formal analogy between sulphuranyl and phosphoranyl radicals. The <sup>33</sup>S hyperfine splitting for (V; R = Bu<sup>t</sup>) corresponds only to about 5% population of the S-3s orbital, and the unpaired electron is probably in an M.O. composed mainly of an S-3p orbital perpendicular to the plane containing the three oxygen atoms.

<sup>1</sup> A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738; *J.C.S. Perkin II*, 1972, 2224.

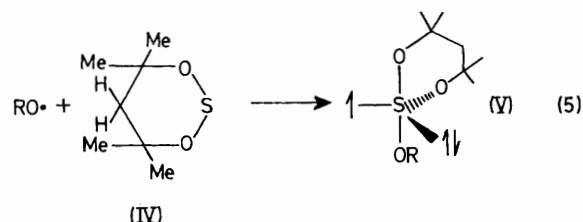
<sup>2</sup> W. G. Bentrude in 'Free Radicals', ed. J. K. Kochi, Wiley, New York, 1973, Vol. II, ch. 22.

<sup>3</sup> T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Letters*, 1972, 4075.

<sup>4</sup> J. R. Morton and K. F. Preston, *J. Phys. Chem.*, 1973, **77**, 2645; A. J. Colussi, J. R. Morton, K. F. Preston, and R. W. Fessenden, *J. Chem. Phys.*, 1974, **61**, 1247.

trapped by (I) or by trialkyl phosphites. The spectra of (III; R = Me or Et) exhibit hyperfine splittings (see Table) which we assign to protons of the apical alkoxy groups in quasi-trigonal bipyramidal sulphuranyl radicals, in which apical and equatorial ligands are not exchanging rapidly on the e.s.r. time scale at ca. 170 K. These conclusions are consistent with the spectroscopic data reported recently for sulphuranyl radicals generated by indirect methods.<sup>4</sup>

In view of the absence of resolvable hyperfine interaction with the equatorial alkoxy groups, we sought further evidence for the formation of (RO)<sub>3</sub>S· [rather than, for example, (RO)<sub>2</sub>S<sup>+</sup>]. Photolysis of the cyclic sulphoxylate (IV) in cyclopropane gave rise to a relatively weak unresolved e.s.r. signal (*g* 2.0068); however if an excess of



di-*t*-butyl peroxide was also present an extremely intense single-line spectrum which may be assigned to (V; R = Bu<sup>t</sup>) was obtained, and <sup>33</sup>S satellites could be readily detected without isotopic enrichment (see Figure).¶

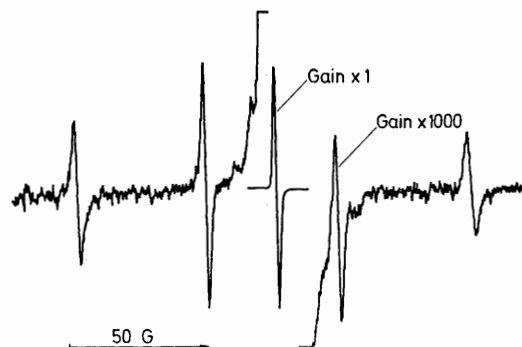


FIGURE. E.s.r. spectrum of the radical (V; R = Bu<sup>t</sup>) obtained by photolysis of a cyclopropane solution containing (IV) and di-*t*-butyl peroxide at 180 K. (Nuclear spin of <sup>33</sup>S is 3/2).

Photolysis of a mixture of (IV) and diethyl peroxide [or (EtO)<sub>2</sub>S] in cyclopropane yielded the spectrum of (V; R = Et) which showed splitting from two protons of the ethoxy group. We believe that these results strongly support the proposal that alkoxy radicals add rapidly to dialkyl sulphoxylates to produce trialkoxysulphuranyl radicals.

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