[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

An Electron Diffraction Study of Disulfur Decafluorodioxide

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A compound (disulfur decafluorodioxide), isolated from the products of the reaction of sulfur and fluorine, has been prepared by other investigators. To it they have assigned the formula $S_2F_{10}O_2$. Its physical properties are similar to those for disulfur decafluoride; it is diamagnetic. An electron diffraction study of the vapor was made both with and without the use of a rotating sector. Resolution of the radial distribution curve into a series of Gaussian probability peaks for some of the interatomic spacings led to a peroxide-type structure for the molecule, very similar in configuration to that of H_2O_2, with (SF_5) groups replacing the hydrogen atoms. The (SF_6) groups are octahedral, as in SF_6, with the (S–F) spacing (1.56 ± 0.02 Å.). Analysis of the data leads to an (O–O) separation of (1.47 ± 0.03 Å.), and an (S–O) separation of (1.66 ± 0.05 Å.). The S–O–O bond angle is (105 ± 3°) and the angle between the planes specified by the atoms $S_1O_1O_2$ and $O_1O_2S_2$ of the (SF_5) groups out of the axis of the (O–O) link is (107 ± 5°).

Introduction

Fluorine forms compounds with sulfur in all its valency states from the effectively divalent S_2F_2 to the hexavalent SF_6. A second compound of hexavalent sulfur, disulfur decafluoride, prepared by Denbigh and Whytlaw-Gray[2] and by others,[3,4] is very similar to SF_6 in its chemical stability and general properties. The results of an electron diffraction study of the compound support a model consisting of two (SF_5) groups linked by a sulfur–sulfur bond.[5]

Other investigators have isolated a compound from the condensed residues of sulfur–fluorine reactions with a boiling point about 20° higher than that of disulfur decafluoride but possessing similar chemical and physical properties.[6] Vapor density measurements indicated the molecular weight to be about 30–32 units greater than that for disulfur decafluoride, and this suggested the possibility of the presence of two oxygen atoms in addition to two sulfur and ten fluorine atoms.

Quantitative analyses gave almost the theoretical values for sulfur and fluorine for a molecule of empirical formula $S_2F_{10}O_2$. No positive identification of the oxygen was obtained, but its presence was supported by the fact that, of the various atoms that might explain the extra 30 molecular weight units, phosphorus was excluded by chemical tests; sulfur was excluded on a basis of the quantitative analytical results; and it was virtually impossible to construct a molecule with nitrogen or silicon. The empirical formula, $S_2F_{10}O_2$, was assigned and some of the physical properties of the compound determined, Table I. For comparison, the properties of disulfur decafluoride are listed as well.

TABLE I

PROPERTIES OF S_2F_{10} AND $S_2F_{10}O_2$

Property	$S_2F_{10}O_2$	S_2F_{10}
Mol. wt. (from vapor density)	289 (theor. 286.1)	254.1
Liquid density, g./ml. at 20°	1.82	−2.08
M.p., °C.	−95	−53
B.p., °C. (atm. pressure)	+49	+29

Two structural formulations have been suggested. If the terminal fluorine atoms of the (SF_5) groups in S_2F_{10} are replaced by (OF) groups one obtains $OFS–SF_4–SF_4–OF$. Alternately, the oxygen atoms may form a peroxide linkage $F_5S–O–O–SF_5$. A chemical argument may be cited in favor of the latter configuration; one would expect $FO–SF_4–SF_5$ to appear as a precursor of $FO–SF_4–SF_4–OF$, but no evidence of this intermediate was reported. The configuration $FO–SF_4–O–SF_5$, although not plausible, cannot be rejected on *a priori* grounds. The objective was to establish the molecular configuration by an electron diffraction investigation of the vapor, and to deduce bond lengths and valence angles in this interesting substance.

Experimental

At room temperature a sample, sealed in a glass bulb, appeared as a mobile water-white liquid in which no visible changes were apparent over a period of two years. The boiling point at atmospheric pressure, and the melting point were checked. Vapor density measurements gave results about 1% high for the molecular weight (289 as compared to 286 calculated). A sample of the liquid was found to be diamagnetic at room temperature.

Examination in a mass spectrometer of samples of the gas gave some support to the presence of oxygen. However, impurities from the sample used, or possibly from reaction with stopcock grease or the walls of the reaction vessel, rendered these data not too reliable.

Samples of the material used for diffraction photographs were redistilled *in vacuo*, and vapor density measurements were made as a criterion of purity. A separate gas sample was used for each set of pictures taken. The pressure of the gas admitted to the camera was controlled by a Dry Ice-acetone-bath, about 15–17 mm. pressure being obtained at −30°. The diffraction camera and the techniques employed are described by Hastings and Bauer.[7]

Sector as well as non-sector photographs were taken. The diameters of the rings of the diffraction pictures were measured and the maximum and minimum intensities were estimated visually on an arbitrary scale so that a "visual curve" of intensity *vs.* ring diameter could be drawn. The microphotometer tracings from the sector photographs provided intensity data (relative to unit background) over the range $10 < q < 65$ where $q = 40/\lambda \sin \theta/2$. Structure in the non-sector pictures could be observed to about $q = 92$. A composite curve of intensity *vs.* q was then drawn using (1) a computed curve for a model which, from initial trials, appears to be quite satisfactory for the region $0 < q < 10$ or 12, over which both visual and microphotometer observations are uncertain; (2) microphotometer intensity values from about $q = 10$ or 12 (the end of the computed curve) to $q \simeq$

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[1] Suffield Experimental Station, Ralston P. O., Alberta, Canada.

[2] K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

[3] N. R. S. Hollies and R. L. McIntosh, *Can. J. Chem.*, **29**, 49 (1951).

[4] W. C. Schumb, *Ind. Eng. Chem.*, **39**, 421 (1947).

[5] R. B. Harvey and S. H. Bauer, THIS JOURNAL, **75**, 2840 (1953).

[6] Our sincere thanks are due to Dr. J. W. Dale and Mr. D. A. MacLeod of Defence Research Chemical Laboratories, Ottawa, Canada, for the sample of the compound supplied to us for this investigation; and for making available to us their unpublished results on the density of the liquid (Table I), and the quantitative analysis for sulfur and fluorine.

[7] J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

65; and visual values of peak or valley positions in a few cases where the microphotometer values of positions were somewhat uncertain; and (3) visual estimates both of position and intensity from $65 < q < 92$. Intensity data from the tracings of the microphotometer records were used over the range $10 < q < 65$ (multiplied by 100 for convenience in plotting) the arbitrary scale of the visual curve being matched so that the data for the composite curve might be extended to $q \simeq 92$. This curve now represents the observed data which are summarized in Table II.

TABLE II

INTENSITY DATA FROM DIFFRACTION PHOTOGRAPHS

Max.	Min.	Visually estimated $q_0{}^a$ (non-sector)	Visually estimated relative intensity	Visually estimated q_0 (sector)	Microphotometer intensities (relative to unit background)	Final values q	Intensity
1		..	...	..	.....	..	....
	1	9	(−19)	(8)	−0.077	8	− 7.7
2		11	+19	(11)	+ .108	11	+10.8
	2	15.7	−10	15.6	− .100	15.6	−10.0
3		19.4	+22	19.5	+ .103	19.4	+10.3
	3	23.3	−19	23.3	− .162	23.3	−16.2
4		28.5	+18	28.8	+ .196	28.7	+19.6
	4	34.5	−10	34.0	− .086	34.2	− 8.6
5		38.9	+ 8	39.6	+ .048	39.4	+ 4.8
	5	43.4	− 2	44.4	− .037	44.0	− 3.7
6		46.8	+ 2	47.0	− .022	47.0	− 2.2
	6	50.4	− 4	49.6	− .044	49.9	− 4.4
7		55.2	+ 4	55.0	+ .037	55.1	+ 3.7
	7	60.6	− 4	60.8	− .044	60.8	− 4.4
8		64.9	+ 3	65.1	+ .033	65.0	+ 3
	8	72.6	− 1.5			72.6	− 1.5
Shoulder		78.0	+ 0.5			78.0	+ 0.5
9		80.4	+ 1			80.4	+ 1
	9	86.3	− 0.5			86.3	− 0.5
10		92.0	+ 0.5			92.0	+ 0.5

[a] Refers to observed values.

Analysis of Data

1. **Method.**—The composite intensity curve was inverted to a radial nuclear charge density distribution curve by the method of Bauer and Coffin.[8]

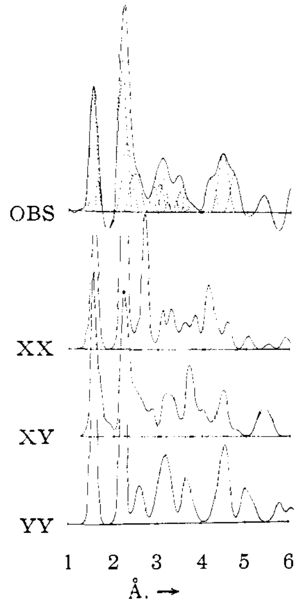


Fig. 1.—The radial nuclear charge density distribution curve derived from the intensity data. The curve from 1–4 Å. has been resolved into a series of Gaussian probability distributions, each corresponding to a spacing in the molecule. A peak in the envelope of the curve from 0–1 Å. is spurious since no atomic spacing corresponds to this distance. The synthetic radial distribution curves XX, XY, YY, correspond to models with a sulfur–sulfur link, a sulfur–oxygen–sulfur link, and a peroxide-type link, respectively.

The integral of the Fourier inversion is approximated by

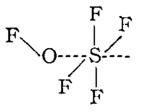
$$2\pi^2 r \underline{D}^*_{\mathrm{m}}(r) \cong \int_0^{s_{\max}} [s_{\mathrm{m}} \underline{J}(s)]_{\mathrm{composite}} \exp[-\gamma^2 s^2] \sin rs \, ds$$

where $\underline{D}^*_{\mathrm{m}}(r)$ is the charge distribution function corresponding to an intensity curve for nuclear scattering $[\underline{J}_{\mathrm{m}}(s)]$ over the range 0 to $s_{\max}$. The parameter γ is adjusted so that the additional temperature factor $\exp[-\gamma^2 s^2] \simeq 0.1$ at $s = s_{\max}$. For convenience in writing formulas the substitution $s = (\pi/10)q_0$ has been used.

When the inversion is carried out in this manner and the intramolecular vibrations are simple harmonic, the resulting radial distribution curve consists of the envelope of superposed Gaussian probability curves, each of which, ideally, represents an interatomic spacing in the molecule. Thus, when the radial distribution curve is prepared from sufficiently accurate data it is possible to resolve it into its component atom-pair distributions. An exact treatment is not always possible, especially with molecules of some complexity where many small contributions are present, and internal rotations are expected.

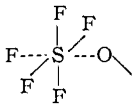
The radial distribution curve in Fig. 1 has been obtained by the procedure outlined above. If any peak of the envelope consists of more than 2 or 3 separate contributions it is not usually possible to obtain a complete resolution, unless some *a priori* information on the structure of the molecule can be used to assist the analysis.[9] This is demonstrated in Fig. 1. The peak at 1.56 Å. can be separated into its three components due to the asymmetry of the two sides. Substantially the same thing can be done for the peak at 2.23 Å. However, it is necessary to have a molecular model to assist in the analysis of the peaks from 2.9 to 3.9 Å.; and the envelope from 4 to 5 Å. has been resolved only broadly, since it is composed of a large number of small contributions which shift with each small change in molecular parameters. The shape of the curve from 0–1 Å., and the negative portion at 5.5–6 Å. are spurious, the result of imperfect intensity data or improper background corrections.

2. **Choice of the Molecular Model.**—On a basis of its physical properties, its considerable chemical stability, and the valences commonly shown by the atoms S, F and O, the molecular configuration of $S_2F_{10}O_2$ is likely to be symmetrical. Such an assumption leads to two (SF_5O) groups joined; with hexavalent sulfur two possibilities arise



X

and



Y

Bridge structures were attempted but failed to give interatomic distances compatible with the results of experiment.

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[8] K. P. Coffin, Ph.D. Thesis, Department of Chemistry, Cornell University (1951). See also brief description in ref. 5.

[9] F. A. Keidel, Ph.D. Thesis, Department of Chemistry, Cornell University, 1951.

From a preliminary calculation of "synthetic" radial distribution curves using reasonable structural parameters[10] it is possible to discriminate between configurations which may be labeled XX, YY and XY, constructed from the above, and to discard any which appear to be unsuitable, before identifying the spacings in the chosen model with the features of the observed radial distribution curve. In the synthetic radial distribution curve, a temperature factor is assigned to each distance which, in effect, allows it to vary about its mean value according to a Gaussian probability distribution function. The following temperature factors were chosen: $\alpha^2 = 0.0015$ for bonded atom pairs; $\alpha^2 = 0.0023$ for next-to-bonded atom pairs; and $\alpha^2 = 0.0034$ for distant atom pairs, in the function

$$r_{ij} = r_{ij}^0 \exp\left[-\frac{(r_{ij}^0 - r_{ij})^2}{4\alpha^2}\right]$$

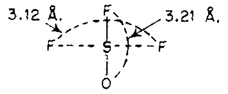
These curves were adjusted to have an area proportional to the scattering power of the atoms concerned. They were plotted on a length scale (Å.) and summed to give an envelope which represents the synthetic radial distribution curve.

In Fig. 1 the observed radial distribution curve is plotted along with those for structures XX, XY and YY and it is clear that the discrepancies for structures XX and XY are of such a nature that minor adjustments of distances would be unlikely to provide a fit. In contrast, structure YY gives a radial distribution curve whose general features match with the observed curve fairly well; the essential difference between them is that the resolution in the observed curve is not quite as good as that assumed in preparation of the synthetic curves.

3. Identification of Molecular Spacings.—Partial resolution of the envelope of the radial charge density distribution into its components can be accomplished before the most probable model is selected. The (S–F) spacing is reported to be 1.56[11,12] and 1.58 Å.[13] A value of 1.56 Å. was reported by Harvey and Bauer[5] in S_2F_{10}.

Both shoulders of the radial distribution envelope forming a peak at about 1.56 Å. are unsymmetrical when they are plotted on a large scale and two small contributions may be separated: one at 1.46 Å. and assumed to be due to the (O–O) bond, and one at about 1.66–1.67 Å. and attributed to the (S–O) bond. With the (S–F) bond length equal to 1.56 Å. and an octahedral (SF_5O) group, one looks for a spacing to be identified with the fluorine atoms (F–F), at about 2.20 Å. This is found in the next large peak, together with a contribution at about 2.30 Å. attributed to an (O–F) spacing, and one near 2.48 Å. suggested to arise from the interaction of the nearest fluorine atoms on the separate (SF_5O) groups. When the upper part of the peak at about 2.23 Å. is plotted on a large scale it is nearly symmetrical with a faint shoulder on the right hand side; the maximum occurs at 2.23_5 Å. Synthesis of a number of peaks with a fixed (S–F) bond (1.56 Å.) and various (S–O) distances indicates that the best fit is obtained when the (S–O) spacing is between 1.65 and 1.70 Å. From this evidence (and the independent peak at 1.66–1.67 Å.) the range of values for the (S–O) bond was restricted to 1.65–1.70 Å.

Identification of the components that make up the peak at 3.1 Å. is less certain. The shoulder on the left-hand side of this peak suggests the occurrence of a spacing at about 2.9 Å. Using the atomic spacings found in the first two peaks for (S–F) and (S–O), *i.e.*, 1.56 and 1.67 Å., respectively, two additional spacings at 3.1 and 3.2 Å., should be found in the (SF_5O) group as indicated in the figure, and a peak between 3.0 and 3.1 Å. is required to form the radial distribution envelope. The peaks at 2.9 and 3.0 Å. are probably due to (O–F) and (S–F) distances, the atoms being located on separate (SF_5O) groups. Calculations of molecular parameters for peroxide-type models suggested that the (S–S) spacing occurs at about 3.5 Å. Since there is a single (S–S) spacing in the molecule, the envelope probably includes (O–F) spacings from atoms in separate (SF_5O) groups at about 3.6 and at 3.8 Å., and a small (F–F) spacing at about 3.4 Å. The resolution is poor from 3.2–3.4 Å. possibly due to small contributions from several spacings which cannot be defined accurately. The broad peaks from 4–5 Å., at 5.4 Å., and at 6 Å. include (S–F) and (F–F) spacings from one (SF_5O) group to the other and are difficult to decompose further.



4. Refinement of Parameters.—A series of radial distribution curves was calculated on a basis of the parameters listed in Table III and the curves

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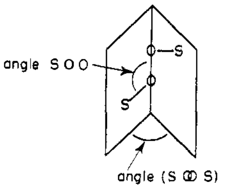
[10] The region in which one may expect to find any given atomic parameter can be defined broadly by a consideration of the covalent radii of the atoms and the experimental values of interatomic distances, (or the bond angles as the case may be). See V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941), and P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950). (a) (S–O) bond—the sum of covalent radii is 1.67 Å. A range of variation of 1.60–1.75 Å. was used for the computation of radial distribution curves. (b) (S–S) bond—the sum of covalent radii is 2.08 Å. Harvey and Bauer[5] report the value 2.21 Å. for the compound S_2F_{10}. (c) (O–F) bond—the sum of covalent radii is 1.42 Å. The (F–O) distance in FNO_3 is 1.42 Å, and in F_2O it is 1.41 Å. A value of 1.40 Å. was used for preliminary calculation. (d) (O–O) bond—for H_2O_2 the bond distance is given as 1.46–1.48 Å. and a range of 1.42–1.48 Å. was used. (e) Bond angle (F–O–S)—this angle was assumed to be 100° although the value may be a bit too small. (f) Bond angle (S–O–O)—for H_2O_2 the value of the analogous angle H–O–O is given as 101.5°. The angle of the bond in divalent oxygen appears to vary from reported values of 100° in F_2O to 115° in Cl_2O. For the case considered here the angle is probably greater than in F_2O for steric reasons, but a range of 100–115° was used. (g) Bond angle out of the axis of the (O–O) link—this angle is referred to as the (S ∞ S) angle and, in H_2O_2, the analogous angle is reported to be 106°. If the



(S ∞ S) angle is not smaller than the corresponding angle in H_2O_2, a sensible range of variation might be 105–115°.

[11] H. Braune and S. Knoke, *Z. physik. Chem.*, **B21**, 297 (1933).

[12] D. P. Stevenson and H. Russel, Jr., THIS JOURNAL, **61**, 3264 (1939).

[13] L. O. Brockway and L. Pauling, *Proc. Natl. Acad. Sci.*, **19**, 68 (1933).

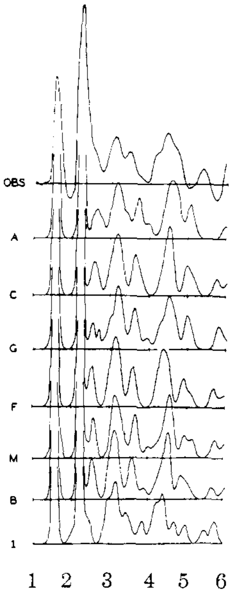


Fig. 2.—Synthetic radial distribution curves for models with a peroxide-type linkage. The details of the parameters are given in Table III.

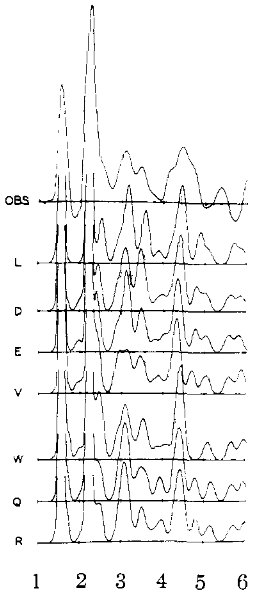


Fig. 3.—Synthetic radial distribution curves for models with a peroxide-type linkage. The details of the parameters are given in Table IV.

were plotted in Fig. 2. In these calculations the (SF_5O) group has been considered to be octahedral, and a constant spacing of 1.56 Å. for the (S–F) bond was used (on a basis of the definite peak of the radial distribution curve, and the evidence of Harvey and Bauer[5]). A few preliminary tests showed that as the angles S O O and S ∞ S were made larger, the bonds (S–O) and (O–O) must be shortened to maintain a general fit between computed and observed distribution curves. Models A, C, G and F suggest that 110° is probably an upper limit. The effects of reducing the angles is shown in models M, B and I. The last model (I) is too small, but if the bond lengths are increased ((S–O) bond from 1.65 to 1.70 Å., and the (O–O) bond from 1.46 to 1.48 Å. models Q and R are obtained with general agreement between observed and computed curves (Fig. 3). A model was tested with angles S O O and S ∞ S equal to 102 and 105°, respectively, and the (S–O) and (O–O) bond lengths equal to 1.70 and 1.48 Å., but the features of the computed curve indicated the model to be too small. Models M and C show good agreement between computed and experimental radial distribution curves.

Table III

Parameters for Molecular Models of $S_2F_{10}O_2$

	Bonds, Å.		Bond angles, deg.		Spaciugs,[14] Å.	
Model	(S–O)	(O–O)	<SOO	<S∞S	S′–S″	F′–F″
A	1.65	1.46	112	112	3.71	2.75
C	1.65	1.46	110	110	3.62	2.67
G	1.65	1.43	110	110	3.61	2.65
F	1.62	1.46	110	110	3.58	2.58
M	1.70	1.46	110	105	3.66	2.55
B	1.65	1.46	110	105	3.56	2.54
I	1.65	1.46	105	105	3.43	2.30

Some further confirmation of this argument may be obtained from the models calculated on a basis of the parameters in Table IV and plotted in Fig. 3. The parameters for model L give a configuration which appears to be too large. Models D and E show peak heights not in strict conformity with those of the observed curve. Progressive reduction of both bond angles and bond lengths to those of model V has given a model which is too small, but lengthening of the (S–O) bond from 1.65 to 1.70 Å. in model W results in a moderately good fit with the observed curve. Models Q and R, in which both bond angles are reduced to 105° but with (S–O) and (O–O) bonds lengthened, result in a fairly good fit between the observed and computed curves.

Table IV

Parameters for Molecular Models of $S_2F_{10}O_2$

	Bonds, Å.		Bond angles, deg.		Spacings, Å.	
Model	(S–O)	(O–O)	<SOO	<S∞S	S′–S″	F′–F″
L	1.62	1.43	110	110	3.56	2.60
D	1.65	1.46	105	110	3.50	2.45
E	1.62	1.46	105	110	3.47	2.40
V	1.65	1.46	102	110	3.41	2.37
W	1.70	1.46	102	110	3.48	2.46
Q	1.70	1.46	105	105	3.48	2.42
R	1.70	1.48	105	105	3.51	2.44

Only general conclusions about atomic parameters and about the relative magnitudes of the angles S O O and S ∞ S, can be drawn from this group. A radial distribution curve calculated for a model with (S–O) = 1.70 Å. (O–O) = 1.48 Å., and angles S O O and S ∞ S of 102 and 105°, respectively, was essentially small in its features and suggested that these values of the angles might represent lower limits. Model C suggests an upper limit of 110° for both angles if the (S–O) and (O–O) bond lengths are not to be seriously shortened. An (S–O) spacing of 1.65–1.70 Å. has received support from the shape of the upper part of the peak at 2.23 Å. of the experimental radial distribution curve, as well as the individual peak at 1.65–1.66 Å. Combined with an (O–O) spacing of 1.46–1.48 Å. suitable radial distribution curves appear to be produced by models with the angles S O O and S ∞ S in the regions 102–105° and 105–110°, respectively.

Included in the tables of molecular parameters are values for the spacings (S′–S″) and (F′–F″). The latter is the distance of closest approach of fluorine atoms of the individual (SF_5O) groups, and this gives an indication of the van der Waals radius for fluorine. The (S′–S″) spacing varied over the region 3.43 < (S′–S″) < 3.62 Å. in Table III, but it can be considerably restricted (3.47 < (S′–S″) < 3.51) if the more satisfactory models are selected, say, D, E, Q, R and W. Similarly the range for (F′–F″) was 2.30 < (F′–F″) < 2.67 Å. in Table III; but it may be reduced to 2.40 < (F′–F″) < 2.46 Å.

5. Comparison of Theoretical and Experimental Intensity Curves.—Further tests of the model proposed are provided by a direct comparison of computed intensity curves with the observed composite

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(14) The primes refer to atoms grouped around separate sulfur atoms.

curve. The parameters for the models listed in Table V were used to compute intensity curves and these were plotted in Fig. 4. No temperature factor was introduced into the calculation of the theoretical intensity curves; the equation being

$$\underline{J}_{\mathrm{m}}(s) = \sum_{ij}{}' Z_i Z_j \frac{\sin r_{ij}^0 s}{r_{ij}^0 s}$$

TABLE V

PARAMETERS OF MODELS FOR INTENSITY CURVES

Model	Bond length, Å. S–F	Bond length, Å. S–O	Bond length, Å. O–O	Bond angle, deg. <SOO	Bond angle, deg. <S∞S	Spacing, Å. S′–S″	Spacing, Å. F′–F″	Av. $q_{\text{calcd.}}/q_{\text{obs}}$	Av. dev.
G	1.56	1.65	1.43	110	110	3.61	2.6_5	0.997_9	0.011_5
C	1.56	1.65	1.46	110	110	3.62	2.6_7	0.997_2	$.018_0$
B	1.56	1.65	1.46	110	105	3.56	2.5_4	1.001_2	$.011_5$
D	1.56	1.65	1.46	105	110	3.50	2.4_5	1.001_6	$.011_5$
F	1.56	1.62	1.46	110	110	3.58	2.5_8	1.001_9	$.012_3$

Consider the calculated and observed intensity curves in the region $10 < q < 45$. The prominent features are the three peaks at q values of 19, 29 and 39, and minima at q values of 16, 23 and 34. The peak at $q = 39$ appears to show a slight loss of intensity in comparison with the others. The minimum at $q \cong 16$ of the observed curve was estimated to fall well below the average background although this is not the case in any of the calculated intensity curves. The over-all agreement is good. At $q = 47$ the observed curve shows a single small peak. The general position and intensity of the feature agrees with the computed curves. The doubling of the peak in models G and C makes them unacceptable and, in fact, they had been criticized earlier as being too large to permit a fit between the observed and synthetic radial distribution curves. The maxima at $q = 55$ and $q = 65$, and the minimum at $q = 61$, of the observed curve agree well with the corresponding features of the calculated intensity curves. The observed curve shows structure in the peak at about $q = 80$, with a shoulder at $q = 78$. All calculated intensity curves have doubled peaks in varying combinations in this region. In the region beyond $q = 70$ non-sector photographs were used to estimate the features of the intensity curve, and the separation and estimation of the relative intensities of peaks at low intensity values is thus less certain. Nevertheless, for this reason, models B and D are not as acceptable as is model F. The last features distinguished on the observed curve are the minimum about $q = 86$ and the maximum at $q = 92$. These features are found in the calculated curves.

All the computed intensity curves were based on a a peroxide-type model with restricted variations in parameters (the parameters are given in Table V). The good general agreement of the calculated curves with the observed curve substantiates the choice of model and parameters as being correct, but the doubling of the peak at $q = 47$ leads to a choice of model F as being the most suitable of those presented. The quotient $q_{\text{calcd.}}/q_{\text{obs.}}$ has been computed for the maxima and minima of each curve. The average of the computed values as well as the average of the deviation of the values from the mean is given in Table V.

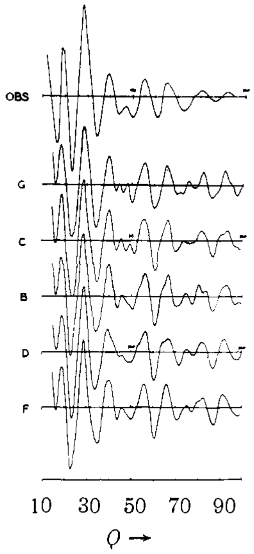

Fig. 4.—Computed intensity curves for $S_2F_{10}O_2$ with a peroxide-type linkage. Details of the parameters are given in Table V.

On a basis of the analysis of the radial distribution curves, and the comparison of computed and observed intensity curves the following molecular parameters are given for $S_2F_{10}O_2$:

(S–F) bond (1.56 ± 0.02 Å.)
(S–O) bond (1.66 ± 0.05 Å.)
(O–O) bond (1.47 ± 0.03 Å.)
Angle (S–O–O) (105 ± 3°)
Angle (S–∞–S) (107 ± 5°)

Discussion

The general configuration of the molecule $S_2F_{10}O_2$ is similar to that of H_2O_2. For H_2O_2 the angles H–O–O and H–∞–H are, respectively, 101.5 and 106° while those for $S_2F_{10}O_2$ are 104 and 107°. The increase is reasonable considering the large groups replacing the hydrogen atoms. The length of the oxygen–oxygen bond in H_2O_2 and in $S_2F_{10}O_2$ is 1.46 Å. Bond lengths are compared below. The

Bond	Bond length, Å. Obsd.	Bond length, Å. Calcd.[10]	Remarks
SF	1.56	1.63	In SF_6: 1.56–1.58 Å. In S_2F_{10}: 1.56 Å.
SO	1.67	1.67	
OO	1.46	1.48	In H_2O_2: 1.46 Å.

short S–F separation is not unexpected, since this is typical for volatile fluorides.[15]

The distance of closest approach of the fluorine atoms on opposing (SF_5O) groups is about 2.4–2.5 Å., a value which is in agreement with that found for S_2F_{10}, and in C_2F_6 for the fluorine–fluorine spacing on opposing (CF_3) groups (2.4 Å.).

The compound $S_2F_{10}O_2$ is stable chemically to acids and bases and, in this property, resembles the organic peroxides with large substituent groups, such as di-*t*-butyl peroxide. Evans[16] and Walsh[17] calculate the dissociation energy of the (O–O) bond to be about 56 kcal. per mole. Walsh suggests that the instability of H_2O_2 is due to little or no negative charge transfer to the oxygen atoms from hydrogen. In H_2O_2 the angle between the planes containing the (O–H) bonds is about 106° giving a skew configuration. A "*trans*" arrangement of

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the molecule, through interference of the charge clouds of the lone pair electrons on the oxygen atoms, would result in a weakening of the peroxide bond by some 10 kcal. The present work corroborates a skew arrangement for $S_2F_{10}O_2$ and, on a basis of Walsh's work, there should be a general increase in stability of the molecule from the charge transfer over that of H_2O_2.

With respect to the formation of $S_2F_{10}O_2$ under the reaction conditions, it has been reported[18] that if any traces of water are present in the acid fluorides which are electrolyzed to obtain fluorine for the sulfur–fluorine reaction, especially during the initial period of electrolysis, they may introduce oxygen as an impurity in the fluorine, either as the element itself or as an oxygen fluoride. When the hydrogen atoms in H_2O_2 are replaced by such groups as $(CH_3)_3C$— or $(C_6H_5)_3C$— the peroxide is quite stable and it is postulated to form readily by a simple chain mechanism from the di-$\{(CH_3)_3C\}$ or di-$\{(C_6H_5)_3C\}$ compound and molecular oxygen. Since $(SF_5{-}SF_5)$ is obtained in the reaction mixture, it does not seem unreasonable that the peroxide $SF_5{-}O{-}O{-}SF_5$ could form in a similar fashion to those mentioned above, especially if molecular oxygen or oxygen fluoride molecules were present to react with (SF_5) groups.

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ITHACA, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Equilibria of Crystalline Zinc Hydroxide in Dilute Hydrochloric Acid and Sodium Hydroxide at 25°. The First and Second Acidic Dissociation Constants of Zinc Hydroxide[1,2]

BY JAMES W. FULTON AND D. F. SWINEHART

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The solubility of orthorhombic zinc hydroxide has been determined at 25° in dilute hydrochloric acid and sodium hydroxide. The solubility product is found to be 7×10^{-18}. The solubility in dilute alkali is represented by one equation from 0.0004 to 1 *m* NaOH. From these data the bizincate ion is found to exist in appreciable concentrations and the first and over-all acid ionization constants of solid zinc hydroxide are calculated to be 1.20×10^{-17} and 2.20×10^{-30}, respectively. The free energies of formation of the bizincate and zincate ions are calculated to be −119,560 and −92,180 cal./mole, respectively.

Introduction

Although zinc hydroxide is one of the classical amphoteric hydroxides and solutions of this substance in acids and alkalies have been the subject of a large number of investigations, substantial disagreement exists in the literature concerning the identification of the ionic species in solution and the values of the equilibrium constants involved. In particular there is disagreement as to the existence of an acid zincate ion and no data exist for the independent determination of the first and second acidic dissociation constants of zinc hydroxide. This paper is written to present data on the solubility of crystalline zinc hydroxide in very dilute sodium hydroxide and hydrochloric acid. From these data it is possible to show the existence of the acid zincate ion and to calculate values of the first and second acid dissociation constants of zinc hydroxide separately.

Previous results for the solubility in water[3–7] lie between 1.3×10^{-5} and 5.2×10^{-5} mole per liter at temperatures between 18 and 25° while values of the solubility product[4,8–13] lie between 1.69×10^{-21} and 1.0×10^{-15}.

Evidence for the existence of the bizincate ion has been obtained from polarographic data by Bernheim and Quintin.[14] Solid sodium bizincate, $NaHZnO_2{\cdot}H_2O$ has been reported as the stable solid phase between 13.5 and 19.6 *m* NaOH by Scholder and Hendrich.[15]

The over-all acid dissociation constant of zinc hydroxide is estimated by Latimer[16] from the data of Dietrich and Johnston[4] to be of the order of 1×10^{-29}.

Experimental

Preparation of Materials.—Crystalline zinc hydroxide was prepared by precipitation of the flocculent hydroxide from a zinc sulfate solution with ammonia followed by

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[1] Taken from the master's thesis of James W. Fulton.

[2] Presented at the Pacific Northwest Regional Meeting of the American Chemical Society, Seattle, Washington, June 8, 1951.

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