Radiation Mechanisms. Part I. Inorganic Salts in Aqueous Solutions: Electron Spin Resonance Studies of γ-Irradiated Aqueous Glasses containing Oxyanions

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Acidic, neutral, and alkaline aqueous glasses containing the anions perchlorate, chlorate, chlorite, perbromate, bromate, sulphate, sulphite, selenate, selenite, phosphate, hydrogen phosphite, and arsenate have been exposed to ^{60}Co γ-rays at 77 K and their e.s.r. spectra recorded. Primary products detected include e_t^-, $\dot{O}H(\dot{O}D)$, $\cdot H(D)$, $\cdot O^-$, and in certain instances species formed from the oxyanions by electron-capture (*e.g.* $\dot{S}eO_4^{3-}$, $\dot{A}sO_4^{4-}$), or hole-capture (*e.g.* $PO{\cdot}_4^{2-}$, $AsO{\cdot}_4^{2-}$).

On annealing above 77 K, reactions between the primary species from water and the oxyanions were observed (*e.g.* $\cdot OH + HPO_3^{2-} \longrightarrow H_2O + \dot{P}O_3^{2-}$; $\cdot OH + SeO_3^{2-} \longrightarrow HO\dot{S}eO_3^{2-}$). These results of 'temperature resolved' processes are compared with those from pulse-radiolysis optical studies, and steady-state e.s.r. studies.

In a related series of studies[1] we have emphasised the structural information obtainable for trapped radicals by the e.s.r. technique: in the present series our attention is centred on the mechanistic aspects of such studies. Much time and effort is currently being directed towards the retrieval of information about chemical reactions at increasingly short time intervals (time-resolved spectroscopy): here we stress the utility of complementary studies at low temperatures (temperature-resolved spectroscopy) and draw comparisons with room temperature work whenever possible. Differences are, of course, only to be expected mainly because of the different entropy factors, but also because of the rigidity of the lattice, which inhibits some processes but leaves others largely unaffected. Nevertheless, the same major patterns of reactivity are expected to emerge, and in addition transient species may be detected that have not yet been 'observed' in room temperature studies.

In our previous work on aqueous salt solutions[2-5] we have thoroughly investigated the behaviour of alkali-metal salts of the halide, cyanide, azide, cyanate, and thiocyanate ions. These studies revealed the presence of several significant intermediates not previously detected or postulated in the aqueous radiation chemistry of these salts, and in particular demonstrated the importance of protonation even at 77 K. Other low-temperature studies include that of Olsen on aqueous

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[1] Unstable Intermediates. Part I. M. C. R. Symons and M. G. Townsend, *J. Chem. Soc.*, 1959, 263; Part CXLVI. S. P. Mishra, G. W. Neilson and M. C. R. Symons, *J.C.S. Faraday II*, 1975, in the press.

[2] I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 201.

[3] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 143, 185.

[4] I. S. Ginns and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 631.

[5] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1973, 3.

oxyanions of bromine,[6] and of Ershov and Pikaev on aqueous oxyanions of chlorine.[7] Pulse radiolysis studies of aqueous solutions of the salts under consideration have been numerous,[8] but the only steady-state radiolysis study of which we are aware is the important work of Behar and Fessenden [9] who in a study of some 15 aqueous salts were able to detect $\cdot SO_3^-$, $\cdot PO_3^{2-}$, $H\dot{P}O_2^-$, and $\cdot CS_2^-$ directly by e.s.r. spectroscopy.

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification provided no evidence was obtained for trace impurities during e.s.r. studies. Thus, for example, aqueous sodium hydrogenphosphite gave e.s.r. spectra characteristic of nitrogen dioxide on irradiation, presumably from nitrate impurity. This was lost after recrystallisation from water.

Glassy beads were prepared by pipetting small droplets directly into liquid nitrogen. It is very important in studies of this type to ensure that no phase separation occurs during solidification.[3,6] In these studies any beads having an opaque appearance were rejected, and in selected cases the Mn^{2+} test [3] was also applied. In all studies of solutions in aqueous (6M) sulphuric acid and aqueous sodium hydroxide (5—10M) clear glasses were invariably obtained. For aqueous solutions, sodium salts usually gave far better glasses than corresponding potassium salts. It was generally possible to detect radiation damage in phase-separated salts as against the same radical product in aqueous solution by comparing linewidths. Thus, those in the separated salts were narrow and essentially the same as those obtained from the pure salt (hydrate), whilst those from radicals in the solution-phase were invariably broad and exhibited somewhat different magnetic parameters from those of the corresponding radicals in the pure salts. We are confident that the results discussed below relate to processes in the solution phase.

Frozen solutions were exposed to ^{60}Co γ-rays in a Vickrad cell at 77 K at a nominal dose-rate of 4 Mrad h^{-1} for up to 2 h. E.s.r. spectra were measured on a Varian E3 spectrometer at 77 K. Most annealing studies comprised slow warming above 77 K *in situ* in the empty insert Dewar with continuous monitoring of the spectrum and immediate re-cooling to 77 K whenever significant changes were observed. Thus the e.s.r. data were always obtained at 77 K. In some cases studies were also made with the Varian variable-temperature accessory.

RESULTS AND DISCUSSION

Identification of Radicals.—All the radicals presently under consideration have been previously studied by e.s.r. spectroscopy and their identifications are generally well established. Data for those species clearly defined are given in the Table. Well defined parallel and perpendicular features were obtained for $\cdot ClO_3$ radicals from aqueous sodium chlorate (Figure 1a) but these radicals were absent in irradiated aqueous sodium perchlorate. Both solutions showed clear ' parallel ' features for ClO_2 radicals and the latter had an extra well-defined feature (Figure 1b) in the region to be expected for one of the stronger features for $\cdot ClO_4^{2-}$ radicals.[10] All other features for $\cdot ClO_4^{2-}$ were potentially present, but were too close to more intense lines from $\cdot ClO_2$ to be clearly defined. The only chlorine-containing radical derived from ClO_2^- was $\cdot ClO_2$, and this differed from the others by rotating ' freely ' in the glass at *ca.* 150 K (Figure 1c).

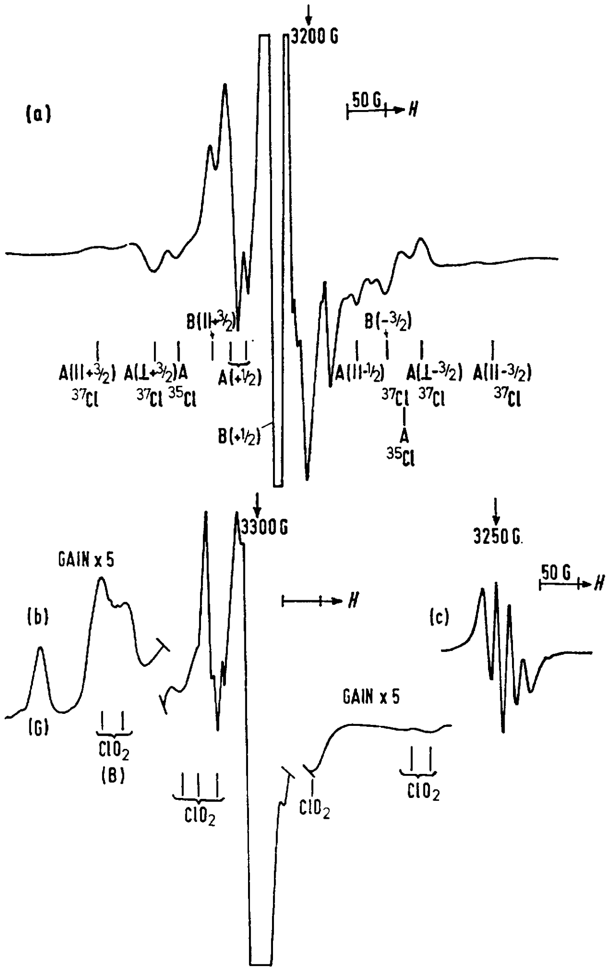

FIGURE 1 First derivative *X*-band e.s.r. spectra for (a) aqueous sodium chlorate glass after exposure to ^{60}Co γ-rays at 77 K and slight annealing, showing features assigned to $\dot{C}lO_3$ (A) and $\dot{C}lO_2$ (B) radicals, (b) aqueous sodium perchlorate glass similarly treated showing features assigned to $\dot{C}lO_2$ (B) and one feature for ClO_4^{2-} (C), and (c) aqueous sodium chlorate glass similarly treated and warmed to *ca.* 150 K, showing features assigned to rotating ClO_2

Radicals thought to be $SO\cdot_4^-$ were identified only by central features which gave the expected *g*-values. No ^{33}S features were detectable because of the large linewidths and low coupling constants. However, $\cdot SO_3^-$ radicals exhibited well-defined ^{33}S features for

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[6] K. J. Olsen, *Trans. Faraday Soc.*, 1971, **67**, 1041.

[7] B. G. Ershov and A. K. Pikaev, *Rad. Res. Rev.*, 1969, **2**, 1.

[8] E. J. Hart and M. Anbar, ' The Hydrated Electron,' Wiley–Interscience, New York, 1970.

[9] D. Behar and R. W. Fessenden, *J. Phys. Chem.*, 1972, **76**, 1706.

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

the $M_I = \pm 3/2$ lines (Figure 2b), so these radicals are quite unambiguously identified. Again, for $\cdot SeO_4^{3-}$ and $\cdot SeO_3^-$ ^{77}Se features were well defined,[11] thus confirming the identifications (Figure 3). Both $PO\cdot_4^{2-}$ and $\cdot PO_3^{2-}$ radicals had well defined spectra, but in both cases the ^{31}P hyperfine coupling proved to be sensitive to the pH of the solutions (Figure 4). A similar effect was observed for variously protonated $\cdot AsO_4^{4-}$ radicals derived from arsenates (Figure 5).

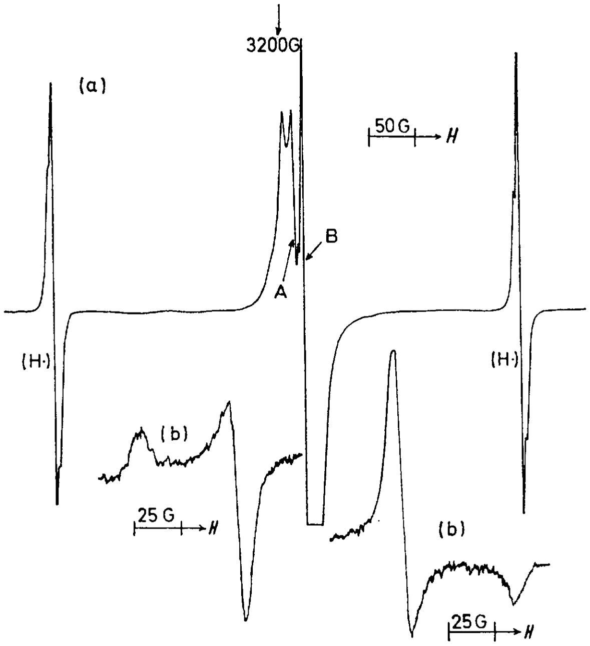

FIGURE 2 First derivative X-band e.s.r. spectrum for aqueous sulphuric acid glass containing sodium sulphate after exposure to ^{60}Co γ-rays at 77 K and slight annealing, (a) at low gain showing features assigned to H•, $\dot{S}O_4^-$ (A) and $\dot{S}O_3^-$ (B), and (b) at high gain, showing ^{33}S hyperfine features ($M_I = \pm 3/2$) for $^{33}\dot{S}O_3^-$

Primary Species.—In all cases, the 'neutral' solutions gave, at 77 K, features assignable to •OH(OD) radicals,[12] trapped electrons (e_t^-) [also clearly defined by the purple-blue colour to which they give rise] and hydrogen (deuterium) atoms. On annealing, e_t^- and H• were initially lost together with some •OH, followed rapidly by the remaining OH radicals. At high gain, features for radicals derived from the oxyions were also detectable in many instances. Loss of e_t^-, H•, and •OH was invariably accompanied by the growth of oxy-radical features, but it was not always possible to say directly which species were derived from a given parent radical.

Alkaline solutions gave spectra for e_t^-, H•(D•), and $\cdot O^-$ [detected by its broad low-field perpendicular feature[13]] and these behaved similarly on annealing. Acidic solutions (generally 6M-H_2SO_4) gave, initially, H•, $\dot{O}H$, and $\dot{S}O_4^-$ radicals, the last two being in roughly equal concentrations. In several instances for these acidic glasses, however, relatively high yields of substrate oxy-radicals were also observed at 77 K. On annealing, all features other than those for $SO\cdot_4^-$ and other oxy-radicals were lost.

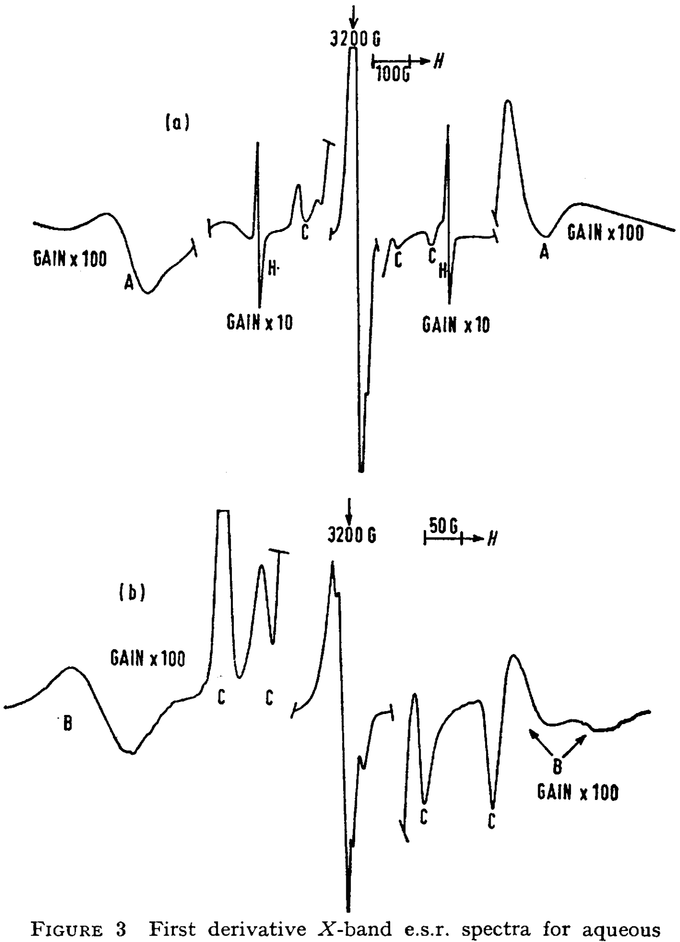

FIGURE 3 First derivative X-band e.s.r. spectra for aqueous sulphuric acid glass (4M) containing sodium selenate after exposure to ^{60}Co γ-rays at 77 K, (a) before annealing, showing the $M_I = \pm\frac{1}{2}$ lines assigned to $^{77}\dot{S}eO_4^{3-}$ [or $^{77}\dot{S}eO_3(OH)^{2-}$] radicals (A) and (H) $\dot{S}eO_2^-$ radicals (C), (b) after annealing, showing the $M_I = \pm\frac{1}{2}$ lines assigned to $^{77}\dot{S}eO_3^-$ [or $^{77}\dot{S}eO_2(OH)$] radicals (B), together with some features thought to be for $^{77}\dot{S}eO_2^-$ [or $^{77}\dot{S}eO(OH)$] radicals (C). The central line is a composite of all three radicals not containing ^{77}Se

Qualitatively, these results show that electrons in the 'conduction band' of these glasses [or 'dry' electrons] have a longer life-time or larger effective range in acidic glasses than in neutral glasses, and a greatly reduced life-time and range in alkaline glasses. It is well established that electrons are efficiently trapped to give e_t^- units (equivalent to 'solvated' electrons) in alkaline glasses, possibly because of the unique ability of hydroxide ions to move by proton transfer away from their initial sites. If this movement can be induced by an incoming electron, then deep

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[11] K. V. S. Rao and M. C. R. Symons, *J.C.S. Dalton*, 1972, 147.

[12] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 2112.

[13] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4352.

and efficient trapping can be understood. In contrast, electron trapping in aqueous-salt glasses requires the presence of molecular sized holes since anion migration is impossible. In acidic glasses reaction with H_3O^+ to give hydrogen atoms can occur, but this apparently does not interfere seriously with electron capture by anions at 77 K. We stress that once electrons are trapped or solvated in these glasses they remain indefinitely stable at 77 K. Thus there can be no doubt that initial electron capture by substrates represents reaction with ' dry ' electrons. The question of similar behaviour by electrons prior to solvation in the liquid-state is currently a matter for controversy.[8,14]

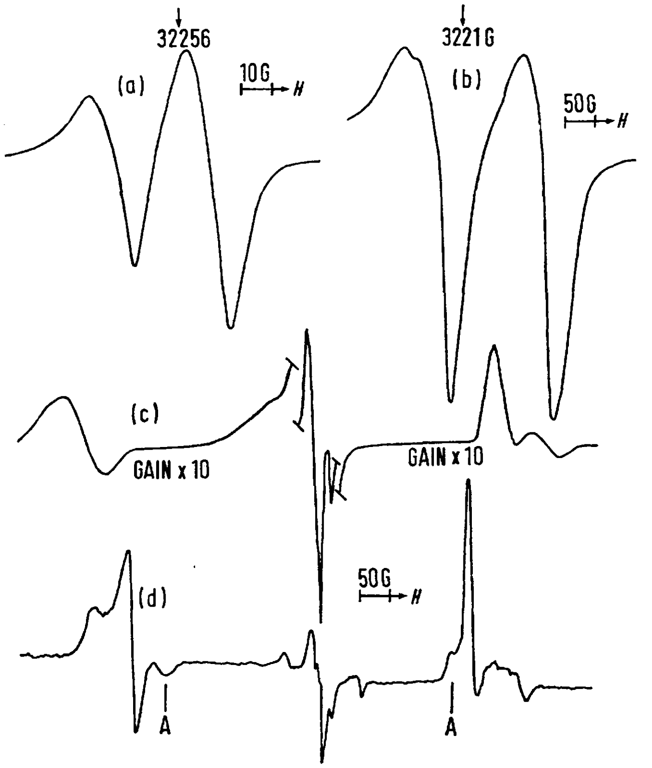

FIGURE 4 First derivative X-band e.s.r. spectra for (a) 10M-aqueous NaOH containing sodium phosphate after exposure to ^{60}Co γ-rays at 77 K after annealing to remove features for H·, ·O^-, and e_t^-, showing features assigned to $\dot{P}O_4^{2-}$ radicals. (b) For 4M-aqueous H_2SO_4 containing sodium phosphate similarly treated, showing features assigned largely to $H_2P\dot{O}_4$ radicals. (c) For acidic Na_2HPO_3 similarly treated prior to annealing, showing features assigned to $\dot{P}O(OH)_2$ radicals. (d) For alkaline Na_2HPO_3 similarly treated after prolonged annealing, showing features assigned to PO_3^{2-} radicals together with shoulders (A) for an unknown radical discussed in the text

Reactions of XO_4^{y-} *Anions*.—These ions are divided into two isoelectronic groups, (A) PO_4^{3-}, SO_4^{2-}, ClO_4^-, and (B) AsO_4^{3-}, SeO_4^{2-}, and BrO_4^-. Group (B) all initially add an electron to give the radical anions which may possibly be subsequently protonated. These anions are thought to have an approximately trigonal bipyramidal structure with the excess electron in one of the equatorial sites. The e.s.r. data are similar to those for these anions in irradiated crystals. Protonated forms of AsO_4^{3-} have been extensively studied by McDowell and his co-workers,[15] particularly in irradiated KH_2AsO_4. We have previously established that in 100% sulphuric acid the species $\dot{A}s(OH)_4$ has a considerably enhanced hyperfine coupling to ^{75}As, as expected on electronegativity grounds.[16] Our present results confirm that on going from AsO_4^{4-} (or $HAsO_4^{3-}$) in concentrated alkaline solution to 6M-aqueous sulphuric acid there is a steady increase in A_{iso} (^{75}As), no doubt as a result of successive protonation. Unfortunately, the lines were always very broad and separate features for individual species were not resolved.

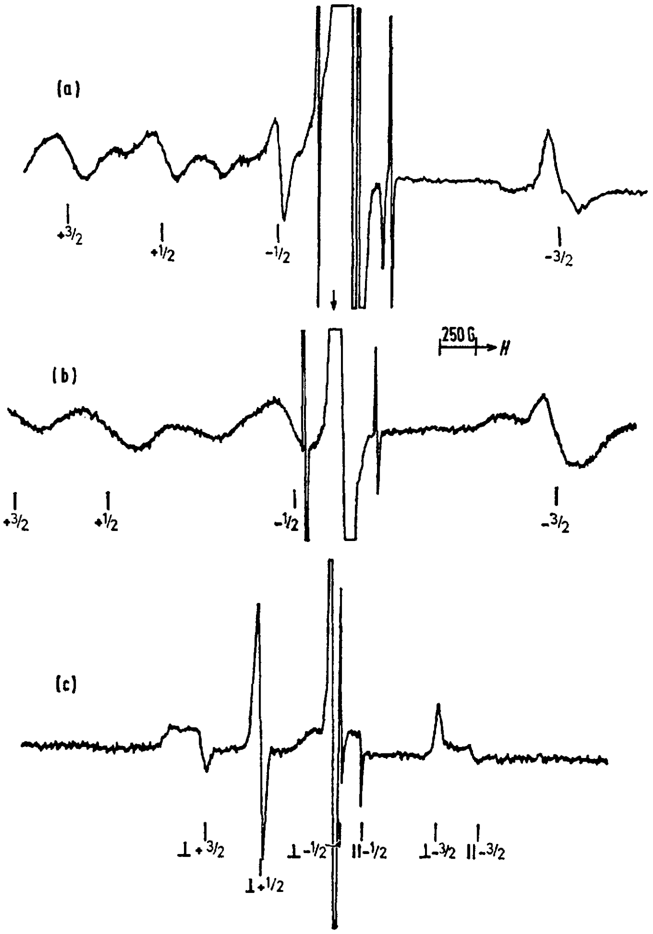

FIGURE 5 First derivative X-band e.s.r. spectra for aqueous sodium arsenate after exposure to ^{60}Co γ-rays at 77 K and slight annealing. (a) Alkaline solutions, showing features assigned to $\dot{A}sO_4^{4-}$ or $H\dot{A}sO_4^{3-}$ and (b) acidic solutions, showing features assigned to $H_2\dot{A}sO_4^{2-}$ or $H_3\dot{A}sO_4^-$ radicals, and (c) as for (a), after prolonged annealing, showing features assigned to $\dot{A}sO_3^{2-}$ radicals

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[14] W. H. Hamill, *J. Phys. Chem.*, 1969, **73**, 1341.

[15] W. C. Lin and C. A. McDowell, *Mol. Phys.*, 1964, **7**, 223; M. Hampton, F. G. Herring, W. C. Lin, and C. A. McDowell, *ibid.*, 1966, **10**, 585.

[16] I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

For group A anions, PO_4^{3-} and its protonated forms clearly do not give stable electron adducts, nor have we been able to detect any $\cdot SO_4^{3-}$ anions although these could well escape clear detection in view of the low abundance of ^{33}S. The unwillingness of protonated phosphate ions to give phosphoranyl radicals under these conditions is surprising in view of the known stability of a range of alkoxyphosphoranyl radicals,[17-19] and the formation of $\cdot PO_4^{4-}$ in a beryllium silicate (phenacite) lattice.[20,21] However, we have recently shown that even $P(OH)_4^+$ does not add an electron to give $\dot{P}(OH)_4$ at 77 K.[16] In this instance, however, in marked contrast with our present results for aqueous phosphates, dissociative electron attachment occurred:

$$e_t^- + P(OH)_4^- \longrightarrow \cdot P(OH)_3^+ + OH^- \qquad (1)$$

The alternative, to give hydrogen atoms and phosphate, would not be detected in our work.

Similarly, sulphate does not capture electrons in neutral or alkaline solution, but in acidic solutions containing HSO_4^- ions, $\cdot SO_3^-$ radicals are formed in good yield:

$$HSO_4^- + e^- \longrightarrow \cdot SO_3^- + OH^- \qquad (2)$$

Because of the high electronegativity of chlorine, ClO_4^- anions are the most likely of this trio to capture electrons, and indeed some evidence for the formation of $\cdot ClO_4^{2-}$ has been outlined above. However, $\cdot ClO_3$ radicals were not detected, whereas in 72% aqueous perchloric acid $\cdot ClO_3$ radicals are formed in high yield. Since some undissociated $HClO_4$ molecules are probably present in this medium, we suggest the process

$$HClO_4 + e^- \longrightarrow \cdot ClO_3 + OH^- \qquad (3)$$

as being reasonable. All these results imply that for XO_4 anions in aqueous solutions the dissociative electron capture process

$$XO_4^{y-} + e^- \longrightarrow XO_3^{(y-1)} + O^{2-} \qquad (4)$$

does not occur. This result is important, since processes of type (4) have been widely postulated for aqueous solutions. They are, in our view, intrinsically improbable because of the excessively large basicity and nucleophilicity of the O^{2-} ion. However, electron capture followed by protonation and subsequent dissociation is, of course, quite reasonable:

$$XO_4^{y-} + e^- \longrightarrow \cdot XO_4^{(y+1)-} + H_2O \longrightarrow H\dot{X}O_4^{y-} \longrightarrow \cdot XO_3^{(y-1)-} + OH^- \qquad (5)$$

Unless $\cdot XO_4^{(y+1)}$ can be detected, this process is indistinguishable from the hydrogen-atom displacement:

$$H\cdot + XO_4^{y-} \longrightarrow OH^- + \cdot XO_3^{(y-1)} \qquad (6)$$

The marked difference in behaviour between groups A and B is clearly nothing to do with relative electronegativities, but may well reflect the higher polarisabilities of group B anions which are thus able to capture electrons (possibly with the aid of the outer *s*-orbital on A or even the 4*d* manifold) prior to deformation to give the stable trigonal-bipyramidal structure.

The tendency to lose electrons, either by direct interation with γ-rays or high energy electrons, or indirectly, by reaction with H_2O^+ 'holes' prior to their immobilisation by proton loss to give $\dot{O}H$ radicals, is clearly exhibited by phosphate and arsenate anions, and less conclusively by sulphate and selenate anions. Which process is involved is again a matter for controversy in liquid-phase reactions, although it has been claimed that recent kinetic data establish the direct process as being most significant at room temperature.[22] It is probable that both processes contribute in these solid-state studies, but it is difficult to obtain quantitative information since the e.s.r. spectral features for species such as $PO_4{\cdot}^{2-}$ overlap strongly with those for $\cdot OH$ radicals and trapped electrons.

The ^{31}P hyperfine data for $PO{\cdot}_4^{2-}$ radicals are again strongly influenced by the pH of the solutions (Table), and these trends undoubtedly reflect the extent of protonation of the radicals. Thus $A(^{31}P)$ for aquated $PO{\cdot}_4^{2-}$ is *ca.* 31 G, that for $HPO{\cdot}_4^-$ *ca.* 35 G, and that for $H_2PO{\cdot}_4$ *ca.* 39 G. Black and Hayon [23] found by optical studies that although the band maxima (*ca.* 500 nm) for these radicals was unaffected by protonation, the extinction coefficients decreased markedly as protonation increased. They were able to derive p*K* values for these species:

$$H_2PO{\cdot}_4 \xrightleftharpoons{pK\ ca.\ 5{\cdot}9} HPO{\cdot}_4^- \xrightleftharpoons{pK\ ca.\ 10{\cdot}7} PO{\cdot}_4^{2-} \qquad (7)$$

Our results agree broadly with these assignments.

It seems probable that $ClO{\cdot}_4$ and $BrO{\cdot}_4$ radicals are also formed by direct interaction with high-energy radiation in these solutions. Byberg [24,25] has presented evidence for these radicals in irradiated $KClO_4$ and $KBrO_4$, and Marov and Symons have tentatively identified $ClO{\cdot}_4$ in irradiated aqueous $KClO_4$.[26] In our present studies we have been unable to avoid extensive formation of $\cdot ClO_2$ radicals which have 'perpendicular' features in the spectral region in which $ClO{\cdot}_4$ radicals absorb so the presence of $ClO{\cdot}_4$, although highly probable, has not been established conclusively. We suggest, however, that $\cdot ClO_2$ formation is also diagnostic of direct electron-loss:

$$ClO_4^- + h\nu \longrightarrow ClO_2 + O_2 + e^- \qquad (8)$$

For aqueous perbromate, however, features for a

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[17] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

[18] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[19] M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885.

[20] M. C. R. Symons, *J. Chem. Phys.*, 1970, **53**, 857.

[21] H. Lozykowski, R. G. Wilson, and F. Holuj, *J. Chem. Phys.*, 1969, **51**, 2309.

[22] R. W. Matthews, H. A. Mahlman, and T. J. Sworski, *J. Phys. Chem.*, 1972, **76**, 1265.

[23] E. D. Black and E. Hayon, *J. Phys. Chem.*, 1970, **74**, 3199.

[24] J. R. Byberg and S. J. K. Jensen, *J. Chem. Phys.*, 1970, **52**, 5902.

[25] J. R. Byberg, *J. Chem. Phys.*, 1971, **55**, 4867.

[26] I. N. Marov and M. C. R. Symons, *Russian J. Inorg. Chem.*, 1971, **16**, 633.

radical containing one bromine atom were clearly observed after loss of ·OH radicals during the annealing process (Figure 7). The g and A-tensor components (Table) accord reasonably well with our expectation for $\dot{\mathrm{B}}\mathrm{rO}_4$ radicals and we favour this assignment. By comparison with results for other radicals of this type, the bromine coupling is somewhat low, but it is difficult to see what other bromine radical could be responsible. Byberg,[25] in his study of potassium perbromate at 4·2 K, detected a species with two equivalent weakly coupled bromine atoms which he described as the dimer, $(\mathrm{BrO}_4)_2^-$. Our results accord well with those for this species, but not at all with the species described by Byberg as BrO_4·.[25] The ^{79}Br tensor components for this species (110·7, 34·3, 37·5 G) do not accord with prediction for BrO·$_4$ and it would be most surprising to find in a single crystal at 4·2 K that some BrO·$_4$ radicals added to their neighbouring anions whilst others did not.

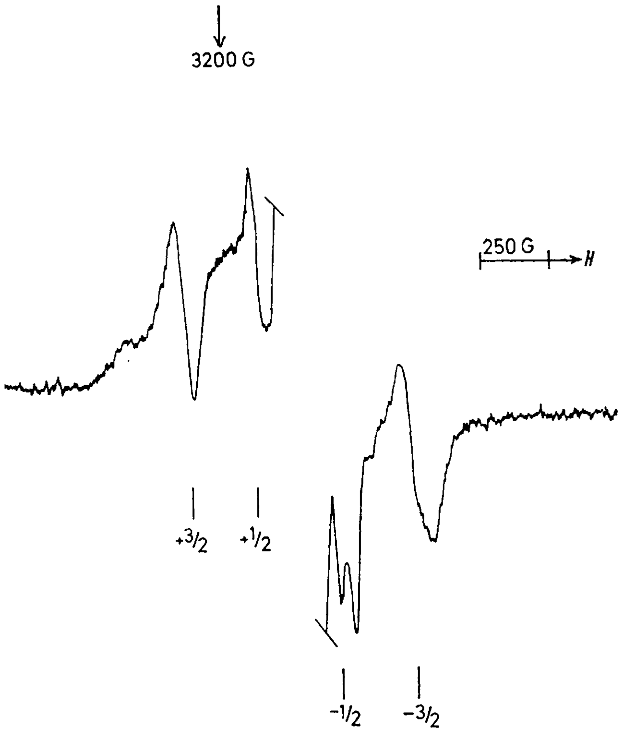

FIGURE 6 First derivative X-band e.s.r. spectrum for sodium arsenate after exposure to ^{60}Co γ-rays at 77 K in 5M-aqueous NaOH after extensive annealing, showing features assigned to $\mathrm{As}\dot{\mathrm{O}}_4^{2-}$ radicals

In all cases, ·OH or ·O$^-$ radicals were trapped in relatively high yield, but were readily lost on annealing. Two alternative modes of reaction are possible with XO_4^{y-} ions, namely

$$\cdot\mathrm{OH} + \mathrm{XO}_4^{y-} \longrightarrow \mathrm{OH}^- + \cdot\mathrm{XO}_4^{(y-1)-} \qquad (9)$$

or

$$\cdot\mathrm{OH} + \mathrm{XO}_4^{y-} \longrightarrow \mathrm{HO{-}O{-}}\dot{\mathrm{X}}\mathrm{O}_3^{y-} \qquad (10)$$

Process (9) seems to be favoured, and (10) can be ruled out for group (A) anions. Thus, for phosphate glasses loss of $\dot{\mathrm{O}}$H resulted in growth of the PO·$_4^{2-}$ type doublet and for arsenate glasses the AsO·$_4^{2-}$ quartet grew appreciably (Figure 6). [AsO·$_4^{2-}$ radicals were previously detected in irradiated calcium tungstate crystals doped with arsenate.[27] The present results show a clear increase in $A(^{75}\mathrm{As})$ just as was found for aqueous PO·$_4^{2-}$ radicals relative to PO·$_4^{2-}$ ions in similar host crystals.[28]] In contrast, loss of $\dot{\mathrm{O}}$H in perchlorate or perbromate glasses did not apparently result in any major gain in chlorine- or bromine-containing radicals.

Reactions of XO_3^{y-} *Anions*.—Aqueous solutions of chlorate ions gave about equal initial yields of ·ClO$_3$ and ·ClO$_2$ radicals, the former being rapidly lost on slight annealing. The former was again formed by direct interaction and possibly by reaction with H$_2$O·$^+$, whilst the latter may have been formed by electron capture to give ·ClO$_3^{2-}$ and subsequent protonation and loss of hydroxide (process 5). We were unable to detect features for the anion ·ClO$_3^{2-}$ which has been recently detected in irradiated potassium chlorate crystals and in calcium carbonate doped with chlorate.[29]

In contrast, only ·BrO$_2$ radicals were obtained from aqueous bromate. This result agrees with that of Olsen,[7] who also concluded that they were formed by an electron-capture process. It is curious that we have not been able to detect ·BrO$_3$ radicals [30] in irradiated

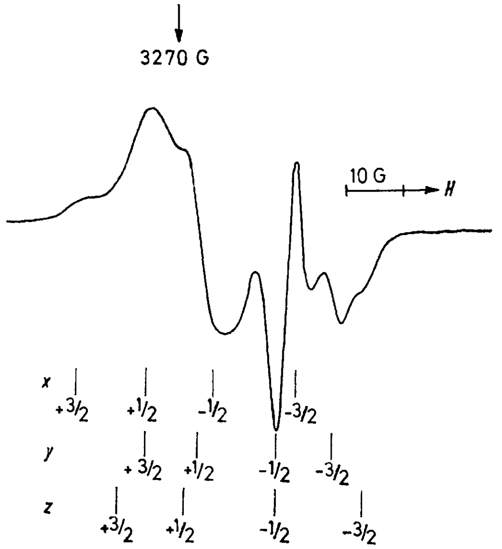

FIGURE 7 First derivative X-band e.s.r. spectrum for potassium perbromate in D$_2$O containing D$_2$SO$_4$ (4M) after exposure to ^{60}Co γ-rays at 77 K for 2 h, followed by slight annealing above 77 K to remove trapped ·OD and other radical species, showing features tentatively assigned to $\mathrm{Br}\dot{\mathrm{O}}_4$ radicals

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[27] S. Subramanian and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 2367.

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

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

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

bromate solution, since direct interaction with high-energy radiation should give $\cdot BrO_3$. However, the absorption lines for this species are spread over a very wide field range, and since they are likely to be very broad in aqueous solution, they may have been too broad to detect. [In this connection, we should mention that Olsen was unable to detect any chlorine- or bromine-containing radicals from aqueous ClO_4^- or BrO_4^- solutions, despite clear evidence that they were involved in the reactions. This may well have been because of the great width of the resonance lines for these radicals when compared with results from the pure salts. This width is not, in general, reduced when H_2O is replaced by D_2O and is, we suggest, a consequence of the presence of a range of solvates of the parent ions in these glasses. Minor modifications in the strengths of hydrogen bonds are expected and because of the sensitivity of e.s.r. parameters to environmental effects,[31,32] this will contribute strongly to the line widths.]

Magnetic data for various oxyanion radicals formed in irradiated aqueous solutions

Radical	Medium	Hyperfine coupling constants (in G) [a,b] A_1	A_2	A_3	A_{iso}	Comments
$\dot{Cl}O_2$	(i) [c] + $NaClO_4$	75	*ca.* 13 [d]	*ca.* 13 [d]	*ca.* 16·3	ClO_2 spectrum became isotropic at *ca.* 150 K for aqueous $NaClO_2$
	(ii) [c] or $NaClO_3$	75	*ca.* 13 [d]	*ca.* 13 [d]	*ca.* 16·3	
	(iii) [c] or $NaClO_2$	75	*ca.* 13 [d]	*ca.* 13 [d]	*ca.* 16·3	
$\dot{Cl}O_3$	(i), (ii), (iii) + $NaClO_3$	131	126	126	127·7	
$\dot{S}O_3^-$	(iii) + SO_4^{2-} (i) and (ii) + SO_3^{2-}	143	123	123	130	Only the ±3/2 (^{33}S) components detected
$Br\dot{O}_4$	(iii) + $KBrO_4$ [e]	15	10	12	12·3	$g_1 = 2{\cdot}008$, $g_2 = 2{\cdot}002$, $g_3 = 2{\cdot}000$
$\dot{S}eO_4^{3-}$	(i), (ii) $\begin{cases} + SeO_4^{2-} \\ \text{or } SeO_3^{2-} \end{cases}$	1110	1010	1010	1043	No clear pH dependence for A (^{77}Se) in SeO_4^{3-}. Central species having $A_{\parallel} \sim 360$ and $A_{\perp} \sim 160$—190 probably SeO_2 or $HSeO_2$
$\dot{S}eO_3^-$	(i), (ii) $\begin{cases} + SeO_4^{2-} \\ \text{or } SeO_3^{2-} \end{cases}$	575	380	380	445	
	(iii) + SeO_4^{2-}	690	510	510	570	Probably $HSeO_3$
$\dot{A}sO_4^{4-}/H\dot{A}sO_4^{3-}$	(i), (ii) + AsO_4^{3-}	*ca.* 1100				A-Values estimated very approximately because of great linewidths
$H\dot{A}sO_4^{3-}/H_2\dot{A}sO_4^{2-}$	(iii) + AsO_4^{3-}	*ca.* 1250				
AsO_3^{2-}	(ii) + AsO_4^{3-}	720	550	550	607	
$P\dot{O}_4^{2-}$	PO_4^{3-} +	(i) 31,	(ii) 35,	(iii) 39		Isotropic within ±2 G
$\dot{P}O_3^{2-}$	(i), (ii) + HPO_3^{2-}	695	535	535	588	
	(iii) + HPO_3^{2-}	870	695	695	753	Coupling reduced on annealing probably $H_2\dot{P}O_3 \longrightarrow H^+ + H\dot{P}O_3^-$
		770	610	610	663	

[a] 1G = 10^{-4} T: corrected using the Breit Rabi equation when necessary. [b] Only hyperfine coupling constants are reported since these are in general more diagnostic. Measured g-values were invariably close to those previously reported. [c] (i), (ii), and (iii) represent 5—10M-aqueous NaOH, H_2O, and 4—6M-aqueous H_2SO_4 or their deuteriated analogues respectively. [d] 'Perpendicular' parameters can only be estimated roughly from powder spectra. [e] Very broad lines in the regions expected for $\dot{Br}O_4^{2-}$ and $\dot{Br}O_2$ were unambiguous but too broad to warrant the extraction of hyperfine data.

Sulphite solutions gave clear evidence for $\cdot SO_3^-$ after partial annealing

$$SO_3^{2-} + \cdot OH \longrightarrow \cdot SO_3^- + OH^- \qquad (11)$$

but no other sulphur-containing radicals were clearly produced. Selenite solutions, however, were of interest because only low concentrations of $\cdot SeO_3$ were detected as primary radicals, whilst $\cdot SeO_4^{3-}$ (or $H\dot{S}eO_4^{2-}$) radicals were clearly formed as $\cdot OH$ radicals were lost:

$$SeO_3^{2-} + \cdot OH \longrightarrow H\dot{S}eO_4^{2-} \qquad (12)$$

This is the only example of such an addition process of which we are aware.

Reactions of HPO_3^{2-} *Anions.* These ions are of interest because of their tendency to form $\cdot PO_3^{2-}$ radicals in their salts, which are readily characterised by their large ^{31}P hyperfine coupling.[31,33] Our results show that $\cdot PO_3^{2-}$ ions are formed in very low primary yields in alkaline glasses, but that they are important secondary products:

$$HPO_3^{2-} + \cdot O^- \longrightarrow OH^- + \cdot PO_3^{2-} \qquad (13)$$

Primary yields of $\cdot PO_3^{2-}$ (or $H\dot{P}O_3^-$) radicals were considerably enhanced in neutral and acidic glasses, and again there was a large increase in yield on annealing:

$$HPO_3^{2-} + \cdot OH \longrightarrow H_2O + \cdot PO_3^{2-} \qquad (14)$$

Electron capture by HPO_3^{2-} is evidently improbable, as with PO_4^{3-}. The species $H\dot{P}O_3^{3-}$ has recently been detected in irradiated Li_2HPO_3 at 77 K [34] but no evidence

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[31] M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1998.

[32] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3075.

[33] A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, 1961, **4**, 475.

[34] S. P. Mishra and M. C. R. Symons, unpublished results.

for its formation in aqueous media could be obtained. Dissociative electron-capture processes such as

$$HPO_3^{2-} + e^- \longrightarrow H\cdot + PO_3^{3-} \quad (15)$$

or

$$\longrightarrow \cdot O^- + HPO_2^{2-} \quad (16)$$

are possible, but the former would simply contribute to the yield of hydrogen atoms whilst the latter is chemically improbable and certainly no evidence for $\cdot O^-$ formation was obtained.

Direct and indirect electron loss to give $HPO\cdot_3^-$ is to be expected, but no good evidence for these ions, which should have e.s.r. spectra resembling $PO\cdot_4^{2-}$, could be obtained. We postulate that rapid intramolecular rearrangement occurs to give $\cdot PO_2(OH)^-$ radicals, and that this is the major process for primary formation of a '$\cdot PO_3^{2-}$' species in neutral and acidic solutions. The radicals $\dot{P}O_3^{2-}$, $\dot{P}O_2(OH)^-$, and $\dot{P}O(OH)_2$ should all have very similar spectra, but with a slight increase in $A(^{31}P)$ on protonation.[16] Our results confirm this increase (Table), and also show that on prolonged annealing of acidic solutions $A(^{31}P)$ falls, which means that proton-loss is occurring.

The only other phosphorus-containing radical detected in these studies was a species having two 'perpendicular' features close to, but inside, those for $\cdot PO_3^{2-}$ in alkaline glasses. This has an apparent $A_\perp$ coupling of *ca.* 470 G and grows in as a minor component after prolonged annealing. It was not detected in neutral or acidic glasses. The species is demonstrably not $H\dot{P}O_3^{3-}$ or $H\dot{P}O_2^-$ [35,36] and we can only suggest a very weakly solvated form of $\cdot PO_3^{2-}$ radicals as a possible candidate. Why this should occur is not clear.

The Chlorite Anion.—The only dioxyanion studied was ClO_2^-, and the only detectable chlorine-containing radical was $\cdot ClO_2$, which was a primary and secondary product:

$$ClO_2^- \longrightarrow \cdot ClO_2 + e^- \quad (17)$$

and

$$\cdot OH + ClO_2^- \longrightarrow OH^- + \cdot ClO_2 \quad (18)$$

We were unable to detect any $\cdot ClO_3^{2-}(H\dot{C}lO_3^-)$ radicals which might have been formed by process (12). Our results therefore agree with the pulse and steady-state radiolysis studies of Buxton and Subhani.[37] These authors also postulated the reactions:

$$e^-_{aq} + ClO_2^- \longrightarrow ClO^- + O\cdot^- \quad (19)$$

and

$$\cdot O^- + ClO_2^- \longrightarrow \cdot ClO_2 + O^{2-} \quad (20)$$

As indicated above, we consider the one-step process (20) to be unlikely, but the formation of ClO_2 on annealing alkaline glasses does suggest a similar composite process (5). Again, no evidence for $\cdot O^-$ formation on loss of e_t^- was obtained, but this result is in no sense definitive, as indicated above.

Finally, we should mention that in many instances, in addition to normal trapped hydrogen atoms, weaker features assigned to $NaH\cdot^+$ and $KH\cdot^+$ were detected.[3] As before, these were generally lost before those for normal atoms.

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[36] P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1963, 250.

[37] G. V. Buxton and M. S. Subhani, *J.C.S. Faraday I*, 1972, 947.