935. *Oxides and Oxy-ions of the Non-metals. Part III.*[1] *Oxy-radicals of Chlorine.*

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Hyperfine and g-tensors for chlorine monoxide, dioxide, and trioxide are presented. The identity of radicals trapped in γ-irradiated perchlorates and chlorates and detected by electron-spin resonance is discussed.

Continuing our studies of simple oxides and oxy-ions of the non-metals,[1,2] we have attempted to prepare the paramagnetic oxides of chlorine, and to measure their electron-spin resonance spectra.

Results for chlorine dioxide both in fluid [3] and rigid solution [4] were interpreted [4] some time ago. Since then Cole [5] reported results for a radical formed on X-radiolysis of a single crystal of potassium perchlorate and trapped in fixed orientations, thus facilitating the calculation of hyperfine and g-tensors. By comparison with the results reported by Ingram and his co-workers,[4] Cole concluded that one of the radicals was chlorine dioxide.

When our studies were well advanced, Cole reported results for X-irradiated ammonium perchlorate containing a radical whose properties led him to postulate that chlorine trioxide had been formed.[6]

Hasty and his co-workers [7] claim to have prepared chlorine monoxide by exposing potassium chlorate crystals to high-energy radiation: this identification is, however, far less certain than that for the dioxide and trioxide, and it is discussed below in the light of present results.

The ultraviolet spectrum of chlorine monoxide in the gas-phase is well known, and Norman and Porter [8] have shown by measuring the change in the ultraviolet spectrum that exposure of rigid solutions of the dioxide to ultraviolet light results in complete conversion into the monoxide. We have used this method to obtain the monoxide unambiguously.

Experimental and Results

Materials.—Chlorine dioxide was generally obtained by heating a mixture of oxalic acid, potassium chlorate, and water to 60°. Chlorine, carbon dioxide, and water were removed from the resulting gas by passage through concentrated aqueous sodium hydroxide and over phosphorus pentoxide. Solutions in sulphuric acid were obtained by adding potassium chlorate, which disproportionates in this medium to give perchloric acid and the dioxide.

Chlorine monoxide was prepared by photolysis of rigid solutions of the dioxide by means of a high-pressure mercury arc supplied by G.E.C., the predominant wavelength being 3650 Å. Irradiation was continued until the orange colour of the dioxide was discharged and no electron-spin resonance spectrum due to this oxide could be detected.

For rigid solutions in sulphuric and in phosphoric acid the electron-spin resonance spectrum assigned to chlorine monoxide (Fig. 3) was well resolved, but, for rigid solutions in hydrocarbons or ethanol, the spectrum of an organic radical was superimposed upon that of the monoxide. In solutions in ethanol, a violet colour developed on photolysis of the dioxide similar to that observed on photolysis of hydrogen peroxide in this medium [9] and on exposure of solid ethanol to high-energy radiation.[10]

[1] Part II, Atkins, Keen, and Symons, *J.*, 1962, 2873.
[2] Mishra and Symons, *J.*, 1962, 1194.
[3] Bennett and Ingram, *Phil. Mag.*, 1956, **1**, 109.
[4] Bennett, Ingram, and Schonland, *Proc. Phys. Soc.*, 1956, **69**, *A*, 556.
[5] Cole, *Proc. Nat. Acad. Sci.*, 1960, **46**, 506.
[6] Cole, *J. Chem. Phys.*, 1961, **35**, 1169.
[7] Hasty, Ard, and Moulton, *Phys. Rev.*, 1959, **116**, 1459.
[8] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.
[9] Symons and Townsend, *J. Chem. Phys.*, 1957, **25**, 1299.
[10] Alger, Anderson, and Webb, *J. Chem. Phys.*, 1959, **30**, 695.

We think that oxygen atoms formed on photolysis of the dioxide extract hydrogen atoms from the media to give trapped organic radicals. However, when sulphuric or phosphoric acid is used, the most probable reaction of oxygen atoms is to add to give corresponding peroxy-acids, which are diamagnetic. That chlorine dioxide is re-formed in good yield on softening is in accord with this postulate.

Other compounds were of the highest available grade. Single crystals were grown from aqueous solution.

γ-Irradiation.—Facilities were kindly made available by the Leicester Royal Infirmary, a 100-c ^{60}Co source being used. Samples were irradiated at room temperature, but for sodium and lithium perchlorate it was necessary to store the materials at 195°K immediately after irradiation in order to prevent decomposition of the trapped species.

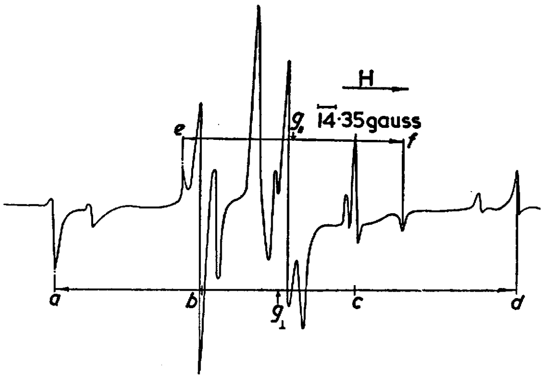

FIG. 1. Electron-spin resonance spectrum of chlorine trioxide in irradiated magnesium perchlorate.

$ab = bc = cd = a_{\perp}(^{35}\text{Cl})$.
$ef = a_{/\!/}(^{35}\text{Cl})$.

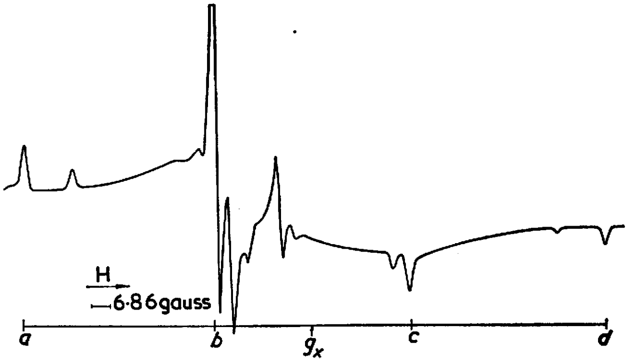

FIG. 2. Electron-spin resonance spectrum of chlorine dioxide in sulphuric acid at 77°K.

$ab = bc = cd = a_{xx}$.

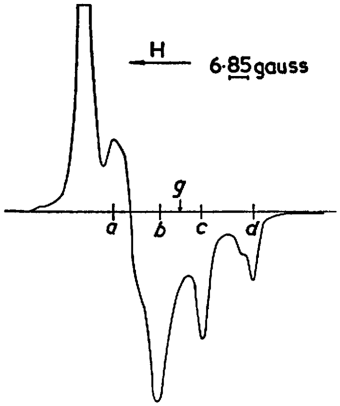

FIG. 3. Electron-spin resonance spectrum of chlorine monoxide in sulphuric acid at 77°K.

$ab = bc = cd = a_{yy}$.

Diffuse-reflectance Spectra.—Precautions were observed as described earlier.[11] The result of Hasty *et al.*,[7] that a band at 460 mμ develops in γ-irradiated potassium chlorate, was confirmed and a similar band was detected in γ-irradiated potassium perchlorate. This we assign to the ozonide ion, O_3^-, for which there is good evidence in these irradiated crystals from spin-resonance measurements. There was definite fine structure in the 460 mμ band from irradiated potassium perchlorate, similar to that found in the spectrum of ozonide ions in liquid ammonia.[12]

Electron-spin Resonance.—Measurements were made at room temperature and 77°K by

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[11] Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

[12] McLachlan, Symons, and Townsend, *J.*, 1959, 952.

means of a 3-cm. high-resolution spectrometer described previously.[13] Single crystals were mounted on rotatable Perspex rods inserted in the HO14 rectangular cavity.

Interpretation of Spectra.—Since it is not generally appreciated that a great deal of information can be derived from powder spectra [2,13] we have given those of irradiated magnesium perchlorate and of chlorine dioxide and monoxide in solid sulphuric acid in Figs. 1—3. In most cases peaks and shoulders are in evidence for ^{37}Cl and ^{35}Cl. Our assignments are indicated in the Figures, and the results are listed in Table 1. As well as for derivation of the tensor parameters, these spectra can be used purely for identifications. For example, the spectrum of the dioxide at 3 cm. wavelength is especially characterised by a strong, symmetrical line with a g-value of about 2·022 and, even when other radicals obliterate a lot of the detail, this feature will often remain and is evidence that chlorine dioxide is one of the components.

TABLE 1.

Experimental data for the chlorine oxides.

System and temp. (K)	^{35}Cl Hyperfine interaction (gauss): observed a_{xx}	a_{yy}	a_{zz}	anisotropic A_{xx}	A_{yy}	A_{zz}	isotropic A_{iso}	g-Values g_{xx}	g_{y}	g_{zz}	g_{av}	g^*
Species ClO												
H_3PO_4/77°	0	−17	0	5·7	−11·4	5·7	−5·7	1·9909	2·0098	1·9909	1·9972	—
Species ClO_2												
$KClO_4$/300° [5,a]	73	−15·5	−11·5	57·6	−30·8	−26·8	15·4	2·0036	2·0183	2·0088	2·0102	
H_2SO_4/300°							16·5				2·0093	
H_2SO_4/77°	70·5							2·0015				2·0216
$KClO_4$/300°	67							2·0015				2·0236
$NaClO_4$/195°												2·0232
Species ClO_3												
NH_4ClO_4/300° [6,a]	115		153	−13		25	128	2·008		2·007	2·008	
$KClO_4$/300°	107		151	−15		29	122	2·0132		2·0066	2·0110	
$Mg(ClO_4)_2$/195°	116		166	−17		33	133	2·0103		2·0069	2·0092	
$LiClO_4$/195°	116							2·0110				
$NaClO_4$/195°	125							2·0110				
Species $Cl \cdots ClO_3^-$ (?)												
$KClO_3$/300° [7,a] (I)				−22·4			44·8	41				
(II)				−2·6			5·2	5·0				
Species O_3^-												
$KClO_3$/77°								2·0025	2·0174	2·0113	2·0104	

g^* = g-value of sharp line characteristic of ClO_2. [a] Single-crystal study.

Determination of Molecular Parameters.—(i) *Chlorine monoxide.* The electron-spin resonance results for this monoxide may be interpreted on the basis that the molecular orbital occupied by the unpaired electron is an antibonding π-level having the form

$$\Psi(\mathrm{ClO}) = a_p\psi_{\mathrm{Cl}}(\pi) - b_p\psi_{\mathrm{O}}(\pi), \tag{i}$$

where

$$\psi_i(\pi) = \frac{1}{\sqrt{2}}[\psi_i(p_x) + \psi_i(p_z)], \tag{ii}$$

$$a_p^2 + b_p^2 = 1, \tag{iii}$$

and the y-axis is the molecular axis.

The hyperfine tensor, which represents the interaction of the unpaired-spin magnetic moment with the chlorine nucleus (spin, $I = 3/2$), may be resolved into an isotropic and an axially symmetric tensor. The former is due to the Fermi contact term and the magnetic interaction $(\mathbf{A})_{\mathrm{iso}}$ is related to the spin population (a_s^2) of a chlorine s-orbital by the expression

$$\mathbf{A}_{\mathrm{iso}} = g_e\beta_e g_N\beta_N(8\pi/3)|\psi_{ns}(0)|^2 a_s^2 \tag{iv}$$

Here g_N and β_N are the nuclear g-value and magneton, respectively, and $\psi_{ns}(0)$ is the amplitude of the wave-function of the ns-orbital at the nucleus. If it is assumed that s-character arises

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[13] Brivati, Keen, and Symons, *J.*, 1962, 237.

from the exchange polarisation of a chlorine 3*s*-orbital, then by using $|\psi_{3s}(0)|^2 = 10{\cdot}66$ a.u. as calculated from Mayer's self-consistent field wave functions by Whiffen,[14] it is found that $a_s^2 = 0{\cdot}004$.

The spin population of the chlorine 3*p*-orbitals may be calculated from the axially symmetric tensor which represents the dipolar interaction of an electron in a non-*s*-state orbital with the nucleus. The contribution of *d*-orbitals cannot be separated from that of the *p*-orbital because of the axial symmetry of the system. The dipolar contribution from an electron in $\psi_{\text{cl}}(3p_z)$ has the symmetry

$$\mathbf{A}_z = \begin{pmatrix} -\alpha & & \\ & -\alpha & \\ & & 2\alpha \end{pmatrix}, \qquad \text{(v)}$$

and that from an electron in $\psi_{\text{cl}}(3p_x)$ the form

$$\mathbf{A}_x = \begin{pmatrix} 2\alpha & & \\ & -\alpha & \\ & & -\alpha \end{pmatrix}. \qquad \text{(vi)}$$

For the doubly degenerate level in the present system the resultant tensor is, therefore,

$$\mathbf{A}_p = \tfrac{1}{2}(\mathbf{A}_z + \mathbf{A}_x) = \begin{pmatrix} \alpha/2 & & \\ & -\alpha & \\ & & \alpha/2 \end{pmatrix}. \qquad \text{(vii)}$$

If *d*-orbitals were invoked to give $d(\pi)$–$p(\pi)$ bonds constructed from chlorine $3d_{xy}$ and $3d_{yz}$ orbitals (Fig. 4) these would contribute a resultant tensor of the form

$$\mathbf{A}_d = \begin{pmatrix} -\beta/2 & & \\ & \beta & \\ & & -\beta/2 \end{pmatrix}. \qquad \text{(viii)}$$

Since both $\mathbf{A}_p$ and $\mathbf{A}_d$ have axial symmetry about *y*, so also will their sum, thus the observed tensor will still be axially symmetric and the *d*- and the *p*-orbital contributions are empirically inseparable when only the chlorine nucleus is considered. Since $\mathbf{A}_d$ and $\mathbf{A}_p$ have opposite signs, if it is assumed that only chlorine 3*p*-orbitals are involved in Ψ(ClO), the value arrived at for a_p^2 can only be equal to, or less than, the true value. Observation of the splitting from ^{17}O-labelled chlorine monoxide would resolve this difficulty.

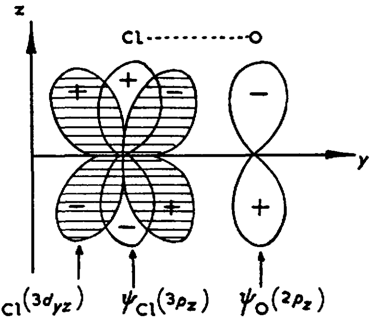

FIG. 4. Atomic orbitals contributing to the *z*-component of Ψ(ClO).

The contribution of a pure *p*-orbital to the dipolar interaction when the external field is applied along its symmetry axis is given by the expression

$$2\alpha = \left(\frac{4}{5}\right) g_e\beta_e g_N\beta_N\langle r^{-3}\rangle_{np} c_p^2, \qquad \text{(ix)}$$

where g_e and β_e refer to the electron, $\langle r^{-3}\rangle_{np}$ is the expectation value of r^{-3}, r being the distance of the electron from the nucleus in an *np*-orbital, and c_p^2 the electronic population of the orbital. Since however, we have the doubly degenerate π-system described above, the contribution from $\psi_{\text{cl}}(3p_z)$ when the field is along the *z*-axis (eqn. vii) is only $\tfrac{1}{2}\alpha$ due to the electron population of the $\psi_{\text{Cl}}(3p_x)$ component of $\psi_{\text{Cl}}(\pi)$. The population of $\psi_{\text{Cl}}(3p_z)$ is then calculated from 2α by eqn. (ix). Since a_p^2 gives the total *p*-character on chlorine it is given by

$$a_p^2 = 2c_p^2 \qquad \text{(x)}$$

By using the value $\langle r^{-3}\rangle_{3p} = 6{\cdot}41$ a.u. obtained from Mayer's values [14] the value $a_p^2 = 0{\cdot}53$ is obtained.

If the isotropic hyperfine contribution is due to inner *s*-shell polarisation, the spin density on oxygen (b_p^2) is $(1 - a_p^2)$, when no *d*-orbital participation is assumed. The interaction of this fraction with the chlorine nucleus is axially symmetric about the *y*-axis and has been estimated [1] to be about 0·3 gauss along *y*. This has been subtracted from the experimental tensor to give the final values listed in Table 2.

(ii) *Chlorine dioxide.* Both Mulliken [15] and Walsh [16] predict the unpaired electron in the dioxide to be in a $4b_1$ molecular orbital and the electron-spin resonance results can be interpreted on this basis. The molecular orbital has the form

$$\Psi(\text{ClO}_2) = a_p\psi_{\text{Cl}}(3_{px}) - b_p\left(\frac{1}{\sqrt{2}}\right)[\psi_{\text{O}}(2_{px}) + \psi_{\text{O}'}(2_{px})], \qquad \text{(xi)}$$

where

$$a_p^2 + b_p^2 = 1, \qquad \text{(xii)}$$

the *x*-axis being perpendicular to the molecular plane which contains the *y* and the *z*-axis, the last bisecting the OClO′ angle. Participation of *d*-orbitals is neglected, and so only apparent 3*p*-character is calculated.

The experimental anisotropic hyperfine interaction tensor ($\mathbf{A}_{\text{exp}}$) does not have the axial symmetry required by (xi), but can be resolved [1,17] into two axially symmetric components

$$\mathbf{A}_{\text{exp}} = \mathbf{A}_1 + \mathbf{A}_2, \qquad \text{(xiii)}$$

$$\textit{i.e.,}\ \begin{pmatrix} 57{\cdot}6 & & \\ & -30{\cdot}8 & \\ & & -26{\cdot}8 \end{pmatrix} = \begin{pmatrix} 58{\cdot}92 & & \\ & -29{\cdot}46 & \\ & & -29{\cdot}46 \end{pmatrix} + \begin{pmatrix} -1{\cdot}33 & & \\ & -1{\cdot}33 & \\ & & 2{\cdot}67 \end{pmatrix} \text{gauss.} \qquad \text{(xiv)}$$

$\mathbf{A}_1$, which is axially symmetric about the *x*-axis, is due to the electron in $\Psi(\text{ClO}_2)$ and from this a_p^2 has been calculated (eqn. ix) to be 0·69. This unpaired electron polarises the $4a_1$ molecular orbital, which has $3p_z$- and 3*s*-character on chlorine, and the spin density which results gives rise to $\mathbf{A}_2$. From eqn. (ix), the spin density in the chlorine $3p_z$-orbital (a_z^2) is 0·031. Spin polarisation leads to an observed isotropic interaction ($\mathbf{A}_{\text{iso}}$) which may (by eqn. iv) be due to 0·01 chlorine 3*s*-character (a_s^2). The experimental results have been associated with the molecular axes indicated on structural grounds. This assignment differs from that of Cole. The experimental bond angle of 118·5° would require $a_s^2 = 0{\cdot}017$, the discrepancy being within experimental error.

TABLE 2.

Molecular parameters.

Species	Source	$a_{p_z}^2$	$a_{p_x}^2$	a_s^2	b_0^2	∠OXO
ClO	H_3PO_4–ClO_2	0·265	0·265	0·004	0·47	—
ClO_2	$KClO_4$ [5,a]	0·031	0·69	0·01	0·31	—
ClO_3	$KClO_4$	0·34	—	0·076	0·58	112°
	$Mg(ClO_4)_2$	0·39	—	0·083	0·53	112
	NH_4ClO_4 [6,a]	0·29	—	0·080	0·63	111
SO_3^-	[a,b]	0·49	—	0·13	0·39	111
PO_3^{2-}	$Na_2HPO_3,5H_2O$ [a,c]	0·53	—	0·16	0·30	110
Cl · · · ClO_3^- (?)	$KClO_3$ (I) [7,a]	0·52	—	0·026	—	—
	(II)	0·07	—	0·003	—	—

[a] Single-crystal study. [b] Chantry, Horsfield, Morton, and Whiffen, unpublished work. [c] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 475.

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[14] Whiffen, personal communication.

[15] Mulliken, *Rev. Mod. Phys.*, 1942, **14**, 204.

[16] Walsh, *J.*, 1953, 2266.

[17] Ovenall and Whiffen, *Mol. Phys.*, 1961, **4**, 135.

(iii) *Chlorine trioxide.* The unpaired electron in the trioxide is in a molecular orbital constructed from chlorine $3s$- and $3p_z$-atomic orbitals overlapping with oxygen $2p_z$-orbitals. The z-axis is the C_{3v} symmetry axis of the molecule. Neglecting d-orbitals gives the molecular orbital the form

$$\Psi(\mathrm{ClO_3}) = a_s\psi_{\mathrm{Cl}}(3s) + a_p\psi_{\mathrm{Cl}}(3p_z) - b_0\left(\frac{1}{\sqrt{3}}\right)[\psi_{\mathrm{O}}(2p_z) + \psi_{\mathrm{O'}}(2p_z) + \psi_{\mathrm{O''}}(2p_z)] \qquad \text{(xv)}$$

with

$$a_s^2 + a_p^2 + b_0^2 = 1. \qquad \text{(xvi)}$$

From the axially symmetric hyperfine tensor, eqn. (ix) gives $a_p^2 = 0{\cdot}30$, the exact value depending on the source, as shown in the Table. Similarly, $\mathbf{A}_{\mathrm{iso}}$ yields $a_s^2 = 0{\cdot}08$. From eqn. (xvi), $b_{\mathrm{O}}^2 = 0{\cdot}6$. If Coulson's relationships[18] between bond angle and hybridisation ratio λ (where $\lambda = a_p/a_s$) are assumed to hold for the system, the OClO bond angle (ϕ) can be calculated from

$$\phi = \cos^{-1}\frac{1}{2}\left[\frac{3}{(2\lambda^2 + 3)} - 1\right] \qquad \text{(xvii)}$$

and is found to be 111°.

These conclusions differ from those of Cole[6] and seem to us to be closer to those expected for this radical.

DISCUSSION

Since our primary aim has been to study oxy-radicals of chlorine rather than radiation damage in oxyhalide salts, we discuss our results for each radical in turn.

Chlorine Dioxide.—A comparison of the results obtained for irradiated potassium perchlorate and frozen solutions of chlorine dioxide in sulphuric acid leaves no doubt that they relate to the same radical, even though we have not been able to distinguish clearly between the g- and the hyperfine parameters for the x- and the y-direction, from the rigid solutions. There is an added check in this instance since the hyperfine splitting derived from fluid solutions of the dioxide agree closely with the isotropic portion of the hyperfine tensor for the oriented radicals, and the g-values for solutions are accurately the average of the principal values from the g-tensor.

The power of the spin-resonance method in elucidating structure in this class of radical is well illustrated by a comparison of the results for dioxides with 17 outer electrons ($\mathrm{NO_2}$) and those with 19 outer electrons ($\mathrm{ClO_2}$). The trend in principal g-values is not very helpful for identification, but the difference in hyperfine splitting from the central atom is. This is because there is a relatively large central-atom s-character in the orbital containing the unpaired electron in the 17-electron radicals, but none, to a first approximation, in that of the 19-electron radicals. This difference can be used as diagnostic, at least for the 17-electron dioxides. This sensitivity to s-character provides, in general, a powerful method for estimating the degree of hybridisation of atomic orbitals.

It is not easy, however, as has been shown in detail for chlorine monoxide, to estimate the relative weights of p- and d-character from the anisotropic part of the hyperfine coupling tensor. For simplicity, we have assumed no d-character, and hence our conclusions, summarised in Table 2, represent limits which must be modified in a better analysis to accommodate the d-orbital contribution. An earlier molecular-orbital treatment[4] gave a result which, in contrast with ours, placed the unpaired electron almost completely in a chlorine $3d$-level: this is, we consider, a chemically improbable situation.

Chlorine Monoxide.—There can be little doubt that the spin-resonance spectrum which develops on photolysis of rigid solutions of the dioxide is a property of the monoxide.

Since no spectrum comparable with this has been detected in irradiated oxychloride salts, derivation of the magnitudes of the principle values of the g- and the hyperfine coupling tensors must rest entirely upon our interpretation of the spectrum. This is indicated in Fig. 1, and is correct provided there are no features such as a third more

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[18] Coulson, Victor Henri Vol. Commemoratif, Contribution à l'Étude de la Structure Moleculaire, 1948, p. 15.

remote set of shoulders, which we have failed to detect. This does not seem to be probable.

The g-values attributed to the monoxide are in accord with expectation for a linear molecule; since there is effectively a hole in the π-system, $g_{/\!/}$ (g_y on our system of axes) should be greater than 2·0023, as is observed. In the absence of any intermolecular interactions the ground state should be $^2\Pi_{3/2}$ giving $g_{/\!/} = 4$ and $g_{\perp} = 0$. Our results (Table 1) show that nearly all the orbital contribution has been removed by interaction with the environment, presumably in the form of strong hydrogen-bonding in solid phosphoric and sulphuric acid. Hence we would expect the g-values to vary strongly with environment, so that if the monoxide were trapped in an ionic crystal the present values could not be used for identification.

The hyperfine coupling tensor is less likely to change markedly with environment and may well be diagnostic. If this is true, then our results show that the radical trapped in irradiated potassium chlorate, and identified by Hasty *et al.*[7] as chlorine monoxide, is some other radical. The results do not resemble those for any of the oxides described here, and we tentatively suggest that they may be due to chlorine atoms, formed by the reaction $ClO_3^- \longrightarrow {\cdot}Cl + O_3^-$ and strongly associated with one specific chlorate ion. It is curious, however, that the results for the second, weakly interacting chlorine,[7] give the same relative s- and p-character as do those for the strongly interacting atom. This is hard to understand in terms of structure in which the unpaired electron is preferentially in the p_z-level of the chlorine atom, where the z-axis is the symmetry axis for the chlorate ion. In this structure one would expect an $s:p$ ratio for the chlorate-chlorine atom close to that for chlorine trioxide, whereas the result given by Hasty *et al.* (Table 2) indicates considerably more p-character. This could only arise if the " chlorate " is greatly flattened.

Chlorine Trioxide.—The radical that we have detected in irradiated potassium and magnesium perchlorate is undoubtedly the same as that found by Cole[6] in irradiated ammonium perchlorate. His reasons for identifying this species as the trioxide were that the only chemically reasonable radicals containing one chlorine atom were ClO, ClO_2, ClO_3, and ClO_4 and, of these, ClO_2 could be rejected because the experimental results for these radicals are quite different. The monoxide was rejected on the grounds that a large deviation of the g-value from 2·0023 would be expected. We agree with this identification and our results for the monoxide show that its g- and hyperfine parameters differ from those of the radical under consideration.

Further, the results obtained are satisfactorily in accord with expectation for the trioxide, as indicated in Table 2. Unfortunately, the bond angle for the trioxide is unknown, but the molecule is probably pyramidal.[19] The bond angle for chlorate ions[20] is 106·7°, so that our value of 111°, estimated on the approximation that the chlorine orbital is an s–p-hybrid, seems reasonable. This result should be compared with that of Horsfield *et al.*[21] for a radical identified as PO_3^{2-} and formed by irradiation of disodium hydrogen phosphite, $HPO_3^{2-} \longrightarrow H{\cdot} + PO_3^{2-}$. We have also detected this radical in a variety of damaged oxy-salts of phosphorus and there can be little doubt that the identification is correct. The results are consistent with those assigned to the iso-electronic chlorine trioxide and recently Chantry *et al.* have completed the series by detecting the radical ion SO_3^- in various irradiated solids.[22] The results for PO_3^{2-} and SO_3^- are included in Table 2 for comparison.

Two features of the results merit attention, namely, the apparent constancy of the bond angle on going from PO_3^{2-} to ClO_3, and the steady increase in delocalisation of the unpaired electron on to oxygen in this sequence. This trend is the same as that for the

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[19] Walsh, *J.*, 1953, 2301.

[20] Kartha, *Acta Cryst.*, 1952, **5**, 845.

[21] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 475.

[22] Chantry, Horsfield, Morton, and Whiffen, to be published.

isoelectronic radicals CO_2^- and NO_2,[1] and arises for similar reasons. Thus the increased oxygen character is a direct consequence of the greater nuclear charge or electron-affinity of the central atom. This results in an increased tendency for the bonding electron-pair in the $4a_1$-level to migrate to the central atom and hence the single anti-bonding $3a_1$-electron is constrained towards oxygen. The bond angle is relatively insensitive to a_p^2 in this region so that, even though the bond angle is fairly constant, an expected trend is observed in p-character on the centre atom.

Other Radicals.—In addition to the simple oxides of chlorine and an unidentified radical formed in potassium chlorate containing two chlorine atoms discussed above, various other radicals have been detected. Of these, all but the ozonide ion, O_3^-, remain unidentified and are being studied further.

In several crystals, notably chlorates, a strong line close to $g = 2$ has been detected. Hasty *et al.*[7] decided that this was a property of the superoxide ion, O_2^-, but the properties they give are not in accord with results for this radical in alkali-metal superoxides.[23] The appearance of an intense absorption band at 461 mμ for such crystals led one of us [24] to postulate that this radical was, in fact, the ozonide ion. We have found that, on cooling to 77°K, the spin-resonance band becomes far better resolved, with marked shoulders at high and low fields and resembling the curve to be expected for a single radical with no magnetic nuclei and three clearly different principal g-values. The values derived from this spectrum are given in Table 1, and are close to those expected for the ozonide ion, the central value being identical with that observed for solid sodium ozonide.[12] The g-tensor for this radical should not have axial symmetry and might be expected to resemble qualitatively that of chlorine dioxide which has a similar electronic structure. This is, in fact, the case, and together with evidence supplied by the visible band at 460 mμ this result constitutes good evidence in favour of our assignment.

Reactivity.—A discussion given earlier [1] for the relative reactivities of CO_2^- and NO_2 is relevant also for the radicals PO_3^{2-}, SO_3^-, and ClO_3. Only the last of these is not completely dimerised under normal conditions, despite the fact that charge repulsion must oppose dimerisation in the other ions. This is due to the greater delocalisation of the unpaired electron on to oxygen in chlorine trioxide. Again, a hydrogen atom adds preferentially to the oxygen in SO_3^- but to the phosphorus in PO_3^{2-}.

Dimerisation of 19-electron dioxides differs from dimerisation of the trioxides discussed above and of the 17-electron dioxides [1] in that two extreme modes of interaction are possible. For chlorine dioxide, for example, dimerisation through chlorine could simply proceed through overlap of the p_x-chlorine orbitals, or, if rehybridisation with the electrons in the $4a_1$-level occurred, a molecule could be formed having an approximately tetrahedral configuration about each chlorine, a lone-pair of electrons occupying one position on each chlorine.

This problem has been discussed by Dunitz,[25] who found that the structure of the dithionite ion in crystalline sodium dithionite is about mid-way between these extremes, the angle between the planes of linked SO_2^- groups being only 30° from parallel, and the ion being in the *cis*-configuration with eclipsed oxygen atoms. This tilting, together with the somewhat surprising conformation and the exceptionally long S–S bond (2·389 Å) has been elegantly explained by Dunitz [25] in terms of hybridisation of sulphur p_x- and d_{xz}-atomic orbitals and the formation of a σ-bond through these. The advantage of this description is that it helps to explain why the oxygen atoms are eclipsed: as it stands, however, it does not explain why the O–S–O angle is reduced to about 109° from the expected angle of about 118° for SO_2^- (cf. ClO_2) nor why the electrons in the $4a_1$-level, which are concentrated along the bisector of this angle and pointing away from oxygen, do not exert a dominating effect in a structure which forces them close together. Our

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[23] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443.

[24] Symons, *Ann. Reports*, 1960, **57**, 68.

[25] Dunitz, *Acta Cryst.*, 1956, **9**, 579.

second representation does explain the last observations qualitatively, but, without invoking arguments based upon p–d-hybridisation we can offer as the only explanation for the *cis*-eclipsed structure that it is dictated by interionic forces in the crystal, or that, in view of the very long, weak, S–S bond there remains some slight vacancy in the oxygen p_x-levels which could result in a lowering of the repulsion between eclipsed oxygens.

If the geometrical requirements are similar for dithionite and Cl_2O_4, then the overriding factor opposing the formation of the latter molecule must again be the extra energy required to localise the unpaired electron in chlorine dioxide, which, for reasons given above, is likely to be more delocalised on to oxygen than that in SO_2^-. We draw attention to the differing tendencies of chlorine dioxide and trioxide to dimerise: whereas the trioxide is largely dimeric at room temperature, we have no evidence for dimerisation of the dioxide in ethanol at about −80°.

However, our results show that the unpaired electron is delocalised far more extensively on to oxygen in the trioxide than the dioxide (Table 2). In our opinion, the geometrical requirements outlined above are of great importance in determining this behaviour, the requirements being stringent for the dioxide and resulting in considerable change in shape on bonding, but mild for the trioxide, which is ideally disposed to form a strong σ-bond on dimerisation.

Effect of Environment.—Whilst no direct evidence for interionic effects, such as those obtained from irradiated formates,[1,17] has resulted from these studies, there are secondary differences in certain hyperfine and g-tensors which must be ascribed to such effects. We draw attention to the results given in Table 1 for chlorine trioxide in different host crystals. It seems that the major change is in the amount of delocalisation on to oxygen rather than in bond angle, the latter being insensitive to small changes in the $s : p$ ratio.

Results for chlorine dioxide are also a function of environment, both for fluid solutions and for radicals trapped in crystals.

In general, these changes are thought to be associated with varying degrees of interaction with cations of the crystal or protons of the solvent, probably primarily through the oxygen atoms; such effects will be considered in more detail later.

The Use of Amorphous Powders or Glasses.—A great deal of recent work in the field of electron-spin resonance has stressed the importance of using single crystals.[24] We hope that our present results will serve as a reminder that, in some instances, results from powders or glasses can be extremely valuable, especially in cases such as those reported in which only one nucleus having I greater than $\frac{1}{2}$ contributes to the hyperfine structure and there are large differences in the principal g-values. Thus we are able to extract parameters from irradiated perchlorates for chlorine trioxide which are comparable with those derived from single crystals, except that the direction cosines of the magnetic axes relative to the crystal axes are not known. These directions are often unimportant chemically, so that one can, on occasion, save much labour by studying powders.

Where results from single crystals containing oriented radicals are unavailable, many assumptions have to be made if results from powders are to be used. Always, one must assume that the principal axes of the hyperfine coupling and g-tensors coincide, and often it is difficult to differentiate between a hyperfine component and a shoulder comprising one extreme of an asymmetric line. However, measurements at two wavelengths, coupled with a knowledge of the chemistry and structure of likely radicals, are generally sufficient to eliminate alternatives.

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