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Oxofluoro Complex Anion Equilibria in Aqueous Hydrofluoric Acid.
II. Iodate(V) in Dilute Hydrofluoric Acid

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The infrared and Raman spectra of $CsIO_2F_2 \cdot {}^1/_3H_2O$, $Cs[H(IO_2F_2)_2] \cdot 2H_2O$, and $Co(NH_3)_6(IO_2F_2)_3 \cdot H_2O$ have been obtained and all compounds are shown to contain water of hydration as opposed to hydroxoiodate anions. Approximate assignments under C_{2v} symmetry have been made for the $IO_2F_2^-$ ion in $CsIO_2F_2 \cdot {}^1/_3H_2O$ and $Co(NH_3)_6(IO_2F_2)_3 \cdot H_2O$. The spectra of $Cs[H(IO_2F_2)_2] \cdot 2H_2O$ show that it contains a complex hydrogen-bridged anion. The Raman spectrum of the $IO_2F_2^-$ ion in aqueous hydrofluoric acid is reported and assigned and the hydrolysis constant, K_h, for the equilibrium

$$IO_2F_2^- + H_2O \overset{K_h}{\rightleftharpoons} IO_3^- + 2HF$$

has been evaluated from Raman peak intensities.

Introduction

Three fluoro anions of iodine(V) are known: IF_6^-, IOF_4^-, and $IO_2F_2^-$. The hexafluoroiodate(V) ion is prepared under rigorously anhydrous conditions[1] and crystals of $CsIOF_4$ have been isolated, from a mixture of CsI and IF_5 in acetonitrile with sufficient oxide for the small amount of product arising from unidentified sources.[2] Simple difluoroiodates, MIO_2F_2 (M = Na, K, Rb and NH_4), may be prepared from 40% HF,[3] and $AgIO_2F_2$ has been prepared from 100% HF.[4] The cesium salt, $CsIO_2F_2$, is reported to crystallize from 15% hydrofluoric acid while $CsIO_2F_2 \cdot HIO_2F_2 \cdot 2H_2O$ results from 40% HF.[5] The crystal structure of KIO_2F_2 has been determined[6] and the shape of the $IO_2F_2^-$ ion shown to be based upon a trigonal bipyramid with the lone electron pair and the oxygens in equatorial positions. Strong interanion bridging over oxygen is indicated. The vibrational spectra of several difluoroiodates have been measured and shown to be consistent with an essentially C_{2v} anion.[4,7,8] The Raman spectrum of this anion in several compounds and in solution forms the subject of this paper. Solutions of iodate(V) in more concentrated hydrofluoric acid (up to 100%) will be dealt with in part III.[9]

Experimental Section

Materials. Iodic acid, 99% (BDH), potassium fluoride, 98% (BDH), and cesium fluoride, 99% (Ozark-Mahoning), were used directly. Hydrofluoric acid, 48% (J. T. Baker), and perchloric acid, 70% (Analar, BDH), were standardized with phenolphthalein and used directly.

Preparation of the Compounds. KIO_2F_2. The method of Helmholz and Rogers was used.[6]

$CsIO_2F_2 \cdot {}^1/_3H_2O$. A 2:1 molar ratio of CsF and HIO_3 was dissolved in hot 15% hydrofluoric acid and large crystals were deposited on cooling. This procedure is essentially that of Weinland and Köppen[5] for the preparation of $CsIO_2F_2$. In our hands this procedure yielded the hydrate $CsIO_2F_2 \cdot {}^1/_3H_2O$. *Anal.* Calcd for $CsIO_2F_2 \cdot {}^1/_3H_2O$: I, 37.79; F, 11.32. Found: I, 37.82; F, 11.41 (calculated from the number of acid equivalents). Crystallization from hot (~95°) 15% HF also yielded the hydrate. Attempts to dehydrate this compound by heating at 90° under vacuum for 12 hr caused some decomposition to $CsIO_3$.

$CsH(IO_2F_2)_2 \cdot 2H_2O$. This compound was prepared from 40% hydrofluoric acid by the method of Weinland and Köppen.[5] *Anal.* Calcd for $CsH(IO_2F_2)_2 \cdot 2H_2O$: I, 45.02; F, 13.48. Found: I, 44.87; F, 13.50 (calculated from the number of acid equivalents). Although this product was formed from solution as well-developed crystals, it was not possible to store it for extended periods. Both H_2O and HF were lost on storage.

$Co(NH_3)_6(IO_2F_2)_3 \cdot H_2O$. $Co(NH_3)_6F_3$ was prepared by dissolving 0.01 mol of $Co(NH_3)_6Cl_3$ in water and adding a saturated solution of AgF (0.03 mol). The precipitated AgCl was filtered off and the resulting solution was concentrated to 50 ml on a vacuum line. Iodic acid (0.03 mol) was dissolved in 30 ml of 48% HF and the resulting solution filtered to remove any suspended particles. Addition to the $Co(NH_3)_6F_3$ solution yielded a good crop of orange crystals on cooling in ice. The product was filtered, washed with a few milliliters of ethanol and then ether, and dried under vacuum. *Anal.* Calcd for $Co(NH_3)_6(IO_2F_2)_3 \cdot H_2O$: I, 49.46; Co, 7.66. Found: I, 50.06; Co, 7.88.

Solutions. Solutions for the determination of the $IO_2F_2^-$ hydrolysis constant were made up from HIO_3 and 24.2 *M* hydrofluoric acid in F:I stoichiometric ratios of interest and diluted with distilled water as required. The molar intensity for ν_4 of HIO_3 was determined using aqueous HIO_3 solutions. In both of these series of solutions $HClO_4$ of known concentration was added for normalization of peak intensities.

Methods. Analysis. Iodine was determined as iodate by titration with sodium thiosulfate.[10] It was found that fluoride analysis by titration with $La(NO_3)_3$ using a fluoride-sensitive electrode[12] was not possible in the presence of iodate(V). The titration of 2:1 KF–HIO_3 mixtures as well as the fluoroiodates gave reasonably sharp end points but the results were ~20% high. Distillation from dilute H_2SO_4 solution failed to separate the iodine which came over with the fluoride. For these reasons the original method used by Weinland was adopted and the total number of acid equivalents was determined using standard sodium hydroxide.[5]

Spectroscopy. Ir spectra were taken as mulls in Nujol and Fluorolube, using CsBr plates, on a Beckman IR 20A spectrometer. Band positions were accurate to ±5 cm^{-1}. Raman spectra were taken with a Jarrell-Ash 300 Raman spectrometer. All spectra were run at 25°. A Spectra-Physics argon ion laser was used (4880 Å) for all spectra except those of $Co(NH_3)_6(IO_2F_2)_3 \cdot H_2O$ which was decomposed at this excitation frequency. A He–Ne excitation at 6328 Å was used for spectra of this compound. Detection was by a cooled photomultiplier tube. A spike filter was used to remove plasma lines from the spectra of the solid. Solid samples were contained in 1-mm o.d. Pyrex tubes, and for solutions, a cylindrical sapphire cell, 10-cm length × 5-mm i.d. (Tyco, Sapphikon Division), closed with a plastic cap, was used. Slit widths were 5 cm^{-1} for spectra of the solids and 10 cm^{-1} for solutions. A Raman spectrum of 48% HF showed no bands that interfered with the spectra of the anions studied. A band identified as due to sapphire (417 cm^{-1}) was observed in the solution spectra. Integrated peak intensities of the Raman bands were measured with a planimeter and were accurate to within ±5%. All integrated peak intensities were relative to $\nu_1(0.34\ M\ ClO_4^-) = 100$.

Results and Discussion

Solids. X-Ray powder photographs of $CsIO_2F_2 \cdot {}^1/_3H_2O$, $CsH(IO_2F_2)_2 \cdot 2H_2O$, and $Co(NH_3)_6(IO_2F_2)_3 \cdot H_2O$ showed that all products were crystalline. The observed powder patterns have been deposited with the American Society for Testing and Materials.

Because of the complexity of the spectra of the solids, a definitive assignment of the bands cannot be made. Moreover without a knowledge of the crystal structures, the effect of factor group splitting cannot be allowed for. However, a tentative assignment is presented here based upon the modes expected under C_{2v} symmetry. The spectra of all of the

Table I. Raman and Infrared Spectra (cm^{-1}) of $IO_2F_2^-$ Species (C_{2v})

Class	Mode. no.	KIO_2F_2[a] Raman	KIO_2F_2[a] Ir	$CsIO_2F_2\cdot{}^1/_3H_2O$[b] Raman	$CsIO_2F_2\cdot{}^1/_3H_2O$[b] Ir	$Co(NH_3)_6(IO_2F_2)_3\cdot H_2O$[c] Raman	$Co(NH_3)_6(IO_2F_2)_3\cdot H_2O$[c] Ir	$IO_2F_2^-$[d] Raman	Approx description of mode
A_1	ν_1	817 vs 814 w, sh	819 m 805 w, sh	814 vs	815 s 805 sh	810 vs 788 s	790 s 760 m, br	840 vs, p (0.16)	$\nu_{sym}(IO_2)$
	ν_2	479 s	485 vs	484 m	475 s	484	500 mw 470 s	483 m, p (0.34)	$\nu_{sym}(IF_2)$
	ν_3	360 m	360 s 351 w, sh	372 w	380 sh	371 w 359 mw	385 sh 378 sh	[335] mw, br, p (?)	$\delta_{sym}(IO_2)$
	ν_4	194 vw	197 s	190 w, br		190 184 m		170 w, p (0.52)	$\delta_{sym}(IF_2)$
A_2	ν_5		220 m, sh	256 vw 213 w, br	283 m		255 w 250 w		τ
B_1	ν_6	838 w	851 m 845 m	836 m 822 m	825 vs	839 w 833 w 817 sh	810 vs		$\nu_{asym}(IO_2)$
	ν_7	346 w	345 s	352 w	345 s	352 w 340 m	350 sh	[335] mw, br	$\delta_{asym}(IO_2)$
B_2	ν_8	456 vw	440 m 407 m	464 m	460 ms 422 s	451 m 435 sh	425 m	420[e]	$\nu_{asym}(IF_2)$
	ν_9[f]	323 s	345 s	314 m	320 sh 305 w	330 mw 311 mw	340 ms, br	[335] mw, br	$\delta_{asym}(IF_2)$

[a] Reference 8. [b] Ir bands due to H_2O: 3425 m, br, 1655 mw, br, 595/615 w, vbr. [c] Ir bands due to H_2O: 3800 vw, 3570 m, 3450 m, 1655 sh. Ir bands due to cation: 3270 s, br, 3150 s, br, 1355 m, 1348 m, 975 vw, 840 s, 330 s, 270 s. Raman bands due to cation: 496 s, 447 m, sh, 321 w. [d] 2 *M* HIO_3 in 24 *M* HF. [e] Superimposed with glass or sapphire peak. [f] Assigned as in ref 8 but see text.

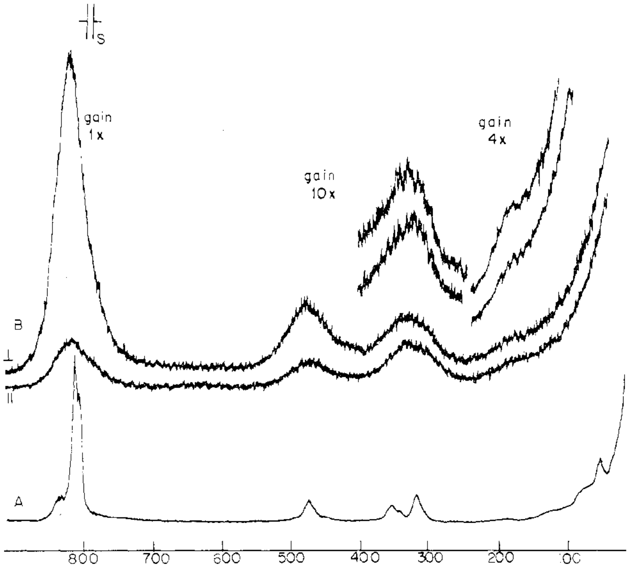

Figure 1. Raman spectra of solid KIO_2F_2 (A) and a 2.0 *M* solution of HIO_3 in 24.2 *M* HF (B). S indicates slit width.

Table II. Raman and Infrared Spectra (cm^{-1}) of $Cs[H(IO_2F_2)_2]\cdot 2H_2O$

Raman[a]	Ir	Description of mode
	3425 m, vbr	ν_{H_2O}
	2900 w, br	ν_{OH}
	1670 m, br	δ_{H_2O}
	1170 vw	δ_{OH}
833 vs	830 ms	ν_{IO}
775 s	800 s	
755 ms	780 m	
737 ms	742 s	
635 w	610 vw, vbr	
600 w, br		
492 m	500 sh	ν_{IF}
	485 s	
455 vw, br	445 sh	
	400 vs, br	
370 ms, br		
355 vw	340 sh	
	332 vs	
310 w	315 ms	
	292 vs	
	270 ms	
230 vw, br	250 m	
150 w, br		

[a] Up to 1800 cm^{-1}.

crystalline difluoroiodates show evidence for the breakdown of the C_{2v} selection rules and oxygen bridging inasmuch as $\nu_5(A_2)$ is active in the ir spectra and more than two IO stretching modes are observed.

The Raman and infrared spectra of the solid difluoroiodate(IV) compounds are given in Table I and the Raman spectrum of KIO_2F_2 is given in Figure 1, trace A. The Raman and infrared spectra of $Cs[H(IO_2F_2)_2]\cdot 2H_2O$ are given in Table II. The spectra recorded for KIO_2F_2 are in excellent agreement with those reported by Finch, *et al.*[8] The X-ray crystal structure of KIO_2F_2[6] shows that there is oxygen bridging between anions, and the appearance of three IO stretching bands where two are expected under C_{2v} symmetry is a result of interanionic coupling. Similar effects have been observed in the case of the isoelectronic $TeO_2F_2^{2-}$ ion.[11]

In the case of the cesium salt, crystallization from 15% hydrofluoric acid did not yield anhydrous $CsIO_2F_2$ in our hands but instead $CsIO_2F_2\cdot{}^1/_3H_2O$ was formed. The Raman and infrared spectra of this compound listed in Table I show no sharp bands in the region of I–O single-bond stretching modes nor an infrared spectrum characteristic of an OH group attached to a heavy atom.[12] The infrared spectrum is, however, characteristic of a hydrate[12] and it is concluded that this compound does not contain a hydroxoiodate ion. It should be noted that there is a considerable difference between the spectra of KIO_2F_2 and those of $CsIO_2F_2\cdot{}^1/_3H_2O$.

The infrared spectrum of $Co(NH_3)_6(IO_2F_2)_3\cdot H_2O$ shows for the same reasons as given for $CsIO_2F_2\cdot{}^1/_3H_2O$ that this compound is also a hydrate. The H_2O deformation appears at 1655 cm^{-1}, characteristic of hydrates,[12] and two OH stretching bands are observed as has been reported for other hydrates.[13] Five bands appear in the IO stretching region, indicating a more complex structure for this compound compared to KIO_2F_2 and $CsIO_2F_2\cdot{}^1/_3H_2O$. The doubling up of many of the bands suggests that there are two types of $IO_2F_2^-$ ion in this substance, differing perhaps by the nature of their oxygen bridging or hydrogen bonding.

Crystallization of 2:1 cesium fluoride–iodic acid mixtures from 40% hydrofluoric acid yields $Cs[H(IO_2F_2)_2]\cdot 2H_2O$.

Raman and infrared spectra listed in Table II suggest that this compound is a hydrate although the presence of H_3O^+ ion cannot be entirely ruled out. The bands at 3425 and 1670 cm^{-1} in the infrared spectrum are characteristic for a hydrate[12] and the band at 610 cm^{-1} may also be due to H_2O. The characteristic bands for $H_5O_2^+$ [14] are not present in the spectrum of this compound. The observation of a weak band at 1170 cm^{-1} shows the presence of a hydroxo group and the broad band at 2900 cm^{-1} is indicative of a strong hydrogen bond, supporting the anion formulation as $H(IO_2F_2)_2^-$. We prefer this interpretation compared to one involving H_3O^+, because the high-frequency limit of the OH stretching band (3750 cm^{-1}) is high for H_3O^+ [15] (3380 cm^{-1} in $H_3O^+NO_3^-$) and because of the parallel in the O–H···O modes with those in the spectrum of $KH(IO_3)_2$.[16] A complete assignment for $Cs[H(IO_2F_2)_2]\cdot 2H_2O$ is not possible due to the complexity of the spectra. The spectra are listed in Table II with a partial assignment.

Solutions. The solution Raman spectrum of the $IO_2F_2^-$ ion is given in Figure 1, trace B, and Table I. No evidence for the formation of HIO_2F_2 was found at the HF concentrations reported here. Polarization measurements confirm the assignment reported for KIO_2F_2[8] except in case of $\nu_3(A_1)$, the symmetric IO_2 deformation. The envelope centered at 335 cm^{-1}, which includes ν_3, ν_7, and possibly ν_9, shows a degree of polarization little different from the 0.75 expected for a depolarized band and the band contour shows no change upon polarization. The polarization measurements confirm the assignment of ν_4 at ~190 cm^{-1} in the solids and not at 319 cm^{-1} as given previously.[11] This shows how uncertain it is to make assignments on the basis of intensity arguments alone and the assignment for the $TeO_2F_2^{2-}$ ion should be reconsidered in this light. We have retained the assignment of the band near 320 cm^{-1} to ν_9 as given by Finch, *et al.*[8] This assignment is based upon the position of this band in spectra of XeO_2F_2 and SeO_2F_2.[17] However in the spectra of the SbF_4^- ion[18] and monomeric TeF_4[19] ν_9 comes at near 185 cm^{-1}. It is possible, therefore, that the band near 320 cm^{-1} assigned to ν_9 is in fact a part of ν_7, appearing in addition to the band near 340 cm^{-1} as a result of anion bridging, and that ν_9 is masked by ν_4 or is too weak for observation.

The Raman spectrum of HIO_3 dissolved in 40% HF shows no peaks that can be attributed to HIO_3 or IO_3^- and the $IO_2F_2^-$ spectrum observed maintains a constant profile over a range of iodate concentration. Further evidence that $IO_2F_2^-$ is the only I(V) species present comes from a plot of the integrated peak intensity of ν_2 of $IO_2F_2^-$ against initial iodic acid concentration, C_{HIO_3} given in Figure 2A, which is a straight line. The measurements for this plot are given in Table III, solutions 1–3. As one reduces HF concentration holding C_{HIO_3} constant, the Raman spectrum changes as shown in Figure 3. As ν_2 of $IO_2F_2^-$ (483 cm^{-1}) falls in intensity, a band at 644 cm^{-1} strengthens. This new band is ν_4 of HIO_3, the I–OH stretching mode.[20] These changes are governed by the equilibria

$$HIO_3 + H_2O \overset{K_d}{\rightleftharpoons} H_3O^+ + IO_3$$

$$IO_3^- + HF \overset{K_{h_1}}{\rightleftharpoons} HIO_3F^-$$

$$HIO_3F^- + HF \overset{K_{h_2}}{\rightleftharpoons} IO_2F_2^- + H_2O$$

$$IO_3^- + 2HF \overset{K_h}{\rightleftharpoons} IO_2F_2^- + H_2O$$

$$K_h = K_{h_1}K_{h_2}$$

The hydrolysis constant is given by

$$K_h = \frac{a_{IO_3^-}a_{HF}^2}{a_{IO_2F_2^-}a_{H_2O}(N)} = \frac{y_{\pm IO_3^-}}{y_{\pm IO_2F_2^-}}\,\frac{[IO_3^-]y_{HF}^2[HF]^2}{[IO_2F_2^-]a_{H_2O}(N)}$$

The term $a_{H_2O}(N)$ denotes the activity of water on the mole

Table III. Calculation of the Hydrolysis Constant, K_h, of the $IO_2F_2^-$ Ion

Soln no.	C_{HIO_3}, M	Integrated peak intens,[a] $\nu(I{-}OH)_{HIO_3}$	$[HIO_3]$, M	$[IO_3^-]$, M	Integrated peak intens,[a] $\nu(IF_2)_{IO_2F_2^-}$	$[IO_2F_2^-]$, M	C_{HF}, M	M_{HF}, M	$[HF]$, M	$a_{H_2O}(N)$	K_h,[b] M^2
1	1.80				428	1.80	24.20				
2	2.69				637	2.69	24.20				
3	2.91				677	2.91	24.20				
4	1.99	265	0.88	0.92	45	0.19	2.35	1.97	1.74	0.968	15
5	1.99	179	0.60	0.83	132	0.56	4.70	3.58	3.12	0.942	15
6	3.01	310	1.03	1.12	203	0.86	5.87	4.15	3.59	0.936	18
7	3.06	230	0.77	0.96	315	1.33	8.22	5.54	4.75	0.913	18
8	3.59	168	0.56	0.88	508	2.15	11.75	7.43	6.33	0.886	18

[a] All integrated peak intensities relative to ν_1 of 0.34 M ClO_4^- = 100. [b] Mean $K_h = 17 \pm 2$ M^2.

Table IV. Calculation of the Molar Intensity for Iodic Acid, $J_{\mathrm{HIO_3}}$

$C_{\mathrm{HIO_3}}$, *M*	Integrated peak intens, ν(I-OH)$_{\mathrm{HIO_3}}$ (ν_4)	$[\mathrm{IO_3}^-]$,^{a} *M*	$y_{\pm\mathrm{HIO_3}}$	$[\mathrm{IO_3}^-]$,^{b} *M*	$[\mathrm{HIO_3}]$, *M*
0.272	47	0.080	0.770	0.110	0.162
0.327	51	0.096	0.756	0.131	0.196
0.429	62	0.120	0.739	0.169	0.260
0.524	73	0.142	0.725	0.203	0.321
1.46	291	0.310	0.656	0.490	0.97
2.29	478	0.430	0.628	0.690	1.60
2.83	580	0.500	0.615	0.822	2.01
4.40	890	0.670			

[a] Calculated assuming $y_{\pm\mathrm{HIO_3}} = 1$. [b] Calculated using $y_{\pm\mathrm{HIO_3}}$ in column 4 (see text).

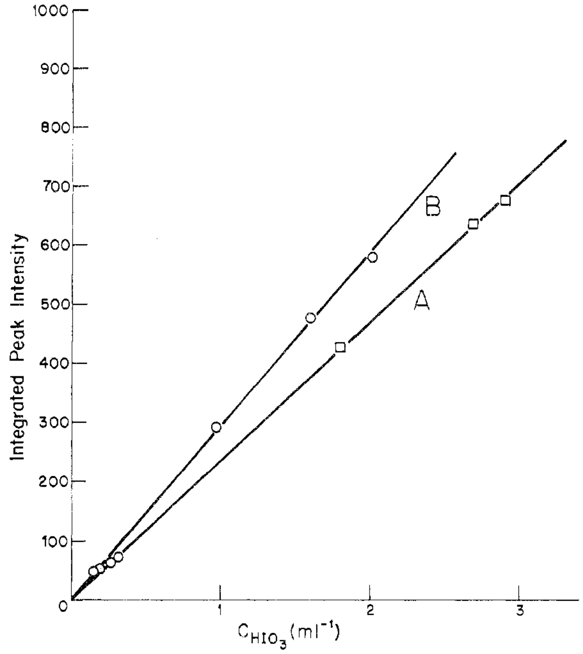

Figure 2. Dependence of integrated peak intensity on concentration: A, ν_2 (483 cm^{-1}) of $\mathrm{IO_2F_2}^-$; B, ν_4 (644 cm^{-1}) of $\mathrm{HIO_3}$.

fraction scale, referred to pure water, where by definition $a_{\mathrm{H_2O}}(\mathrm{N}) = 1$. Since the two I(V) anions have the same charge, their activity coefficients may be assumed to cancel to a good approximation. The concentrations of the various I(V) species may be determined from the integrated peak intensities of ν_2 of $\mathrm{IO_2F_2}^-$ (483 cm^{-1}) and ν_4 of $\mathrm{HIO_3}$ (644 cm^{-1}).

The concentration of $\mathrm{IO_2F_2}^-$ may be determined in a given $\mathrm{HIO_3}$–HF solution from the plot of integrated peak intensity of ν_2 against $\mathrm{IO_2F_2}^-$ concentration given in Figure 2A. However, the concentration of $\mathrm{IO_3}^-$ cannot be determined in this manner due to overlap of the IO stretching modes of $\mathrm{HIO_3}$, $\mathrm{IO_3}^-$, and $\mathrm{IO_2F_2}^-$ ions. Instead, $\mathrm{HIO_3}$ concentration may be determined from the integrated peak intensity of ν_4 of $\mathrm{HIO_3}$ at 644 cm^{-1} and $[\mathrm{IO_3}^-]$ found from the stoichiometry

$$C_{\mathrm{HIO_3}} = [\mathrm{HIO_3}] + [\mathrm{IO_3}^-] + [\mathrm{IO_2F_2}^-]$$

The molar intensity of ν_4 for $\mathrm{HIO_3}$, $J_{\mathrm{HIO_3}}$, may be evaluated from the data in Table IV and the $\mathrm{HIO_3}$ concentration, calculated from the dissociation constant for $\mathrm{HIO_3}$.[20] The molar activity coefficients for the hypothetical completely dissociated iodic acid, $y_{\pm\mathrm{HIO_3}}$, listed in Table IV, have been calculated using the data and method of Durig, *et al.*,[20] and the densities listed in ref 21, p 55. An initial calculation of iodic acid concentration is made, using the dissociation constant for iodic acid, $K_\mathrm{d} = 0.18$ *M*, and, assuming all activity coefficients, $y_{\pm\mathrm{HIO_3}}$, are unity. Hydronium ion concentration was taken as the sum of that arising from iodic acid and the 0.34 *M* $\mathrm{HClO_4}$ present in all solutions. The results of this calculation are given in Table IV and a plot of integrated peak intensity against $[\mathrm{HIO_3}]$ calculated in this way gives a value of $J_{\mathrm{HIO_3}} = 238$. The calculation was now improved by introducing ionic activity coefficients, $y_{\pm\mathrm{HIO_3}}$, as calculated according to Durig, *et al.*,[20] for the iodate ion concentration. The molecular iodic acid activity coefficient was still assumed to be unity. The results of this calculation are given in Table IV and Figure 2B. The highest iodic acid concentration could not be used since the activity coefficient data do not extend to high enough concentrations. This plot gives a value of $J_{\mathrm{HIO_3}} = 295$. This calculation takes no account of the effect of 0.34 *M* $\mathrm{HClO_4}$ on $y_{\pm\mathrm{HIO_3}}$. For the solution of lowest iodic acid concentration an estimate of $y_{\pm\mathrm{HIO_3}}$ could be made, assuming $\mathrm{HClO_4}$ to affect the activity coefficient exactly as hypothetical completely ionized $\mathrm{HIO_3}$ does. Thus, $y_{\pm\mathrm{HIO_3}}$ was taken from ref 20 for an iodate concentration of 0.110 + 0.34 *M* (=0.45 M, $y_{\pm\mathrm{HIO_3}} = 0.620$). Calculation using this value gives $J_{\mathrm{HIO_3}} = 340$. The greatest error in the determination of K_h arises from the uncertainty in $J_{\pm\mathrm{HIO_3}}$. A value of $J_{\pm\mathrm{HIO_3}} = 300 \pm 50$ was chosen for subsequent calculation.

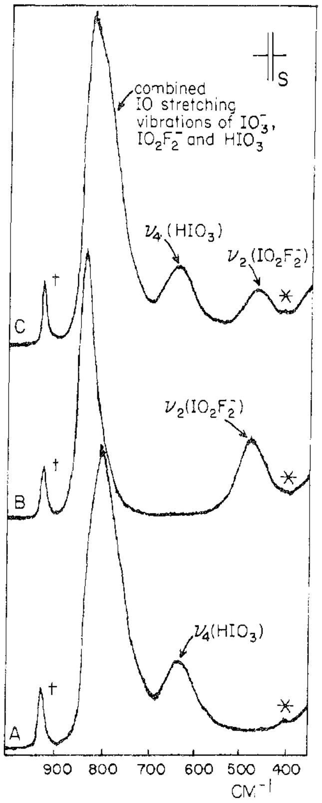

Figure 3. Raman spectra of $\mathrm{HIO_3}$ solutions: A, 2.83 *M* $\mathrm{HIO_3}$ in $\mathrm{H_2O}$; B, 2.91 *M* $\mathrm{HIO_3}$ in 24.2 *M* HF; C, 3.01 *M* $\mathrm{HIO_3}$ in 4.15 *M* HF. S indicates slit width, asterisk indicates sapphire, and the dagger indicates ν_1 of $\mathrm{ClO_4}^-$.

The other parameters in the expression for K_h were evaluated as in part I.[22] The initial concentration of HF, C_{HF}, was corrected for reaction with iodate to give a partially corrected HF concentration, M_{HF}

$$M_{HF} = C_{HF} - 2[IO_2F_2^-]$$

Equilibrium molalities of HF in aqueous solutions have been measured up to an initial HF concentration of 4 *m*[23] and [HF] listed in Table III has been evaluated from these data by interpolation and using density data in ref 21, p 54. It was assumed that $y_{HF} = 1$. The [HF] at higher concentrations than 4 *m* (3.82 *M*) have been arrived at by a linear extension of Hamer and Wu's data.[23] The justification for this procedure comes from Fredenhagen's work[24] where it was shown that the partial pressure of HF over aqueous solutions shows a linear dependence on HF concentration up to above 7.0 *M*. Hydrogen fluoride vapor is known to be monomeric up to vapor pressures above those measured over 7.0 *M* HF.[25] Water activities have been calculated from H_2O vapor pressure measurements over aqueous HF solutions[24] as was done in previous work.[22] The effect of $HClO_4$, present for peak normalization purposes, and the I(V) anions on [HF] and a_{H_2O}(N) in these solutions has not been taken into consideration. In spite of this, there is satisfactory agreement in K_h over a wide range of C_{HIO_3} and C_{HF} as shown in Table III, solutions 4–8. The hydrolysis constant, K_h, was found to be 17 ± 2 m^2 $l.^{-2}$.

The hydrolysis of I(V) in 24 *M* HF solutions is much more extensive than that for Te(IV)[22] and Sb(III)[9] under the same conditions. The TeF_5^- ion is observed in 6 *M* HF while iodine pentafluoride appears in HF solutions only at HF concentrations of ~55 *M* and above.[9]

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Registry No. $CsIO_2F_2\cdot{}^1/_3H_2O$, 54275-79-5; $Co(NH_3)_6(IO_2F_2)_3\cdot H_2O$, 54275-81-9; $Cs[H(IO_2F_2)_2]\cdot 2H_2O$, 54275-82-0; $IO_2F_2^-$, 30669-35-3; HIO_3, 7782-68-5.

References and Notes

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Molecular Structure of Octadecahedral Carboranes by Gas-Phase Electron Diffraction. 1,2-Dicarba-*closo*-hexaborane(6) and Carbahexaborane(7)

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Gas-phase electron diffraction patterns of 1,2-dicarba-*closo*-hexaborane(6) and carbahexaborane(7) were recorded at room temperature. Least-squares analyses of the reduced intensity data confirm the distorted octahedral geometry of the respective carboranes in the gas phase. The following structural parameters have been obtained for 1,2-$B_4C_2H_6$, r_g: C(1)–C(2) = 1.535 Å, C(1)–B(5) = 1.621 Å, C(1)–B(4) = 1.618 Å, B(4)–B(3) = 1.745 Å, and B(3)–B(5) = 1.723 Å. The bond angles are B(5)C(1)B(6) = 96.7°, B(5)B(3)B(6) = 89.4°, and C(1)B(5)B(3) = 86.9°. The angles are measured in terms of r_α and the uncertainties set at 3σ (σ is the least-squares standard deviation). The structural parameters (r_g) of CB_5H_7 are B(2)–B(3) = 1.921 Å, B(3)–B(4) = 1.685 Å, B(4)–B(5) = 1.756 Å, C(1)–B(2) = 1.602 Å, C(1)–B(4) = 1.659 Å, B(2)–B(6) = 1.909 Å, and B(4)–B(6) = 1.689 Å. The bond distance for the bridging H(7) to B(2) is 1.399 Å and from H(7) to B(6) is 1.397 Å indicating the bridge hydrogen is located at a nearly central position on the B(2)B(3)B(6) face. The bond angles are B(3)C(1)B(2) = 73.7°, B(3)C(1)B(4) = 62.2°, B(4)C(1)B(5) = 63.9°, B(2)B(3)B(6) = 59.8°, B(2)B(6)B(3) = 60.4°, B(2)B(6)B(5) = 55.4°, and B(4)B(6)B(5) = 62.6°. The structural data for the carbahexaborane(7) confirms the structure predicted by low-temperature NMR experiments. Comparisons of the structural data are made with the 1,6-dicarba-*closo*-hexaborane(7).

Introduction

Both electron diffraction[1–4] and rotation–vibration spectra[5–7] have been valuable in determining the molecular structure, geometric parameters, and vibrational amplitudes of the volatile carboranes and boron hydrides. Because crystalline samples of the more volatile carboranes are difficult to isolate, X-ray crystal analysis has not been used in the area of small carboranes.

In this report we present structural data for the octahedral carboranes 1,2-dicarba-*closo*-hexaborane(6) and carbahex-