Electron Spin Resonance Spectra of Selenuranyl Radicals $R_2Se\dot{-}X$

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Summary E.s.r. spectra assigned to the σ^* selenuranyl radicals $R_2Se\dot{-}X$ (R = alkyl or aryl) are detected in solution during photochemical generation of X• [CF_3S•, R′C(O)S•, Me_3CO•, or Me_3SiO•] in the presence of dialkyl or alkyl aryl selenides.

ALTHOUGH a number of homolytic substitution reactions of dialkyl selenides are known [equation (1)],[1,2] intermediate selenuranyl radicals $[R_2SeX]$• have never been detected by e.s.r. spectroscopy.

$$X\bullet + R_2Se \rightarrow RSeX + R\bullet \qquad (1)$$

We have shown previously that trimethylsiloxyl radicals and thiyl radicals with electron-withdrawing substituents add to dialkyl sulphides to give sulphuranyl radicals of the type $R_2S\dot{-}X$ [**1**; X = Me_3SiO, CF_3S, or R′C(O)S] in which the singly occupied molecular orbital (SOMO) is probably an S–O or S–S σ^* orbital.[3,4]

$$R_2S\dot{-}X$$

(1)

We now report that dialkyl selenides also react with these addenda to form selenuranyl radicals which are readily detectable in fluid solution by e.s.r. spectroscopy. During u.v. photolysis of a cyclopropane solution containing Me_2Se and CF_3SSCF_3 the e.s.r. spectrum shown in Figure (a) was obtained and we ascribe the signals to the radical $Me_2Se\dot{-}SCF_3$ [equation (2; R = Me, X = CF_3)]. The spectrum of [**2**; R = 1-adamantyl (1-Ad), X = CF_3S] from di-1-adamantyl selenide[5] showed only coupling to the three fluorine nuclei. Diethyl selenide gave a similar adduct with $CF_3S\cdot$; acylthiyl radicals [from photolysis of R′C(O)-SSC(O)R′, R′ = Bu^t or Et] also gave selenuranyl adducts with all three dialkyl selenides [Figure (b)]. Aryl alkyl selenides[5] also afforded selenuranyl adducts with $CF_3S\cdot$, although splittings from the aryl protons were not resolved. Photolysis of Et_2Se or $1\text{-}Ad_2Se$ alone in hydrocarbon solvents did not give rise to e.s.r. signals, but photolysis of Me_2Se afforded the spectrum of the methyl radical.

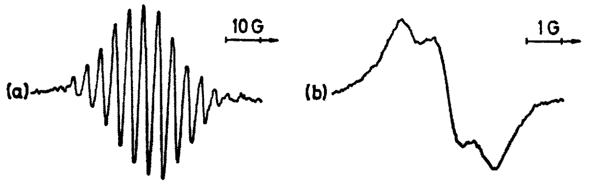


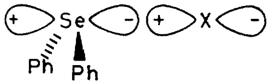
FIGURE. E.s.r. spectra in cyclopropane solvent of the selenuranyl radicals (a) $Me_2Se\dot{-}SCF_3$ at 158 K and (b) $1\text{-}Ad_2Se\dot{-}SC(O)Et$ at 238 K.

$$X\cdot + R_2Se \rightarrow R_2Se\dot{-}X \qquad (2)$$

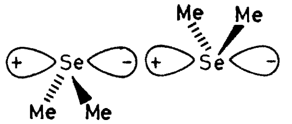
(2)

With trimethylsiloxyl radicals (from photolysis of $Me_3SiOOSiMe_3$) a selenuranyl adduct was detected only with dimethyl selenide.† Selenuranyl adducts were not detected in a previous study[2] of the reaction of t-butoxyl radicals with dialkyl selenides. However, during the photolysis of Bu^tOOBu^t in the presence of Me_2Se we observed, in addition to the spectrum of the methyl radical, a signal which we assign to $Me_2Se\dot{-}OBu^t$. The e.s.r. parameters of the selenuranyl radicals are given in the Table.

There have been three previous reports[6,7] of e.s.r. spectra ascribed to 3-co-ordinate selenium-centred radicals, all trapped in single crystals. The selenuranyl radicals[6] $Ph_2Se\dot{-}Cl$ and $Ph_2Se\dot{-}Br$ appear to adopt the σ^* structures (**3**; X = Cl or Br) related to that proposed for the dimer cation of dimethyl selenide[7] [(**4**), a(12H) 4·6 G, g 2·0344]. The SOMO of (**4**) is a σ^* orbital comprised mainly of Se-4p atomic orbitals.



(3)



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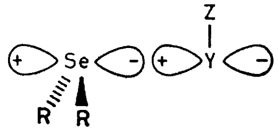

(5)

Y = O, Z = Me_3Si or Me_3C
Y = S, Z = CF_3 or RC(O)

We propose that the selenuranyl radicals (**2**) adopt the similar geometrical and electronic structure (**5**), as probably do the sulphuranyl radicals (**1**).[3,4]‡ The low value of $a(^{77}Se)$ for $1\text{-}Ad_2Se\dot{-}SC(O)Bu^t$ (see Table) corresponds[8] to only *ca.* 3% population of the Se-4s orbital and is consistent with the electronic structure (**5**). The g factors of (**2**) are significantly

TABLE. E.s.r. parameters for the radicals $R^1R^2Se\dot{-}X$ in cyclopropane solution.

R^1	R^2	X	T/K	g-Factor[a]	Hyperfine splittings/G[b]
Me	Me	Me_3SiO	190	2·0206	6·5 (6H)
Me	Me	Me_3CO	148	2·0162	4·9 (6H)
Me	Me	EtC(O)S[c]	160	2·0184	3·5 (6H), 0·7(2H)
Et	Et	EtC(O)S	164	2·0177	3·5 (4H)[d]
1-Ad	1-Ad	EtC(O)S	160	2·0196	1·1 (2H)
Me	Me	$Bu^tC(O)S$	158	2·0189	3·5 (6H)
Et	Et	$Bu^tC(O)S$	160	2·0183	3·5 (4H)
1-Ad	1-Ad	$Bu^tC(O)S$	162	2·0206	162·6 ($1\,^{77}Se$)[e]
Me	Me	CF_3S	158	2·0196	3·8 (6H), 8·4 (3F)
Et	Et	CF_3S	162	2·0191	4·0 (4H), 8·6 (3F)
1-Ad	1-Ad	CF_3S	160	2·0209	9·6 (3F)
p-PhC_6H_4	Me	CF_3S[f]	162	2·0208	4·0 (3H), 8·3 (3F)[g]
Ph	1-Ad	CF_3S[f]	160	2·0200	9·3 (3F)[h]

[a] The g-factors are essentially independent of temperature. [b] Number of equivalent nuclei shown in parentheses. [c] A singlet (g *ca.* 2·0240), assigned[4b] to R′C(O)SS·, was also detected in all experiments involving photolysis of R′C(O)SSC(O)R′. [d] Splitting from the methylene protons of the propionyl group not resolved (ΔB_{p-p} 1·8 G). [e] At 238 K; natural abundance of ^{77}Se ($I = \frac{1}{2}$) is 7·6%. [f] Solvent toluene + cyclopropane *ca.* 1 : 1 v/v. [g] Aryl group splittings not resolved (ΔB_{p-p} 1·6 G). [h] Phenyl group splittings not resolved (ΔB_{p-p} 1·3 G).

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† Diethyl selenide appeared to undergo a rapid thermal reaction with $Me_3SiOOSiMe_3$. Di-1-adamantyl selenide, like Bu^t_2S,[3] is apparently too hindered to give a detectable concentration of adduct with $Me_3SiO\cdot$. Photolysis of MeSSMe in the presence of R_2Se failed to afford spectra attributable to $R_2Se\dot{-}SMe$.

‡ Attempts to detect analogous telluranyl radical adducts of Me_2Te have been unsuccessful.

greater than those of (**1**)[3,4] and this difference can be associated with the relatively large spin–orbit coupling constant for selenium (1688 cm^{-1}) compared with that for sulphur (382 cm^{-1}).[8] The spin population (ρ_{Se}) in the Se-4p orbital may be estimated by comparison of the magnitudes of the methyl proton splittings for (**2**; R = Me) and for (**4**) (in which $\rho_{Se} = 0{\cdot}5$) provided that the usual type of relationship[7] [equation (3)] holds and that the value of B is the same for (**2**) and (**4**). For freely rotating methyl groups the average value of $\cos^2\theta$ is 0·5 and hence B is 18·4 G.

$$a(CH_3) = \rho_{Se}B\cos^2\theta \qquad (3)$$

With these assumptions, ρ_{Se} in (**2**; R = Me) is 0·38 [X = Bu^{t}C(O)S], 0·41 (CF_3S), 0·53 (Me_3CO), and 0·71 (Me_3SiO). The shift of spin density to selenium in $Me_2Se\dot{-}X$ along the series $X = R'C(O)S < CF_3S < Me_3CO < Me_3SiO$ is in accord with the antibonding nature of the SOMO coupled with the higher electronegativity of oxygen compared with that of sulphur.

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