An Electron Spin Resonance Study of Dialkylaminothiyl ($R_2NS\cdot$), Dialkylaminosulphinyl ($R_2N\dot{S}O$), and Alkyl(sulphinyl)aminyl [$R\dot{N}S(O)X$] Radicals. Radical Addition to *N*-Sulphinylamines

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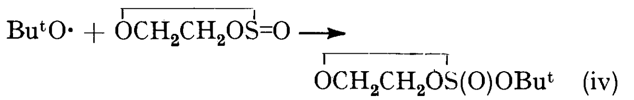
Photochemically generated t-butoxyl (or trimethylsiloxyl) radicals react with bis(dialkylamino) sulphides or sulphoxides, containing primary *N*-alkyl groups, to produce dialkylaminothiyl ($R_2NS\cdot$) or dialkylaminosulphinyl ($R_2N\dot{S}O$) radicals, respectively. The e.s.r. spectra of these radicals have been detected and show *a*(N) 10.7 G, *g* 2.0155 ($R_2NS\cdot$) and *a*(N) *ca.* 6.5 G, *g* 2.0060 ($R_2N\dot{S}O$). t-Butoxyl, trimethylsiloxyl, methyl, and t-butyl radicals (X•) add rapidly to the sulphur atom of *N*-sulphinylalkylamines to produce alkyl(sulphinyl)aminyl radicals [$R\dot{N}S(O)X$], which are detected by e.s.r. spectroscopy [*a*(N) 8.4—10.3 G, *g ca.* 2.0042]. The e.s.r. spectra are discussed in terms of the electronic structure and conformation of these radicals. The 1-hydroxy-1-methylethyl radical reduces *N*-sulphinyl-t-butylamine, probably to give the radical $Bu^tN{=}\dot{S}OH$ rather than the tautomeric aminosulphinyl radical $Bu^tN(H)\dot{S}{=}O$.

REACTIVE free radicals readily add to compounds of trivalent phosphorus to produce phosphoranyl radicals. For example, alkoxyl radicals add rapidly to trialkyl phosphites to form tetra-alkoxyphosphoranyl radicals (1).[1] Using e.s.r. spectroscopy, it has recently been shown that analogous hypervalent sulphuranyl radicals are produced by addition of alkoxyl radicals to dialkyl sulphoxylates (2; X = RO)[2] or to alkyl alkanesulphenates (2; X = R).[3] Related oxysulphuranyl radicals are formed by radical addition to sulphonyl fluoride[4] [equation (iii)] or to ethylene sulphite[5] [equation (iv)], and similar species may be transient intermediates in the homolytic dealkylation of dialkyl sulphoxides.[6]

$$RO\cdot + (RO)_3P \longrightarrow \underset{(1)}{(RO)_4P\cdot} \qquad \text{(i)}$$

$$RO\cdot + \underset{(2)}{ROSX} \longrightarrow (RO)_2\dot{S}X \qquad \text{(ii)}$$

$$F\cdot + F_2S{=}O \longrightarrow F_3\dot{S}{=}O \qquad \text{(iii)}$$



$$Bu^tO\cdot + \overline{OCH_2CH_2OS}{=}O \longrightarrow \overline{OCH_2CH_2OS}(O)OBu^t \qquad \text{(iv)}$$

Our original aim in studying the homolytic reactions of compounds containing S–N bonds was to identify further examples of such hypervalent sulphur-centred radicals. In the event such adducts were not detected by e.s.r. spectroscopy, although they may have been involved as short-lived intermediates leading to the observed radicals.

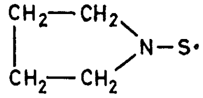
RESULTS

Solutions (usually in cyclopropane) of the sulphur compound, alone or in the presence of a photochemical source of free radicals, were irradiated with high intensity u.v. light whilst the samples were in the cavity of an e.s.r. spectrometer. The radicals produced were all transient, and their e.s.r. spectra were recorded during continuous photolysis.

(a) *Dialkylaminothiyl Radicals.*—Photolysis of a mixture of bis(diethylamino) sulphide and di-t-butyl peroxide in cyclopropane at 160 K gave rise to a spectrum which showed *a*(N) 10.7, *a*(4H) 6.1 G, *g* 2.0156. A radical showing identical e.s.r. parameters was detected when the di-t-butyl peroxide was replaced by bis(trimethylsilyl) peroxide or by acetone, and in the latter experiment the signal from the 1-hydroxy-1-methylethyl radical was also observed. We assign this spectrum to the diethylaminothiyl radical (3) since the e.s.r. parameters are very similar to those obtained previously for dialkylaminothiyl radicals (see Discussion section).

$(MeCH_2)_2N{-}S\cdot$

(3)



(4)

$(R_2N)_2S{=}O$

(5)

$R_2N{-}\dot{S}{=}O$

(6)

Analogous results were obtained for bis(pyrrolidino) sulphide when the radical (4) was detected. The e.s.r. parameters are given in Table 1.

Photolysis of the bis(dialkylamino) sulphides alone did not give rise to detectable concentrations of dialkylaminothiyl radicals. Some broad, unidentified signals were apparent during photolysis in the presence or absence of peroxides. The spectra of the dialkylaminothiyl radicals were strongest at low temperatures and were undetectable above *ca.* 220 K. The line-width (*ca.* 1.3 G) was essentially independent of temperature.

(b) *Dialkylaminosulphinyl Radicals.*—Photolysis of bis(dialkylamino) sulphoxides (5) in cyclopropane (sometimes with dichloromethane to increase solubility) yielded weak signals assigned to the dialkylaminosulphinyl radicals (6). The radical (6; R = Me) was also detected during photolysis of dimethylaminosulphinyl chloride [$Me_2NS(O)Cl$] in

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[1] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993, 2224.

[2] J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 835.

[3] W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, 152(S), 1748(M).

[4] J. R. Morton and K. F. Preston, *J. Chem. Phys.*, 1973, **58**, 2657.

[5] W. B. Gara, B. P. Roberts, C. M. Kirk, B. C. Gilbert, and R. O. C. Norman, *J. Magnetic Resonance*, 1977, **27**, 509.

[6] W. B. Gara and B. P. Roberts, *J.C.S. Perkin II*, 1977, 1708

cyclopropane–dichloromethane solvent. Much more intense spectra of (6) were obtained by irradiation of mixtures of di-t-butyl peroxide [or bis(trimethylsilyl) peroxide] and (5) than were obtained in the absence of peroxide. The spectroscopic parameters of (6) are given in Table 1, and the spectrum of (6; R = Me) is shown in the Figure.

TABLE 1

E.s.r. parameters for dialkylaminothiyl ($R_2NS\cdot$) and dialkylaminosulphinyl ($R_2N\dot{S}O$) radicals in cyclopropane at *ca.* 170 K. The parameters for the corresponding nitroxides (at *ca.* 300 K) are also given

Radical	*g* Factor	Hyperfine splitting (G) *a*(N)	Hyperfine splitting (G) *a*(H) [a]	Reference
$(MeCH_2)_2NS\cdot$	2 0156	10.7	6.1 (4)	This work
$CH_2(CH_2)_2CH_2NS\cdot$ [b]	2.0154	10.7	14.5 (4)	This work
$(Me_2CH)_2NS\cdot$	2.0159	10.9	2.4 (2)	*c*
$(CH_3)_2N\dot{S}O$ [d]	2.0060	6.8	3.8 (6)	This work
$(MeCH_2)_2N\dot{S}O$	2.0060	6.1	2.3 (4)	This work
$CH_2(CH_2)_2CH_2N\dot{S}O$ [b]	2.0061	6.3	3.7 (4)	This work
$Bu^tN{=}\dot{S}OH$ [e]	2.0071	1.4	9.5 (1)	This work
$Bu^tN{=}\dot{S}OD$ [e]	2.0072	1.4	1.4 (1D)	This work
$(CH_3)_2NO\cdot$		15.2	12.3 (6)	*f*
$(MeCH_2)_2NO\cdot$		15.2	10.3 (4)	*f*
$(Me_2CH)_2NO\cdot$		14.7	4.5 (2)	*f*
$CH_2(CH_2)CH_2NO\cdot$		14.9	19.6 (4)	*g*

[a] Number of nuclei coupling given in parentheses. [b] In cyclopropane–ethylene oxide (6 : 1 v/v). [c] Refs. 12 and 13: at 233 K. [d] In cyclopropane–dichloromethane (1 : 1 v/v). [e] At 200 K. [f] In CCl_4; J. Q. Adams, S. N. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654. [g] In CH_2Cl_2; G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France.*, 1965, 3283.

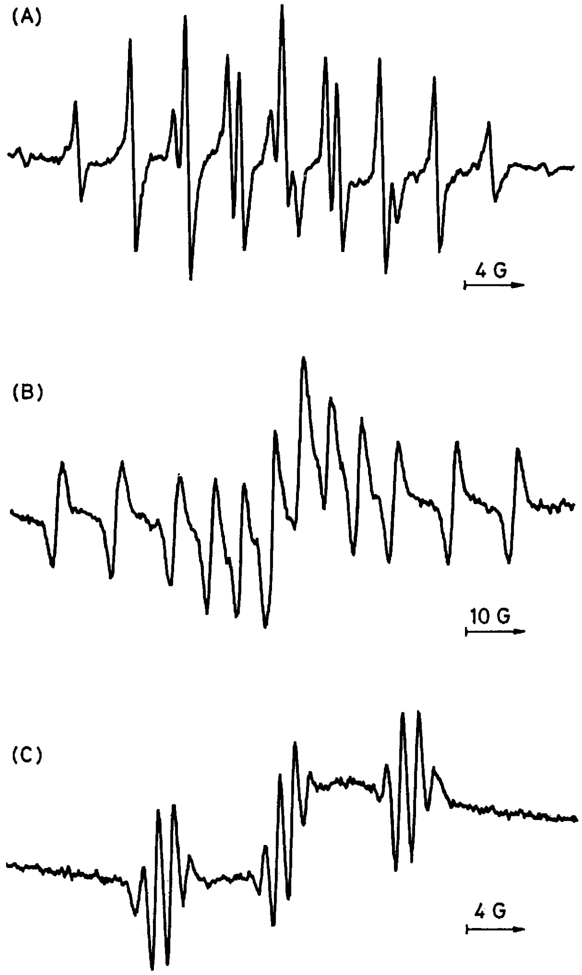
Apart from the spectrum of (6; R = Me), a sharp singlet (*g* 2.0054, peak–peak line-width 0.45 G at 175 K) was detected during irradiation of (5; R = Me) in the presence or absence of peroxides. This unidentified singlet grew in intensity as the photolysis progressed, and thus appears to derive from a secondary product. Gilbert *et al.*[7] have detected a singlet, *g ca.* 2.0053, which they could not assign with certainty, during photolysis of dialkyl sulphites alone or in the presence of di-t-butyl peroxide. The spectra of the radicals (6), like those of (3) and (4), were most intense at low temperatures, and the decrease in amplitude at higher temperatures was not accounted for by an increase in linewidth.

(c) *Radical Addition to* N-*Sulphinylamines*.—E.s.r. spectra were recorded during the photochemical generation of t-butoxyl (from Bu^tOOBu^t), methyl (from MeN=NMe), and t-butyl radicals (from $Bu^tN{=}NBu^t$) in the presence of a series of *N*-sulphinylamines (RNSO). t-Butoxyl and alkyl radicals add to sulphur to produce radicals of the type (7; X = Bu^tO or alkyl), which are characterised by *g* factors of *ca.* 2.0042 and nitrogen splittings of 9—10 G.

$$X\cdot + RN{=}S{=}O \longrightarrow \underset{(7)}{R\dot{N}{-}S(O)X} \qquad \text{(v)}$$

The methyleneamino protons in (7; R = Et) were non-equivalent, and small long-range splittings, which were sometimes difficult to assign, were detected for most adducts. The spectroscopic parameters for (7) are gathered in Table 2, and the spectra of (7; R = Et, X = Bu^tO) and of (7; R = Bu^t, X = Me) are shown in the Figure.

Apart from the signal due to (7; R = X = Bu^t), the spectrum of a radical showing *g* 2.0042 and hyperfine splitting (9.9 G) probably from two equivalent nitrogen nuclei was detected during irradiation of a mixture of Bu^tNSO and $Bu^tN{=}NBu^t$. This spectrum, which increased in intensity as the photolysis progressed and thus derives from a secondary product, is very tentatively ascribed to (8) which might be formed as shown in equations (vi)—(viii). α-Scission of (7; R = X = Bu^t) is also a possible source of t-butylnitrene.



E.s.r. spectra of the radicals (A) $Me_2N\dot{S}O$ in cyclopropane–dichloromethane at 160 K, (B) $Et\dot{N}S(O)OBu^t$ in cyclopropane at 157 K, (C) $Bu^t\dot{N}S(O)CH_3$ in cyclopropane at 210 K

$$Bu^tNSO \xrightarrow{h\nu} Bu^tN + SO \qquad \text{(vi)}$$

$$Bu^tN + Bu^tNSO \longrightarrow Bu^tN{=}S(O){=}NBu^t \qquad \text{(vii)}$$

$$Bu^t\cdot + Bu^tN{=}S(O){=}NBu^t \longrightarrow \underset{(8)}{Bu^tN{=}S(O)(Bu^t){-}\dot{N}Bu^t} \qquad \text{(viii)}$$

Photolysis of a mixture of Bu^tNSO and Bu^tOOBu^t in isobutane solvent gave rise to the spectrum of (7; R = X = Bu^t) and of that ascribed to (8) as a secondary product, but *not* to that of the t-butyl radical. Photolysis, in propene solvent at 200 K gave rise to overlapping signals from the allyl radical and from a species assigned as

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[7] B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, 173(S), 1974(M).

(7; $\mathrm{R = Bu^t}$, X = allyl) which showed a(N) 8.8 G, g 2.0044 (peak–peak line width 2 G).

Photolysis of a mixture containing $\mathrm{Bu^tNSO}$, $\mathrm{Bu^tOOBu^t}$, and isopropyl alcohol * gave rise to an e.s.r. spectrum which we ascribe to the radical (9), although it is difficult to eliminate with certainty the tautomeric aminosulphinyl radical (10). The nitrogen splitting (1.4 G) is much smaller

$\mathrm{Bu^tN{=}\dot{S}OH}$ (9) $\mathrm{Bu^tN(H)\dot{S}{=}O}$ (10)

and the g value higher than expected for the aminosulphinyl radical (10). The proton splitting (9.5 G) is similar to that observed previously [7] for the hydroxysulphinyl radical, $\mathrm{HO\dot{S}{=}O}$. Replacement of the isopropyl alcohol by the O-deuterio-compound brought about the expected changes in the spectrum (see Table 1).

Photolysis of N-sulphinylamines alone in cyclopropane resulted in the formation of some insoluble white solid and gave rise to a broad featureless e.s.r. signal (g *ca.* 2.00) which persisted when photolysis ceased. This signal was detected when a source of radicals was also present [see Figure (C)] and solid was deposited, especially in experiments with the azoalkanes.

TABLE 2

E.s.r. parameters for alkyl(sulphinyl)aminyl radicals, $\mathrm{R\dot{N}S(O)X}$, produced by radical addition to N-sulphinylalkylamines in cyclopropane at *ca.* 200 K

Radical	g Factor	Hyperfine splitting (G) a(N)	a(H) [a]
$\mathrm{MeCH_2\dot{N}S(O)OBu^t}$	2.0041	10.3 [b]	29.2 (1); [c] 25.2 (1); [c] *d,e*
$\mathrm{MeCH_2\dot{N}S(O)OSiMe_3}$ [f]	2.0041	10.0	31.1 (1); 26.0 (1)
$\mathrm{MeCH_2\dot{N}S(O)CH_3}$	2.0043	9.3	22.2 (1); 18.7 (1); 1.3 (3)
$\mathrm{MeCH_2\dot{N}S(O)Bu^t}$	2.0042	9.3	18.5 (1); [g] 17.1 (1); [g] 1.1 (9)
$\mathrm{Me_2CH\dot{N}S(O)OBu^t}$ [h]	2.0041	9.6	10.0 (1); *d, i*
$\mathrm{Me_2CH\dot{N}S(O)CH_3}$	2.0041	9.0	9.4 (1); *j*
$\mathrm{Me_2CH\dot{N}S(O)Bu^t}$	2.0041	*ca.* 9.0	*ca.* 9.0 (1); *k*
$\mathrm{\overline{CH_2(CH_2)_4CH}\dot{N}SO(O)Bu^t}$	2.0041	*ca.* 9.5	*ca.* 9.5
$\mathrm{Bu^t\dot{N}S(O)OBu^t}$	2.0042	8.7	*d,l*
$\mathrm{Bu^t\dot{N}S(O)CH_3}$	2.0044	8.4	1.1 (3)
$\mathrm{Bu^t\dot{N}S(O)Bu^t}$ [m]	2.0042	8.7	1.0 (9)

[a] Number of nuclei coupling given in parentheses. [b] Independent of temperature (±0.1 G) from 150 to 268 K. [c] Temperature dependent. Proton splittings in G (T/K): 34.2, 27.8 (151); 32.0, 26.8 (168); 30.4, 26.2 (186); 28.2, 25.2 (223); 27.6, 24.9 (245); 26.9, 24.8 (268). [d] Small long-range splittings were detected from both the γ-protons of the N-alkyl group and from the protons of the t-butoxy group. These were difficult to assign. [e] Long-range splitting; $\geqslant 8$ lines spaced by 0.45 G. [f] At 162 K. [g] Temperature dependent. Proton splittings in G (T/K): 18.9, 17.3 (188); 19.5, 17.6 (173); 20.0, 18.0 (163). [h] Secondary product spectrum detected showing a(N) 9.8, a(6 H) 1.4 G, g 2.0028, tentatively ascribed to $\mathrm{Me_2C{=}N{-}\dot{S}O_2}$. [i] Long-range splitting; $\geqslant 10$ lines spaced by 0.43 G. [j] Wing lines showed a further splitting into $\geqslant 10$ components spaced by 0.6 G. [k] Wing lines showed a further splitting into $\geqslant 8$ components spaced by 1.0 G. [l] Long-range splitting; $\geqslant 14$ lines spaced by 0.25 G. [m] Secondary product spectrum detected showing a(2N) 9.9 G, g 2.0042, peak to peak line-width 2.3 G (see text).

(d) *Radical Decay Rates.*—We have briefly investigated the rates of decay of the different types of radical using kinetic e.s.r. spectroscopy.[9,10] The radicals $\mathrm{Et_2NS\cdot}$, $\mathrm{Et_2N\dot{S}O}$, and $\mathrm{Et\dot{N}S(O)OBu^t}$ were chosen as typical examples, and the decay of their e.s.r. signals was monitored as a function of time at *ca.* 160 K after shuttering the u.v. light with a rotating sectored disc. The measured rate constants are given in Table 3.

The radicals $\mathrm{Et_2NS\cdot}$ and $\mathrm{Et_2N\dot{S}O}$ decay in second-order reactions at close to the diffusion-controlled limiting rate, whilst $\mathrm{Et\dot{N}S(O)OBu^t}$ decays by a first-order process.

TABLE 3

Rate constants for the decay of selected radicals in cyclopropane

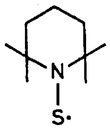
Radical	T/K	Initial concentration (M)	Kinetic order of decay	Rate constant (l mol^{-1} s^{-1} or s^{-1})
$\mathrm{Et_2NS\cdot}$	153	1.9×10^{-7}	Second	1.3×10^9
$\mathrm{Et_2N\dot{S}O}$	163	3.1×10^{-7}	Second	1.1×10^9
$\mathrm{Et\dot{N}S(O)OBu^t}$	153	2.8×10^{-7}	First	4.2×10^1

DISCUSSION

(a) *E.s.r. Spectra.*—(i) *Dialkylaminothiyl radicals.* A relatively small number of these radicals has been studied previously by e.s.r. spectroscopy.[11-13] The species (11)—(14) were generated by thermolysis and/or photolysis of the appropriate bis(dialkylamino) disulphide [equation (ix)].

$\mathrm{(Me_2CH)_2NS\cdot}$

(11)



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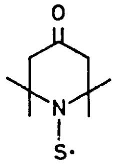

(13)

$\mathrm{Ph_2NS\cdot}$

(14)

$$\mathrm{R_2NSSNR_2} \xrightarrow{h\nu \text{ or heat}} \mathrm{2R_2NS\cdot} \qquad \text{(ix)}$$

The reported g values are in the range 2.015—2.018 and the nitrogen splitting constants are 10.9 (11),[12,13] 11.4 (12),[11-13] 10.9 (13),[11] and 8.0 G (14).[13] A further splitting from two equivalent protons (2.4 G) was detected for (11). An e.s.r. spectrum consisting of a single broad line (g 2.017) was obtained during photolysis of bis(diethylamino) disulphide and tentatively attributed to the radical (3).[13] The spectrum which we assign to (3) exhibits well resolved nitrogen and proton splittings of the expected [11-13] magnitudes. Danen and

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* Isopropyl alcohol does not react directly with $\mathrm{Bu^tNSO}$ under the conditions employed.[8]

[8] W. T. Smith, jun. and L. D. Grinninger, *J. Org. Chem.*, 1961, **26**, 2133.

[9] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902.

[10] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.

[11] J. E. Bennett, H. Sieper, and P. Tavs, *Tetrahedron*, 1967, **23**, 1697.

[12] W. C. Danen and D. D. Newkirk, *J. Amer. Chem. Soc.*, 1976, **98**, 516.

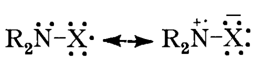
[13] B. Maillard and K. U. Ingold, *J. Amer. Chem. Soc.*, 1976, **98**, 520.

Newkirk[12] report that photolysis of bis(pyrrolidino) disulphide yielded only very weak, uninterpretable spectra, whilst we have shown that the reaction of t-butoxyl radicals with bis(pyrrolidino) sulphide gives rise to the spectrum of (4). The reasons for these differences are not immediately obvious, but it is conceivable that the spectra of the dialkylaminothiyl radicals with less bulky substituents generated from the disulphides are broadened as a result of the S_H2 exchange reaction (x).

$$R_2NS\cdot + R_2NSSNR_2 \rightleftharpoons R_2NSSNR_2 + R_2NS\cdot \quad \text{(x)}$$

However, we were unable to detect any signal in the g 2.016—2.017 region during photolysis of $Et_2NSSNEt_2$ in cyclopropane or t-butylbenzene over a wide range of temperature and disulphide concentration, although other weak signals [12,13] were present.

The relationship of the dialkylaminothiyl radicals (15; X = S) to the well known dialkyl nitroxides (15; X = O) has been pointed out previously.[11-13] The

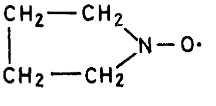


$$R_2\ddot{N}-\underset{\cdot\cdot}{\ddot{X}}\cdot \longleftrightarrow R_2\overset{+\,\cdot\cdot}{N}-\underset{\cdot\cdot}{\overset{-}{X}}\!:$$

(15a) (15b)

smaller magnitudes of the nitrogen and β-proton splitting constants in (15; X = S) compared with those in (15; X = O) are consistent with the lower electronegativity of sulphur and consequent smaller contribution from (15b). The much higher g factors of (15; X = S) compared with those (*ca.* 2.006) of (15; X = O) are related to the relatively high spin density on sulphur in the former radicals, and to the higher spin-orbit coupling constant for sulphur compared with those for oxygen and nitrogen.

Whilst the nitrogen splittings for (3), (4), and (11) are almost identical, the β-proton coupling constants differ markedly and in a similar manner to those found for the analogous nitroxides (see Table 1). This is to be expected if the magnitude of a(β-H) in both (15; X = S and O) depends mainly upon the π-spin density at nitrogen and θ, the dihedral angle between the β-C–H bond and the axis of the $2p_\pi$ orbital on nitrogen, provided that this angle is similar for the two types of radical. The cyclic radicals (4) and (16), for which the average values of θ should be very similar, both show $a(N)/a(\beta\text{-H}) = 0.75 \pm 0.01$.



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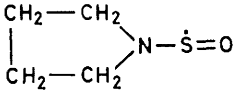


(17)

(ii) *Dialkylaminosulphinyl radicals.* These species are closely related to the alkoxysulphinyl radicals, $RO\dot{S}O$, recently characterised by Gilbert *et al.*[7] The g value of $R_2N\dot{S}O$ is intermediate between those found for alkanesulphinyl radicals [14,15] $R\dot{S}O$ (*ca.* 2.010) and alkoxysulphinyl radicals [7] (*ca.* 2.0049). The ratio $a(N)/a(\beta\text{-H})$ for (17) is greater (1.7) than that found for (4) and (16), probably as a result of the much smaller π-spin density on nitrogen in $R_2N\dot{S}O$ compared with $R_2NS\cdot$ and $R_2NO\cdot$.

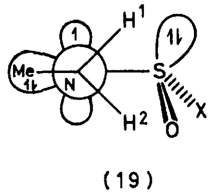
(iii) *Alkyl(sulphinyl)aminyl radicals.* These radicals are characterised by g factors of 2.0040—2.0045, very close to the values for simple dialkylaminyl and amidyl radicals,[16] and nitrogen splittings in the range 9—10 G. From the large magnitudes of the splittings from the protons of C–H groups α to nitrogen,[16] it appears that the unpaired electron is localised mainly (60—70%) on nitrogen with structures such as (18; Y = NR) being relatively unimportant.

$X\dot{S}(O)=Y$ (18a)

$X\overset{+}{\dot{S}}(O)-\bar{Y}$ (18b)

For the isoelectronic alkanesulphonyl radicals, $R\dot{S}O_2$, it has been deduced that about half the unpaired spin density resides on sulphur with the remainder equally distributed between the two oxygen atoms.[17,18] Hence structures (18) would appear to be more important when Y = O than when Y = NR, in line with the greater electronegativity of oxygen compared with that of nitrogen. The localisation of the unpaired electron on N rather than O in $RS(O)\dot{N}X$ is also in accord with the greater electronegativity of oxygen.

For the radicals $RS(O)\dot{C}R_2$ it has been demonstrated that the spin-withdrawing power of the sulphinyl substituent is small.[19] It is presumably fortuitous that the methyl proton splittings in $CH_3\dot{S}O_2$ (0.6 G [20]) and in $CH_3S(O)\dot{N}X$ (*ca.* 1 G) are so similar.



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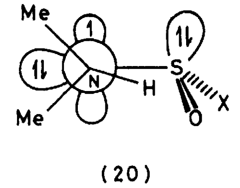

(20)

The magnitudes and temperature dependence of the β-proton splittings in $Et\dot{N}S(O)X$ (X = Bu^{t}O, Me, Bu^t) indicate that the most stable conformation of these radicals is probably (19) * (the nitrogen is assumed to be sp^2-hybridised and the sulphur quasi-tetrahedral).

The non-equivalence of H^1 and H^2 probably arises because of a relatively large barrier to rotation about the S–N bond, which would lead to different average

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* The ethyl group could be *cis* or *trans* to X. Since only one spectrum was detected one isomer presumably predominates, for steric reasons probably that shown.

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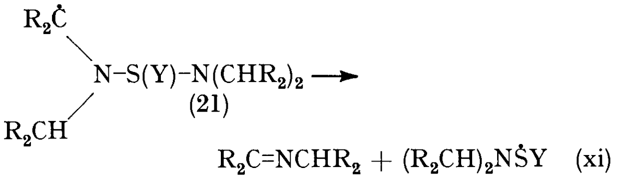
environments for the two protons even if exchange between rotamers about the C–N bond were fast on the e.s.r. time scale. The temperature dependence (see Table 2) of the β-proton splittings for $\mathrm{Et\dot{N}S(O)X}$ ($\mathrm{X} = \mathrm{Bu^tO}$, $\mathrm{Bu^t}$) is indicative of fast exchange of (19) with less stable conformations in which one or both β-C–H bonds subtend larger dihedral angles with the axis of the orbital of the unpaired electron on nitrogen. The large barrier to rotation about the S–N bond is probably related to the interactions represented by (18; $\mathrm{Y} = \mathrm{NR}$).

The small magnitudes (*ca.* 10 G) of the splittings from the β-protons in the adducts of *N*-sulphinylamines containing secondary *N*-alkyl groups are consistent with a most stable conformation of the type (20). The nitrogen splittings for $\mathrm{R\dot{N}S(O)X}$ vary in such a manner as to indicate that both the bulk of R and the electronic properties of X are important in determining $a(\mathrm{N})$.

(b) *Mechanistic Aspects.*—Photolysis of bis(dialkylamino) sulphides or sulphoxides alone produces much weaker signals from the radicals $\mathrm{R_2NS\cdot}$ or $\mathrm{R_2N\dot{S}O}$, respectively, than when mixtures of the compounds with peroxides are irradiated. By analogy with the mechanism proposed for the formation of $\mathrm{RO\dot{S}O}$ from the reaction of t-butoxyl radicals with dialkyl sulphites,[7] we suggest that β-scission of the species (21; $\mathrm{Y} = \mathrm{O}$ or lone pair) is the major source of aminothiyl or aminosulphinyl radicals when peroxides are present.


(21)

$$\mathrm{R_2C{=}NCHR_2 + (R_2CH)_2N\dot{S}Y} \qquad \text{(xi)}$$

There are two reasonable mechanisms for the formation of (21), one involving abstraction of hydrogen from carbon [equation (xii)], and the other proceeding by way of an intermediate (oxy)sulphuranyl radical adduct (22) which undergoes subsequent loss of alcohol to produce (21) [equations (xiii) and (xiv)].

$$\mathrm{Bu^tO\cdot + [(R_2CH)_2N]_2SY \longrightarrow Bu^tOH + (21)} \qquad \text{(xii)}$$

$$\mathrm{Bu^tO\cdot + [(R_2CH)_2N]_2SY \longrightarrow \underset{(22)}{[(R_2CH)_2N]_2\dot{S}(Y)OBu^t}} \qquad \text{(xiii)}$$

$$\mathrm{(22) \longrightarrow (21) + Bu^tOH} \qquad \text{(xiv)}$$

It is difficult to choose between these alternatives at present, but the second appears attractive in view of the known propensity of oxygen-centred radicals to attack at sulphur, particularly when charge transfer from sulphur to oxygen is favourable. Pulse radiolytic studies have shown that the radical $\mathrm{MeS\dot{C}H_2}$ is formed by loss of water from an initial sulphuranyl radical adduct ($\mathrm{Me_2\dot{S}OH}$) in the reaction of hydroxyl radicals with dimethyl sulphide.[21] An oxysulphuranyl radical is formed by addition of t-butoxyl radicals to ethylene sulphite [equation (iv)].[5] The ionisation potential of bis(dimethylamino) sulphoxide (8.53 eV) is considerably less than those of dimethyl (10.25 eV) and ethylene (10.93 eV) sulphites,[22] and thus the interaction between the HOMO of $\mathrm{(R_2N)_2SO}$ and the SOMO of $\mathrm{RO\cdot}$ will be more favourable than the corresponding interaction for $\mathrm{(RO)_2SO}$.*

The diethylaminothiyl radical, like $\mathrm{Pr^i{}_2NS\cdot}$,[13] probably decays by diffusion-controlled S–S coupling to give the disulphide. Similarly, the radical $\mathrm{Et_2N\dot{S}O}$ presumably dimerises to give the S–S or S–O coupled product.

Addition to N-*Sulphinylamines.*—Primary or tertiary alkyl radicals, but not allyl radicals, add essentially irreversibly to *N*-sulphinylalkylamines to produce alkyl(alkanesulphinyl)aminyl radicals. Addition of alkyl and alkoxyl radicals occurs at sulphur, and not at nitrogen which would yield aminosulphinyl radicals. Alkyl and alkoxyl radicals also add rapidly to the sulphur atom of sulphur dioxide to give alkyl- or alkoxy-sulphonyl radicals respectively [equation (xv; $\mathrm{X} = \mathrm{R}$ or RO)].[19,24,25]

$$\mathrm{X\cdot + SO_2 \longrightarrow X\dot{S}O_2} \qquad \text{(xv)}$$

Alkoxysulphinyl radicals [7] are not detected during the reaction of alkyl radicals with sulphur dioxide.[19] Brunton *et al.* have shown that the radicals [$\mathrm{X\cdot}$ in equation (xvi)] $\mathrm{CF_3\cdot}$, $\mathrm{R_3Si\cdot}$, $\mathrm{(EtO)_2\dot{P}O}$, and $\mathrm{CF_3S\cdot}$ add to di-t-butylsulphur di-imide (23) to give adducts assigned structure (24).[26] For example, (24; $\mathrm{X} = \mathrm{CF_3S}$) shows

$$\mathrm{X\cdot \times \underset{(23)}{Bu^tN{=}S{=}NBu^t} \longrightarrow \underset{(24)}{Bu^t\dot{N}{-}S{-}N(X)Bu^t}} \qquad \text{(xvi)}$$

$a(\mathrm{N_1})$ 12.6, $a(\mathrm{N_2})$ 0.9, $a(3\mathrm{F})$ 2.0 G, g 2.0060, $t_{\frac{1}{2}}$ (293 K) *ca.* 3 min. The balance between addition to S or to Y in Y=S=Y (Y = O or NR) must be quite fine, and it is possible that the longevity of the adducts (24) gives a false idea of their ease of formation.

The radical $\mathrm{Bu^tN{=}\dot{S}OH}$ (9) presumably arises by a direct hydrogen transfer from $\mathrm{Me_2\dot{C}OH}$ [equation

$$\mathrm{Bu^tO\cdot + Me_2CHOH \longrightarrow Me_2\dot{C}OH + Bu^tOH} \qquad \text{(xvii)}$$

$$\mathrm{Me_2\dot{C}OH + Bu^tNSO \longrightarrow Me_2CO + Bu^tN{=}\dot{S}OH} \qquad \text{(xviii)}$$

$$\mathrm{Me_2\dot{C}OH + Bu^tNSO \longrightarrow Bu^t\dot{N}S(O)C(OH)Me_2} \qquad \text{(xix)}$$

$$\mathrm{Bu^t\dot{N}S(O)C(OH)Me_2 \longrightarrow Bu^tN{=}\dot{S}OH + Me_2CO} \qquad \text{(xx)}$$

(xviii)] or by an addition–elimination sequence [equations (xix) and (xx)].

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* In the limit of complete electron transfer the adduct (22) would be an ion pair $\{[\mathrm{(R_2CH)_2N}]_2\overset{+}{\dot{\mathrm{S}}}\mathrm{Y}\ \bar{\mathrm{O}}\mathrm{Bu^t}\}$ in which much of the spin and charge density resides on nitrogen and there is no covalent S–O bond. The radical cations $[\mathrm{(R_2N)_2SY}]^{+\cdot}$, which are readily detectable by e.s.r. spectroscopy, are produced by electrochemical oxidation of $\mathrm{(R_2N)_2SY}$.[23]

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The nature of the process responsible for the first-order decay of $\mathrm{Et\dot{N}S(O)OBu^t}$ is not clear. It is unlikely to be a γ-scission [equation (xxi)] since the activation energy for such a reaction must be appreciable and the spectrum of the sulphinylaminyl radical does not vary markedly in intensity between 150 and 270 K.

$$\mathrm{Et\dot{N}S(O)OBu^t} \xcancel{\longrightarrow} \mathrm{EtNSO_2} + \mathrm{Bu^t\cdot} \qquad \text{(xxi)}$$

No spectrum from the t-butyl radical adduct of EtNSO was detected at high temperatures. It is possible that the addition of t-butoxyl radicals to *N*-sulphinylethylamine is reversible.

EXPERIMENTAL

E.s.r. Spectroscopy.—The techniques employed for the detection of e.s.r. spectra during continuous u.v. irradiation of samples in the cavity of the spectrometer have been described previously.[27] The kinetics of radical removal were measured by computer-averaging of a large number of e.s.r. signal decay curves produced by positioning a rotating sectored disc in the light path.[9,10] *g* Factors were obtained by measurement of the microwave frequency and the magnetic field at the centre of resonance, and are considered accurate to ±0.0001.

Materials.—Di-t-butyl peroxide was obtained commercially and purified before use: bis(trimethylsilyl) peroxide,[28] azomethane,[29] and azoisobutane [30] were prepared according to published procedures. Bis(diethylamino) sulphide [31] and disulphide,[12,13] bis(dimethylamino) [32] and bis(diethylamino) [33] sulphoxides, *N*-sulphinyl-ethylamine,[34] -cyclohexylamine,[35] and -t-butylamine,[36] and dimethylaminosulphinyl chloride [37] were all synthesised by methods in the literature. The preparations of new compounds are described below. *Bis(pyrrolidino) sulphide*, prepared using the method described for bis(diethylamino) sulphide,[31] had b.p. 66—68 °C at 1 Torr (Found: C, 55.8; H, 9.4; N, 16.4; S, 18.3. $C_8H_{16}N_2S$ requires C, 55.8; H, 9.4; N, 16.3; S, 18.6%). *Bis(pyrrolidino) sulphoxide*, prepared using the method described for bis(diethylamino) sulphoxide [33] but employing 1,4-diazabicyclo[2.2.2]octane as the base, had b.p. 78—79 °C at 0.5 Torr (Found: C, 50.8; H, 8.5; N, 14.6; S, 17.3. $C_8H_{16}N_2OS$ requires C, 51.0; H, 8.6; N, 14.8; S, 17.0%). N-*Sulphinylisopropylamine*, prepared using the method described for *N*-sulphinylethylamine,[34] had b.p. 86 °C at 760 Torr (Found: C, 34.3; H, 6.9; N, 13.0. C_3H_7NOS requires C, 34.3; H, 6.7; N, 13.3%).

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