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Iodine Oxides. Part V. The Crystal Structure of $(IO)_2SO_4$

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The crystal structure of $(IO)_2SO_4$ at 100 ± 5 K has been determined from three-dimensional X-ray data. The structure is monoclinic, space group $C2/c$. The elementary cell contains four formula units and has the dimensions: $a = 15.177(3)$ Å, $b = 4.6854(8)$ Å, $c = 9.810(2)$ Å, $\beta = 125.17(2)°$. The following values were found for the positional parameters: $x = 0.16348(7)$, $y = 0.7066(2)$, $z = 0.2519(1)$ for I in 8(f); $y = 0.1773(11)$ for S in 4(e); $x = 0.2835(8)$, $y = 0.9861(24)$, $z = 0.3576(13)$ for O(1) in 8(f); $x = 0.0960(8)$, $y = -0.0032(26)$, $z = 0.3677(14)$ for O(2) in 8(f); $x = 0.0212(8)$, $y = 0.3550(25)$, $z = 0.1471(13)$ for O(3) in 8(f).

The structure comprises distinct, sandwich-like layers arranged parallel to (001). Within the layers infinite $(IO)_n$ spiral chains along [010] are linked together by SO_4 tetrahedra. A tentative discussion of the chemical bonding in $(IO)_2SO_4$ is presented.

Iodine dioxide (I_2O_4) decomposes irreversibly in I_2O_5 and I_2 at a temperature of about 125°C. However, on introducing H_2SO_4 (or H_2SeO_4) as a reaction medium for I_2O_5 and I_2, the process can be reversed through a two-stage reaction. The first stage terminates by the isolation of an intermediate product with the composition I_2SO_6 (or I_2SeO_6).

Although I_2SO_6 was first isolated as early as 1844 [1] and subjected to regular studies [2–22] thereafter, very little decisive information concerning its properties is available. In fact, most of the research effort on the compound has been concentrated on establishing its correct composition. (The controversy, which seems now unequivocally resolved, concerned the question of whether one,[9,14,15] one half,[4,5,7,11] or no [11–13,16–22] molecule of water is to be included in the formula.) Another subject open to discussion is whether I_2SO_6 is to be regarded as essentially ionic,[12,13,16,18] *i.e.* $(IO^+)_2(SO_4)^{2-}$ (iodosyl sulphate), as a covalent inorganic polymer [17] containing $(IO)_n$ groups linked to SO_4 tetrahedra, or as an addition compound[11–13] of the type $I_2O_3.SO_3$. The latter problem can only be resolved by means of a complete structure determination, and the results of such a study are presented here.

EXPERIMENTAL

Several batches of I_2SO_6 were prepared by shaking the theoretical quantities of finely powdered I_2O_5 and I_2 in conc. H_2SO_4, *cf.*, *e.g.*, Ref. 20. The products were thoroughly washed with conc. H_2SO_4. Well shaped single crystals were obtained by recrystallization from a hot solution of I_2SO_6 in conc. H_2SO_4.

Crystals were removed from the mother liquor by pipetting, quickly dried on a porous plate, and immediately picked up with a goniometer head readied with a glass fibre and adhesive. The crystal was then placed in a cold gas stream on a Syntex $P\bar{1}$ diffractometer fitted with a modified Enraf-Nonius cooling device. The time elapsed from a crystal had been dried until it was positioned in the cold gas stream was ~ 10 s. This quick manipulation is necessary because a ~ 30 s exposure to laboratory atmosphere will cause serious decomposition. The temperature at the crystal site (constant to ± 0.2 K) was 100 ± 5 K. Under these conditions no crystal decay was observed.

The crystals showed a marked tendency towards twinning, and 5 – 10 specimens were examined before one which gave a reasonably good ω scan for several reflections was found. As became apparent later (see section on structure determination and refinement) the crystal used for data collection was not entirely free of twinning symptoms.

Three-dimensional intensity data were obtained by diffractometer measurements using graphite crystal monochromatized Mo$K\alpha$-radiation. Reflections with $2\theta < 55°$ were

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measured with the ω-2θ scan technique in a variable scan rate mode (2° min^{-1} for the majority of the reflections, but up to 6° min^{-1} for the strongest reflection), very weak reflections (*viz.* those with intensities below a threshold value) being automatically omitted. The scan range was $2\theta(\alpha_1) - 1.4$ to $2\theta(\alpha_2) + 1.1°$, and the background was measured (for 70 % of the scan time) at each of the scan range limits. Measurement of check reflections was repeated every 50th reflection, no systematic variation being detected. A total of 648 unique reflections were recorded as "observed" [$I_{net.} > 3\sigma(I)$]. Unobserved reflections were not included in the calculations.

The crystal was sufficiently large to warrant absorption corrections to be made. However, the amount of adhesive needed to pick up the crystal quickly was large enough to impede subsequent measurement of crystal dimensions, and absorption correction was accordingly not performed.

The calculations were performed on CD 3300 and CD 7600 computers using programmes by Dahl *et al.*[23] and Hope.[24] The atomic scattering factors used in the final refinements were taken from Doyle and Turner [25] and the values for the real and imaginary parts of the dispersion (for iodine only) from Cromer and Liberman.[26]

Throughout this paper estimated standard deviations (e.s.d.) applying to the least significant digits are given in parentheses following the corresponding parameter values.

CRYSTAL DATA

I_2SO_6, $M = 381.85$.
Transparent, approximately prismatically shaped crystals of yellow colour.
Monoclinic.
$a = 15.177(3)$ Å, $b = 4.6854(8)$ Å,
$c = 9.810(2)$ Å, $\beta = 125.17(2)°$.
Unit cell volume: 570.2(4) Å^3.
Unit cell content: 4 I_2SO_6 groups.
Calculated density: 4.447 g cm^{-3}.
Systematic extinctions:
hkl absent when $h + k = 2n + 1$
$h0l$ absent when $l = 2n + 1 (h = 2n + 1)$
Space group: $C2/c$
(The preliminary crystallographic data reported in the preceding paper of this series [22] refer to a pseudo cell defined by: $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = 1/3\mathbf{a} + \mathbf{c}$, which give $\beta' \approx 90°$.)

STRUCTURE DETERMINATION AND REFINEMENT

Space group extinct reflections with l odd were recorded for the $h0l$ zone. A number of these reflections with $h = \pm 4, \pm 12$ were found to have significant intensities. The dimensions of the reciprocal lattice are such that a 180° rotation about the vector $\mathbf{b}^* \times \mathbf{c}^*$ places even l lattice points of the original lattice with $h = \pm 4, \pm 12$ at odd l points in the rotated lattice, whereas for $h = 0, \pm 8, \pm 16$ the coincidence is even-even. The relative magnitudes of the individual parts of a crystal assumed to be twinned as described were established from the $h0l$ intensities to be near 10:1. Based on this model the intensities of all $4n,k,l$ reflections were adjusted to correspond to those of the major crystal.

The approximate positions of the crystallographic equivalent iodine atoms were easily deduced from a three-dimensional Patterson synthesis. A set of structure factors calculated on the basis of these iodine parameters gave $R = 0.32$, and the corresponding Fourier map produced the location of the sulphur atoms in addition to shifts of the iodine atoms. After a preliminary refinement of the atomic coordinates of iodine and sulphur (giving $R = 0.18$), the positions of the three non-equivalent oxygen atoms were deduced from a second Fourier map. Subsequent full matrix least squares refinement with isotropic temperature factors converged to $R = 0.092$. A refinement with anisotropic temperature factors for all atoms lowered R to 0.057, but it is clear that the indicated anisotropy is, at least partly, a result of lacking absorption correction rather than of anisotropic motion. The β_{22} values for I and S are nearly zero. We therefore decided to base the description of the structure on the results from the isotropic refinement. Because the low-order reflections normally are most seriously affected by experimental errors, we excluded observations with $\sin\theta/\lambda < 0.25$ from the refinement. Although e.s.d. for F_{obs} based on counting statistics was available, the model errors indicated above led us to use the weighting scheme of Hughes,[27] with $4I_{min.} = 67$.

The final R factor is higher than normally seen for good diffractometer data. We therefore have used additional criteria to establish the essential correctness of the structure. A difference Fourier synthesis showed that all atoms had been accounted for, and that no atom had been grossly misplaced. A listing of F_{obs}/F_{calc} ratios in groups with constant h,k and varying l shows a uniform variation of the ratio as a function of l. Individual ratios within each

Table 1. Final positional and thermal parameters for the crystal structure of $(IO)_2SO_4$. [I, O(1), O(2), and O(3) in position 8(*f*) and S in position 4(*e*) of space group $C2/c$.]

Atom	*x*	*y*	*z*	B(Å^2)
I	0.16348(7)	0.7066(2)	0.2519(1)	0.48(4)
S	0	0.1773(11)	1/4	0.56(9)
O(1)	0.2835(8)	0.9861(24)	0.3576(13)	0.71(15)
O(2)	0.0960(8)	−0.0032(26)	0.3677(14)	1.03(17)
O(3)	0.0212(8)	0.3550(25)	0.1471(13)	0.83(16)

group rarely deviate by as much as 5 % from values estimated from a smooth curve fitted for the group. This is a strong indication that the positional parameters are reliable in spite of a poor determination of the thermal parameters.

The final positional and thermal parameters are listed in Table 1. The observed and calculated structure factor data are available from the authors upon request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Important interatomic distances and angles calculated from the unit cell dimensions and the positional parameters in Table 1 are given in Table 2.

As shown in Fig. 1, the crystal structure of I_2SO_6 comprises distinct, sandwich-like layers arranged parallel to (001). The layers are in turn built up of infinite $(IO)_n$ spiral chains along [010] linked together by SO_4 tetrahedra. Hence, the complete structure may to a reasonable approximation be illustrated by a schematic, two-dimensional diagram of the type postulated by Dasent and Waddington.[17] The overall structural inferences of the latter authors are, in fact, remarkably correct when it is borne in mind that they were based on somewhat poorly resolved infra-red spectroscopic data.

The immediate coordination of each I is most usefully regarded as an almost planar arrangement, comprising two O(1), one O(2), and one O(3). However, the corresponding iodine-oxygen distances separate in two categories [I−O(1) *versus* I−O(2) and I−O(3)], which differ considerably. (The difference between the two I−O(1) distances is not significant, whereas that between I−O(2) and I−O(3) is to be classified as highly signifi-

Table 2. Important interatomic distances and angles in the crystal structure of $(IO)_2SO_4$. (The standard deviations correspond to those in the positional parameters.)

Interatomic distances (Å)			
I−O(1′)	1.966(8)	I−O(3)	2.424(9)
I−O(1)	1.983(9)	2S−O(2)	1.494(11)
I−O(2′)	2.351(9)	2S−O(3)	1.480(10)

Interatomic angles (°)			
O(1) −I−O(1′)	95.2(.3)	O(2)−S−O(2′)	111.1(.7)
O(1) −I−O(2′)	83.7(.3)	2O(2)−S−O(3)	106.8(.6)
O(1′)−I−O(3)	87.5(.3)	2O(2)−S−O(3′)	110.3(.4)
O(2′)−I−O(3)	93.9(.3)	O(3)−S−O(3′)	111.5(.7)
O(1′)−I−O(2′)	175.7(.4)	I−O(1)−I	127.1(.6)
O(1) −I−O(3)	175.0(.4)	I−O(2′)−S	117.1(.6)
		I−O(3)−S	125.7(.6)

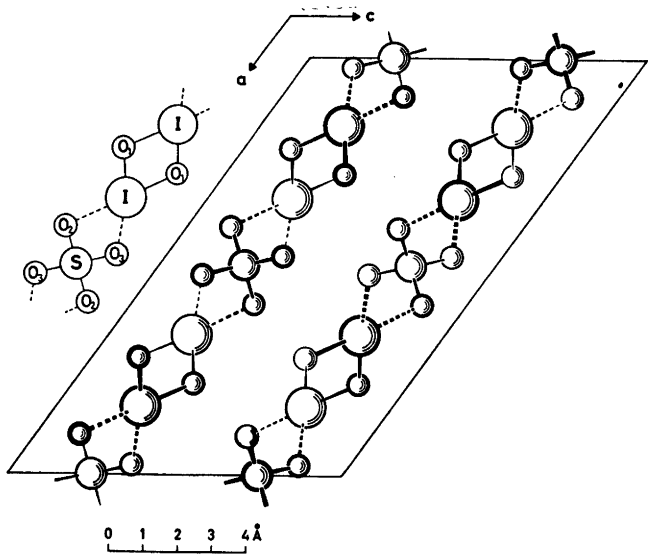


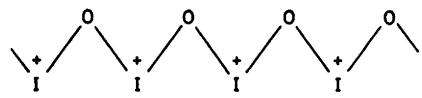
Fig. 1. The crystal structure of $(IO)_2SO_4$ projected along [010]. The numbering of the crystallographically non-equivalent atoms is shown on the left hand side of the diagram. Broken lines indicate contacts between $(IO)_n$ chains and SO_4 tetrahedra.

cant according to the significance test of Cruickshank.[28,29]) This distinction gives rise to the characteristic $(IO)_n$ spiral chains of the structure, the short I–O(1) distances being located within these chains. The longer I–O(2) and I–O(3) contacts join the $(IO)_n$ and SO_4 units of the structure, and as a consequence the already commonly used formula $(IO)_2SO_4$ is appropriate whatever conclusion one may arrive at regarding the nature of the bonding.

The SO_4 units, which are easily recognized in Fig. 1, are of almost perfect tetrahedral symmetry (*viz.* T_d rather than C_2 symmetry imposed by the space group). The bonding S–O(2) and S–O(3) distances are virtually identical and the mutual differences between the O–S–O bond angles as well as their deviations from the ideal tetrahedral value of 109.47° are unimportant (Table 2).

The almost conjectural formulation of $(IO)_2SO_4$ as a simple salt between IO^+ and SO_4^{2-} must immediately be rejected as incompatible with the actual structure. The fact that the S–O bond length in $(IO)_2SO_4$ coincides with the corresponding distances in the ionic sulphates is to be regarded as an accidental circumstance in view of the relatively strong I–O(2) and I–O(3) bonds (*vide infra*).

It has been suggested [17,21] that effective IO^+ cations are present as



This extreme distribution of positive unit-charges located on iodine and, hence, approximately neutral oxygen atoms within the $(IO)_n$ chains seems intuitively improbable. On the contrary, the fact that the intra-chain I–O(1) bond lengths very nearly match the expected value for the I–O single-bond, and the close correspondence in the values for the angles I–O(1)–I, I–O(2)–S, and I–O(3)–S (Table 2 and *vide infra*) strongly suggest that only comparatively small effective charges are located on the different atoms in $(IO)_2SO_4$. However, although the bonding is predominantly covalent, there is a degree of uneven charge distribution on iodine, sulphur, and oxygen, due to their different electronegativities. These partial charge separations may *inter alia* be responsible for the yellow colour of $(IO)_2SO_4$, as suggested by Dasent and Waddington.[17] The following simplified discussion, nevertheless, neglects the polarity of the bonds, and considers $(IO)_2SO_4$ as an idealized covalent macromolecule.

A comprehensive discussion of the bonding characteristics of iodine is difficult due to the many atomic orbitals potentially available for bonding, and the relatively large size and easy polarizability of this atom. In general, a considerable number of possible hybridization schemes for iodine are open for consideration. However, the situation for I in $(IO)_2SO_4$ appears fortunately to be relatively simple and clearcut. The simplest bonding scheme for I involves that two of its p-orbitals are engaged in regular σ-bonds to two O(1) and the (originally empty) $d_{x^2-y^2}$ and d_{z^2} orbitals are used in dative σ-bonding with O(2) and O(3). [The three remaining d-orbitals (d_{xy}, d_{yz}, and d_{xz}) on each iodine are of appropriate symmetry for π-contribution to the I–O(1) bonds (*vide infra*).] This interpretation is consistent with the almost coplanar arrangement of I, two O(1), O(2), and O(3), and the approximately 90° O–I–O bond angles. The differences between the I–O(1) bond lengths on the one hand and I–O(2) and I–O(3) on the other suggest that it is justified to neglect hybridization of the iodine orbitals in this case. The fact that the I–O(2) and I–O(3) bond distances exceed the regular single bond length (*vide infra*) is attributed to the use of d- rather than p- (or s-) orbitals on iodine.

Alternatively, the electron arrangement at I can be compared with that at Xe in, *e.g.*, XeF_4.[30] A twelve-electron system at the central I atom would be arranged in six pairs in a quadrangular bipyramid with the electrons in its basal plane involved in ligand bonding and the apical ones left as unshared pairs. In the present structure we observe a distorted planar arrangement around I, but otherwise the analogy may be reasonable. This picture corresponds well with the assumption of only a small degree of charge separation in $(IO)_2SO_4$.

Because of the non-availability of atomic d-orbitals, the bonding situation associated with oxygen is simpler than for sulphur and iodine. Each oxygen is bonded to either two iodine or one iodine and one sulphur atom. In common with the vast majority of compounds containing two-coordinate oxygen, the arrangements I–O(1)–I, I–O(2)–S, and I–O(3)–S are non-linear. The situation with respect to these bond angles is analogous to that discussed[31] for the intra- and intermolecular I–O–I bond angles in I_2O_5. Following the arguments advocated for the latter case, the two bonding orbitals on each oxygen may be either:

(i) essentially pure p-orbitals for which the theoretical 90° bond angle has been enlarged due to iodine-iodine or iodine-sulphur repulsion* (including charge as well as size effects), or

(ii) result from incomplete sp-hybridization.

Although the average I–O(1) bond distance of 1.97(2) Å is only insignificantly shorter than the currently accepted I–O single-bond length of 1.99 Å (*cf.*, *e.g.*, Ref. 31) we suggest that the I–O(1) bonds possess a slight, but finite degree of π-character (*viz.* p_π–d_π back-bonding from O(1) to I) in addition to a normal single σ-bond. In the S–O(2) and S–O(3) bonds the contribution of π-bonding is unquestionable, since the average S–O bond distance of 1.48(2) Å is 0.21 Å shorter than the presumed S–O single-bond length (derived from the Schomaker-Stevenson[32,33] rule). The theoretically best founded scheme for deriving π-bond order for the type of compounds under consideration appears to be due to Cruickshank.[34] Following Cruickshank the observed S–O bond distances in $(IO)_2SO_4$ amount to an average π-bond order of 0.52(4), which is a quite reasonable value from the point of view of the I–O skeleton of the structure. The implied large degree of freedom for the SO_4 tetrahedra to arrange themselves in favourable positions relative to the $(IO)_n$ chains is also reflected in their almost perfect T_d symmetry. Hence, the sulphur employs four virtually ideally sp^3-hybridized orbitals for the σ-bonds and the originally empty atomic $d_{x^2-y^2}$ and d_{z^2} orbitals for the π-bonding system.

The crystal structure of $(IO)_2SO_4$ is consistent with its instability towards moisture. The H_2O molecules clearly attack the crystals at the SO_4 units. This reaction produces H_2SO_4 and, at least in principle, asymmetric I_2O_3 fragments as may be imagined from Fig. 1. The further separation of I_2 and the rearrangement of the residual unit to form the crystal structure of I_2O_4 is another problem, however.

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*The interatomic I–I ($\geqq$3.53 Å), I–S ($\geqq$3.32 Å), and O–O ($\geqq$2.38 Å) distances in $(IO)_2SO_4$ appear to be consequences of the crystal structure and are therefore regarded as virtually non-bonding, even when they are shorter than the corresponding van der Waals distances of 4.3, 4.0, and 2.8 Å, respectively.

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