MASTER

AN ESR STUDY OF THE IO_2F^- RADICAL IN γ -IRRADIATED SINGLE CRYSTALS OF
POTASSIUM OXYFLUOROIODATE

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ABSTRACT

Single crystals of KIO_2F_2 γ -irradiated at room temperature, or irradiated at 77°K and allowed to warm above 140°K, give ESR spectra characteristic of the 27-electron radical anion IO_2F^- . The g , $A(^{19}\text{F})$ and $A(^{127}\text{I})$ tensors have been evaluated, and the ^{127}I quadrupole interaction parameters Q' and Q'' have been estimated, from the spectra. The unpaired electron is predominantly delocalized over the iodine and oxygen atoms and interacts only weakly with the fluorine atom. Loss of a fluorine atom from IO_2F_2^- would lead to a radical structure based on a trigonal bipyramid with the electron pair and two oxygen atoms in equatorial positions and the fluorine atom and odd electron in apical positions. The ESR data are consistent with an arrangement of this type and with some involvement of iodine 5d orbitals in the bonding.

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INTRODUCTION

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ESR studies of paramagnetic oxyions of non-metals, usually produced by γ -irradiation of salts of the appropriate diamagnetic ion, have been studied extensively.¹⁻¹⁷ Information concerning their electronic structures and geometry have been largely deduced from the g values and the hyperfine splittings by nuclei of the central atoms,^{18,19} since ligand splittings can only be seen by enrichment with ^{17}O and this has only rarely been done.²⁰ Study of the isoelectronic fluoroxy ions has the advantage that ligand hyperfine splittings may be observed, as in the tetrahedral series²¹ PO_4^{2-} , PO_3F^- and PO_2F_2 each with 31 valence electrons. Also, substitution of oxygen by fluorine may lead to stable species in which the central atom apparently uses more than four orbitals; thus, the ESR spectra of the 33-valence electron radical PF_4 indicates that d orbitals are used in bonding and that the structure is approximately trigonal pyramidal.^{18,22}

In the present article we report the radical anion IO_2F^- in γ -irradiated single crystals of KIO_2F_2 . This ion is of unusual interest because it is the first paramagnetic oxyion of iodine which has been observed and the first tetratomic radical reported with more than 26 valence electrons. Although reports of ESR investigations of oxyions of chlorine^{3,4} and bromine²³ have appeared, no iodine containing oxyions appear to have been studied. The only reported species showing iodine hyperfine interaction are the V_k centers^{24,25} I_2^- and IF^- . The maximum number of valence electrons which can be accommodated in species of the type $\text{XO}_y\text{F}_{3-y}^{n-}$ and $\text{XO}_y\text{F}_{4-y}^{n-}$ without the use of d orbitals is 26 and 32, respectively. Species with less than these numbers would be expected to have approximately tetrahedral arrangements as observed for ClO_3 (25 electrons),²⁶ PO_3F^- (31 electrons)²¹

and IO_4^- (32 electrons).²⁷ However, species where these numbers are exceeded have different structures such as ClF_3 (28 electrons) with a distorted T-shape^{28,29} and IO_2F_2^- (34 electrons) with a distorted trigonal pyramidal arrangement,³⁰ unshared pairs on the central atom being sterically active in each case. The radical IO_2F^- might therefore be expected to have a molecular orbital scheme similar to ClF_3 and an unusual structure and this proves to be the case.

Spectra of a second species, believed to be $\text{IO}_2\text{F}_2^{\cdot-}$ or IO_2F_2 , are obtained in crystals of KIO_2F_2 irradiated and observed at 77°K but analysis of these very complex spectra is not yet complete and a description of that species must be deferred.

EXPERIMENTAL ~~~~~

KIO_2F_2 crystals were prepared by dissolving analytically pure KIO_3 in excess of 48% hydrofluoric acid in a Teflon container and allowing the solution to evaporate slowly.³⁰ The crystals of KIO_2F_2 obtained were washed with HF and were purified further by recrystallization from HF. Transparent rectangular single crystals obtained by the above process were examined under a polarizing microscope to eliminate twinned crystals. The crystals were invariably single and showed all the morphological characteristics listed by Groth.³¹

Selected crystals of KIO_2F_2 were irradiated with γ -rays from a ^{60}Co source producing an effective dose of 20×10^6 rads/hr. Irradiations at 300°K were performed by placing the samples in screw-capped vials in the gamma source, and for irradiation at 77°K sealed samples were immersed under liquid nitrogen in a Dewar vessel designed to fit inside the radiation compartment of the gamma source. Samples were usually irradiated for a period of 3 to 4 hours.

ESR measurements were carried out using a Varian V-4502 X-band spectrometer with 100 KHz field modulation and a Varian V-4503 Q-band spectrometer. Magnetic field calibration and klystron frequency measurements were achieved by methods previously described.³² Measurements at 77°K were done by immersing the crystal in a Dewar filled with liquid nitrogen the quartz tip of which fitted inside the Varian V-4531 multi-purpose cavity.

Single crystals were mounted in selected orientations ($\pm 3^\circ$) by thin copper springs attached to one end of a quartz rod which fitted inside the Dewar; a large protractor calibrated in degrees permitted measurement of orientation in the magnetic field. Rotations were performed about the a, b and c crystallographic axes of KIO_2F_2 with spectra recorded every 10° or, near certain orientations, every 5° .

A detailed X-ray crystallographic study of KIO_2F_2 showed³⁰ that the crystals are orthorhombic, four molecules per unit cell, with space group $C_{2v}^5(Pca)$. The unit cell dimensions are: $a_0 = 8.38$, $b_0 = 5.97$ and $c_0 = 8.41$ Å. We follow the notation of Rogers and Helmholtz for the axes (which differs from that of Groth); the structure of the IO_2F_2^- ion is shown in Fig. 1.

RESULTS

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Single crystals of KIO_2F_2 γ -irradiated and observed at 77°K without warmup showed ESR spectra spread over a range of about 4500 G (Fig. 2); these are attributed to the species $\text{IO}_2\text{F}_2^\cdot$ (or IO_2F_2). When the crystals were warmed above 140°K the lines from this primary radical were replaced

Fig. 1

Fig. 2

by a new set spread over about 2500 G belonging to a secondary radical species which was stable even at room temperature. The ESR spectrum of the 300°K radical with $H_0 || \underline{C}$, shown in Fig. 3(A), consists of a sextet of lines of equal intensity with hyperfine spacing 520 G from hyperfine interaction with one iodine nucleus, split into doublets with spacing 40 G from hyperfine interaction with one fluorine nucleus. An extra feature marked "X" in the middle of the spectrum does not belong to the main radical since it is shifted relative to the main sextet at Q band (Fig. 3(B)).

Fig 3

INTERPRETATION OF THE SPECTRA

It can be seen in the X-band spectrum, Fig. 3(A), that there are a few weak doublets between the six main strong lines and the intensity of these weaker lines relative to the main lines is reduced in the corresponding Q-band spectrum of Fig. 3(B). Since ^{127}I has a nuclear spin of 5/2 and a large quadrupole moment ($eQ = -0.75$ barns) the latter will affect the ESR spectrum in two ways; first, the six lines arising from the interaction of the unpaired electron with the iodine nucleus will not be equally spaced but should show a frequency dependence on m_I and, second, the off-diagonal matrix elements stemming from the quadrupole Hamiltonian (see Discussion) cause a mixing of the various nuclear energy levels and the so-called "forbidden" transitions with $\Delta m_I = \pm 1$, ± 2 become allowed.^{33,34} This can be physically pictured as follows: the magnetic field (from the unpaired electron and the external field) and the electric field at the nucleus each try to quantize the nucleus along their respective (but differently oriented) axes and the quantization of

the nucleus will therefore depend upon the relative strengths of the magnetic and electric fields; hence, at orientations when the two fields are not parallel to each other, the first-order assumption that the nucleus is always quantized along the external magnetic field is no longer true. The considerable mixing of the nuclear m_I levels leads to the breakdown of the selection rules $\Delta m_S = \pm 1$ and $\Delta m_I = 0$ and the appearance of forbidden transitions_A which are strong enough in the spectra of the room-temperature radical to confuse their interpretation. When the external field is parallel to the a or b axis at X-band the intensity of the forbidden transitions is as high as the normal $\Delta m_I = 0$ transitions (Fig. 4). The six ^{127}I hyperfine lines from a given site are never equally spaced at any orientation. The hyperfine coupling to iodine is so high that the low-field lines occur at X-band at magnetic fields which are only four times larger than the hyperfine field. This causes a progressive increase in the separation between the component hyperfine lines from low to high field as a consequence of the "second-order field effect".^{35,36} The observed hyperfine coupling constants were therefore corrected using the Breit-Rabi equation.³⁷ This second-order field effect was less noticeable at Q-band since the fourfold increase in the external magnetic field reduces the magnitude of the off-diagonal elements. Also, at Q-band the separations between the centers of the hyperfine lines from magnetically distinct sites are increased since their g values differ. Extensive use of Q-band spectra has therefore been made in completing the analysis.

Fig. 4

For an arbitrary orientation of the magnetic field with respect to the crystal axes there are four sets of lines corresponding to the four magnetically distinct sites of the space group Pca . However, for $H \parallel \underline{b}$ or $H \parallel \underline{c}$ there are only two distinct sites, and for $H \parallel \underline{a}$ only a single site is observed (Fig. 3). The angular variation of the six lines of the main multiplet is shown in Fig. 5(A) and (B) for rotation of the magnetic field in the $\underline{bc}$ and $\underline{ac}$ planes, respectively. The doublet spacing varied little with orientation, remaining in the range 39-41 G, and is not shown in Fig. 5 to simplify the plots which are based on the positions of the centers of the doublets. The principal values of the g tensor and the ^{127}I hyperfine interaction tensor, along with their direction cosines relative to the crystallographic axes, were evaluated by the method of Schonland³⁸ and are listed in Table I; it is seen that they are nearly coincident.

Fig 5

An attempt was made to evaluate, for ^{127}I in the radical, the quadrupolar parameters Q' and Q'' , where

$$Q' = Q_{zz} - 1/2(Q_{xx} + Q_{yy}), \quad (1)$$

$$\text{and } Q'' = 1/2(Q_{xx} - Q_{yy}). \quad (2)$$

Excluding the nearly isotropic hyperfine coupling to ^{19}F and assuming that the ^{127}I nuclear gyromagnetic ratio is isotropic, the Hamiltonian for the system can be written³⁹ as:

$$\begin{aligned} = & \beta(g_{xx} H_x S_x + g_{yy} H_y S_y + g_{zz} H_z S_z) + A_{xx} I_x S_x + A_{yy} I_y S_y \\ & + A_{zz} I_z S_z + Q' [I_z^2 - 1/3 I(I+1)] + Q'' (I_x^2 - I_y^2) \\ & - g_n \beta_n (H_x I_x + H_y I_y + H_z I_z) \end{aligned} \quad (3)$$

where the terms have their usual significance. If the magnetic field H makes polar angle θ and azimuthal angle ϕ with the right-handed coordinate system of the principal axes of the g tensor (which are coincident with those of the hyperfine tensor) we may write:

$$\begin{aligned} g_{\perp}^2 &= g_{xx}^2 \cos^2 \phi + g_{yy}^2 \sin^2 \phi, \\ g_{\parallel}^2 &= g_{zz}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta, \\ A_{\perp}^2 g_{\perp}^2 &= A_{xx}^2 g_{xx}^2 \cos^2 \phi + A_{yy}^2 g_{yy}^2 \sin^2 \phi, \\ K^2 g_{\parallel}^2 &= A_{zz}^2 g_{zz}^2 \cos^2 \theta + A_{\perp}^2 g_{\perp}^2 \sin^2 \theta. \end{aligned} \quad (4)$$

By use of these quantities the Hamiltonian of Eq. 3 was diagonalized to second order by the method of Tseng and Kikuchi.⁴⁰ The values of Q' and Q'' were adjusted until the difference between the calculated and experimental line positions for the normal ($\Delta m_I = 0$) transitions for ^{127}I reached a minimum, the values so obtained are listed in Table II and the agreement between calculated and observed spectra is shown in Fig. 6. From the values of Q' and Q'' a quadrupole coupling constant $e^2 q Q = 1095.5 \text{ MHz}$ for ^{127}I is obtained and an asymmetry parameter $\eta = 0.110$. Unfortunately, the method is not very accurate since the "normal" transitions are not as sensitive as the "forbidden" transitions⁴¹ to changes in Q' . The angular variation of these forbidden transitions, however, could not be analyzed completely in the three orthogonal planes because of overlap of resonances from the four magnetically distinct sites.

DISCUSSION

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From the hyperfine structure of the spectra it is apparent that the odd electron interacts with one iodine nucleus and one fluorine nucleus plus an undetermined number of oxygen nuclei ($I = 0$ for ^{16}O). Since the 77°K

best
(Fig. 6)
here

radical is IO_2F_2^- (or IO_2F_2), and the secondary radical has lost a fluorine atom, the room temperature radical studied here could be IO_2F^- formed by the process

The possibility IOF^- appears less likely since maximum stability should be achieved with the maximum number of I-O bonds; IF^- may be excluded since $A_{||}(\text{F})$ has been observed for that species²⁵ and is ~630G (with $A_{\perp} \approx 0$).

The experimental hyperfine splitting tensor for ^{127}I may be broken down in the usual manner⁴² into isotropic and dipolar terms and the spin density in the iodine valence shell orbital estimated from these components. Thus,

$$\begin{vmatrix} 759.1 \text{ MHz} \\ 917.8 \\ 1433.3 \end{vmatrix} = \begin{vmatrix} 1036.7 \\ 1036.7 \\ 1036.7 \end{vmatrix} + \begin{vmatrix} -224.7 \\ -224.7 \\ +449.4 \end{vmatrix} + \begin{vmatrix} -52.9 \\ +105.8 \\ -52.9 \end{vmatrix}$$

where the last term takes into account the deviation of the dipolar term from axial symmetry. Using the Hartree-Fock values⁴³

for the isotropic and anisotropic iodine 5s and 5p hyperfine interactions

$a_{5s}(^{127}\text{I}) = 26,000 \text{ MHz}$ and $2B_o(^{127}\text{I}) = 1624 \text{ MHz}$, the unpaired spin densities in the iodine 5s and 5p orbitals are 0.04 and 0.28, respectively. Similarly,

for fluorine the small observed isotropic and anisotropic splittings lead to $\rho_{2s}(^{19}\text{F}) \approx 0.002$ and $\rho_{2p}(^{19}\text{F}) \approx 0.002$. Together these account for only 33% of the total spin density.

Although no value for the dipolar splitting for an odd electron in the iodine $5d$ orbitals is available, we have estimated a value by extrapolation of the Hartree-Fock $\langle r^{-3} \rangle$ values for the second-row transition elements^{44,45}. In this way we obtain $2B_o(^{127}\text{I}, 5d) \approx 1225$ MHz, and the value of $2B = 105.8$ MHz from the smaller dipolar tensor (above) then leads to $\rho_{5d}(^{127}\text{I}) \approx 0.09$. This is an upper limit since some of the asymmetry of the ^{127}I tensor could arise from odd electron density in the bonding p_σ orbitals.

The remaining spin density not accounted for in this way may be on the oxygen ligands. However, it is also possible that we may have underestimated the true unpaired spin density in the iodine $5s$ orbital. The observed $a(^{127}\text{I})$ is only a net contribution from all the iodine s orbitals and spin polarization of the inner s electrons by the p and d unpaired electron density on iodine can occur, part of which can be negative. Taking into account that the true iodine $5s$ spin density is, therefore, somewhat greater than 0.04 the observed $s:p:d$ ratios for iodine from Table I (0.04:0.28:0.09) are not inconsistent with the expected sp^3d hybridization. Also, as has been pointed out by Higuchi⁴⁶ for PF_4 , the hybridization ratios would not be expected to correspond exactly to sp^3d .

The low isotropic and anisotropic fluorine hyperfine interactions appear to be most consistent with the structure of the radical shown in Fig. 1 where a fluorine atom has been removed from IO_2F_2^- leaving the odd electron in a hybrid orbital directed 180° to the remaining fluorine.

Under these conditions the overlap with both the $2s$ and $2p_{\pi}$ orbitals of fluorine would be small. In the case of PF_4 it has been shown^{22,46} that, as the angle between the PF bond and the hybrid orbital of phosphorus carrying the unpaired electron increases from $\sim 90^\circ$ to $\sim 130^\circ$, $a(F)$ decreases from 360 to 45 G (at the same time $2B(F)$ which is 28 G in the first case becomes unobservable in the second case). While the electronic structure of IO_2F^- will be more complex than that of PF_4 the values of $a(^{19}F) = 111.1 \text{ MHz}$ and $2B(^{19}F) = 6.5 \text{ MHz}$ in IO_2F^- seem reasonable for an angle of 180° between the odd electron orbital and the I-F bond. Also, the directions of g_{zz} and $A_{zz}(^{127}I)$ lie parallel to the F-I-F bond of the IO_2F_2 species in the crystal (Table I) which suggests that the odd electron orbital has nearly the direction of one of the original I-F bonds.

The large quadrupole coupling constant eqQ for ^{127}I (1095.5 MHz) also suggests a pyramidal configuration for IO_2F^- since the value for IO_3^- is quite close⁴⁷ (1025 MHz, Table II). The observed asymmetry parameter $\eta = 0.11$ also is in agreement with the pyramidal arrangement, which lacks axial symmetry. It should be noted that the quadrupole coupling constants for ICl_2^- , ICl_4^- , I_3^- and similar molecules can be accounted for without use of iodine d orbitals in bonding⁴⁷ and, indeed, where there are ligands of high electronegativity it is not unreasonable that only the sp^3 orbitals of the central atom would suffice. We are, of course, not able to exclude this possibility for IO_2F^- in view of the many assumptions made in interpreting the ESR data.

Table I. Magnetic Parameters for the IO_2F^- radical in KIO_2F_2 .

Tensor Components ^b	Direction Cosines ^a		
<u>g</u> -Tensor			
	<u>a</u>	<u>b</u>	<u>c</u>
$g_{xx} = 2.0989$	0.971	0.233	0.055
$g_{yy} = 2.0164$	-0.121	0.280	0.952
$g_{zz} = 1.9432$	-0.206	0.931	-0.301
<u>A</u> (¹²⁷ I) Tensor			
$A_{xx} = 759.1$	0.984	0.180	0.101
$A_{yy} = 917.8$	-0.079	0.276	0.983
$A_{zz} = 1433.3$	-0.154	0.977	-0.180
I-F bond direction in KIO_2F_2	0.336	0.860	+0.379

A(¹⁹F) Tensor

$$A_{xx} = A_{yy} = 107.8; A_{zz} = 117.6; a(F) = 111.1; 2B(F) = 6.5.$$

Estimated Spin Densities

Iodine: $\rho_{5s} = 0.04$ (Original experimental dipolar tensor)
 Or $\rho_{5p} = 0.28$ (Deviation from axial symmetry of the tensor included)
 Plus $\rho_{5d} = 0.09$ (Estimated)
 Fluorine: $\rho_{2s} = 0.002$ and $\rho_{2p} = 0.002$
 Oxygen: ρ_{2s} and $\rho_{2p} \leq 0.54$ (Both oxygens, by difference)

^a Relative to the a,b,c crystallographic axes of KIO_2F_2 .

^b All hyperfine interactions are in MHz.

Table II. Quadrupolar parameters for IO_2F^- and for some related species.

Molecule	$e^2Qq(\text{MHz})$	η	Ref.
IO_2F^- in KIO_2F_2 $\underline{Q}' = 123.24 \text{ MHz}$ $\underline{Q}'' = 4.53 \text{ MHz}$	1095.5	0.110	This work
HIO_6	1126.9	0.45	47
IO_3^- in $\text{Ca}(\text{IO}_3)_2$	1025.36	0	47
I_3^- in NH_4I_3 (Central I)	1725	0.151	47

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CAPTIONS FOR FIGURES

- Fig.1. Molecular structure of IO_2F_2^- and suggested structure of the radical anion $\text{IO}_2\text{F}_2^{\cdot -}$.
- Fig.2. Second-derivative ESR spectrum of γ -irradiated KIO_2F_2 at 77°K; the magnetic field is parallel to the b axis of the crystal.
- Fig.3. (A) First-derivative X-band spectrum of KIO_2F_2 γ -irradiated at 77°K and observed at room temperature; the magnetic field is parallel to the b axis of the crystal. (B) The same but at Q-band.
- Fig.4. (A) First-derivative X-band spectrum of γ -irradiated KIO_2F_2 at room temperature with the magnetic field parallel to the a axis of the crystal. (B) The same but with the magnetic field parallel to the c axis of the crystal. The "forbidden" lines are of moderate intensity.
- Fig.5. Variation of the resonance magnetic field with orientation for the six main lines from ^{127}I interaction in the spectrum of $\text{IO}_2\text{F}_2^{\cdot -}$ for (A) the field in the bc plane, and (B) the magnetic field in the ac plane.
- Fig.6. Experimental (solid lines) and calculated (circles) field positions for the six ^{127}I hyperfine lines in the spectrum of $\text{IO}_2\text{F}_2^{\cdot -}$. The magnetic field is in the bc plane and, for $\theta = 0^\circ$ is parallel to the c axis of the crystal. Values represented by the circles were calculated using the parameters in Tables I and II.

Fig.1. Molecular structure of IO_2F_2 and suggested structure of the radical anion IO_2F_2^- .

500 G

Fig.2. Second-derivative ESR spectrum of γ -irradiated KIO_2F_2 at 77°K ;
the magnetic field is parallel to the b axis of the crystal.

Fig.3. (A) First-derivative X-band spectrum of KIO_2F_2 γ -irradiated at 77°K and observed at room temperature; the magnetic field is parallel to the b axis of the crystal. (B) The same but at Q-band.

Fig.4. (A) First-derivative X-band spectrum of γ -irradiated KIO_2F_2 at room temperature with the magnetic field parallel to the a axis of the crystal. (B) The same but with the magnetic field parallel to the c axis of the crystal. The "forbidden" lines are of moderate intensity.

Fig.5. Variation of the resonance magnetic field with orientation for the six main lines from ^{127}I interaction in the spectrum of IO_2F^- for (A) the field in the bc plane, and (B) the magnetic field in the ac plane.

Fig.6. Experimental (solid lines) and calculated (circles) field positions for the six ^{127}I hyperfine lines in the spectrum of IO_2P^m . The magnetic field is in the bc plane and, for $\theta = 0^\circ$ is parallel to the c axis of the crystal. Values represented by the circles were calculated using the parameters in Tables I and II.