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ESR STUDY OF THE PHENYLSELENINYL RADICAL TRAPPED IN A SINGLE CRYSTAL MATRIX

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Summary

The phenylseleninyl radical has been trapped in an X-irradiated single crystal of Ph_2SeO. The analysis of the hyperfine interaction with ^{77}Se shows that the unpaired electron is mainly localized (~80%) in a selenium $4p_x$-orbital. The ESR parameters are quite similar to those obtained for the radical $Ph_2\dot{As}$ and indicate that the p_x-orbital is probably perpendicular to the CSeO plane. The spin density on the selenium atom in the phenylseleninyl radical is twice as great as that in the phenylselenonyl radical.

Introduction

The identification of paramagnetic damage produced by irradiating compounds containing sulfur or selenium is important to understanding the mechanisms of radiation protection and sensitization [1,2]. Furthermore, when such studies are performed by electron spin resonance (ESR), it is also possible to get information about the electronic configuration of these radical species.

We have previously shown that irradiation of R_3SeHal (R = phenyl group, Hal = Cl or Br) and of R_2SeO_2 lead respectively to the formation of $R_2\dot{Se}Hal$ [3] and $R\dot{Se}O_2$ [4]. In the present work we have produced the radical $R\dot{Se}O$ by irradiating diphenylselenoxide and report (as far as we know) the first ESR study of an organic seleninyl radical trapped in a single crystal matrix. Analysis of the $\bar{g}$ tensor and of the hyperfine interaction with ^{77}Se ($I = \frac{1}{2}$, natural abundance = 7.6%) enables us to determine the localization of the unpaired electron and to propose a structure for the phenylseleninyl radical.

Experimental

Diphenylselenoxide was synthesized by following a published method [5]. Single crystals (obtained by slow evaporation of a solution in benzene) generally have the form of thin needles. Some recrystallizations also gave rise to small plates of larger dimensions, but the crystalline state of these last crystals was not perfect (twinning).

X-irradiation was performed by using a Philips tube no 2184 (tungsten anticathode, 30 mA, 30 kV).

ESR spectra were recorded on a Varian-E9 spectrometer (100 kHz field modulation) at 77 K or at room temperature. The angular dependance of the ESR signals was analysed by using a second order perturbation and a least squares fitting subroutine. The accuracy of the $\bar{g}$ and ^{77}Se hyperfine interaction tensors was checked by comparing the positions of the experimental signals with those obtained by a direct diagonalization of the Hamiltonian.

Results

After an irradiation at 77 K many different radical species are trapped in the crystal, giving rise to unresolved broad lines. The best resolved spectra are obtained by irradiating (at room temperature) a crystal lying on a metallic stem cooled at —90° C. In Fig. 1 we show a spectrum recorded at 77 K and obtained with a crystal (needle) which was irradiated in such conditions. Two kinds of lines are clearly seen in this spectrum, i) very intense lines marked A; ii) satellite lines of very low intensity marked A′. Relative intensities of A and A′

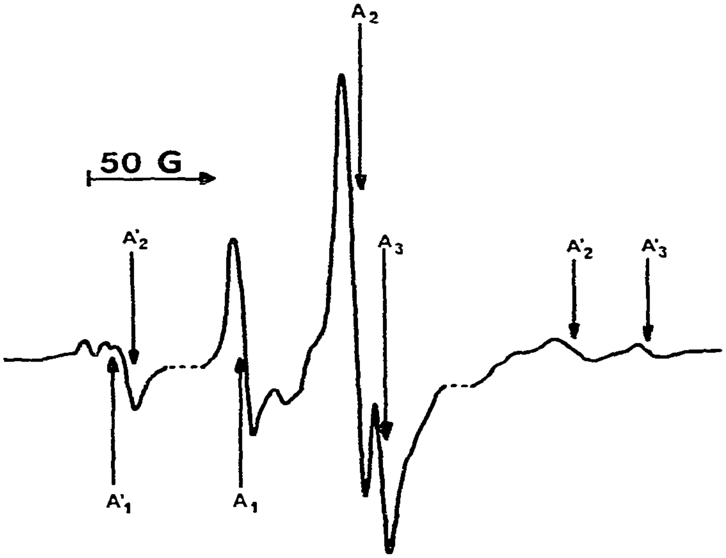


Fig. 1. ESR spectrum obtained at 77 K with an X-irradiated single crystal of Ph_2SeO. (Lines A'_1, A'_2, and A'_3 are due to hyperfine coupling with ^{77}Se and refer respectively to sites 1, 2 and 3. Amplitude gain for A′ lines = 4 × amplitude gain for A lines).

TABLE 1

ESR PARAMETERS OBTAINED AT 77K WITH AN X-IRRADIATED SINGLE CRYSTAL OF Ph_2SeO

		Principal values	direction cosines			Angle g_{min}, T_{max} (°)
Site 1	g	2.052	0.288	0.633	−0.717	
		2.023	−0.465	−0.562	−0.683	
		1.998	−0.836	0.531	0.132	
	^{77}Se-T	256.4	0.843	−0.519	−0.134	
		−86.6	0.161	0.006	+0.986	
		−64.8	−0.511	−0.854	0.089	1
Site 2	g	2.054	0.546	−0.822	−0.156	
		2.023	0.663	0.539	−0.519	
		1.997	0.511	0.179	0.840	
	^{77}Se-T	246.1	0.538	0.190	0.820	
		−90.7	−0.537	0.827	0.160	
		−74.8	−0.648	−0.528	0.548	2
Site 3	g	2.056	0.590	−0.802	−0.088	
		2.023	0.717	0.572	−0.397	
		1.996	0.368	0.171	0.913	

together with the angular variation of these lines show that the signals A′ are due to hyperfine interaction with ^{77}Se. Two sites of a same radical species are in general observed though some orientations even show the different lines of two other sites. The instability of the radicals does not allow studying of an X-irradiated needle at room temperature. Nevertheless this room temperature study has been performed on a crystal of larger size (plate). However, the

TABLE 2

ESR PARAMETERS OBTAINED AT ROOM TEMPERATURE WITH AN X-IRRADIATED SINGLE CRYSTAL OF Ph_2SeO

		Principal values	direction cosines			Angle g_{min}, T_{max} (°)
Site 1	g	2.055	0.649	−0.586	0.483	
		2.019	0.567	0.797	0.206	
		1.998	−0.506	0.141	0.850	
	^{77}Se-T	228.7	0.527	−0.107	−0.842	
		−81.4	0.279	0.958	0.052	
		−74.6	+0.802	−0.262	0.535	25
Site 2	g	2.054	0.243	0.917	0.315	
		2.021	−0.332	−0.226	0.915	
		1.994	0.911	−0.327	0.250	
	^{77}Se-T	223.4	0.933	−0.112	0.341	
		−88.2	0.217	0.932	−0.288	
		−64.0	−0.286	0.343	0.894	13
Site 3	g	2.052	0.335	−0.634	−0.696	
		2.017	0.119	0.761	−0.636	
		1.999	0.934	0.130	0.331	
	^{77}Se-T	244.5	0.924	0.186	0.332	
		−114.9	−0.031	0.906	−0.420	
		−38.6	−0.380	0.378	0.843	3

poor crystallinity of these crystals makes it difficult to determine the angular dependance of the ESR spectra. In these conditions three sites have clearly been seen and a fourth pattern has been detected for some orientations.

In Table 1 and 2 we report the principal values of the $\bar{g}$ and hyperfine coupling tensors respectively obtained in the two experiments previously described.

Discussion

The ^{77}Se hyperfine coupling tensors obtained at 77 K are characterized by an almost axial symmetry. This result (similar to that found for the ^{33}S hyperfine interaction in MeSO [6]) is in good agreement with the identification of PhSeO. A property common to OSCl [7], SO_2^- [8], MeSO [6] and SeO_2^- [9,10] concerns the alignment of the $T_\parallel$ direction for the central atom with the g_{min} direction. This property is also observed for the present radical since the two sites respectively show a g_{min}, ^{77}Se-$T_\parallel$ angle equal to 1° and 2°. As for SeO_2^-, the g_{min} value is particularly low and suggests some participation of the selenium 4*d* orbitals [10].

By studying the coupling with ^{17}O and ^{33}S, Reuveni et al. have shown that for SO_2^- the perpendicular components for ^{33}S are negative. We will assume that this is also true for PhSėO.

The isotropic and anisotropic coupling constants with ^{77}Se are given in Table 3. These parameters can be compared with the values of A^*_{iso} and $2B_0$ which correspond to the coupling constants respectively associated with a 4*s* and a 4*p* electron of atomic selenium. For A^*_{iso} we have used the value given by Morton and Preston [11] (7185 G) whereas $2B_0$ (279.5 G) has been obtained from the semi experimental value of $(1/r^3)$ given by Barnes and Smith [12]. The spin densities have been calculated in the approximation of an axial symmetry of the ^{77}Se coupling tensor. These values are reported in Table 3. It is clear that 80% of the total spin density is localized in a selenium 4*p* orbital. Thus the spin density on the selenium is considerably higher for the seleninyl radical than for the selenonyl radical (39%) [4]. As a comparison, Table 4 shows the spin densities on the central atom observed for O^{77}SeCl, $^{33}SO_2^-$, SeO_2^- and Me^{33}SO. (These data have been calculated by using the atomic parameters reported in [11] and in [12]).

It is worthwhile pointing out that the ESR results for PhSėO are quite similar to those obtained for the radical Ph$_2$Aṡ [13]: the *g* tensors have almost

TABLE 3

ISOTROPIC AND ANISOTROPIC ^{77}Se COUPLING CONSTANTS AND SPIN DENSITIES FOR PhSeO TRAPPED IN Ph$_2$SeO

	A_{iso} (G)	T_1 (G)	T_2 (G)	T_3 (G)	c_s^2	c_p^2
Site 1 (77K)	35.0	221.4	−121.6	−99.8	0.004	0.79
Site 2 (77K)	26.8	219.3	−117.5	−101.6	0.003	0.78
Site 1 (RT)	24.2	204.5	−105.6	−98.8	0.003	0.73
Site 2 (RT)	23.7	199.7	−111.9	−87.7	0.003	0.71
Site 3 (RT)	30.3	214.2	−145.2	−68.9	0.004	0.76

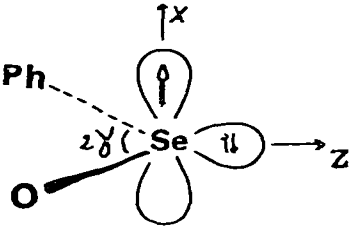
TABLE 4

SPIN DENSITIES ON THE CENTRAL ATOM FOR SOME SULFUR- AND SELENIUM-CONTAINING RADICALS [a]

	c_s^2 (central atom)	c_p^2 (central atom)	Reference
SO_2^-	0.01	0.70	8
MeSO	0.00	0.87	6
SeO_2^-	0.00	0.78	9
OSeCl	0.00	0.99	7

[a] Atomic parameters are obtained from refs. 11 and 12.

the same principal values, the g_{min} direction is parallel to $T_{\parallel}$, the unpaired electron is confined to a *p*-orbital of the central atom. This favours the limiting formula $\mathrm{PhSe^+{-}O^-}$, isoelectronic with $\mathrm{Ph_2\dot{A}s}$, for which a structure in accordance with the ESR results, is given below:



A measure of the angle 2 γ cannot be obtained from hyperfine interaction with ^{77}Se. However, for $\mathrm{Ph_2\dot{A}s}$ the quadrupolar interaction with ^{75}As permitted us to get a value of 98° for this angle and this certainly constitutes a rough estimation for the CSeO angle.

Data reported in Table 2 show that, at room temperature, two sites (marked 1 and 2) have ESR tensors very similar to those obtained at 77 K. In particular, the ^{77}Se-T tensors have a marked axial symmetry and the angle g_{min}, $T_{\parallel}$ is small. The apparent decrease of the spin density in the selenium 4*p* orbital (Table 3) is certainly due to some movement of the radical. For example, oscillations of 25° around the bisector of CSeO lead to a 10% decrease for $T_{\parallel}$ and one of the perpendicular components. However the complexity of the spectra obtained with a large crystal (plate) at room temperature together with the great variety of possible movements prevent any accurate study of this temperature effect.

A third site (marked 3 in Table 2) is observed at room temperature. The corresponding ^{77}Se hyperfine tensor does not present an axial symmetry. An additional site, similar to site 3, is also detected for some orientations. The identification of the radical species giving rise to these signals is rather difficult. Nevertheless, as the g tensor is close to those obtained for $\mathrm{PhS\dot{e}O}$ (see above) and the g_{min} direction is aligned along the T_{max} direction we suggest that these spectra are due to a phenylseleninyl radical trapped in a conformation slightly different of that found for sites 1 and 2. Diphenylselenoxide is isomorphous with diphenylsulfoxide [14]. For $\mathrm{Ph_2SO}$ the crystalline structure shows that weak CH ... O bonding occurs between one of the phenyl groups and an oxygen of a neighboring molecule. The difference between sites 1 and 2 and site 3 can be due to the non-equivalence of the two phenyl groups; the presence of an interaction between a benzenic hydrogen and an oxygen preventing the radical of site 3 adopting its most stable conformation. From the crystallographic data the angle between the normals to the planes C_1SO and C_7SO is found to be equal to 78°; this value is in good agreement with our interpretation since the angle T_{max} (site 1), T_{max} (site 3) is equal to 77°. We have already discussed [15] important matrix effects for molecules, such as $Ph_2\dot{P}$, bearing a lone pair on the central atom. Furthermore marked matrix dependances have also been reported for the ESR parameters of SeO_2^- [10].

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