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The Crystal Structure of Potassium Fluoroiodate, KIO_2F_2

BY LINDSAY HELMHOLZ AND M. T. ROGERS

Introduction

A complete knowledge of the crystal structure of potassium fluoroiodate should afford considerable evidence concerning the steric effect of unshared electron pairs in molecules and ions and concerning the influence of relative electronegativity on the interatomic distances. The structure determination has been carried out to investigate these questions. Unfortunately it has turned out that the number of parameters to be determined is so great that, although the general characteristics of the structure are certain, the accuracy of the determination permits us to make only qualitative remarks about the effects mentioned above.

It has been found that the $IO_2F_2^-$ group approximates an octahedral group with two of the positions unoccupied. A tetrahedral configuration for the ion, which might have been anticipated from the similarity of the unit dimensions of this crystal and those of KIO_4, is clearly impossible.

A distinction between oxygen and fluorine atoms or ions in the structure is suggested by the intensities and the interatomic distances, but it is impossible for us to insist on our assignment and so to give any detailed discussion of the influence of electronegativity on bond distance.

The observation that potassium iodate, formed by the hydrolysis of the compound in moist air, is oriented to a considerable extent on the surface of the fluoroiodate suggests (as is borne out by the structure) that the crystal resembles KIO_3 much more than KIO_4.

Procedure.—Potassium fluoroiodate was prepared by dissolving potassium iodate in concentrated hydrofluoric acid and allowing the resulting solution to stand until, after a few days, tabular crystals were precipitated. Some smaller crystals were formed for which the principal direction of growth was normal to the plate. Goniometric measurements showed the crystals to be identical with those described by Groth.[1] In order to prevent reaction of the crystals with atmospheric moisture they were coated with a layer of lacquer.

Oscillation photographs were taken with CuK_α and MoK_α radiations and Laue photographs with continuous radiation ($\lambda_{\text{min.}} = 0.24$ Å.) from a tungsten target. Intensities were estimated visually using a calibrated scale and photographs of different exposure times. For the CuK_α pictures the influence of absorption was considered; for the Mo pictures the crystals were small enough so that the absorption correction was shown to be negligibly small.

Space Group and Unit Cell.—Laue photographs taken with the X-ray beam normal to the plates showed the Laue symmetry D_{2h}. The regular absences $h0l$, $h \neq 2n$ and $0kl$, $l \neq 2n$ were observed giving C_{2v}^5 and D_{2h}^{11} as possible space groups. A pyroelectric experiment which gave a positive result eliminated D_{2h} and established $C_{2v}^5 - Pca$ as the correct space group for the crystal.

The dimensions of the unit cell were found, from oscillation photographs, to be $a_0 = 8.38 \pm 0.02$ Å.; $b_0 = 5.97 \pm 0.02$ Å.; $c_0 = 8.41 \pm 0.02$ Å. The data from which these values were obtained are listed in Table I. The X-ray data give the axial ratios $a:b:c = 0.996:0.7098:1$ to be compared with the crystallographic axial ratios $a:b:c = 0.9925:2 \times 0.7074:1$ given by Groth.[1]

Assuming the density of the fluoroiodate to have a value close to the densities of potassium iodate (3.89 g./cm.^{3}) and periodate (3.61 g./cm.^{3}) the number of molecules in the orthorhombic unit was found to be four. The density calculated for four molecules per unit cell is 3.71 g./cm.^{3} Numerous Laue photographs of long exposure time showed no reflections requiring a large unit.

Determination of the Structure.—For the space group $C_{2v}^5 - Pca$ there exists only one set of positions, the general four-fold positions $4a$):[2] $x, y, z;\ \bar{x}, \bar{y}, \tfrac{1}{2} + z;\ \tfrac{1}{2} - x, y, \tfrac{1}{2} + z;\ \tfrac{1}{2} + x, \bar{y}, z.$

There are then three parameters to be determined for iodine and three for potassium. The eight fluorine atoms in the unit are to be placed in two sets of positions $4a$, and the eight oxygen atoms also in two sets of the four-fold positions.

The first step in the structure analysis was the determination of the iodine parameters. For this

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[1] Groth, "Chemische Krystallographie," Teil II, Leipzig, 1908, p. 94.

[2] "Int. Tab. z. Bestimmung v. Kriststrukturen."

TABLE I

a_0			b_0			c_0		
$(h00)$	a_0 (obsd.)	a_0 (calcd.)	$0k0$	b_0 (obsd.)	b_0 (calcd.)	$00l$	c_0 (obsd.)	c_0 (calcd.)
(200)	8.346	8.38	010	5.963	5.97	(002)	8.30	8.41
(400)	8.376		020	5.974		(004)	8.37	
(600)	8.382		030	5.990		(006)	8.47	
(800)	8.368		050	5.960		(008)	8.408	
(10,00)α_1	8.381		060	5.984		(00,10)α_1	8.412	
α_2	8.378		070α_1	5.978		α_2	8.409	
			α_2	5.974				

purpose a Patterson projection on the x–z plane was made using $h0l$ data. This projection (Fig. 1) shows strong peaks, corresponding to iodine–iodine interactions, at $x = \frac{1}{2}$, $z = 0$; $x = 0$, $z = \frac{1}{2}$; and $x = z = \frac{1}{2}$. This distribution can be accounted for only if the iodine parameters $x_1 = z_1 = 0$, or an arrangement equivalent to this. This assignment of parameters may be checked by a qualitative consideration of the intensities. The intensities of reflection from planes (hkl), with $h + l \neq 2n$ were observed to be very much weaker than the reflections with $h + l = 2n$ even for large values of h, k and l. For the iodine parameters $x_1 = z_1 = 0$ the iodine contribution to the intensities of the type of planes first mentioned is zero.

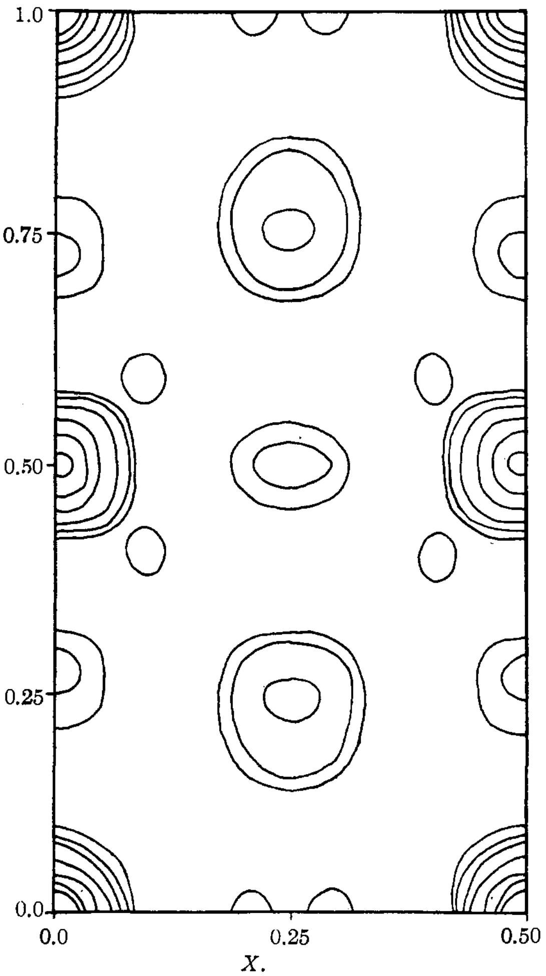

Fig. 1.—Patterson projection, $P(x,z)$, on x–z plane.

A Harker projection, $H(xy\frac{1}{2})$, making use of the two-fold screw axis parallel to z, was calculated as the next step in the determination. This gave a value for the y-parameter for iodine, $2y = 0.135$. Complete data were not used in preparing this projection but the final structure indicates that the 200 important reflections which were used gave a very reliable value for the parameter. No other use was made of the projection.

Since the projection of the scattering matter in the cell on the x–y plane contains a center of symmetry it was profitable next to make a Fourier projection on this plane using the $(hk0)$ data. The signs of the F's for all strong reflections are unambiguously determined by the iodine contribution, so that, starting with these reflections, a complete Fourier projection could be made by a process of successive approximations. From the first of these the potassium ions were found to have $x \approx 0.25$, $y \approx 0.50$.

As long as only reflections to which iodine contributes were used, a plane of symmetry, not present in the crystal, persists along a line $x = 0$. The strongest F to which iodine does not contribute, F_{310}, was next introduced arbitrarily with positive sign. The introduction of this single F_{310} destroys the plane of symmetry and permits the assignment of approximate x and y parameters for potassium ions, fluorine and oxygen atoms. The final projection, shown in Fig. 2, was obtained by including all the $F_{(hk0)}$'s in the Fourier series. The letters refer to the atoms with parameter z, the primed letters to equivalent atoms at $z + \frac{1}{2}$. The c-glide planes are indicated by dotted lines, the a-glide plane by the dashed line. Contour lines have been drawn at 20, 30, 40, 50, 100, 150, 250, and 350 on an arbitrary scale.

Figure 2 shows clearly the iodine atoms at I and

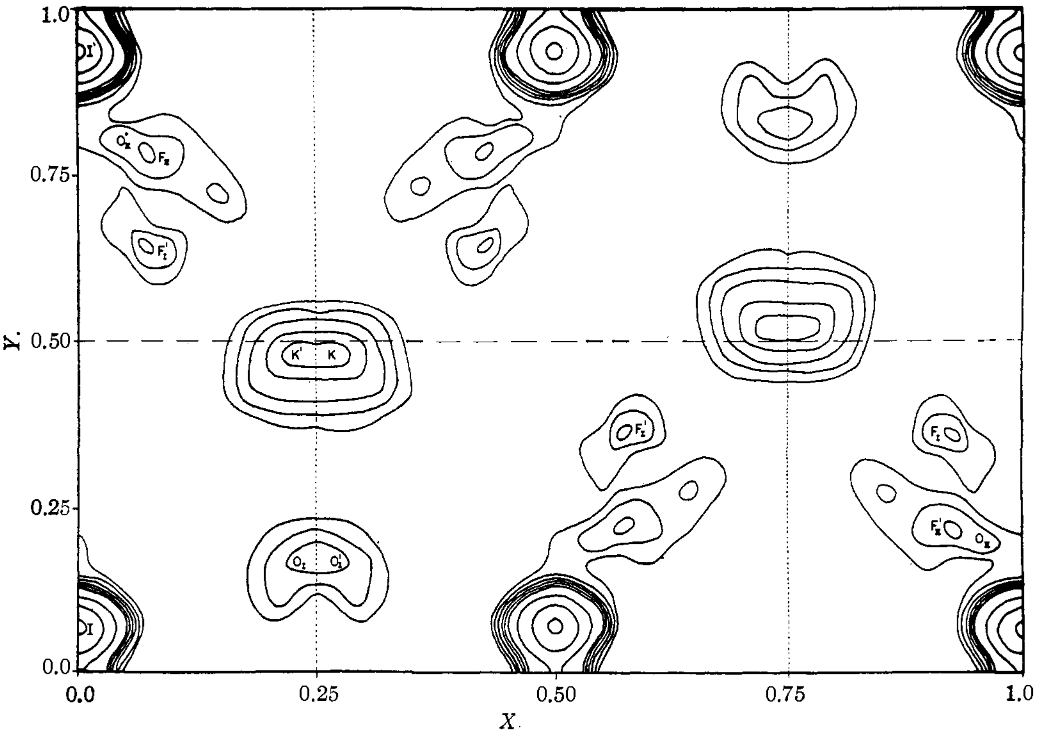

Fig. 2.—Fourier projection of scattering matter on (001) face.

I'. The peak K (and K') is unresolved and due to equivalent potassium ions at *xyz* and $\frac{1}{2} - x, y, z + \frac{1}{2}$. The differentiation of oxygen and fluorine atoms cannot be made on the basis of the projection, and evidence for the distinction finally made is not entirely conclusive but the discussion will be continued on the basis of the final assignment and it will be borne in mind that an exchange of oxygen atoms for fluorine in the structure is possible within the limits of error of the X-ray data. The unresolved peak at O_I (O_I') is due to oxygen atoms and the clearly defined maximum at F_I can be identified as a fluorine atom. The remaining somewhat diffuse maximum in the neighborhood of F_{II} and O_{II} is believed to be due to the superposition of two maxima.

The atoms were given *x*- and *y*-parameters as indicated by the lettering of the maxima and as seem reasonably definite from the size of the maxima for all cases except that of O_{II}. Two possible positions for this atom are compatible with the projection; (1) the maximum corresponding to O_{II} lies so close to I that it is not observed, or (2) the maximum for O_{II} is part of the O_{II}–F_{II} maximum which is unresolved. A decision in favor of the second alternative was made with reasonable certainty on the basis of the intensities of reflection which are independent of the iodine atoms.

The evaluation of the *z* parameter was carried out by making use of the general characteristics of the X-ray spectra, the Patterson projection, and structural arguments as outlined below. It is seen (most clearly on Laue photographs) that, for all pairs of reflections (*hkl*) and (*lkh*) having the same type of structure factor, the intensities are very nearly equal for all values of *h* and *l*. This fact together with the evidence of the Patterson projection indicates that a projection of the scattering matter on the *x*–*z* plane has approximately tetragonal symmetry.

If F_I is associated with any iodine atom it must be bonded to I and not to I' since the projection of the distance I' – F_I on the *x*–*y* plane (see Fig. 2) is greater than could correspond to an iodine–oxygen bond. The projection places another fluorine atom at F_{II}, which might be bonded to I' as far as the projection is concerned. If this were the case and if I – F_I were equal to I' – F_{II} then the projection of the interatomic distance on the *x*–*z* plane should show up on the Patterson projection where no maximum is observed. Since F_{II} is the same distance from I as F_I and lies on a straight line through I and F_I (in the projection) it is suggested that these two atoms form opposed bonds with iodine and by referring to the argument in the previous paragraph the values of x_{F_I} and $x_{F_{II}}$ will be approximately ±0.08. This assignment of parameters is made more probable by the small maximum at $z = 0.40$, $x = 0.10$ on the Patterson projection.

The oxygen atom O_I may be assigned fairly definite parameters, the Patterson projection indicating that z_{O_I} cannot be very large. From the projection x has two possible values $\approx 0.25 \pm 0.025$. This choice must be made on the basis of structural arguments and intensities of *hkl* planes. If $IO_2F_2^-$ groups are postulated then certainly x must be less than 0.25. The possibility that x is larger than 0.25 is not altogether unreasonable and was considered seriously but no fit between experimental and calculated intensities could be obtained on this basis. With F_I, F_{II} and O_I placed the choice of parameters for O_{II} was made by concluding from the Patterson projection that it must have a position relative to the z-axis similar to that of O_I relative to the x-axis. In trying to find the proper parameters the iodine to fluorine distances were considered to be equal, as were the iodine to oxygen distances.

The potassium parameters were determined roughly from the projections and then refined by comparison of observed and calculated intensities. The parameters were varied subject to the condition that distances from potassium to oxygen and fluorine be larger than 2.60 Å.

The atomic positions fixed by the means described in the previous paragraphs were finally varied by small amounts (0.005 to 0.01) to obtain the best fit between experimental and observed intensities. The resulting parameters are given below:

	x	*y*	*z*
I	0.00	0.067 ± 0.001	0.00
K	.215 ± 0.005	.465 ± .005	.29 ± 0.005
F_I	− .08 ± .01	.355 ± .01	.09 ± .01
F_{II}	.08 ± .01	− .22 ± .01	− .09 ± .01
O_I	.215 ± .01	.175 ± .01	.035 ± .01
O_{II}	− .02 ± .01	.19 ± .01	.210 ± .01

The atoms occupying the positions F_I and F_{II} it was felt must be the same, either oxygen or fluorine. The position of these atoms is fairly well fixed and it is found that the agreement is considerably better for some of the weak reflections if fluorine atoms are placed in positions F_I and F_{II}. The fact that the I–O distance for this assignment is so closely equal to the same interatomic distance in $(NH_4)_2H_3IO_6$ also lends support to this arrangement.

Tables II and III give the calculated and observed F_{hkl}'s. Pauling–Sherman *f*-values were used in calculating the F's.

TABLE II

VALUES OF F_{hkl}

(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.
(010)	70	100	(310)	54	68	(600)	64	56
(020)	81	79	(320)	abs	10	(610)	82	89
(030)	14	17	(330)	abs	4	(620)	50	52
(040)	abs	6	(340)	18	26	(630)	23	19
(050)	30	24	(350)	abs	6	(640)	abs	7
(060)	35	30	(360)	abs	2	(650)	28	24
(070)	46	50	(370)	abs	12	(660)	23	30
(080)	28	35				(670)	abs	25
						(680)	28	30
(110)	abs	6	(400)	112	152			
(120)	abs	3	(410)	81	94	(710)	abs	1
(130)	20	24	(420)	92	80	(720)	abs	5
(140)	26	28	(430)	abs	0.0	(730)	abs	1
(150)	14	15	(440)	abs	1.0	(740)	abs	4
(160)	15	20	(450)	23	27	(750)	abs	1
(170)	abs	16	(460)	24	28			
			(470)	27	32	(800)	35	42
(200)	94	136	(480)	31	31	(810)	50	54
(210)	129	169				(820)	31	32
(220)	45	35	(510)	abs	14			
(230)	69	61	(520)	abs	2	(10,00)	36	50
(240)	15	20	(530)	abs	10	(10,10)	31	28
(250)	16	19	(540)	abs	5	(10,20)	28	27
(260)	38	43	(550)	abs	8			
(270)	37	43				(12,00)	abs	22
(280)	33	27				(12,10)	23	34

TABLE III

VALUES OF F_{hkl}

(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.
002	87	145	(801)	abs	9	(211)	30	30
004	98	148	(802)	63	55	(212)	85	94
006	68	70				(213)	23	24
008	56	49				(214)	100	126
00,10	29	61	(111)	71	78	(215)	abs	3
			(112)	abs	10	(216)	69	80
(201)	10	8	(113)	55	76	(217)	abs	14
(202)	130	172	(114)	abs	29	(218)	50	50
(203)	53	65	(115)	52	57			
(204)	88	89	(116)	abs	12	(221)	25	33
(205)	abs	14				(222)	102	134
(206)	73	68	(121)	83	98	(223)	abs	13
			(122)	37	46	(224)	49	64
(208)	50	62	(123)	70	89	(226)	49	64
			(124)	abs	5	(228)	38	45
(401)	33	47	(125)	78	96			
(402)	84	91	(126)	abs	16	(231)	23	25
(403)	abs	31	(127)	39	50	(232)	32	33
(404)	119	128	(128)	abs				
(405)	25	22						
(406)	74	80	(131)	98	131			
			(132)	12	28			
			(133)	106	105			
(601)	22	33						
(602)	80	73						
(603)	27	32	(141)	125	103			
(604)	65	83	(142)	abs	9			
(605)	abs	22	(143)	101	83			
(606)	65	68						
(608)	45	45						

As an additional check on the parameters the ratio of intensities I_{hkl}/I_{lkh} were compared with the calculated intensity ratio. Since the interplanar distances d_{hkl} and d_{lkh} are so nearly equal quantitative use could be made of the Laue intensities for such pairs of reflections. Reflections with $n\lambda$ in the neighborhood of the critical absorption limit for iodine were not used in these comparisons. The intensities were estimated visually with the use of a calibrated scale. Table IV gives the results.

TABLE IV

hkl	I_{hkl}/I_{lkh} obsd.	I_{hkl}/I_{lkh} calcd.
1 (415)	15.0	13.10
2 (611)	5.5	4.22
3 (613)	2.4	2.02
4 (614)	1.0	0.98
5 (615)	7.5	6.30
6 (617)	7.5	10.8
7 (811)	4.5	4.5
8 (813)	3.5	4.9
9 837	2.0	30.0[a]
10 429	8.0	6.2

[a] The calculated F's for both reflections are so small for this case 5.7 and 1.0 that a very small error in parameters makes a very large error in the calculated intensities.

Discussion of the Structure.—The crystal structure derived from the above parameters is shown in Fig. 3. The fluoroiodate ion, as shown in the figure, consists of a central iodine atom forming bonds to two fluorine and two oxygen atoms. The fluorine atoms lie on a straight line through the iodine atom and may be thought of as forming opposed bonds. The oxygen atoms lie in a plane perpendicular to the I–F bonds and form bonds with the iodine atom at about 100°. This arrangement gives the group as a whole the appearance of an octahedron with two of the corners removed. It may perhaps better be thought of as a trigonal bipyramid in which one of the three equivalent orbitals is occupied by an unshared pair and the angle between the remaining two decreased from 120 to approximately 100°. The interatomic distances are: $I{-}O_I = 1.93 \pm 0.05$ Å.; $I{-}O_{II} = 1.92 \pm 0.05$ Å.; $I{-}F_I = 2.00 \pm 0.05$ Å.; $I{-}F_{II} = 1.99 \pm 0.05$ Å.; $O_I{-}O_{II} = 2.85 \pm 0.10$ Å.; and the angle $O_I{-}I{-}O_{II} = 100 \pm 7°$. The fluorine–oxygen contacts are the same within the limits of error and equal to 2.75 ± 0.10 Å.

This configuration of the $IO_2F_2^-$ group is the same, within the limits of error, as that reported by Stevenson and Schomaker[3] for $TeCl_4$ in which the unshared pair of electrons has apparently the same steric effect as in the $IO_2F_2^-$ ion.

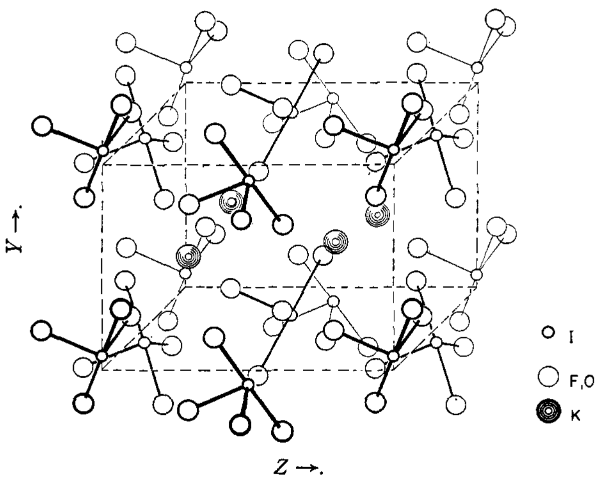

Fig. 3.—Structure of potassium fluoroiodate.

The effect of the unshared pair of electrons on the bond distances may be discussed by comparing the effective iodine radius in this compound with the iodine radii in other related compounds. The data for a number of these compounds are shown in Table V. The table shows that a considerable decrease in the effective iodine radius can be correlated with an increase in formal charge. Since the unshared pair in $IO_2F_2^-$ contributes the same number to the formal charge of iodine as the two additional electron pair bonds in IO_6^{5-} the I–O distances in the two ions might be expected to be nearly the same. The iodine radii for the cases of the iodates and of IF_5 seem to be much too large to be accounted for on the assumption that the radius is a simple function of the formal charge. It is true, however, that the determinations of these two distances are not completely reliable, and satisfactory answer has not yet been given to the question of the existence of discrete IO_3^- ions in iodate crystals.

TABLE V

Compd.	I − X, Å.	Configuration	Formal charge	I-radius
KIO_4[a]	2.23	Octahedral	+3	1.18
$(NH_4)_2H_3IO_6$[b]	1.93	Octahedral	+1	1.27
KIO_2F_2	1.93 (O)	Octahedral or	+1	1.27
	2.00 (F)	trig. bipyr.	+1	1.36
IF_5[c]	2.56	Trig. bipyr.	0	1.90
KI Cl_4[d]	2.34	Octahedral	−1	1.35
KIO_3[e]	2.23	Octahedral	−1	1.58

[a] E. A. Hazelwood, *Z. Krist.*, **98**, 439 (1938).
[b] L. Helmholz, THIS JOURNAL, **59**, 2036 (1937).
[c] Braune and Pinnow, *Z. physik. Chem.*, **35**, 239 (1937).
[d] R. C. L. Mooney, *Z. Krist.*, **98**, 377 (1938).
[e] Zachariasen, *Phys. Rev.*, **37**, 1626 (1931).

If the iodine–oxygen and iodine–fluorine dis-

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(3) D. P. Stevenson and Verner Schomaker, THIS JOURNAL, **62**, 1267 (1940).

tances in potassium iodate and iodine pentafluoride are assumed to be even approximately correct then it would seem evident that two cases must be distinguished. If a vacant orbital exists in the coördination polyhedron, the unshared pair may occupy that orbital and its effect on the iodine radius will be small and may be correlated with the formal charge on the central atom. If no such vacant orbital exists, then the extra electrons become an "inert pair" having no steric effect, but causing a relatively large increase in the iodine radius.

The Structure.—The coördination of oxygen and fluorine atoms about potassium is irregular but it is probable that the packing of the $IO_2F_2^-$ groups is the determining factor in the structure. The K–O and K–F contacts are: $O_I - K = 2.75$, 2.76 Å.; $O_{II} - K = 2.63$, 3.03 Å.; $F_I - K = 2.64$, 3.06 Å.; $F_{II} - K = 2.74$, 3.04 Å.

The interatomic distances which are less than 3.50 Å. between oxygen and fluorine atoms of different anion groups are: $F_I - F_{II} = 2.77$, 3.23 Å.; $F_I - O_{II} = 3.40$ Å.; $F_{II} - O_I = 3.24$ Å.

There are, in addition, two distances between iodine atoms and oxygen atoms in different $IO_2F_2^-$ groups that are shorter than three Ångströms: $I\text{-}O_I = 2.82$ Å.; $I\text{-}O_{II} = 2.88$ Å.

The similarity between this structure and that reported for potassium iodate may be seen if one considers an altered KIO_2F_2 in which the I–O contacts just mentioned are made real bonds so that each oxygen atom is shared between two iodine atoms. If, then, the iodine atoms and bonds to oxygen atoms are placed in the *x–z* plane, then this plane will be identical with a plane $z = 0$ for the potassium iodate structure. In this altered structure the I–F bonds will be in a vertical position along the lines $x = z = 0$, etc. If now one atom of oxygen is substituted for two atoms of fluorine and this atom shared between two iodine atoms the structure would become the cubic structure attributed to potassium iodate. It is suggested that the similarity, although not very great, is sufficient to cause the orientation effects observed on photographs of KIO_2F_2 in which some of the salt had hydrolyzed. The powder lines had quite definite maxima at positions corresponding to the equator and layer lines for potassium iodate oriented with the cube edges parallel to the orthorhombic axes of KIO_2F_2.

Summary

From a determination of the crystal structure of KIO_2F_2 it has been found that the $IO_2F_2^-$ group is composed of an iodine atom forming bonds at approximately 100° with two oxygen atoms, and perpendicular to the plane of these three atoms, two opposed bonds at 180° to fluorine. The configuration may perhaps best be thought of as that of a trigonal bipyramid in which one of the three equivalent orbitals is occupied by an unshared electron pair. The interatomic distances in the ion were found to be: $I - O = 1.93 \pm 0.05$ Å.; $I - F = 2.00$ Å. ± 0.05 Å. The O–I–O bond angle = 100 ± 10°. The influence of the unshared pair on the bond distance is discussed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. VIII. The Relative Affinity of Mercury and Lead for Methyl and Ethyl Radicals

BY GEORGE CALINGAERT, HAROLD SOROOS AND GEORGE W. THOMSON

Previous papers[1,2] of this series have described the redistribution reaction for the interchange of alkyl radicals in alkyl compounds of lead, tin, silicon, or mercury. Redistribution of alkyl groups is not confined to systems containing a single metal, but under suitable conditions can take place between compounds of more than one metal. This was illustrated in the first paper[1] of this series by an analytical distillation[3] curve for the reaction product of tetramethyltin with tetraethyllead, which indicated the presence of all ten possible R_4M compounds.

The fact that the equilibrium composition of a redistributed mixture corresponds to a random distribution of all the organic radicals present indicates that the relative affinity of a given radical for a given metal is independent of the

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[1] Calingaert and Beatty, THIS JOURNAL, **61**, 2748 (1939).

[2] Calingaert, Beatty and Soroos, *ibid.*, **62**, 1099 (1940); Calingaert, Soroos and Hnizda, *ibid.*, **62**, 1107 (1940).

[3] Calingaert, Beatty and Neal, *ibid.*, **61**, 2755 (1939).