

**997. Oxides and Oxyions of the Non-metals. Part VI.¹
Radical Anions of Selenium.**

By P. W. ATKINS, M. C. R. SYMONS, and H. W. WARDALE.

Exposure of sodium and potassium selenates and selenites to γ -radiation, both at 77°K and room temperature, gave paramagnetic centres whose hyperfine and g -tensors are as expected for the radical ions SeO_2^- and SeO_3^- . The results are compared with those for the corresponding radicals of chlorine and sulphur. A further radical is tentatively identified as SeO_4^- .

CONTINUING our studies of the structure of non-metal oxides, we have used the technique of γ -radiolysis in an attempt to prepare paramagnetic oxyions of selenium. So far as we are aware, no oxy-radical of selenium has yet been described, although analogous oxy-radicals of chlorine, sulphur, and phosphorus are known,¹ and recently Horsfield² has reported the radical AsO_3^- .

EXPERIMENTAL AND RESULTS

Materials.—Sodium and potassium selenates and selenites of the highest available grade were used as finely ground powders.

γ -Irradiation.—Samples were irradiated at either room temperature or 77°K with a 1900C ⁶⁰Co source for at least twelve hours.

Electron-spin Resonance.—Measurements were made at room temperature or 77°K at X-band frequencies on a spectrometer described previously³ and on a Varian V4502-03 EPR spectrometer.

Parameters were obtained from the spectra by the method recommended by Kneubühl⁴ and are recorded in Table 1. The quoted g -values have been corrected, where applicable, for the effect of the off-diagonal elements of the spin-Hamiltonian arising from the large hyperfine interactions. Typical spectra are given in Figs. 1—3.

Derivation of Molecular Parameters.—Electron populations were calculated by using the atomic self-consistent field values⁵ $|\psi_s(0)|^2 = 15.7791$ a.u. and $\langle r^{-3} \rangle_{4p} = 9.2284$ a.u. and are recorded in Table 2. The bond angle in SeO_3^- was calculated on the assumption that Coulson's formulae⁶ were applicable. All overlap contributions were neglected.

DISCUSSION

Identification.—In common with most studies of radiation damage, there is no direct method for identifying the paramagnetic species formed. Ordinary analytical methods are of little use since many diamagnetic break-down products are also formed.

However, since the electron-spin resonance spectra of a variety of oxy-radicals of first- and second-row elements are known,¹ a reasonably firm identification can be made by

¹ Considered as Part V of this series, Symons, *Advances in Chemistry Series*, 1962, **36**, 76.

² Horsfield, personal communication.

³ Brivati, Keen, and Symons, *J.*, 1962, **237**.

⁴ Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

⁵ Morton, Rowlands, and Whiffen, National Physical Laboratory Report No. B.P.R. 13, 1962.

⁶ Coulson, Victor Henri Vol. Commemoratif, "Contribution a l'Etude de la Structure Moleculaire."

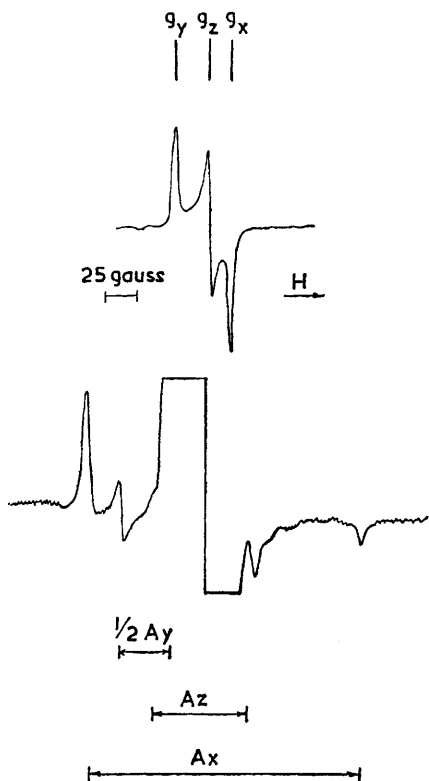


FIG. 1. Electron-spin resonance spectrum from γ -irradiated potassium selenite at 300°K.

FIG. 2. Electron-spin resonance spectrum from γ -irradiated potassium selenate at 300°K.

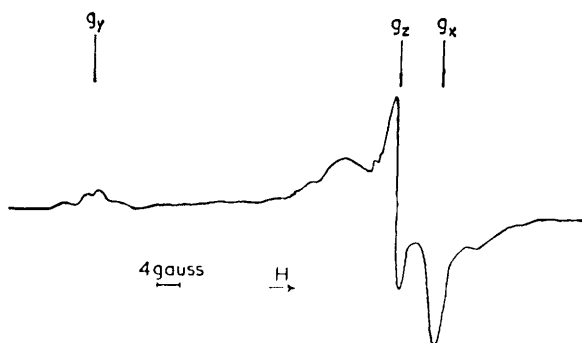
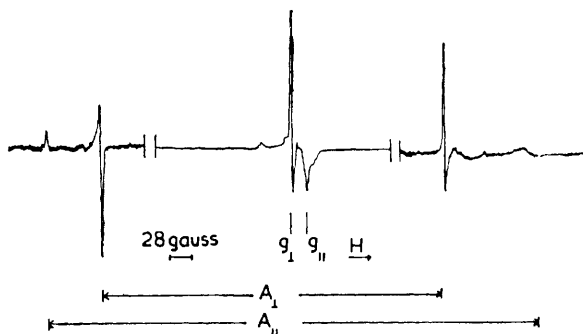


FIG. 3. Electron-spin resonance spectrum from γ -irradiated potassium selenate at 77°K.

TABLE 1.

Electron spin resonance results for γ -irradiated selenates and selenites.

Radical	Medium	Measure-		g Values				A_x	A_y	A_z	A_{iso}
		temp.	ment temp.	g_x	g_y	g_z	g_{av}				
I (SeO_3^-)	Na_2SeO_4	77°	77°	1.9975	2.0317	2.0066	2.0119				
		77	300	1.9973	2.0306	2.0068	2.0116				
		77	77 ^a	1.9974	2.0318	2.0072	2.0121				
		300	300	1.9971	2.0301	2.0065	2.0112				
		300	300	1.9986	2.03	2.0090	—	130	-80	-48	160 ^b
		300	300	1.9976	2.0309	2.0096	2.0127				
	K_2SeO_3	77	77	1.9987	2.0304	2.0102	2.0131				
		77	77 ^a	1.9976	2.0305	2.0094	2.0125				
		300	300	1.9985	2.0297	2.0097	2.0126				
		300	300	1.9986	2.03	2.0118	—	109	-59	-50	141 ^b
		77	300	1.9970	2.0305	2.0050	2.0108				
		300	300	1.9974	2.0310	2.0059	2.0114				
II (SeO_3^-)	K_2SeO_4	300	300	2.0156	2.0156	2.0030	2.0114				
		300	300	2.0150	2.0150	2.0037	2.0112	-63	-63	126	490 ^c
		77	77	2.0148	2.0148	2.0025	2.0107				
III (SeO_4^-)	K_2SeO_4	77	77	2.0021	2.0452	2.0072	2.0182				
					2.0423		2.0172				
		77	300	2.0013	2.0394	2.0076	2.0161				
	77	77 ^a	2.0016	2.0455	2.0069	2.0180					
	Na_2SeO_4	77	77	—	2.0436	—	—				

^a Re-cooled from 300°K. ^b g -Values measured from hyperfine components. ^c g -Values measured from hyperfine components and corrected for second order shifts.

TABLE 2.

Calculated spin populations in SeO_3^- and SeO_2^- .

Species	Medium	a_z^2	a_{px}^2	a_{pz}^2	a_o^2	p/s ratio	ϕ
SeO_3^-	K_2SeO_4	0.10	—	0.47	0.43	4.7	112°
SeO_2^-	K_2SeO_3	0.03	0.39	0.02	0.61	13	—
	Na_2SeO_4	0.03	0.44	0.01	0.56	14.7	—

Parameters refer to a co-ordinate system in which z is the major rotation axis and, in C_{2v} , x is perpendicular to the molecular plane. ϕ is the $\angle\text{OXO}$ angle.

comparison with the results for isostructural radicals, and these identifications can be reinforced by theoretical considerations.

Comparison of the results for radicals trapped in irradiated selenates and selenites, with those for oxyradicals of sulphur, chlorine, and arsenic (Table 3), strongly suggests that these are primarily SeO_2^- and SeO_3^- . The results are discussed in terms of this postulate.

TABLE 3.

 g -Tensors and molecular parameters for related radicals.

Radical	Medium	g_x	g_y	g_z	g_{av}	a_z^2	a_{px}^2	a_{pz}^2	a_o^2	p/s ratio	ϕ	Ref.
SO_4^-	$\text{K}_2\text{S}_2\text{O}_8$	2.0035	2.0327	2.0084	2.0149							^a
ClO_3^-	NH_4ClO_4	2.008	2.008	2.007	2.0076	0.08		0.34	0.58	4.5	112°	^b
SO_3^-		2.004	2.004	2.003	2.0036	0.13		0.49	0.38	3.8	111	^c
PO_3^{2-}	Na_2HPO_3	2.001	2.001	1.999	2.0003	0.16		0.53	0.31	3.3	110	^d
AsO_3^{2-}		1.999	1.999	1.992	1.997	0.18		0.60	0.22	3.3	110	^e
ClO_2^-	KClO_4	2.0036	2.0183	2.0088	2.0102	0.01	0.69	0.03	0.31			^b
NO_2^{2-}	KCl	2.0038	2.0099	2.0070	2.0070	0.03	0.64		0.36			^f

^a Atkins, Brivati, Horsfield, Symons, and Trevalion, Sixth International Symposium on Free Radicals, Cambridge, 1963. ^b Atkins, Brivati, Keen, Symons, and Trevalion, *J.*, 1962, 4785. ^c Chantry, Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1962, 5, 233. ^d Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, 4, 473. ^e Horsfield, personal communication. ^f Atkins and Symons, *J.*, 1962, 4794.

The identification of Radical III as SeO_4^- is less firm since no hyperfine features from ^{77}Se could be detected. Furthermore, although there is a well-defined feature giving one g -value, the other features are concealed by the spectra of SeO_3^- and SeO_2^- and hence only

approximate values can be derived (Table I). Nevertheless the approximate g -tensor is in accord with expectation for distorted SeO_4^- radicals, being quite similar to that for SO_4^- in irradiated potassium persulphate.⁷ The absence of hyperfine features is then reasonable since the unpaired electron is expected to be largely confined to a non-bonding molecular orbital on oxygen. Finally, since Radical III is only obtained by irradiation at 77°K, it must be a precursor of SeO_3^- and SeO_2^- formed at room temperature. This could well be SeO_4^- .

The Radical SeO_2^- .—Because of the greater magnitude of the spin-orbit coupling constant for selenium (1688 cm^{-1}) than that for sulphur (382 cm^{-1}), we would expect a larger variation in the g -factor, as found. However, the low value for g_{xx} is surprising since on simple theory one might expect Δg_{xx} to be very small, as is found for SO_2^- and ClO_2 , since the g -shift for this direction arises from the mixing of b_1 and a_2 or a_1 and b_2 orbitals. The occupied orbital in SeO_2^- is a b_1 orbital, so that one would expect the g -shift to be due to the virtual excitation $a_2 \rightarrow b_1$. However, if we assume that the molecular orbital is built only from atomic p_x orbitals, then these orbitals have no component of angular momentum about the x -axis, in other words, the matrix elements $\langle a_2 | L_x | b_1 \rangle$ disappear and no g -shift would be expected. If, however, there are empty selenium d -orbitals not too far removed from the b_1 energy, it is quite probable that we should properly write the b_1 molecular orbital as

$$\Psi(b_1) = \alpha\psi_x + \delta\psi_{xz} - \frac{\beta}{\sqrt{2}}(\phi_{x_1} + \phi_{x_2}) \quad (1)$$

with $\alpha^2 + \delta^2 + \beta^2 = 1$. Here the ψ_x and ψ_{xz} are selenium p_x and d_{xz} orbitals and the ϕ_{x_i} are p_x orbitals on the oxygen atoms. For a linear molecule δ is necessarily zero, but for the

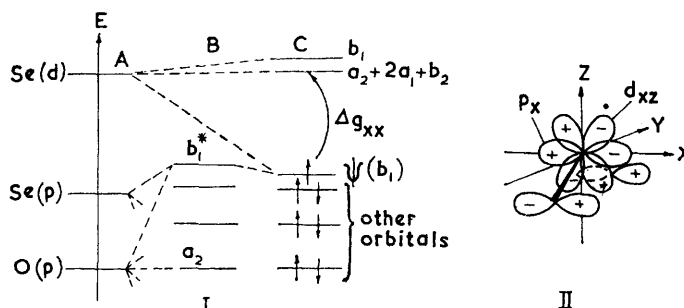


FIG. 4. (I) Proposed energy level diagram for SeO_2^- . A, Atomic orbital energy levels. B, Molecular orbital energies excluding d orbitals. C, Molecular orbital energy levels including d -orbitals.

(II) Atomic orbitals involved in the b_1 molecular orbital.

C_{2v} molecule we are considering, involvement of the d_{xz} orbital is favourable as it is *bonding* between the selenium and oxygen atoms. Since, on the basis of Walsh's diagrams⁸ for 19-electron oxides, the b_1 orbital is probably closest to the d orbitals under consideration, the other d orbitals (which transform as $a_2 + b_2 + 2a_1$ in C_{2v}) are probably less involved in bonding. The situation envisaged is indicated in Fig. 4. With the molecular orbital $\Psi(b_1)$ of eqn. (1), the matrix elements $\langle a_2 | L_x | b_1 \rangle$ do not disappear when we remain within the d -manifold, that is, the g_{xx} -shift can arise by mixing a d -orbital of a_2 symmetry with one of b_1 symmetry. Since the upper a_2 molecular orbital is essentially a pure d_{xy} orbital on selenium we can estimate that

$$\Delta g_{xx} \simeq \frac{4\lambda(\text{Se})\delta^2}{E(b_1) - E(a_2)} \quad (2)$$

⁷ Atkins, Brivati, Horsfield, Symons, and Trevalion, Sixth International Symposium on Free Radicals, Cambridge, 1963.

⁸ Walsh, *J.*, 1953, 2266.

where $\lambda(\text{Se})$ is the spin-orbit coupling constant of selenium (1688 cm.^{-1}) and $E(a_2) - E(b_1)$ is the separation of the a_2 and b_1 orbitals. This predicts a negative Δg_{zx} , as is observed, and, using the $4s^2 4p^2 4d^5 D - 4s^2 4p^4 {}^3P$ energy separation of $63,400 \text{ cm.}^{-1}$ given by Moore⁹ for the value of $E(b_1) - E(a_2)$, we can estimate that $\delta^2 \sim 0.04$, which on this theory is the amount of selenium d orbital involved in $\Psi(b_1)$.

The anisotropic hyperfine coupling tensor, \mathbf{A} , of SeO_2^- has not the axial symmetry expected for the tensor if it arose from an electron in a pure p orbital on selenium. It is possible to approximate the observed tensor by the sum of two tensors axially symmetric about different axes, \mathbf{A}^x and \mathbf{A}^z say. Then

$$\mathbf{A} = \mathbf{A}_\xi^x + \mathbf{A}^z \quad (3)$$

The superscripts refer to the principal axis and the subscript indicates that \mathbf{A}^x depends upon the choice of ξ . We can obtain solutions of (3) within experimental accuracy when ξ is

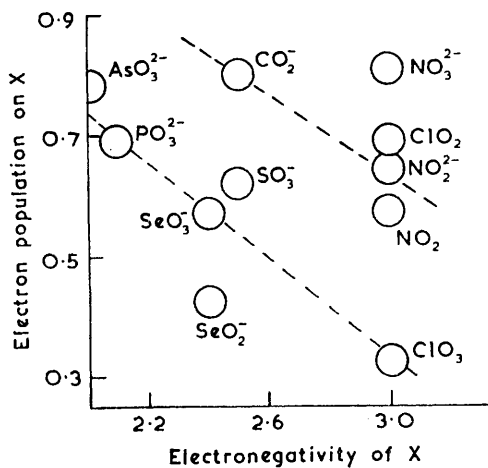


FIG. 5. Variation of the total electron population on X with electronegativity of X for the two isoelectronic series XO_2^{n-} and XO_3^{n-} .

y or z . For $\mathbf{A} = (109.3, -59.1, -50.2)$ gauss, we have (i) $\mathbf{A}_y^x = (106.4, -53.2, -53.2)$, $\mathbf{A}^y = -(-3.0, 6.0, -3.0)$ gauss, (ii) $\mathbf{A}_z^x = (112.2, -56.1, -56.1)$, $\mathbf{A}^z = (-3.0, -3.0, 6.0)$ gauss.

Ordinarily, we would reject (i) as giving the wrong sign of \mathbf{A}^z , then (ii) would correspond to a polarisation of the full $p_z(a_1)$ orbital. However, (i) could be acceptable if contributions from selenium d orbitals were important, since if in $\Psi(b_1)$ δ was not zero the ψ_{zx} would give a contribution of the form $\mathbf{A}^y = (\gamma, -2\gamma, \gamma)$, that is, a tensor axially symmetric about the y axis. If both ψ_{zx} and p_z contributed to the observed tensor, then only their *difference* would be measured by a tensor of the form \mathbf{A} , this is because two equal tensors \mathbf{A}^z and \mathbf{A}^y would have a sum which would itself be axially symmetric about the x -axis and hence indistinguishable from \mathbf{A}^x ; thus the analysis cannot lead to a direct determination of δ^2 .

It is interesting to note the trend of electron populations in the series XO_2^{n-} and XO_3^{n-} , illustrated in Fig. 5, where the population on X is plotted against its electronegativity χ . The value for SeO_2^- is remarkably at variance to the expected trend. This is difficult to account for at the moment, but it may be due either to d -orbital involvement or to a major change in bond angle, of the sort which removes NO_3^{2-} from the XO_3^{n-} curve.¹ If by a reduction in the $\angle \text{OSeO}$ angle the O-O bonding increases, then the electron may well be more localised on the oxygens than would normally be expected.

The Radical SeO_3^- .—The electron populations in this radical are in line with those of analogous radicals¹ and the estimated bond angle of 112° is reasonable for such a radical. The g value of SeO_3^- is greater than for SO_3^- and PO_3^{2-} as would be expected. As both the

⁹ Moore, "Atomic Energy Levels," Vol. 2, National Bureau of Standards, Washington, 1952.

g and A tensors are axially symmetric nothing can be said about possible d -orbital involvement.

The Radical SeO_4^- .—If the tentative identification of radical III as SeO_4^- be accepted, then we must conclude that, as with SO_4^- ,⁷ there is considerable distortion from tetrahedral configuration. This may, in part, arise because of an unsymmetrical "crystal field" from surrounding ions, but the remarkable similarity between g_{xx} for the radicals in K_2SeO_4 and Na_2SeO_4 at 77°K suggests that the distortion is very much a property of the radical itself. The reduction in Δg_{xx} for the radical in K_2SeO_4 at higher temperatures is probably a result of a general loosening of environmental constraints. The marked broadening of all features is thought to be a consequence of efficient spin-lattice relaxation. Indeed, if the radical had T_d symmetry, the unpaired electron would be in a t_1 orbital, and under these circumstances relaxation would be expected to be efficient.¹

This distortion, reflected in the g -tensor, may also account for the fact that the magnetic centre is not mobile. This alone is unlikely to cause permanent trapping on one site, however, and thus it is possible either that the SeO_4^- unit moves towards a neighbouring SeO_4^{2-} to give a weakly bonded dimer, in a manner comparable with the hal_2^- centres in alkali halide crystals, or that the trapped radical is closely associated with a cation vacancy which is required to give charge compensation.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
LEICESTER.

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