Electron-gain and -loss Centres in Irradiated Periodates: an Electron Spin Resonance Study †

By **Martyn C. R. Symons** * and **Shuddhodan P. Mishra**, Department of Chemistry, The University, Leicester LE1 7RH

Exposure of octahedrally co-ordinated periodates ($H_3IO_6^{2-}$, H_5IO_6, or $H_6IO_6^+$) to ^{60}Co γ-rays at 77 K results in electron-capture centres having large, almost isotropic ^{127}I hyperfine coupling constants corresponding to *ca.* 21% 5*s* character. On annealing to *ca.* 120 K these centres decompose to give axially symmetrical centres with a reduced 5*s* character, thought to be five-co-ordinate iodine(VI) complexes [*e.g.* $^{\cdot}I(OH)_5^+$ or $^{\cdot}IO(OH)_4$]. The electron-loss centres in these systems, exhibiting weak coupling to ^{127}I nuclei, have their unpaired electron confined to one or more oxygen ligands. For H_5IO_6, a dimeric centre having two equivalent ^{127}I nuclei is obtained. The tetrahedral periodate ion, IO_4^- (in K[IO_4] and Na[IO_4]), gives similar electron-loss centres, but markedly different electron-gain centres, having low spin density on iodine (a_s^2 *ca.* 0.038, a_p^2 *ca.* 0.16). These centres are thought to be the anion $^{\cdot}IO_4^{2-}$. The results are comparable with those previously reported for $^{\cdot}BrO_4^{2-}$ and $^{\cdot}ClO_4^{2-}$ anions.

SALTS containing non-metal oxy-anions have been extensively studied by radiation chemists, and in particular, e.s.r. spectroscopy has been widely used to probe the nature of paramagnetic centres trapped in such salts.[1] Alkali-metal perchlorates and perbromates have been studied, and all the expected primary centres, $ClO_4^{\cdot}$, $^{\cdot}ClO_4^{2-}$, $BrO_4^{\cdot}$, and $^{\cdot}BrO_4^{2-}$, have been reported.[2,3] In addition, we have prepared the $^{\cdot}ClO_4^{2-}$ anion by electron addition to ClO_4^- ions incorporated in barium sulphate.[4]

Curiously, periodates do not seem to have been similarly studied, and there is a dearth of information on iodine oxy-radicals. A radical formed from $IO_2F_2^-$ anions was thought to be $^{\cdot}IO_2F^-$ by Subramanian and Rogers,[5] but in our view, and that of Morton and Preston,[6] should be ascribed to $^{\cdot}IO_2$ weakly interacting with a fluoride ion. A species described as an iodine atom was trapped in irradiated HIO_3,[7] and a comparable species, thought to be $^{\cdot}IO_3^{2-}$, was formed in Li[IO_3] crystals.[8] Both these identifications are open to question. The former is chemically improbable, whilst the latter is confusing because the data, as reported, give a negative value for the anisotropic coupling, *i.e.* $|A_{\parallel}(^{127}I)| < |A_{\perp}(^{127}I)|$, which is quite exceptional and, if correct, probably reflects some form of motional averaging. An interesting aspect of both centres is the presence of a large proton coupling. This is too large for dipolar coupling, or coupling to OH protons, and may indicate the formation of a species containing an H–I unit such as HIO_2^+, HIO_3^+, HIO_2^-, or HIO_3^-. Further work on these centres is required. Pulse-radiolysis studies of aqueous periodates [9,10] gave two intermediates identified as $^{\cdot}IO_4^{2-}$ ($\lambda_{max.}$ 360 nm) and $IO_4^{\cdot}$ ($\lambda_{max.}$ 520 nm). The final stable product was iodate ion.[11]

We have had a long-standing interest in oxy-radicals,[1] and also in periodates.[12-15] Periodates differ from their chlorine and bromine analogues in existing in tetrahedral (IO_4^-) and octahedral ($H_3IO_6^{2-}$, $H_4IO_6^-$, H_5IO_6) forms, and we thought it of interest to compare the types of centres formed from these alternative structures.

EXPERIMENTAL

AnalaR grade Na[IO_4], K[IO_4], and H_5IO_6 were used as supplied. Sodium orthoperiodate trihydrate, Na[H_4IO_6]·H_2O,[16] and the D_2O derivative were prepared by recrystallisation from purified water or 99% D_2O. The ion $H_6IO_6^+$ [14] was derived from orthoperiodic acid by dissolution in sulphuric acid (6 mol dm^{-3}).

Solids were irradiated as finely ground powders at 77 K. Solutions of orthoperiodic acid in sulphuric acid were frozen in liquid nitrogen as small beads. Samples were irradiated at 77 K in a Vickrad ^{60}Co source using doses of *ca.* 2 Mrad.‡ E.s.r. spectra were measured with a Varian E109 *X*-band spectrometer at 77 K. The spectrometer was calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe.

Samples were annealed using a Varian variable-temperature accessory or by decanting liquid nitrogen from the insert Dewar and allowing the samples to warm slowly until significant spectral changes were observed. They were then re-cooled to 77 K for study.

RESULTS AND DISCUSSION

Octahedral Complexes.—Four systems were studied, namely $Na_2[H_3IO_6]$, Na[IO_4]·$3H_2O$, H_5IO_6, and $H_6IO_6^+$ ions in sulphuric acid. The salt Na[IO_4]·$3H_2O$ has been shown to contain $H_4IO_6^-$ ions.[12,16] In all cases, two distinct centres were detected at 77 K, one exhibiting an anisotropic set of lines in the free-spin region (Figure 1) and the other exhibiting a single nearly isotropic hyperfine component in the 8 500 G region (Figure 2). The former centres have ^{127}I hyperfine coupling constants in the 10—40 G range and hence have little, if any, direct spin density on iodine. They must therefore be electron-loss centres.[1] In contrast, the latter centres have extremely large hyperfine coupling constants, and thus have properties expected for electron-gain centres.

Electron-loss Centres.—Pure orthoperiodic acid gave a well defined species at 77 K (Table 1), having 11 hyperfine components characteristic of two equivalent ^{127}I nuclei. On annealing to *ca.* 120 K this species changed irreversibly to a species having only one coupled ^{127}I nucleus.

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† Taken as Unstable Intermediates, Part 197; for Part 196 see ref. 18.

‡ Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

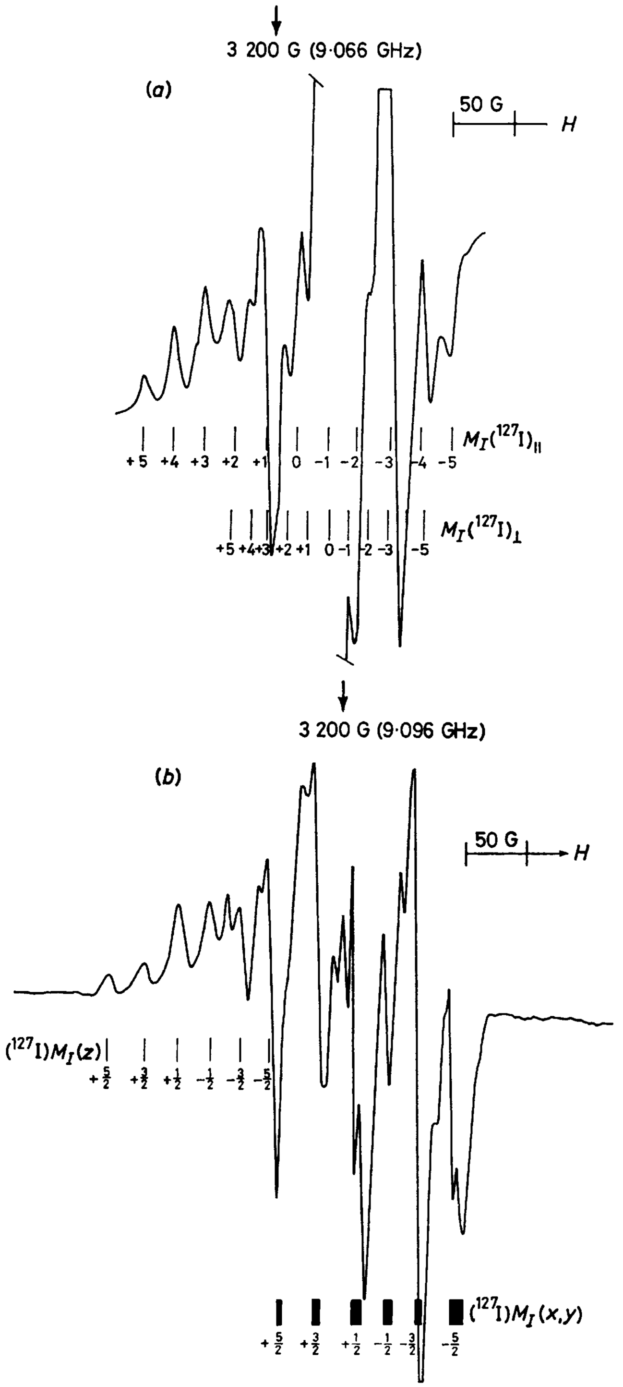


FIGURE 1 First-derivative e.s.r. spectra for H_5IO_6 after exposure to ^{60}Co γ-rays at 77 K showing (a) features assigned to $(HO)_5IO\dot{-}OI(OH)_5^+$ radicals, and (b), after annealing, to $L_xIO^•$ radicals

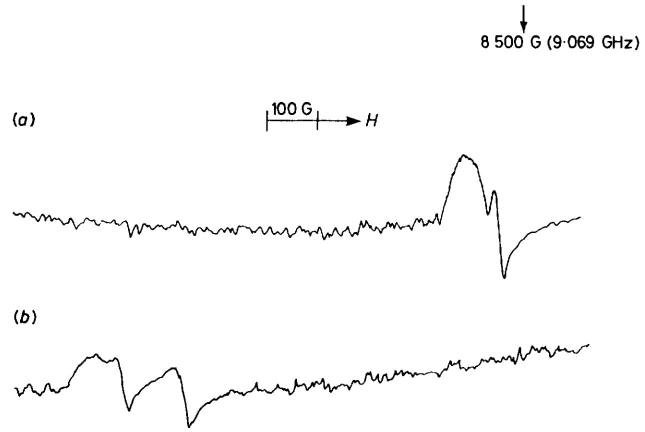
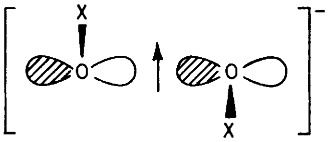


FIGURE 2 As in Figure 1, showing features assigned (a) to $H_5IO_6^-$ and possibly $^•I(OH)_6$ radicals, and (b), after annealing, to $^•IO(OH)_4$ radicals

Similar, but less well defined species were obtained from $Na_2[H_3IO_6]$, $Na[IO_4]·3H_2O$, and $H_6IO_6^+$ ions.[14]

The small coupling to ^{127}I for all these centres is in accord with electron-loss radicals having their unpaired electrons confined to one or more oxygen ligands, the ^{127}I hyperfine coupling arising from spin polarisation of the I–O σ electrons.[1] Dimer hole centres were reported for irradiated perchlorates and perbromates at 4 K,[2,3] and have been previously observed in irradiated calcium tungstate crystals.[17] Their structure is by no means clear. One interesting possibility is that they are σ* radicals of the type shown (I), where X is BrO_3, WO_3, or in the present case $H_5IO_4^+$ for example.[18] So far as we know, such $XO\dot{-}OX$ σ* structures have not previously been postulated. They are comparable with the well known $RS\dot{-}SR^-$ and $R_2S\dot{-}SR_2^+$ σ* radicals,[19] and with $O_3S\text{-}S\dot{-}S\text{-}SO_3^{3-}$ radicals.[20] The bonding seems to be relatively weak, and in the present case the dimer centres change irreversibly into monomeric hole centres on annealing. It is not clear to us why this should occur. If, for example, BrO_4 is formed by electron loss in $K[BrO_4]$ at 4 K, and reacts to form $(BrO_4)_2^-$,[3] why should this change back irreversibly into BrO_4 on annealing? For the octahedral periodate species this could be a result of conversion of one half of the dimer into its tetrahedral form as a result of dehydration, but for the perchlorates and perbromates it is difficult to understand what extra factors are involved. The situation is not clear cut, since the e.s.r. data reported for the $ClO_4^•$ and $BrO_4^•$ centres formed on annealing differ markedly from expectation,[18] the orbital populations on halogen estimated from the hyperfine coupling being much larger than expected. Thus it seems probable that there is some structural change involved, but we do not know what this is. One possibility is that $ClO_4^•$ and $BrO_4^•$ radicals decompose unimolecularly to give species described as $^•ClO_2$ and $^•BrO_2$ weakly associated with dioxygen molecules.[21]



(I)

Data for the monomeric periodate hole centres formed on annealing above 77 K closely resemble those for monomeric centres formed from tetrahedral periodate

TABLE 1

E.s.r. parameters for electron-loss centres formed by ionising radiation in various periodates

Centre	^{127}I Hyperfine coupling/G $A_{\parallel}$	$A_{\perp}$	$A_{iso.}$	g Values $g_{\parallel}$	$g_{\perp}$
A [a] (H_5IO_6)	25	15.9	18.9	2.010	2.005
B [b] (H_5IO_6)	27	*ca.* 35	*ca.* 32.3	2.080	*ca.* 2.002
$IO_4^{\bullet}$/K[IO_4]	47	35	39	2.02	2.004
$IO_4^{\bullet}$/Na[IO_4]	25	15	18.3	2.046	2.003
$H_4IO_6^{\bullet}$/Na[IO_4]·$3H_2O$					
$H_3IO_6^{\bullet -}$/Na_2[H_3IO_6]	*ca.* 22	*ca.* 15	*ca.* 17.3	*ca.* 2.01	*ca.* 2.00

[a] Two equivalent ^{127}I nuclei: $(HO)_5IO\dot{-}OI(OH)_5^+$. [b] One ^{127}I nucleus: from A on annealing $H_5IO_6^{\bullet +}$, $H_4IO_6^{\bullet}$, or a partially dehydrated species.

ions (see below and Table 1), and accord well with expectation for $\geqslant$I–$\dot{O}$ type centres. It is not possible to obtain accurate e.s.r. parameters from the powder spectra, partly because the features overlap extensively, and partly because quadrupole effects distort the symmetry of the sets of hyperfine features, and may introduce extra transitions ($\Delta M = \pm 1$, *etc.*), and partly because for low-symmetry centres the turning points detected in powder spectra do not necessarily provide principal values of the g and A components. However, our concern is not with precise numbers but with identification and basic structural assignments: these are clear cut for the species concerned.

It is noteworthy that the form of the spectra for the monomeric electron-loss centres varies markedly depending on the parent from which it is derived. Large variations in g values and ^{31}P coupling constants were also observed for $^{\bullet}PO_4^{2-}$ radicals in a range of crystalline environments.[22] These changes were interpreted in terms of variable delocalisation onto different oxygen ligands, which will control the form of the g tensor, and crystal-field effects which will control the isotropic hyperfine coupling.[22] Similar arguments probably apply to the present centres, but we feel that the results are too approximate to warrant detailed consideration.

TABLE 2

E.s.r. parameters for electron-gain centres formed by ionising radiation on various periodates

Radical host	^{127}I Hyperfine coupling/G $A_{\parallel}$	$A_{\perp}$	$A_{iso.}$	g Values $g_{\parallel}$	$g_{\perp}$		$g_{av.}$
$H_3IO_6^{3-}$/Na_2[H_3IO_6]			*ca.* 3 100				2.00 [a]
$H_4IO_6^{2-}$/Na[IO_4]·$3H_2O$			*ca.* 2 610 [b]				2.000
$H_5IO_6^-$/H_5IO_6			(*i*) 3 095 [a] 3 120				2.00 [a]
			(*ii*) 2 603 [b]				2 000 [b]
H_6IO_6/$H_6IO_6^+$			(*i*) 3 121 [a]				2.00 [a]
			(*ii*) 2 605 [b]				2.000 [b]
IO_4^{2-}/K[IO_4]	(*i*) 350,	242,	278 (±3)	2.003,	1.994	(±0.001),	1.997
	(*ii*) 338,	238,	271 (±3)				
	(*iii*) 294,	204,	234 (±3)	2.002,	1.995	(±0.001),	1.997
IO_4^{2-}/Na[IO_4]	350,	240,	277 (±5)	2.002,	1.993	(±0.002),	1.996

[a] Calculated using equation (1) on the assumption that $g = 2.00$. [b] Calculated from equations (1) and (2).

Electron-gain Centres.—The centres formed at 77 K have a single feature in the 8 500 G region which is assigned to the $-\frac{5}{2}$ hyperfine component ($M_I = \frac{5}{2}$). Thus the centre is comparable with the IF_6 molecule studied by Boate *et al.*,[23] which had its $M_I = -\frac{5}{2}$ feature at *ca.* 11 000 G. Assuming a g value of 2.0, this corresponds to an isotropic coupling to ^{127}I of *ca.* 3 100 G [*cf.* for IF_6 Boate *et al.* found $A(^{127}I) \approx 6\,230$ G]. For this value of the hyperfine coupling, none of the so-called n.m.r. transitions could be detected on our spectrometer. The e.s.r. feature at *ca.* 8 500 G was always broad, but appeared to be isotropic. We therefore used equation (1) to calculate A, where B_2 is the field

$$A = 2B_0(B_2 - B_0)/[B_0(2I + 1) - B_2] \qquad (1)$$

value for the $-\frac{5}{2}$ component. However, for H_5IO_6, two features of approximately equal intensities were detected (Figure 2).

We suggest that these species, detected in irradiated $Na_2[H_3IO_6]$, $Na[IO_4]\cdot 3H_2O$, H_5IO_6, and $H_6IO_6^+$ (in aqueous sulphuric acid) (Table 2), are all six-co-ordinated extra-electron species such as $^{\bullet}I(OH)_6$, $^{\bullet}IO(OH)_5^-$, *etc.* The two very similar species obtained from H_5IO_6 could well be $^{\bullet}IO(OH)_5^-$ together with $^{\bullet}I(OH)_6$ formed by protonation of the anion. Data from $H_6IO_6^+$ were not sufficiently precise for us to make clear assignments, but the species with the larger A value is expected to be $^{\bullet}I(OH)_6$.

On annealing between *ca.* 120 and 150 K the 8 500 G feature was lost irreversibly and two slightly asymmetric features grew in the 7 800 G region (Figure 2). As shown by Boate *et al.*[23] the $M_I = -\frac{5}{2}$ and the n.m.r. (I) transitions occur close together in this region, and are usually of comparable intensity. This is the case, for example, for AsF_6^{2-} anions.[23] From the field values for these two features, using equations (1) and (2), we

$$B_{n.m.r.} = B_0[2I(I + 1)A - 2B_0]/(2B_0 - A) \qquad (2)$$

obtained the values $g = 2.000$, $A = 2\,610$ G for the centre in H_5IO_6. The asymmetry of these features was too poorly defined to warrant any attempt to estimate anisotropic parameters.

We suggest that these features are due to five-co-ordinate iodine derivatives, formed by loss of water or hydroxide ions, as, for example (3). On further annealing, they were also lost irreversibly, but no other features appeared elsewhere in the spectra.

$$^{\bullet}I(OH)_6 \longrightarrow {}^{\bullet}IO(OH)_4 + H_2O \qquad (3)$$

No high-field features of this type were detected in irradiated $Na[IO_4]$ or $K[IO_4]$. Instead, well defined sets of parallel and perpendicular features occurred as shown in Figure 3 for $K[IO_4]$ at 77 K. For this salt, three sets of features with similar parameters were obtained. On annealing, set (*iii*) grew at the expense of (*i*) and (*ii*) (Table 2). For the sodium salt, only one set was obtained. Since, for both salts, the only other detectable centre was the electron-loss radical $IO_4^{\bullet}$, it seems most probable that the centres under consideration were formed by electron capture. The ^{127}I hyperfine coupling constants are comparable with those assigned to ClO_4^{2-} and BrO_4^{2-},[2-4] but the difference in these data, compared with the results for five- and six-co-ordinated iodine electron-gain centres, is quite remarkable.

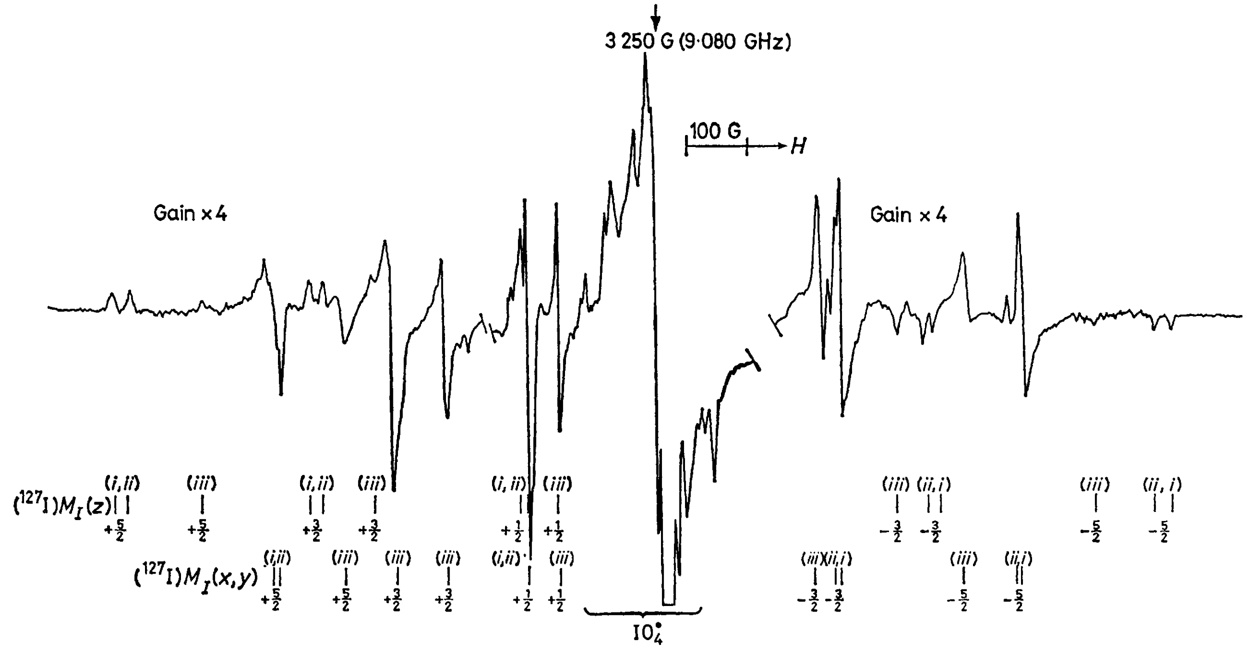


FIGURE 3 First-derivative e.s.r. spectrum for $K[IO_4]$ after exposure to ^{60}Co γ-rays at 77 K, showing central features assigned to $IO_4^{\bullet}$ radicals, and outer features assigned to $^{\bullet}IO_4^{2-}$ radicals

It is noteworthy that there is a steady downward trend in $A_{iso.}$ and in total spin density on the central atom, on going from PO_4^{4-} [24,25] and AsO_4^{4-},[26] *via* SeO_4^{2-},[27] to ClO_4 and BrO_4. This trend follows expectations for an electron in an antibonding orbital, but is much more marked than that for the family of XF_6 electron-gain centres.[23] Indeed, the results show that the total spin density on iodine for $^{\bullet}IO_4^{2-}$ is only *ca.* 8%.

We conclude that the species is probably $^{\bullet}IO_4^{2-}$. Other chemically reasonable assignments can be rejected. Thus $^{\bullet}IO_3^{2-}$ and $^{\bullet}IO_3$ radicals should resemble their bromine and chlorine analogues and have far higher isotropic hyperfine coupling constants. Data for $^{\bullet}IO_2$ should give comparable isotropic but far larger anisotropic coupling constants. The possibility that librating $^{\bullet}IO_2$ radicals were responsible (*cf.* $^{\bullet}ClO_2$ [28]) was rejected since the same features were obtained at 4.2 K. The three species (*i*)—(*iii*) detected in $K[IO_4]$ after irradiation are almost certainly all $^{\bullet}IO_4^{2-}$ radicals in effectively different environments. In their studies of irradiated $K[ClO_4]$ and $K[BrO_4]$, Byberg and Jensen [2,3] detected a range of subtly different radicals rather than single species. The changes are especially marked for radicals having major spin density on the ligands, since this can be directly modified by the cations. The central features assigned to $IO_4^{\bullet}$ radicals also changed on annealing and the poor resolution obtained is probably due to the presence of two or more environmental modifications.

Aspects of Structure.—The electron-gain $^{\bullet}I(OH)_6$ and related centres clearly have their unpaired electrons centred in the iodine 5*s* orbital, the spin densities estimated from the $A°$ values recommended by Morton and Preston [29] being *ca.* 21%. This value is only half that for the isostructural $^{\bullet}IF_6$ radicals. This reduction accords with expectation for antibonding electrons. In both cases, the spectra give no indication of hyperfine anisotropy so it seems that no major distortion results from electron addition. This is confirmed by the equivalence of the six ^{19}F nuclei for $^{\bullet}IF_6$.

In contrast, for $^{\bullet}XF_5$ species such as $^{\bullet}SF_5$ [29] and $^{\bullet}PF_5^-$ [30] there are four equivalent ligands, the fifth giving an almost undetectably small hyperfine coupling. The central-atom hyperfine coupling is anisotropic, but the anisotropy is small relative to the large isotropic coupling. This is observed for the centres formed from $^{\bullet}I(OH)_6$ and related radicals on annealing, the reduction of 5*s* character to *ca.* 17.7% and acquisition of slight anisotropy being in good accord with expectation. The idealised structure assigned to these five-co-ordinate species is square pyramidal, the unpaired electron effectively occupying the sixth position.

There is clearly a drastic change in structure on going to the four-co-ordinate radicals, the 5*s* character falling to *ca.* 4%, the total spin density on iodine being *ca.* 8%. Such a marked change in parameters is not observed in examples taken from rows 5 and 6 of the Periodic Table. For example, $A_{\text{iso.}}$ (^{31}P) for $^{\bullet}PF_5^-$ is *ca.* 1 330 G, the value for $^{\bullet}PF_4$ being comparable. On going from $^{\bullet}PF_4$ to $^{\bullet}PO_4^{4-}$ there is a fall in $A_{\text{iso.}}$ of only *ca.* 1 500 G.[25] Thus it seems that, as with $^{\bullet}ClO_4^{2-}$ and $^{\bullet}BrO_4^{2-}$, most of the spin density is now on the ligands. Byberg's results [2,3] clearly establish that there is some distortion from a T_d symmetry for ClO_4^{2-} and BrO_4^{2-}, but in the absence of hyperfine information from the ligands the form of this distortion is not clear. For $^{\bullet}IO_4^{2-}$, axial symmetry is observed, but we still cannot say much about the nature of the distortions involved.

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