Inorganica Chimica Acta, 12 (1975) 247–249

Preparation and Properties of Barium Monofluorotrioxoiodate(V), $BaIO_3F$

S. OKRASINSKI*, R. JOST**, R. RAKSHAPAL*** and G. MITRA
King's College, Department of Chemistry, Wilkes–Barre, Pa. 18711, U.S.A.
Received August 18, 1974

Introduction

The oxo-, fluoro-, and oxyfluoro- anions of iodine(V) have received a great deal of attention. In fact, the salts of the difluorodioxoiodate(V) ion are reported by R. F. Weinland and O. Lauenstein as early as in 1899[1,2]. In more recent years single crystal X-ray diffraction has shown that the steric effect caused by iodine's lone pair of electrons is quite noticeable. This is evidenced through the observation that the O–I–O angle in the $IO_2F_2^-$ ion measure approximately 100°, a value appreciably smaller than that expected for a regular trigonal bipyrimidal structure[3].

Up until this time the difluorodioxoiodate(V) ion is possibly the only well-defined oxyhalo anion of a halogen that has been reported. In this paper the preparation and properties of a salt of a new oxyhalo ion of iodine, the monofluorotrioxoiodate(V) ion will be described.

All previous attempts to isolate salts of IO_3F^{2-} ion have ended in failure. Reaction (1) occurs very fast in aqueous media and the pH

$$KIO_2F_2 + 2KOH = KIO_3 + 2KF + H_2O \qquad (1)$$

titration curve gives no evidence to support the existence of a 1:1 addition product as in (2).

$$KIO_2F_2 + KOH = K_2IO_3F + HF$$
or
$$KIO_2F_2 + KOH = KHIO_3F + KF \qquad (2)$$

However, the formation of the IO_3F^{2-} ion can reasonably be assumed possible by analogy to KIO_2F_2 and $NaIO_2F_2$, as the $\Delta H°_f$ for these compounds are –209.52 and –202.85 kcal/mol respectively[4], which would help to indicate that the IO_3F^{2-} ion would possess some thermodynamic stability. The problems represented in the reactions (1) and (2) can be overcome in the laboratory by reacting $Ba(OH)_2 \cdot H_2O$ with KIO_2F_2 in an alcohol medium. Barium hydroxide is a weaker base than KOH and one can logically expect that $BaIO_3F$ would be a sparingly soluble compound. Thus the formation of $BaIO_3F$ would be further enhanced since the IO_3F^{2-} ion would be constantly removed from the equilibrium as the solid compound.

Experimental

All reagents used in the preparation of the compound were reagent grade, and the starting material KIO_2F_2 was prepared by dissolving KIO_3 in 40% HF at 80° C and then allowing KIO_2F_2 to crystallize from the solution upon cooling.

The isolation of $BaIO_3F$ is accomplished as follows: 4.0 g of KIO_2F_2 and 3.3 g of $Ba(OH)_2 \cdot H_2O$ is ground to a fine powder and placed into a 250 ml nalgene erlenmeyer flask along with a teflon coated stirring bar. To this mixture 200 ml of absolute ethanol is then added and the flask is stoppered with an anhydrous calcium chloride drying tube. The contents of the flask are then stirred for 48 hr at approximately 60° C and the resulting solid material is then collected by filtration. The solid is then washed repeatedly with hot concentrated ammonium chloride solution, hot water, and dilute HCl followed by 95% ethanol. The wash solution was found to contain an appreciable amount of fluoride and only traces of IO_3^- after use.

It should be noted however, that the presence of water in the reaction medium in excess of the single water of crystallization of the barium hydroxide is fatal. It has also been observed that the use of $Ba(OH)_2 \cdot H_2O$ that has been given a chance to absorb carbon dioxide from the air also results in negative results. From time to time the reaction mixture may take on a deep yellow color before 48 hr. has transpired, indicating that uncontrolled hydrolysis has taken place. In these cases the reaction mixture was filtered without waiting for the entire 48 hr to pass, and the resulting solid washed and identified.

Considerable difficulty is met in the synthesis of $BaIO_3F$ if adequate provisions are not made for the exclusion of water and for the use of pure $Ba(OH)_2 \cdot H_2O$.

---

* Present Address: Department of Chemistry, Princeton University, Princeton, N. J.

** Present Address: Department of Chemistry, University of Syracuse, Syracuse, N. Y.

*** Present Address: Department of Chemistry, Howard University, Washington, D. C.

Attempts to prepare $BaIO_3F$ from $Ba(OH)_2 \cdot 8H_2O$, $BaCO_3$ and $Ba(C_2H_3O_2)_2 \cdot H_2O$ were unsuccessful.

The analysis of the compound gave the following results. Found: Ba, 41.30; I, 38.67; F, 5.40%. Calculated: Ba, 41.46; I, 38.31; F, 5.74%.

Discussion of Results

The accurate interpretation of the vibrational spectra of $BaIO_3F$ is not easily accomplished. The difluorodioxoiodate(V) ion, $IO_2F_2^-$ ideally belongs to the C_{2v} symmetry group, but the replacement of a fluorine atom by an oxygen atom to form the IO_3F^{2-} ion reduces the symmetry of the ion to C_s. However, as the compound is probably isostructural with KIO_2F_2, it may be concluded that the two anions $IO_2F_2^-$ and IO_3F^{2-} have basically the same structural configuration. For this type of structure (tbp) the equatorial bonds are usually shorter than the axial bonds, however this is not the case for KIO_2F_2 as the I–O and I–F bond lengths are found to be almost identical, 1.93 and 2.00 respectively. Because of this similarity the assignments of the I. R. bands would take on added difficulties. Using this as a basis it is reasonable to expect that this slight increase of $r_{(I-O)}$ axial over $r_{(I-O)}$ equatorial would result only in the broadening of the I. R. band for $BaIO_3F$. Using this same type of reasoning it can be seen that the interpretation of the I.R. spectra for both the I–F and I–O stretches presents problems. The close similarity between the I–O and I–F bond lengths results in an isotope type shift in frequency as the only means of differentiation between the two types of bands, and overlap between the two bands would be extensive. A similar observation has previously been reported.[5]

A Beckman Laser Raman 700 equipped with an argon-ion laser (480 nm) was used for studying the Raman spectra of the compound. It was found that KIO_2F_2 decomposed under the laser beam. The very strong 810 cm^{-1} stretch attributed to $\nu(I\text{–}O)_{sym}$ of KIO_2F_2 shifts to the well established 750 cm^{-1} I–O stretch of KIO_3. We think barium monofluorotrioxoiodate(V) also decomposes under the prolonged exposure of the laser beam.

The infra-red and Raman spectra of $BaIO_3F$ was taken in the solid state and the results are given in Table I.

The 785 cm^{-1} Raman and 790 cm^{-1} I.R. bands are attributed to the I–O stretching modes[6]. The characteristic I–O frequencies of a series of similar compounds are given in Table II.

It is seen that as the F:I ratio decreases the I–O stretching bands shift towards lower frequency. This effect is also reflected in the bond distances as the I–O bond lengths are 1.93 and 2.23 Å in KIO_2F_2 and KIO_3 respectively. Thus, as expected, the bond order between iodine and oxygen increases as increasing amounts of electron density are shifted from iodine to fluorine atoms.

TABLE I. Vibrational Spectra of $BaIO_3F$.

IR (cm^{-1})	Raman (cm^{-1})
1460 (m)	807
1430 (m)	785
790 (s)	755
750 (vs)	730
620 (w)	310
525 (vw)	335
375 (m)	365
310 (m)	415
	380
	215
	165

TABLE II. Reported I–O Stretches in Oxyfluorides and Oxyfluoro Anions of Iodine(V).

Compounds	I.R. (cm^{-1})	Raman (cm^{-1})
IOF_3	883	907
$IO_2F_2^-$	844	830
	816	808
IO_2F	809	807
IO_3F^{2-}	790	785
IO_3^-	746	

I–F stretching vibrations occur in the 500 cm^{-1} to 650 cm^{-1} region[7]. Weak peaks were found at 620 and 525 for $BaIO_3F$. However, barium iodate also exhibits a few peaks in this region and the exact assignments of the $BaIO_3F$ bands could not be made. Similary the 472 cm^{-1} strong Raman band of KIO_2F_2 was replaced by two very weak peaks at 415 and 380 cm^{-1} in $BaIO_3F$. The peak in the region of 480 for KIO_2F_2 is attributed to $\nu(IF_2)_{sym}$. This peak disappears when KIO_2F_2 is dissolved in pyridine. In addition, $BaIO_3F$ shows a strong peak at 165 cm^{-1} (rock) which is not present in barium iodate.

The X-ray powder diffraction pattern clearly differentiates the resulting compound, $BaIO_3F$, from the possible impurities BaF_2, KIO_2F_2, $Ba(IO_3)_2$ and $Ba(OH)_2 \cdot H_2O$ thus indicating the the product is not the result of an uncontrolled hydrolysis. Table III lists the diffraction pattern as indexed for an orthorhombic crystal system. The orthorhombic system appears to be the most probable at this time but it is not definitely established as the correct system.

The thermal behavior of $BaIO_3F$ provides yet another means of differentiation of the compound from the possible impurities and products of uncontrolled hydrolysis. The DTA behavior, as obtained on a Perkin–Elmer DSC-1, is summarized in Table IV for the pertinent compounds.

TABLE III. Diffraction Pattern.

d obs.	d calc.	hkl	I/I_o
3.767	3.758	102	12
3.373	3.426	210	82
3.218	3.186	112	10
3.162	3.173	211	10
2.986	3.004	020	21
2.790	2.780	300	33
2.638	2.640	301	100
2.348	2.347	122	35
2.252	2.320	302	16
2.187	2.171	213	30
2.109	2.109	222	28
2.023	2.024	401	37
1.992	1.992	123	16
1.977	1.975	303	12
1.898	1.897	131	16
1.861	1.868	402	25
1.804	1.805	230	12
1.670	1.668	500	26
1.631	1.630	033	56
1.244	1.246	603	23
1.156	1.156	207	14
1.147	1.146	702	16

Unit Cell: a_o = 8.340, b_o = 6.008, c_o = 8.420; Volume = 421.9 Å^3

TABLE IV. Differential Thermal Analysis Data.

Compounds	Endotherms (° C)	Exotherms (° C)
$Ba(IO_3)_2$	403	360 (broad)
BaF_2	135–215 (broad)	300 (broad)
$Ba(OH)_2 \cdot H_2O$	90 (broad)	
	252	
	375	
	390 (broad)	
KIO_2F_2		250 (broad)
$BaIO_3F$		177
		380

It should be noted that decomposition of $BaIO_3F$ is observed at the 177° C point for $BaIO_3F$, and a gaseous substance is given off along with the appearance of the exotherm. This gaseous material has not yet been identified.

Conclusion

The monofluoro iodate ion, IO_3F^{2-}, discribed in this paper is the only divalent oxy or oxfluoro anion formed by iodine as the central element. Some physical properties of iodic acid suggest the existence of a dimer $H_2I_2O_6$. This is however, controversial. During the disproportionation of hypoiodite a relatively stable intermediate ion $I_2O_2^{2-}$ has been postulated by a kinetics study. In IO_3F^{2-} ion the three oxygen atoms are situated almost at the same distance from iodine. For this reason, the ion breaks easily in aqueous solution to IO_3^- and F^- ions.

The X-ray diffraction analysis of $BaIO_3F$ shows its structural similarity with KIO_2F_2. Our assignments for the d values of $BaIO_3F$ are tentative and further investigation is necessary.

This work was supported in part by a grant received from ONR.

References

1 R.F. Weinland and O. Lauenstein, *Z. Anorg. Allgem. Chem., 30* (1899).

2 R.F. Weinland and O. Koppen, *Ibid., 22,* 256 (1900).

3 L. Helmholz and M.T. Rogers, *J. Am. Chem. Soc., 62,* 1537 (1940).

4 A. Finch, P.N. Gates and M.A. Jenkinson, *J. Fluor. Chem. 2,* 111 (1972–73).

5 J. Pitts, S. Kongpricha and A.W. Jache, *Inorg. Chem., 4,* 257 (1965).

6 H.A. Carter and F. Awkle, *Inorg. Chem., 10,* 2296 (1971).

7 R.C. Lord, M.A. Lynch, W.C. Schumb and E.J. Slowinski, *J. Am. Chem. Soc., 72,* 522 (1950).