

Oxides and Oxyions of the Non-metals. Part XV.¹ Electron Spin Resonance Spectra of Some Selenium and Bromine Radicals

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Exposure of various crystalline bromates to ⁶⁰Co γ -rays at 77 K gave radicals identified by their e.s.r. spectra as BrO₂ and BrO₃. Barium sulphate doped with bromate gave BrO₃ together with another bromine-containing radical tentatively identified as BrO₃²⁻. Frozen aqueous glasses containing bromate ions gave only BrO₂ on irradiation and annealing.

Similar treatment of selenates gave the radicals SeO₂⁻, SeO₃⁻, and SeO₄⁻, together with the previously unknown radical SeO₄³⁻. The latter was formed predominantly when aqueous glasses containing selenate ions were irradiated at 77 K. They were also formed in aqueous selenite glasses.

The electronic structures of these radicals are discussed in the light of these results and compared with those for other isoelectronic species.

In an earlier study of γ -irradiated potassium bromate at 77 K, only the BrO₃ radical was detected² by e.s.r. spectroscopy. Since many other oxy-radicals of chlorine are known,³⁻⁵ a search was initiated for comparable radicals of bromine, especially BrO₂. During the course of this study, a brief report on the formation of BrO₂ in irradiated zinc bromate has appeared.⁶

In extending our studies of the oxyions of selenium,⁷ we sought in particular the ion SeO₄³⁻, which is isoelectronic with the known ion AsO₄⁴⁻.⁸ The hyperfine

tensor for ⁷⁷Se in this ion was of potential interest since there is a marked difference in the hyperfine tensors for AsO₄⁴⁻ and PO₄⁴⁻⁹ on the one hand, and ClO₄²⁻ on the other.⁵ We previously envisaged a rather sharp switch in structure⁵ and on this basis expected that SeO₄³⁻ would clearly resemble one type or the other rather than having intermediate properties.

Three methods have been used in these studies: irradiation of pure salts, irradiation of doped host salts,

¹ Part XIV, S. Subramanian and M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 2367.

² A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 918.

³ R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. (A)*, 1968, 2433.

⁴ R. S. Eachus, P. R. Edwards, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1968, 1704.

⁵ M. B. D. Bloom, R. S. Eachus, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 1235.

⁶ M. A. Collins, M. M. Cosgrove, and G. P. Betteridge, *J. Phys. (B)*, 1970, 3, L40.

⁷ P. W. Atkins, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. (A)*, 1964, 5215.

⁸ M. Hampton, F. G. Herring, W. C. Lin, and C. A. McDowell, *Mol. Phys.*, 1966, 10, 565.

⁹ M. C. R. Symons, *J. Chem. Phys.*, 1970, 53, 857.

and irradiation of frozen aqueous glasses. The first is the most direct, but suffers from the fact that both electron-excess and electron-deficient radicals are often formed together, and initial products are often not readily trapped because of their mobility *via* electron transfer. The second method is particularly useful for the preparation of radicals having the same charge as the host anions. Thus if the dopant ion has one less charge, electron gain is achieved,¹⁰ whilst dopant ions having one extra charge commonly lose one electron readily.¹¹ The last method is only effective provided good glasses are obtained.¹² If the salt in question is not a glass-former in aqueous solution, then various additives can be included to eliminate phase-separation. In this work we generally used magnesium chloride, which gives excellent aqueous glasses.

EXPERIMENTAL

Materials were of reagent grade and were not further purified. Samples were prepared as described previously.^{3,5,10,11} They were irradiated, generally at 77 K, in a Vickrad source at a nominal dose-rate of 4 Mrad h⁻¹ for periods up to 2 h. E.s.r. spectra were run on a Varian E3 spectrometer at 77 K. Samples were annealed by controlled warming for suitable intervals and re-cooling to 77 K for measurement.

RESULTS AND DISCUSSION

Identification.—There can be little doubt that the radical designated as BrO₂ in Table 1 is correctly identified. Bromine has two almost equally abundant isotopes, ⁷⁹Br and ⁸¹Br, both having $I = \frac{3}{2}$. Features from both are clearly resolved, showing that the radical contains one bromine atom with the unpaired electron in a π^* orbital. The form of the g - and A -tensors is very similar to that for ClO₂,⁴ the larger spread in g -values being an expected consequence of the greater spin-orbit coupling constant for bromine. Our results differ somewhat from those of others,⁶ especially in the perpendicular region. The powder spectra rule out the value of 172 G for A_{yy} (Figure 1). As in previous studies,^{2,4,13} we have estimated the 'perpendicular' parameters from the $\pm \frac{3}{2}$ lines, which are clearly defined in the powder spectra. This procedure has been found to give parameters close to those derived from detailed single-crystal studies of the same radicals, in which large quadrupole effects have been detected. Such effects are to be expected for BrO₂, but we believe that our numerical data are not significantly influenced thereby, and can be taken as sufficiently accurate for use in estimating spin-densities by the normal approximate methods.

The major isotope for selenium is non-magnetic, but ⁷⁷Se with $I = \frac{1}{2}$ is present in 7.5% abundance. The isotropic contribution to the ⁷⁷Se hyperfine tensor for radicals described as SeO₄³⁻ (Table 2) is far greater even than that for SeO₃⁻ radicals,⁷ and the estimated spin-

density is comparable with those for AsO₄⁴⁻ and PO₄⁴⁻ radicals.^{8,9} This strongly supports our identification, and we know of no other reasonable formulation.

The radical designated BrO₃²⁻ in Table 1 is only tentatively identified. Certainly it is expected to be formed in barium sulphate doped with bromate ions, but unfortunately many of its expected features are concealed

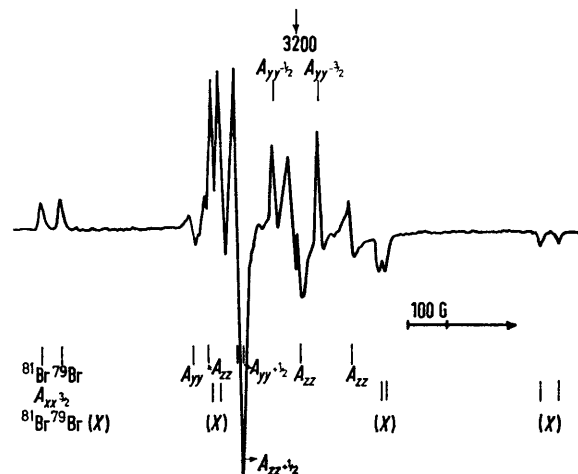


FIGURE 1 E.s.r. powder spectrum of γ -irradiated $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 300 K. The parallel and outermost 'perpendicular' features assigned to BrO₂ are indicated

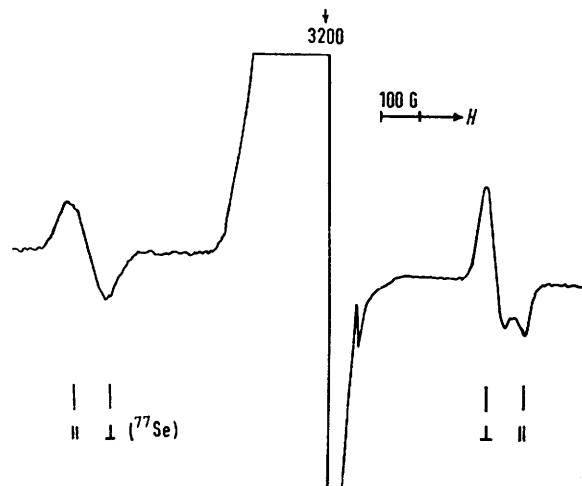


FIGURE 2 E.s.r. spectrum of a γ -irradiated frozen aqueous solution of potassium selenate at 77 K, showing features assigned to ⁷⁷SeO₄³⁻

by more intense lines from BrO₃, which is formed in relatively high yield in these crystals. Only one set of features were clearly resolved, so we are not able to estimate the g - or A -tensors for this species, and hence unfortunately cannot compare it with the ion ClO₃²⁻, identified in irradiated potassium chlorate.³

Sodium and potassium bromate both gave BrO₃ in good yield, the former being trapped in two quite distinct

¹⁰ R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. (A)*, 1968, 790.

¹¹ S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. (A)*, 1970, 1239.

¹² K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc. (A)*, 1971, 2163.

¹³ R. C. Catton and M. C. R. Symons, *J. Chem. Soc. (A)*, 1969, 446.

sites. Low yields of BrO_2 were obtained for the potassium salt only. Barium bromate gave BrO_3 only, again in two sites, but in contrast zinc bromate gave only BrO_2 , with no trace of BrO_3 . Again, the only bromine radical detected in irradiated aqueous solutions at 77 K was BrO_2 .

be positive, and A_{\perp} positive or negative) (Table 3). The resulting spin-densities on bromine are compared with those for similar radicals in Figure 3, whence it can be seen that only the negative sign for A_{\perp} gives a reasonable result. Indeed, by use of this sign the plot is so good that a reasonable value for the spin-density on bromine

TABLE 1
E.s.r. parameters for some oxy-radicals of bromine in γ -irradiated bromates

| Medium | Species | g_{xx} | g_{yy} | g_{zz} | A_{xx} | A_{yy} | A_{zz} |
|--|--------------------------------|----------|----------|----------|----------|----------|----------|
| NaBrO ₃ ^{a,b} | BrO ₃ (I) | 2.037 | | | 908 | | |
| | BrO ₃ (II) | 2.036 | | | 845 | | |
| MgCl ₂ .6H ₂ O ^{a,b} | | | | | | | |
| NaBrO ₃ | BrO ₂ | 1.979 | 2.057 | | 364 | 120 | |
| aqueous glass | | | | | | | |
| KBrO ₃ ^{a,c} | BrO ₃ | 2.027 | 2.102 | 2.076 | 853 | 501 | 497 |
| KBrO ₃ ^{a,b} | BrO ₂ | 1.980 | | | 446 | | |
| Ba(BrO ₃) ₂ ^{a,b} | BrO ₃ (I) | 2.033 | | | 920 | | |
| | BrO ₃ (II) | 2.032 | | | 877 | | |
| BrO ₃ ⁻ doped ^{a,b} | BrO ₃ | 2.036 | | | 872 | | |
| BaSO ₄ | | | | | | | |
| | BrO ₃ ²⁻ | 2.012 | | | 659 | | |
| Zn(BrO ₃) ₂ .6H ₂ O ^a | BrO ₂ | 1.981 | 2.055 | 2.046 | 450 | 130 | 110 |
| Zn(BrO ₃) ₂ .6H ₂ O ^d | BrO ₂ | 2.005 | 2.056 | 2.068 | 483 | 172 | 121 |

^a Present work. The g - and A -values have been calculated for ⁸¹Br isotope using the Breit-Rabi equation. The errors in g -values are ± 0.001 and those in A values are ± 1 G. ^b The blank spaces correspond to features which were either poorly defined or hidden by lines from other radicals. ^c Values reported in ref. 2. ^d Values reported in ref. 6. These g - and A -values have probably not been corrected using the Breit-Rabi equation. Only data for ⁸¹Br isotope has been included for comparison.

TABLE 2
E.s.r. parameters for some oxy-radicals of selenium

| Medium | Radical | g_{xx} | g_{yy} | g_{zz} | A_{xx} | A_{yy} | A_{zz} | A_{iso} |
|---|--------------------------------|----------|----------|----------|----------|----------|----------|-----------|
| BaSeO ₄ ^{a,b} | SeO ₂ ⁻ | | | 2.011 | | | 120 | |
| Na ₂ SeO ₄ ^b | SeO ₂ ⁻ | 1.9975 | 2.0317 | 2.0066 | 290 | 80 | 112 | 160 |
| K ₂ SeO ₃ ^c | SeO ₃ ⁻ | 1.9976 | 2.0309 | 2.0096 | 250 | 82 | 91 | 141 |
| BaSeO ₄ ^a | SeO ₃ ⁻ | 2.016 | 2.016 | 2.001 | 379 | 379 | 575 | 444 |
| K ₂ SeO ₃ ^c | SeO ₃ ⁻ | 2.0148 | 2.0148 | 2.0025 | 427 | 427 | 616 | 490 |
| BaSeO ₄ ^d | SeO ₄ ⁻ | 2.001 | 2.041 | 2.007 | ~50 | | | |
| K ₂ SeO ₄ ^c | SeO ₄ ⁻ | 2.0021 | 2.0452 | 2.0072 | | | | |
| BaSeO ₄ ^d | SeO ₄ ³⁻ | | | | ~980 | | | |
| SeO ₄ ²⁻ ^a | SeO ₄ ³⁻ | 2.033 | 2.003 | 1.999 | 977 | 995 | 1148 | 1040 |
| doped Ba ₃ (PO ₄) ₂ | | | | | | | | |
| K ₂ SeO ₄ ^a | SeO ₄ ³⁻ | 2.031 | 2.002 | 2.000 | 1023 | 1032 | 1193 | 1082 |
| aqueous glass | | | | | | | | |
| K ₂ SeO ₃ | SeO ₄ ³⁻ | 2.031 | 2.002 | 2.000 | 1023 | 1032 | 1193 | 1082 |
| aqueous glass | | | | | | | | |

^a Present work. The g - and A -values have been calculated using the Breit-Rabi equation. The errors in g -values ± 0.001 and those in A values are ± 1 G. ^b The blank spaces correspond to features which are not well defined for measurement. ^c Values reported in ref. 7. ^d The g - and A -values have been calculated without applying Breit-Rabi correction.

TABLE 3
Calculated spin populations for some 33-electron XO₄-type radicals and for BrO₂

| Radical | B_{xx} | B_{yy} | B_{zz} | A_{iso} | a_s^2 | a_p^2 | $a_s^3 + a_p^3$ | p/s |
|-----------------------------------|----------|----------|----------|-----------|---------|---------|-----------------|-------|
| ClO ₄ ²⁻ | -3.3 | 0 | 3.3 | 67.8 | 0.044 | 0.03 | 0.074 | 1 |
| PO ₄ ⁴⁻ | -49.6 | -36.3 | 86.1 | 1146.1 | 0.31 | 0.42 | 0.73 | 1.3 |
| AsO ₄ ⁴⁻ | -38.2 | -38.2 | 76.4 | 1084.7 | 0.32 | 0.42 | 0.74 | 1.3 |
| SeO ₄ ³⁻ | -63 | -45 | 108 | 1040 | 0.22 | 0.40 | 0.62 | 1.7 |
| BrO ₂ ^{a(i)} | 380 | -200 | -180 | 70 | 0.008 | 0.674 | 0.682 | 84 |
| BrO ₂ ^{a(ii)} | 220 | -100 | -110 | 230 | 0.027 | 0.390 | 0.417 | 14.44 |

^a (i) Taking A_{\perp} as negative. (ii) Taking A_{\perp} as positive.

All the radicals in Table 2, namely SeO_2^- , SeO_3^- , and SeO_4^{3-} , were detected in irradiated barium selenate, but only the last of them was clearly formed in irradiated frozen aqueous solutions (Figure 2).

Electronic Structure.—Approximate spin-densities in the 4s and 4p orbitals for bromine in BrO_2 have been calculated from the two reasonable tensors (A_{\parallel} taken to

could have been predicted from the electronegativity value. This correlation lends some support to our approximate method for estimating orbital populations, and also supports our neglect of bromine d orbitals.

A similar plot for the 33-electron XO_4 radicals (Figure 4) shows that the results for ClO_4^{2-} (if indeed this species has been correctly identified) are quite anomalous.

Possible reasons for this dramatic difference have been given earlier.⁵ Again there is no call for the inclusion of *d* orbitals on selenium to explain the hyperfine parameters, and indeed the major positive deviation in g_{xx}

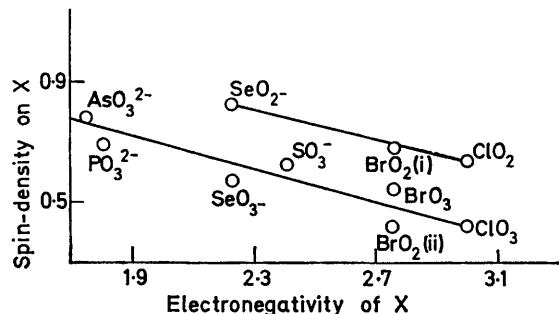
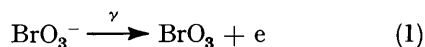


FIGURE 3 Spin density on the central atom X in XO_2 as a function of electronegativity of X. Results for XO_3 radicals are given also for comparative purposes (i) BrO_2 taking A_{\perp} negative, (ii) taking A_{\perp} positive

is opposite to expectation for significant *d* orbital participation.

Reaction Mechanisms.—It seems that BrO_3^- can lose an electron fairly readily [reaction (1)], and the resulting



trioxide is readily trapped; but the expected electron-trapping step (2), if it occurs, must be followed by further



reactions even at 77 K, since BrO_3^{2-} was detected in one instance, and then only tentatively. In water, and

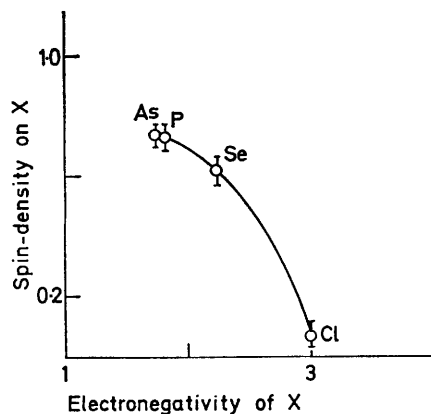
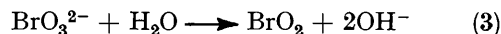


FIGURE 4 Spin density on the central atom X in XO_4 as a function of electronegativity of X

hydrated zinc bromate, it is probable that BrO_3^{2-} becomes protonated, with concomitant loss (3) of hydr-

oxide ion. It is now clear that such protonation, even



at 77 K, can be most important¹⁴ and we suggest that this explains the predominant formation of BrO_2 in these aqueous lattices. Another route for BrO_2 formation in such lattices is reaction (4) with hydrogen atoms. The fate of BrO_3^{2-} or the liberated electrons in



the anhydrous bromate is not clear. We have previously suggested that ClO_3^{2-} may break down [reaction (5)] to give chloride and ozonide ions, and as ozonide ions are certainly formed in these bromates, it may be significant here also. Oxygen-atom transfer is known



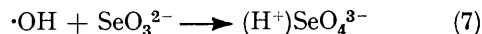
to be important since BrO_4^- has been shown to be a significant final damage product,¹⁵ but this is far more likely to arise [reaction (6)] from BrO_3 on warming,



rather than from BrO_3^{2-} . However, no clear evidence for reaction (6) was obtained on annealing, in contrast with our results for chlorates.³

Both BrO and BrO_2 have been reported as intermediates in the steady-state radiolysis of aqueous solutions of bromates.¹⁶ Our results confirm the formation of BrO_2 , but although BrO was not detected by e.s.r. spectroscopy this does not imply its absence, since the π^* electron in this linear radical is expected to have considerable orbital angular momentum, which could well result in very broad lines. We note that the species detected by e.s.r. spectroscopy, originally thought to be ClO , is now known to be the peroxy-radical $ClOO$,⁴ and ClO has, so far as we know, never been clearly identified by e.s.r. in irradiated solids.

In contrast with bromate, selenite ions in aqueous glasses give SeO_4^{3-} ions, presumably by reaction (7) with hydroxyl radicals, which may or may not be protonated.



The possibility that the species identified as BrO_2 is really $\cdot BrO_4^{2-}$ formed by reaction with $\cdot OH$ radicals in an analogous manner can, we believe, be rejected. Even if *A* is taken as positive, the calculated *p*-character is far greater than that for the isostructural ClO_4^{2-} ion (Table 3). We therefore strongly favour the BrO_2 formulation.

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¹⁴ I. S. Ginns and M. C. R. Symons, *Chem. Comm.*, 1971, 893.
¹⁵ L. C. Brown, G. M. Begun, and G. E. Boyd, *J. Amer. Chem. Soc.*, 1969, **91**, 2250.

¹⁶ G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc.*, 1968, *A*, **309**, 427.