B from diffusion measurements. It would appear that a ratio of about 4 for *a/b*, and a hydration of about 0.3 g. of water per g. of protein would be in good agreement with all the available data.

Summary

1. The effect of polarization capacity upon the measurements of dielectric constants of conducting solutions has been further investigated.

2. The dielectric constants of solutions of lactoglobulin in 0.25 and 0.50 *M* glycine have been measured at 0 and 25° over a frequency range of 10,000 to 5,000,000 cycles.

3. The low-frequency dielectric increments per gram per liter, extrapolated to zero concentration of lactoglobulin, are in both solvents 1.51 at 25°, and 1.84 at 0°. These figures diminish with increasing concentration.

4. The dipole moments are estimated to be 730 Debye units at 25° and 770 at 0°.

5. The mean mid-point frequency is approximately proportional to the ratio of absolute temperature and relative viscosity of the solvent.

6. The dispersion curves have been analyzed and the results compared with those obtained from ultracentrifuge, diffusion and viscosity measurements. All these data can be interpreted in terms of an elongated ellipsoidal molecule of axial ratio (*a/b*) 4 and hydration 0.3 g. of water per gram of protein.

The Crystal Structure of Iodic Acid

BY MAX T. ROGERS AND LINDSAY HELMHOLZ

Introduction

Although reports have been published on the crystal structures of all the alkali iodates, no completely satisfactory structure determination of any iodate has been made. The isomorphous crystals cesium iodate, rubidium iodate, potassium iodate, and ammonium iodate are pseudocubic and are said to give no powder lines indicating any deviation from the ideal perovskite structure assigned to them.[1,2,3] This places a regular octahedron of six oxygen atoms around each iodine atom with the distance I–O = 2.23 Å. and gives the alkali atom a coördination number of twelve. Sodium iodate, which is orthorhombic, has been assigned a deformed anti-perovskite structure the alkali atom having a coördination number of six and the iodine atom twelve. Lithium iodate is hexagonal with a reported structure based on hexagonal closest packing,[4] in which octahedra of oxygen atoms surround both lithium and iodine atoms, the IO_6 octahedra sharing corners and the LiO_6 octahedra sharing faces.

Potassium iodate and the isomorphous rubidium, cesium and ammonium compounds are known to be monoclinic hemihedral from crystallographic and piezoelectric measurements and the assignment of a simple cubic structure to them on the basis of powder pictures is unsatisfactory, since the intensities of the lines are rather insensitive to the oxygen parameters and could be roughly accounted for by an essentially incorrect structure. The deviations from the ideal perovskite structure may also be appreciable for sodium iodate since the observed axial ratios 0.903:1:0.636 differ considerably from those of a cubic perovskite structure in that orientation, *viz.*, 1:1:0.707. The oxygen parameter in lithium iodate is not closely enough known to give the oxygen positions with any certainty. Hence none of the structure determintions can be accepted as showing what the configuration of the iodate group is.

One might expect on chemical grounds and from the correlation of Raman spectra in crystals and solution[5] that discrete iodate groups or simple polymers would exist in the crystal rather than regular IO_6 octahedra with shared corners. The observed I–O distance (2.23 to 2.33 Å.) in these crystals seems rather large in view of the value 1.93 Å. observed in KIO_2F_2 and $(NH_4)_2H_3IO_6$,[6]

(1) V. M. Goldschmidt, "Geochem. Vert. Gesetze der Elemente," VII and VIII.

(2) W. H. Zachariasen, *Skrifter Norske Videnskapsakad. Oslo I, Mat. Natur. Klasse*, 1928, No. 4.

(3) J. Garrido, *Anales soc. españ. fis. quím.*, 30, 811 (1932).

(4) W. H. Zachariasen and F. A. Barta, *Phys. Rev.*, 37, 1628 (1931).

(5) James Hibben, "The Raman Effect and Its Chemical Applications," A. C. S. Monograph, 1939, p. 378.

(6) L. Helmholz and M. T. Rogers, THIS JOURNAL, 62, 1537 (1940).

and the sum of the covalent single bond radii, 2.02 A., obtained using the octahedra iodine radius, 1.35 Å., found for KICl$_4$[7] in which iodine has a formal charge of -1 as in the iodates. The distances I–O = 2.87 Å., 2.95 Å., 3.18 Å. reported for sodium iodate[2] seem especially unlikely.

In this paper we report the results of a thorough investigation of the structure of the α-modification of crystalline iodic acid. The only previous work on this compound reported is a determination of unit cell and probable space group.[2]

The presence of discrete pyramidal IO$_3$$^-$ groups in the crystal has been shown, with the observed I–O distances 1.80 Å., 1.81 Å., and the O–I–O angles 96°, 98°, and 101°. Three oxygen atoms in positions approximately opposed to the three bonded IO$_3$ oxygens and at distances 2.45, 2.70, 2.95 Å. complete a distorted IO$_6$ octahedron with three strong bonds and three weaker ones. The hydroxyl oxygen atom of each iodate group has two nearest oxygen neighbors at 2.78 Å. There are thus two hydrogen bonds for each iodate group forming a moderately strong bifurcated bond of the type observed in glycine.[8] The oxygen atoms are in a somewhat distorted closest packed arrangement. The structure resembles somewhat that of perovskite with the oxygen atoms moved from a central position between iodine atoms to form iodate groups. The formation of hydrogen bonds has displaced the oxygen atoms slightly from the line joining the iodine atoms and the iodine atoms are no longer in the perovskite arrangement although each has six nearest iodine neighbors. Crystalline iodic acid is an aggregate of HIO$_3$ molecules held together by hydrogen bonds, and secondary I–O bonds of the type observed for arsenic and oxygen in arsenolite.[9]

Procedure

Iodic acid was prepared by oxidizing iodine with concd. nitric acid. The solution was evaporated at 150° to a thick sirup which was allowed to crystallize. Goniometric measurements agreed with those given by Groth[10] for the α-modification of iodic acid.

Laue photographs were taken with X-rays normal to each axis using continuous radiation from a tungsten target. Oscillation photographs of 12° and 24° angular range were obtained with each axis vertical using MoKα radiation and a zirconium filter. The crystals were dissolved down to an approximately cylindrical shape and such a

size that the influence of absorption was negligible for pictures taken with the "a" and "c" axes vertical. The radius of the cylindrical crystal with b vertical was such that an absorption correction was necessary. The correction was taken from tables for powder rod absorption with $\mu r = 3.0$.[11] The intensities of all equatorial and of 75 hkl reflections were estimated visually using a calibrated scale. The estimation of intensities was facilitated by using two films with a sheet of 0.0015″ copper between so that the intensity of the reflections on the second film was about one-fifth of that on the first.

In order to obtain correct estimates of the relative intensities of strong reflections a powder picture was taken using CuKα radiation of a film of powder held by a thin coating of vaseline to a small diameter glass fiber.

Space Group and Unit Cell.—Laue photographs showed the Laue symmetry to be D$_{2h}$-mm. The regular absences $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; and $00l \neq 2n$, were observed on Laue and oscillation photographs. The space group is thus D$_2^4$-P$_{2_12_12_1}$. This is in agreement with the crystallographic evidence that α-iodic acid is rhombic bisphenoidal, and the absence of a center of symmetry has been confirmed by a positive piezoelectric experiment.[12] The dimensions of the unit cell are $a_0 = 5.525 \pm 0.010$ Å., $b_0 = 5.855 \pm 0.010$ Å., and $c_0 = 7.715 \pm 0.010$ Å. This gives the axial ratios 0.944:1:1.317 from X-ray data to be compared with the crystallographic values 0.9388:1:1.3181 given by Groth.[8] Using the observed density, 4.63 g./cc. the number of molecules in the orthorhombic unit cell is found to be four. Long exposure Laue photographs gave no reflections requiring a larger unit.

This is in essential agreement with the values $a_0 = 5.53 \pm 0.05$ Å., $b_0 = 5.92 \pm 0.05$ Å., $c_0 = 7.75 \pm 0.05$ Å. and $Z = 4$ with possible space groups V^1 – V^4 found by Zachariasen[2] from measurements of powder pictures.

Determination of Structure.—The space group D$_2^4$ has only the fourfold positions

4:(a) x,y,z; $1/2-x,\bar{y},1/2+z$; $1/2+x,1/2-y,\bar{z}$; $\bar{x},1/2+y,1/2-z$

There are thus three parameters each to be determined for iodine and for the three oxygen atoms. The hydrogen parameters cannot be found directly.

The iodine parameters were obtained from Patterson projections made with $(0kl)$ and $(hk0)$ data. The Patterson projection on the xy plane

$$P(X, Y) = \Sigma h \Sigma k \mid F_{hk_0} \mid^2 \cos 2\pi(hX + kY)$$

was made using observed intensities for 58 reflec-

(7) R. C. L. Mooney, Z. Krist., **98**, 377 (1938).

(8) Albrecht and Corey, THIS JOURNAL, **61**, 1087 (1939).

(9) R. M. Bozorth, ibid., **45**, 1621 (1923).

(10) P. Groth, "Chemische Kristallographie," Teil II, Leipzig, 1908, p. 74.

(11) "Int. Tab. zur Bestimmung von Kristallstrukturen II," Ch. XI.

(12) A. Hettich and H. Steinmetz, Z. Physik, **76**, 700 (1932).

tions $(hk0)$. From this the iodine parameters x = 0.204, y = −0.088 were obtained. The intensities of 70 reflections $(0kl)$ were used to make a Patterson projection on (100) from which the iodine parameter z = 0.156 was obtained and the value y = −0.088 confirmed. These projections were not used to obtain the oxygen parameters.

The oscillation photographs with the b-axis vertical gave 200 equatorial reflections $(h0l)$ going out to sin θ/λ = 1.38. The signs of the F's of about 175 of these were determined at once from the sign of the iodine contribution using the above parameters in the structure factor. A preliminary Fourier projection of relative electron density on the x-z plane

$$\rho(x, y) = \Sigma h \Sigma l\ F_{(h0l)} \cos 2\pi(hx + lz)$$

was then made. This gave the approximate positions of the oxygen atoms so that the signs of most of the remaining reflections could be calculated and these added to the Fourier plot. The intensities of the strong reflections, which are observed relatively too weak due to extinction, were corrected using the method of Darwin.[11] The corrected intensity I_0 was obtained from the observed I using the formula $I = I_0/1 + gI_0$ with g = 0.005. The final Fourier plot, shown in Fig. 1,
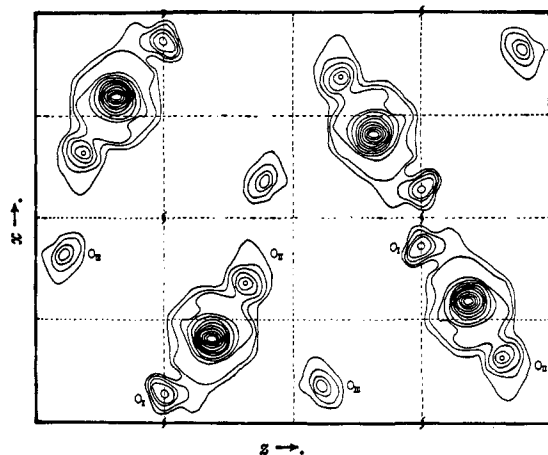

Fig. 1.—Fourier projection of the scattering matter on the x-z plane.

gave resolved peaks for the oxygen atoms from which their x and z parameters were obtained by reading maximum values of contour lines. The parameter values obtained from this projection are

O_I: x = 0.069, z = 0.250; O_{II}: x = 0.341, z = 0.090
O_{III}: x = 0.407, z = 0.447

The y-parameters of the oxygen atoms were obtained from a Fourier projection of scattering

matter on the x-y plane. The signs of the F's for most of the reflections were determined by the iodine contribution alone and a preliminary projection made with these. This was then refined by adding the remaining reflections, a correction for extinction being applied as before. The projection is shown in Fig. 2. The peaks are not as well
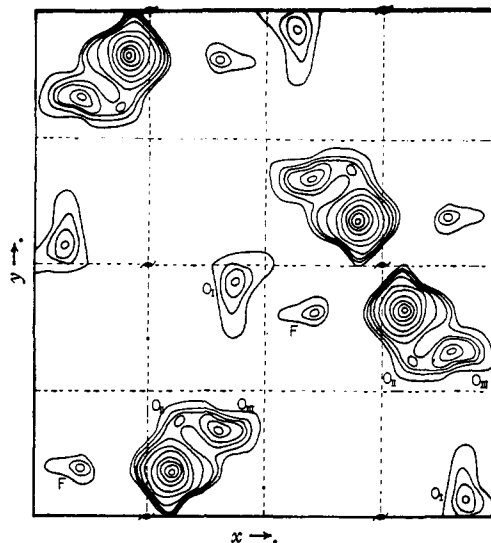

Fig. 2.—Fourier projection of the scattering matter on the x-y plane.

resolved as in the projection on (010) since O_{II}, O_{III}, and iodine fall close to one another. It was possible to correlate the two Fourier projections in the manner shown and so to derive the structure. The y-parameters for the three oxygen atoms and a check on the x-parameters are thus obtained. The values found are:

O_I: x = 0.063, y = 0.534; O_{II}: x = 0.315, y = 0.193
O_{III}: x = 0.407, y = 0.173

The peak marked F (Fig. 2) is believed to be false since any structure which could be derived interpreting it as due to an oxygen atom, and taking the x and z parameters from the Fourier projection on (010), was ruled out on spatial grounds. It also introduces serious discrepancies in the comparison of relative calculated intensities with observed values. This peak may arise from the incompleteness of the data for $(hk0)$.

A confirmation of these parameter assignments and a more accurate value of the y-parameter for O_{II}, which was difficult to obtain from the projection on (001), was obtained by making a Fourier projection on (100). About 70 reflections $(0kl)$ were used. The parameters obtained from this projection are

O$_I$: $y = 0.533$, $z = 0.242$; O$_{II}$: $y = 0.187$, $z = 0.086$
O$_{III}$: $y = 0.160$, $z = 0.458$

We thus have two independent estimates of each parameter agreeing with but one exception, to 0.01 Å. or better. Slight changes in some parameters were then made to give the best agreement with observed intensities. The final parameter values are shown in Table I.

TABLE I

	x	y	z
I	0.204 ± 0.002	−0.088 ± 0.002	0.156 ± 0.002
O$_I$	.068 ± 0.005	.534 ± 0.005	.250 ± 0.005
O$_{II}$	.340 ± 0.005	.195 ± 0.005	.090 ± 0.005
O$_{III}$	.407 ± 0.005	.170 ± 0.005	.447 ± 0.005

The values of F_{hkl} were calculated for all equatorial and for 75 hkl reflections using the Pauling–Sherman tables of F-values and a Debye–Waller temperature factor with $B = 1.0$.[11] Tables III and IV give observed and calculated F's for approximately one-third of the experimental data

used in the determination. The strongest reflections are usually observed somewhat weaker than they are calculated. That this is due to extinction was verified by estimating the intensities of some lines on the powder photograph. The observed amplitudes, shown in Table V, give the same relative values for strong and weak reflections as calculated. The empirical correction for extinction applied to the stronger amplitudes used in the final Fourier projections is therefore justified.

Discussion

The structure of iodic acid is shown in Fig. 3 and its projection on the y-z plane in Fig. 4.

The iodate group is pyramidal with the distances I–O$_I$ = 1.81 Å., I–O$_{II}$ = 1.89 Å., I–O$_{III}$ = 1.80 Å., and O$_I$–O$_{III}$ = 2.78 Å. O$_{II}$–O$_{III}$ = 2.78 Å., O$_I$–O$_{II}$ = 2.75 Å., giving the angles O–I–O the values 95°40′, 98°10′, 101°25′. The distances are probably not in error by more than

TABLE II[a]

VALUES OF F_{hkl}

(hkl)	Obsd.	Calcd.	(hkl)	Obsd.	Calcd.	(hkl)	Obsd.	Calcd.	(hkl)	Obsd.	Calcd.
(002)	50	70	(180)	28	18	(01, 12)	abs.	6	(102)	100	190
(004)	76	112	(1, 10, 0)	16	12	(021)	77	112	(104)	72	112
(006)	64	88	(210)	78	98	(023)	abs.	7	(106)	45	49
(008)	13	22	(230)	75	71	(025)	100	118	(108)	63	74
(00, 10)	57	66	(250)	17	17	(027)	57	52	(10, 10)	40	36
(00, 12)	42	45	(270)	abs.	10	(029)	37	28	(10, 12)	31	29
(00, 14)	abs.	8	(290)	25	22	(02, 11)	43	49	(10, 14)	39	43
(00, 16)	30	27	(220)	41	42	(022)	63	75	(10, 16)	abs.	4
(00, 18)	12	8	(240)	52	58	(024)	39	26	(10, 18)	23	16
(00, 20)	14	11	(260)	68	65	(026)	59	48	(10, 20)	18	11
(200)	77	134	(280)	16	14	(028)	24	10	(201)	46	59
(400)	35	35	(310)	64	90	(031)	75	100	(203)	63	66
(600)	10	10	(330)	15	18	(033)	91	146	(205)	36	29
(800)	43	34	(350)	47	50	(035)	35	19	(207)	43	45
(10, 00)	30	23	(370)	30	28	(037)	70	71	(209)	41	38
(12, 00)	17	24	(320)	102	105	(039)	68	60	(20, 11)	12	14
(020)	70	75	(340)	58	54	(03, 11)	abs.	5	(20, 13)	26	20
(040)	74	67	(360)	abs.	1	(032)	17	14	(20, 15)	16	9
(060)	84	67	(380)	25	31	(034)	abs.	11	(20, 17)	6	4
(080)	22	25	(011)	50	65	(036)	abs.	13	(20, 19)	15	10
(0, 10, 0)	30	26	(013)	71	110	(038)	abs.	5	(202)	50	45
(0, 12, 0)	17	18	(015)	45	31	(101)	49	66	(204)	77	120
(110)	91	180	(017)	58	46	(103)	40	50	(206)	73	93
(130)	36	41	(019)	53	42	(105)	44	39	(208)	11	7
(150)	90	77	(01, 11)	18	14	(107)	12	7	(20, 10)	44	43
(170)	57	49	(012)	80	155	(109)	22	19	(20, 12)	31	33
(1, 11, 0)	30	25	(014)	82	105	(10, 11)	20	20	(20, 14)	15	13
(120)	63	65	(016)	57	42	(10, 13)	7	9	(20, 16)	29	26
(140)	abs.	1	(018)	79	71	(10, 15)	6	6	(20, 18)	10	7
(160)	abs.	5	(01, 10)	22	26	(10, 17)	abs.	2	(20, 20)	10	6

[a] The X-ray photographs from which the $(hk0)$ and $(0kl)$ data were obtained were considerably less intense than the $(h0l)$ pictures; hence the fact that some reflections $(hk0)$ and $(0kl)$ are not observed, in spite of the fact that the calculated F's are larger than for reflections $(h0l)$ which are observed, does not indicate a discrepancy between calculated intensities and experimental data.

TABLE III

VALUES OF F_{hkl}

(hkl)	Obsd.	Calcd.	(hkl)	Obsd.	Calcd.
(111)	71	75	(223)	51	50
(112)	50	46	(224)	69	58
(121)	92	106	(331)	68	76
(122)	56	52	(332)	78	79
(123)	103	125	(333)	14	12
(131)	103	135	(411)	81	93
(132)	41	35	(412)	47	46
(133)	39	35	(413)	30	31
(231)	71	72	(431)	24	24
(232)	42	41	(432)	33	31
(233)	100	106	(433)	38	41
(241)	81	83	(441)	36	37
(242)	57	54	(442)	32	47
(221)	85	100	(443)	32	47
(222)	69	71			

TABLE IV

VALUES OF F_{hkl} FROM A POWDER PHOTOGRAPH

(hkl)	Calcd.	Obsd.
(020)	73	72
(200)	134	142
(011)	65	55
(110)	179	150
(101)	66	59
(102)	190	172
(012)	155	146
(021)	112	100
(111)	75	78
(013)	110	99
(031)	100	115
(022)	75	70
(204)	120	122

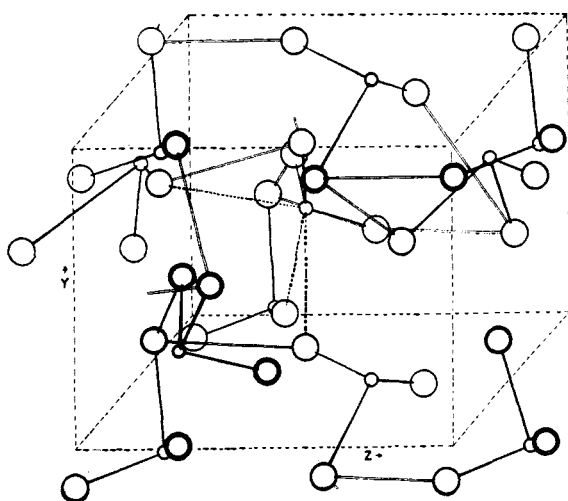± 0.04 Å. or the angles by more than $\pm 5°$. Each iodine atom has, in addition to these three closest

Fig. 3.—Crystal structure of the α-modification of iodic acid showing I–O bonds with solid lines and secondary (weak) I–O bonds with dotted lines. Hydrogen bonds between oxygen atoms are represented by double lines.

oxygen neighbors, three more at distances considerably less than the sum of the van der Waals radii, 3.55 Å. These are I–O$'_{I}$ = 2.45 Å., I–O$'_{III}$ = 2.70 Å., I–O$''_{III}$ = 2.90 Å. (the prime and double prime refer to the oxygen atoms of second and third iodate groups) (the next iodine–oxygen contacts are at 3.30 Å. and 3.45 Å.). These six nearest oxygen atoms form a distorted octahedron about the iodine atom; the angles between the four atoms approximately in a plane are 66°, 84°, 100° and 110°, while these make angles of 79°, 90°, 97° and 101° with O$_{I}$ at one apex. The longer I–O distances are intermediate between bonded and non-bonded values and so correspond to secondary bonds of the type formed in arsenolite and senarmontite.[9] The angles I–O–I = 114°, 131° and 138° for these weak bonds differ considerably from the tetrahedral value expected for two covalent bonds with oxygen but are not far from the tetrahedral single bond-double bond value—indeed they are close to the angles Sb–O–Sb = 116° and 132° observed in valentinite[13] where the Sb–O bond has less double bond character than the I–O$_{I}$, I–O$_{III}$ bonds here. Each iodine atom has six nearest neighbors, two at each of the
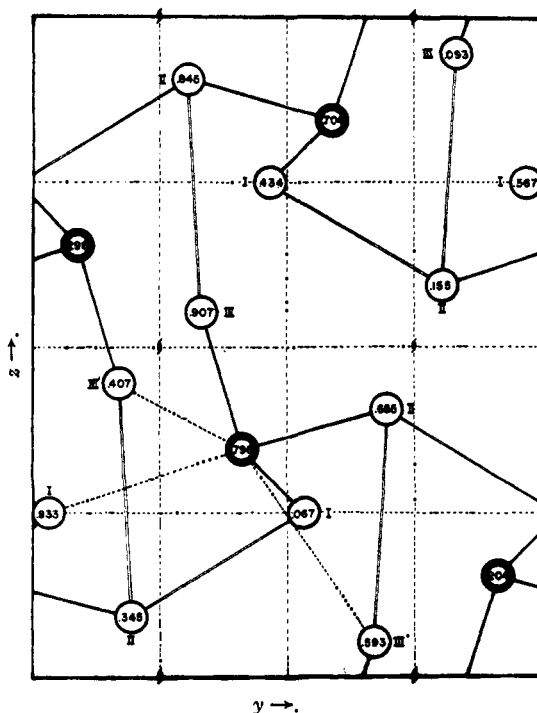

Fig. 4.—Projection of iodic acid structure on y-z plane. Bonds are designated as in Fig. 3. The numbers within the circles give the x-parameters.

(13) M. J. Buerger and S. B. Hendricks, Z. Krist., 98, 1 (1937).

three distances 3.79 Å., 4.03 Å., and 4.13 Å. There is an oxygen atom of the distorted octahedron between each of the six iodine nearest neighbors and the central iodine atom but these are displaced both from the position central between the iodine atoms and from the line joining them. This is not a true distorted perovskite structure although it bears certain analogies to such an arrangement.

The observed closest I–I contacts are 0.20 Å. to 0.33 Å. less than the sum of the van der Waals radii, 4.30 Å. (the I–I contacts reported for KIO_2-F_2 are 4.40 Å. and for the alkali iodates 4.45 to 4.65 Å.). This shortening is to be expected since the direction of the I–I contact makes only a small angle with either one or two covalent I–O bonds and the electron pairs which give the atom size in that direction are pulled in to form the bond, thus reducing the effective van der Waals radius. The oxygen–oxygen distances of 2.78 Å. between oxygen atoms of the same group are not abnormal for this reason. The partial double-bond character of the I–O bonds indicating the use of a second electron pair from the oxygen atom in the bond will further tend to reduce the oxygen radius in directions near that of the bond.

Each of the three types of oxygen atoms has a different set of iodine contacts which correspond to no simple arrangement. O_{II} has four nearest neighbors at 3.40 Å., 3.44 Å., 3.60 Å., 3.85 Å., O_{III} four at 2.70, 2.90, 3.70, and 4.30 Å. and O_I three at 2.45, 3.70, 4.00 Å. exclusive of the iodine atom of the group to which each belongs. The oxygen atoms form a nearly closest packed structure. There are twelve nearest neighbors for O_I, three at 2.78 $\pm$ 0.02 Å. and nine at 2.90, 3.00, 3.00, 3.07, 3.12, 3.20, 3.25, 3.32, 3.60 Å.; for O_{II} four at 2.78 $\pm$ 0.02 Å. and eight at 3.10, 3.13, 3.16, 3.16, 3.20, 3.35, 3.58, 4.12 Å.; for O_{III} three at 2.78 $\pm$ 0.02 Å. and nine at 2.90, 3.00, 3.00, 3.11, 3.14, 3.22, 3.37, 3.38, 4.30 Å. The formation of iodate groups and hydrogen bonds has considerably distorted the true hexagonal closest packed arrangement. The volume per oxygen atom is 2.1 cu. Å.

In addition to two oxygen contacts of 2.78 and 2.76 Å. within the group O_{II} has two neighbors O'_I and O''_{III}, one from each of two other groups, at 2.76 and 2.78 Å. Since the distance I–O_{II} = 1.89 Å., O_{II} may be considered to be the hydroxyl oxygen. It forms the two hydrogen bonds O_{II}–H–O'_I and O_{II}–H–O''_{III} of equal strength. The

oxygen–oxygen distances indicate that the bifurcated bond is strong (there are here two bonds per iodate group each of which is about the strength of the single hydrogen bond in water and ice). The hydrogen atom was now given parameters such that the distance O_{II}–H = 1.01 Å., the angle I–O–H = 109°, and the O_{II}–H bond bisected the O''_{III}–O_{II}–O'_I angle. The parameters so derived are x = 0.340, y = 0.300 and z = 0.197 making the angles O–H–O $\cong$ 121°. The hydrogen bonds along with the weaker iodine–oxygen bonds link the iodate groups together forming a relatively hard crystal (hardness = 3). The observed complete cleavage (101) breaks two hydrogen bonds and one of the two weakest I–O bonds; the incomplete cleavage (011) must also break the stronger I–O bond corresponding to the distance I–O'_I = 2.45 Å. The O–I–O angles, with an average value of 98° $\pm$ 3°, indicate that the orbitals involved in bonding are between p-orbitals (three at right angles to one another) and sp^3 (tetrahedral) orbitals. The radius of iodine may thus be taken as intermediate between the tetrahedral and octahedral radii, 1.27 Å. and 1.35 Å., respectively. Using the value 1.29 Å. the I–O single bond distance would be 1.95 Å. and the double bond distance 1.75 Å. Although there is nominally a formal charge of −1 on the iodine atom no correction to the radius value has been made for this since resonance with structures in which unshared electron pairs from the oxygen atoms form additional covalent bonds will leave the iodine neutral or perhaps with a slight residual positive charge. The observed interatomic distances within the group I–O = 1.80, 1.81 and 1.89 Å. thus correspond to a slight amount of double bond character for the bond to the hydroxyl oxygen and a large amount for the remaining oxygen atoms. The formation of the three weaker iodine–oxygen bonds might be expected to decrease the double-bond character of the oxygen atoms of the group and make the distances correspondingly longer as for the As–O bonds in arsenolite[9]; however, the sharing of oxygen atoms by SiO_4 tetrahedra in silica and the silicates and of PO_4 tetrahedra in the pyrophosphates causes no lengthening of the Si–O or P–O distances.[14] In KIO_2F_2[6] the distance I–O = 1.93 $\pm$ 0.05 Å. and the angles O–I–O = 100 $\pm$ 7° were observed.

The influence of the various factors in deter-

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 226.

mining the structure may now be seen clearly. The HIO_3 molecule contains essentially covalent bonds, the pyramidal shape of the IO_3 group being determined by the type of iodine orbitals used for the single bonds (p-orbitals with some s character). The hydrogen atom of the hyroxyl group might form either one strong hydrogen bond to one of the two remaining oxygen atoms (of another iodate group) or two weaker bonds, one to each of them; it actually forms the bifurcated bond. The iodine atom has less stable orbitals available to form additional octahedral bonds which it now can do partially by forming weak bonds with three oxygen atoms of other iodate groups. Since the hydroxyl oxygen (O_{II}) is not available for these bonds the iodine atom must form the three weak bonds with the remaining two oxygen atoms and it does this by forming one weak bond with one of them (O'_I) and two weaker bonds with the other (O'_{III} and O''_{III}).

Considering the relation of the structure of HIO_3 to that reported for the iodates it seems likely that in those crystals the oxygen atoms are displaced from the symmetry positions of the perovskite structure in such a manner as to form iodate groups. An investigation of one of the pseudocubic iodates using the proper monoclinic

hemihedral space group and unit cell would settle this question.

The authors are indebted to Professor Linus Pauling for detailed discussion of this work and many helpful suggestions.

Summary

The structure of the α-modification of crystalline iodic acid has been determined. Laue and oscillation photographs show that the orthorhombic unit cell with $a_0 = 5.520 \pm 0.005$, $b_0 = 5.855 \pm 0.005$, $c_0 = 7.715 \pm 0.005$ contains four molecules of HIO_3. The space group is $D_2^4 - P_{2_1 2_1 2_1}$. Patterson and Fourier projections on the three axial planes calculated from visually observed intensity data gave the twelve parameters for the oxygen and iodine atoms (Table II). The structure is an aggregate of HIO_3 molecules held together by hydrogen bonds of the bifurcated type and weak iodine oxygen bonds. Iodine atoms are surrounded by distorted octahedra of oxygen atoms and the oxygen atoms are in a nearly closest packed arrangement. The influence of the different types of bond on the structure has been discussed and its relation to the perovskite structure shown.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NEW YORK UNIVERSITY]

Dissolution and Diffusion Rates in Alcohol–Water Mixtures

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Numerous studies have been made of the rate of dissolution of magnesium in aqueous acid solutions, and a thorough study of the rate in absolute ethyl alcohol has been reported by Sclar and Kilpatrick.[1a] Only a few experiments have been carried out in solutions of acids in alcohol–water mixtures. These have indicated that, in relatively dilute alcohol, the rate is inversely proportional to the viscosity of the mixture.[2] The comparatively low rates in absolute alcohol[1a] indicate that this proportionality does not hold over the entire range of alcohol concentration; the fluidity of pure ethyl alcohol is only 20% less than that of water, while the dissolution rate is 70%

less, and there is evidence that part of this rate is due to reaction with the solvent itself.[1a]

Diffusion coefficients have been found in general to be nearly proportional to the fluidity of the medium (for example, measurements of Arrhenius on hydrochloric acid in dilute ethyl alcohol[3]). However, few measurements have been made in water–alcohol mixtures, and many of the measurements in concentrated or "absolute" ethyl and methyl alcohol are of doubtful accuracy.

While the diffusion rates of non-solvated non-electrolytes might be expected to follow the fluidity in mixed solvents, this could hardly be true of solvated electrolytes. In order to clarify the relations between dissolution rate, viscosity, and diffusion rate of acids, we have measured dissolution and diffusion rates in ethyl alcohol–water

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(1a) Sclar and Kilpatrick, THIS JOURNAL, 59, 584 (1937).

(2) King and Braverman, ibid., 54, 1744 (1932); Van Name and Hill, Am. J. Sci., (4) 36, 543 (1913).

(3) Arrhenius, Z. physik. Chem., 10, 51 (1892).