at −196 °C and heated at 165 °C for 2.2 h. The product was checked by infrared spectroscopy, but it was found that no reaction took place. The reaction mixture was again heated at 250–260 °C for 5 h. The products were separated by trap-to-trap distillation through a trap at −196 °C which retained the compound found to be $(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$ (0.46 mmol).

Reaction of $CF_2CF_2CF_2CF_2S{=}NLi$ with $CF_2CF_2CF_2CF_2S{=}NC(CF_3)_2$. Into a 100-mL reaction vessel which retained 2.0 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ was condensed 2.15 mmol of $CF_2CF_2CF_2CF_2S{=}NCF(CF_3)_2$ at −196 °C. The reaction mixture was gradually warmed to 25 °C.[3] After 6 h, the product was separated by trap-to-trap distillation. However, only starting material ($CF_2CF_2CF_2CF_2S{=}NCF(CF_3)_2$, 1.76 mmol) and small amounts of $CF_2CF_2CF_2CF_2S$ were found.

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Registry No. $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$, 77110-78-2; $CF_2CF_2CF_2CF_2S{=}NC(O)CF_3$, 77110-79-3; $CF_2CF_2CF_2CF_2S{=}NSO_2CF_3$, 77110-80-6; $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$, 77110-81-7; $CF_2CF_2CF_2CF_2S{=}NC(O)N{=}SCF_2CF_2CF_2CF_2$, 77110-82-8; $CF_2CF_2CF_2CF_2S{=}NC(O)C(O)N{=}SCF_2CF_2CF_2CF_2$, 77110-83-9; $CF_2CF_2CF_2CF_2S{=}NCN$, 77110-84-0; $(CF_3)_2N{=}SC(O)C(O)S{=}N(CF_3)_2$, 77110-85-1; bis(trifluoromethyl)diazirine, 3024-50-8; $CF_2CF_2CF_2CF_2S$, 706-76-3; $(CF_3)_2C{=}NN{=}C(CF_3)_2$, 1619-84-7; $CF_2CF_2CF_2CF_2S{=}NLi$, 77110-86-2; $(CF_3)_2S{=}NLi$, 61097-18-5; $CF_2CF_2CF_2CF_2S{=}NH$, 77110-87-3; $(CF_3)_2S{=}NH$, 60646-40-4; $(CH_3)_3SiCl$, 75-77-4; $CF_3C(O)Cl$, 354-32-5; ClCN, 506-77-4; CF_3SO_2F, 335-05-7; $ClSO_2F$, 13637-84-8; $COCl_2$, 75-44-5; FC(O)C(O)F, 359-40-0; $FN{=}C(CF_3)_2$, 2802-70-2.

Contribution from Rocketdyne,
a Division of Rockwell International Corporation, Canoga Park, California 91304

Syntheses and Properties of $FOIF_4O$, $ClOIF_4O$, $HOIF_4O$, and Tetrafluoroperiodates

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Mixtures of *cis*- and *trans*-$CsIF_4O_2$ were prepared by the interaction of $CsIO_4$ with either anhydrous HF, BrF_5, ClF_3, ClF_5, or F_2. The vibrational spectra of these mixtures were recorded, and partial assignments are given for *cis*- and *trans*-$IF_4O_2^-$. The assignments for *trans*-$IF_4O_2^-$ were supported by a normal-coordinate analysis. The $CsIF_4O_2$ salt dissolves in CH_3CN with the formation of $IF_4O_2^-$ anions but undergoes solvolysis in anhydrous HF with formation of $HOIF_4O$. An improved synthesis of $HOIF_4O$ from $CsIF_4O_2$ and BiF_5 in anhydrous HF is reported, and its Raman and ^{19}F NMR spectra were recorded. The interaction of $CsIF_4O_2$ with NF_4SbF_6 in anhydrous HF results in solutions containing NF_4^+, HF_2^-, and $HOIF_4O$. When standing or when pumped to dryness, these mixtures decompose to yield NF_3 and the new compound $FOIF_4O$ in high yield. The latter compound, the first known example of an iodine hypofluorite, was thoroughly characterized and shown by vibrational and NMR spectroscopy to be a mixture of the cis and trans isomers. For comparison, the vibrational spectra of IF_5O have also been recorded. The reaction of $CsIF_4O_2$ with $ClOSO_2F$ was shown to yield the novel compound $ClOIF_4O$. The fluorination reactions of $CsIO_4$, $CsIF_4O_2$, IF_5O, and $HOIF_4O$ with elementary fluorine were also studied.

Introduction

The number of elements known to form stable hypofluorites is very limited.[1] Thus stable hypofluorites are known only for carbon-, nitrogen-, sulfur-, selenium-; fluorine-, and chlorine-containing compounds. In addition, the unstable hypofluorous acid, HOF, has been prepared.[2] Since recent work in our laboratory had shown that the thermal decomposition of certain NF_4^+ salts of oxyanions such as NF_4ClO_4[3] and NF_4SO_3F[4] produces the corresponding hypofluorites in high yield, it was interesting to apply this method to the synthesis of novel hypofluorites. Preliminary results[5] showed that $FOIF_4O$, the first known example of an iodine hypofluorite, can be prepared in this manner. In this paper, detailed information is given on the synthesis, properties, and reaction chemistry of this interesting compound and of related iodine oxyfluoride derivatives such as $ClOIF_4O$, $HOIF_4O$, and the $IF_4O_2^-$ anion.

The literature on the synthesis and properties of salts containing the $IF_4O_2^-$ anion is scant. The first report on the existence of $IF_4O_2^-$ salts was published in 1971 by Engelbrecht and co-workers[6] but was limited to a one-sentence statement that $HOIF_4O$ interacts with either alkali-metal fluorides or trifluoroacetates to yield the corresponding salts. In a subsequent paper,[7] this statement was repeated, but again no data were given. In 1975, Aubke and co-workers reported[8] that CsF combines with an excess of IF_3O_2 to give $Cs^+IF_4O_2^-$. A melting point, elemental analysis, and incomplete vibrational spectra were given, which were incorrectly interpreted in terms of a cis isomer. In 1976, Selig and Elgad reported[9] that partial hydrolysis of IF_7 produces IF_5O, $HOIF_4O$, and, with increased water addition, the $IF_4O_2^-$ anion, which was identified by ^{19}F NMR and vibrational spectroscopy as the cis isomer. Although Selig and Elgad reported only solution data, their vibrational spectra strongly disagreed with those reported by Aubke for solid $Cs^+IF_4O_2^-$. In 1977, Gillespie and Krasznai reported[10] that solutions of KIO_4 in IF_5 contain a mixture of IO_2F, IOF_3, and *cis*- and *trans*-$IF_4O_2^-$. On cooling solutions of KIO_4 dissolved in boiling IF_5, they isolated a $KIF_4O_2{\cdot}2IF_5$ adduct, which could be converted into KIF_4O_2. Both compounds were shown by ^{19}F NMR and Raman spectroscopy to

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contain in the solid state and in CH_3CN solution *trans*-$IF_4O_2^-$. In IF_5 solution, however, $IF_4O_2^-$ was shown to exist in a cis–trans equilibrium, with the cis isomer being favored.

Tetrafluoroorthoperiodic acid, $HOIF_4O$, was first prepared by Engelbrecht and co-workers[11] according to

$$Ba_3H_4(IO_6)_2 + 14HSO_3F \rightarrow 2HOIF_4O + 8H_2SO_4 + 3Ba(SO_3F)_2$$

Since $HOIF_4O$ could not be separated from HSO_3F by distillation, it was converted into the more volatile IF_3O_2

$$HOIF_4O + SO_3 \rightarrow IF_3O_2 + HSO_3F$$

which was distilled off and then reconverted to $HOIF_4O$ by HF addition according to

$$IF_3O_2 + HF \rightarrow HOIF_4O$$

The acid was characterized[6,11] by its physical constants and mass and NMR spectra, which showed the compound to be a mixture of the cis and trans isomers, with the cis isomer being more abundant. Selig and Elgad found[9] that solutions of $NaIO_4$ in anhydrous HF contain $HOIF_4O$, as well as other unidentified fluorine species, and reported the ^{19}F NMR spectra of both isomers in HF solution. Gillespie and Krasznai[10] also listed chemical shifts for *cis*- and *trans*-$HOIF_4O$, without specifying the solvent, and gave a coupling constant of 21 Hz for the cis isomer, which disagrees with the values of about 220 Hz reported by others.[6,9,11]

Experimental Section

Caution. Two explosions were encountered in reactions involving $FOIF_4O$. Most hypofluorites are shock-sensitive materials[1] and appropriate precautions should therefore be taken when one is working with larger amounts of $FOIF_4O$.

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[12] IF_5O,[13,14] and $ClOSO_2F$.[15] $CsIO_4$ was prepared by slowly combining, with stirring, stoichiometric amounts of concentrated aqueous solutions of CsCl and $NaIO_4$. The mixture was cooled to 0 °C, and the $CsIO_4$ precipitate was filtered off, washed three times with ice water, and dried for 16 h in an oven at 110 °C. Its vibrational spectra showed no detectable impurities. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. BrF_5 (Matheson) was treated with 35 atm of F_2 at 200 °C for 24 h and then purified by fractional condensation through traps kept at −64 and −95 °C, with the material retained in the latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_5 to remove the last traces of H_2O.[16] ClF_3 (Matheson) and ClF_5 (Rocketdyne) were purified by fractional condensation prior to their use.

Apparatus. Volatile materials used in this work were handled in either a Monel–Teflon FEP, a stainless steel–Teflon FEP, or a Teflon PFA vacuum line. The last was constructed exclusively from injection-molded PFA fittings and valves (Fluoroware, Inc.). The anhydrous HF was preferentially handled in the PFA or Monel line, whereas the halogen fluorides were handled mainly in a steel line. All lines were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Metathetical reactions were carried out in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref 17). For NMR or low-temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4-mm Teflon FEP or a thin-walled Kel-F tube.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Room-temperature spectra of solids were obtained by using dry powders pressed between AgCl disks. Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The spectra of matrix-isolated $FOIF_4O$ and IF_5O were obtained at 6 K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ne (Matheson) was used as a matrix material in a mole ratio of 1000:1. The spectrometer was calibrated by comparison with standard gas calibration points,[18,19] and the reported frequencies are believed to be accurate to ±2 cm^{-1}.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[20] for the elimination of plasma lines. Sealed quartz, Teflon FEP, or Kel-F Tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. Polarization measurements were carried out according to method VIII listed by Claassen et al.[20] Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external $CFCl_3$ with positive shifts being downfield from $CFCl_3$.[21a]

The mass spectra were recorded with an EAI Quad 300 quadrupole spectrometer at an ionization potential of 70 eV.

Preparation of $CsIF_4O_2$. In a typical experiment, $CsIO_4$ (31.44 mmol) was placed in a $^3/_4$-in. o.d. Teflon FEP ampule equipped with a stainless-steel valve. Anhydrous HF (20 mL of liquid) was condensed into the ampule, and the mixture was stirred with a magnetic stirring bar for 4 days at ambient temperature. Volatile products were pumped off overnight at ambient temperature and for an additional 2 h at 50 °C. The solid residue (11.402 g, weight calculated for 31.44 mmol of $CsIF_4O_2$ 11.564 g) was shown by Raman spectroscopy to still contain some unreacted $CsIO_4$. It was treated again, as described above, with fresh anhydrous HF (15 mL of liquid). After the residue was pumped to dryness, the Raman spectrum of the solid residue (11.532 g) showed *cis*- and *trans*-$CsIF_4O_2$ as the principal products and only a trace of unreacted $CsIO_4$.

A total of eight preparations were carried out in a similar manner, with use of shorter reaction times, slightly higher reaction temperatures (~50 °C), and rapid HF removal at elevated temperature. The conversion of $CsIO_4$ to $CsIF_4O_2$ after the first HF treatment was generally in the range of 75–90%, and the Raman spectra showed the presence of some unreacted $CsIO_4$. This unreacted $CsIO_4$ was readily converted to $CsIF_4O_2$ by repeated treatment with anhydrous HF; however in most cases, repeated HF treatments resulted in a slight weight decrease and the appearance of bands due to HF_2^- (infrared 1435 s, br, 1228 ms cm^{-1}; Raman complex band at 790–740 cm^{-1} with maximum at 759 cm^{-1}). This is caused by the solvolysis of $CsIF_4O_2$ in anhydrous HF and the volatility of the resulting $HOIF_4O$ (see below). The ratio between the cis and trans isomers of $CsIF_4O_2$ varied somewhat for the different preparations, with the trans isomer being slightly favored at the lower and the cis isomer being somewhat favored at the higher reaction temperatures.

The $CsIO_4$–BrF_5 System. Cesium periodate (2.453 mmol) was placed in a passivated sapphire reactor equipped with a stainless-steel valve and a magnetic stirring bar. Bromine pentafluoride (14.99 mmol) was added at −196 °C, and the mixture was allowed to react during warm-up to room temperature. A fast reaction with gas evolution occurred, which was moderated by intermittent cooling with liquid N_2. After completion of the warm-up cycles, the mixture was stirred at 20 °C for 24 h, resulting in a clear, pale yellow solution. The Raman spectrum of this solution showed the presence of BrF_5, BrF_3O, and $IF_4O_2^-$ (mainly trans with a small amount of cis isomer). The solution was kept at 22 °C for 4 days and then cooled to −196 °C. The materials volatile at −196 °C consisted of 1.92 mmol of oxygen. The materials volatile at 22 °C were separated by fractional condensation and identified by Raman spectroscopy. They consisted of unreacted

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BrF_5 (9.9 mmol) and a mixture of BrF_3 and BrF_3O (found 682 mg, calcd for 3.84 mmol of BrF_3 + 1.06 mmol of BrF_3O 688 mg). The solid residue (found 804 mg, weight calcd for 2.453 mmol of $CsIF_4O_2$ 787 mg) was shown by Raman spectroscopy to consist mainly of *trans*-$CsIF_4O_2$, $CsBrF_4$, and smaller amounts of *cis*-$CsIF_4O_2$, and possibly some solvated BrF_3O. Vacuum pyrolysis at 90 °C resulted in a solid residue consisting again of *trans*-$CsIF_4O_2$, $CsBrF_4$ and a small amount of cis $CsIF_4O_2$ and also in the evolution of some IF_5 (~8 weight %).

The $CsIO_4$–ClF_3 System. A well-passivated (with ClF_3) sapphire tube equipped with a stainless-steel valve and containing a Teflon-coated stirring bar was loaded with $CsIO_4$ (1.14 mmol), followed by ClF_3 (10.6 mmol). The liquid ClF_3 and solid periodate were stirred magnetically overnight at 0–20 °C. This resulted in a clear, very pale yellow solution. Upon removal of the volatile material and several hours of pumping at ambient temperature, a white powder (0.493 g) remained in the tube, which was identified by vibrational spectroscopy as a mixture of $CsF{\cdot}3IF_5$ and $CsClF_4$ (weight calculated for the conversion of 1.14 mmol of $CsIO_4$ to 0.38 mmol of $CsF{\cdot}3IF_5$ and 0.76 mmol of $CsClF_4$ was 0.497 g). The volatile materials consisted of ClF, $FClO_2$, and unreacted ClF_3.

The $CsIO_4$–ClF_5 System. When $CsIO_4$ was allowed to interact with a large excess of ClF_5 in a stainless-steel reactor at room temperature, the composition of the solid reaction product depended on the reaction time. After short reaction times (about several hours) the solid consisted, on the basis of its weight change and Raman spectra, mainly of unreacted $CsIO_4$ and smaller amounts of *trans*-$CsIF_4O_2$. After longer reaction times (in excess of 1 month), the solid consisted mainly of $CsIF_8$ and *trans*-$CsIF_4O_2$ and some $CsIF_4O$.

The $CsIO_4$–F_2 System. The fluorination of $CsIO_4$ with elemental fluorine in a static system at temperatures up to 60 °C resulted in a solid product, which, on the basis of its vibrational spectra, was a mixture of mainly $CsIF_8$, $CsIF_6$, and $CsIO_4$ with smaller amounts of $CsIF_4O$ and *cis*- and *trans*-$CsIF_4O_2$ also being present.

Synthesis of $HOIF_4O$. In a typical experiment, $CsIF_4O_2$ (2.0 mmol) and BiF_5 (2.0 mmol) were placed in a passivated Teflon FEP U-trap containing a magnetic stirring bar. One arm of the trap was closed off by the stainless-steel valve, while the other one was connected through a porous Teflon filter to a second Teflon U-trap, which was capped off by another valve. Anhydrous HF (5 mL of liquid) was condensed into the U-trap, and the $CsIF_4O_2$–BiF_5–HF mixture was stirred at 25 °C for 1 h. The double U-trap assembly was cooled to −78 °C and inverted, and the $HOIF_4O$-containing HF solution was separated from the $CsBiF_6$ precipitate by pressure filtration. The HF solvent was pumped off at −45 and −13 °C. The residue was allowed to warm to ambient temperature, and the material volatile at 25 °C was collected at −78 °C in a 4-mm o.d. external Teflon U-trap. This trap was shown to contain $HOIF_4O$ (~2 mmol), which was identified by its Raman and ^{19}F NMR spectra. The filter cake (0.9 g) was identified by its Raman spectrum as $CsBiF_6$.

Synthesis of $FOIF_4O$. In a typical experiment, $CsIF_4O_2$ (5.0 mmol) and NF_4SbF_6 (5.0 mmol) were placed in the Teflon FEP metathesis apparatus (see above), and anhydrous HF (5 mL of liquid) was condensed in at −78 °C. The mixture was stirred for 1 h at room temperature. The apparatus was cooled to −78 °C and inverted, and the white precipitate was separated from the solution by pressure filtration. Most of the HF solvent was pumped off over several hours at temperatures ranging from −64 to −30 °C. The resulting white solid residue was allowed to decompose during slow warm-up from −30 °C to ambient temperature. The volatile products were passed through a Teflon U-trap containing passivated NaF pellets, followed by a series of cold traps kept at −78, −95, −112, and −210 °C. The −78 °C trap contained a small amount of unidentified material, which was discarded, the −95 °C fraction consisted of pure $FOIF_4O$ (2.36 mmol), the −112 °C trap had 1.69 mmol of $FOIF_4O$ containing a small amount of IF_5O as an impurity, and the −210 °C trap contained NF_3 (4.0 mmol). A small amount of white solid residue, which was left behind after the thermal decomposition of the filtrate, was shown by vibrational spectroscopy to consist mainly of *trans*-$CsIF_4O_2$. The filter cake (1.8 g) was identified by Raman spectroscopy as $CsSbF_6$. The −95 °C fraction was used for the characterization of $FOIF_4O$ and was shown by vibrational and ^{19}F NMR analysis to be free of IF_5O.

For the elemental analysis, 278.7 mg of the material was condensed at −196 °C into an ampule containing 12 mL of frozen 1 N NaOH. The mixture was warmed to ambient temperature for 12 h and then analyzed for total iodine by energy-dispersive X-ray fluorescence spectrometry, for IO_4^- by iodometric titration, for base consumption by back-titration with 0.1 N HCl using a pH electrode and for fluoride by titration using $La(NO_3)_3$ and an Orion specific-ion electrode. Anal. Calcd for $FOIF_4O$: I, 49.98; F, 37.42; OH^- consumed, 6.0 equiv/mol; iodometric titration, 8.0 equiv/mol, with the assumption of the hydrolysis reaction $FOIF_4O + 6OH^- \rightarrow IO_4^- + 5F^- + 0.5O_2(g) + 3H_2O$. Found: I, 50.0; F, 36.0; OH^- consumed, 6.1 equiv/mol; iodometric titration, 7.8 equiv/mol.

Synthesis of $ClOIF_4O$. A 30-mL stainless-steel cylinder was loaded with 2.32 mmol of $CsIF_4O_2$, and 2.12 mmol of $ClSO_3F$ was added at −196 °C. After the cylinder was kept for 5 days at −78 °C, the volatile products were removed from the cylinder. The solid residue was identified by vibrational spectroscopy as $CsSO_3F$. The volatiles were fractionated through traps cooled to −45, −78, and −196 °C. The lowest temperature fraction (0.77 mmol) was mainly Cl_2 together with some $FClO_2$, while the −45 °C trap contained a white solid, which melted above 0 °C and which was identified by its infrared spectra as IF_5. The −78 °C trap contained a yellow-orange solid, which on slight warming melted to an orange liquid. Its gas-phase infrared spectrum was recorded at 25 °C and showed the following bands (cm^{-1}; relative intensity, assignment): 912 m, I=O stretch; 763 mw, O—Cl stretch; 678 vs, 635 s, 532 mw, I—F and I—O stretching. The compound was found to be thermally unstable and very difficult to handle. It readily decomposed to IF_5, and its synthesis required careful temperature control. When the synthesis was carried out for example at −45 °C, only decomposition products were obtained. Attempts to isolate fluorocarbon derivatives of $ClOIF_4O$ by adding it across the C=C double bond of C_2F_4 resulted at −78 °C in no reaction and at room temperature in the oxygenation, fluorination, and decomposition products COF_2, CF_3COF, $ClCF_2COF$, C_2F_5Cl, and IF_5.

Results and Discussion

Synthesis of $CsIO_2F_4$. In our work the known[9] equilibrium

$$IO_4^- + 4HF \rightleftarrows IF_4O_2^- + 2H_2O$$

was utilized for a convenient synthesis of $CsIF_4O_2$. So that this equilibrium can be shifted to the right, a large excess of HF must be used and the HF treatment must be repeated at least once. The resulting $CsIF_4O_2$ consists of a mixture of the cis and trans isomers, as shown by ^{19}F NMR and vibrational spectroscopy (see below). The ratio of cis to trans isomer varies somewhat with the reaction conditions used, but the formation of the cis isomer appears to be slightly favored. The ^{19}F NMR and Raman spectra were recorded for solutions of $CsIF_4O_2$ in anhydrous HF and CH_3CN. Whereas the CH_3CN solution spectra show the presence of the $IF_4O_2^-$ anion, the spectra of the HF solutions are characteristic (see below) for those of $HOIF_4O$. This finding is in excellent agreement with the previous report by Selig and Elgad[9] that solutions of $NaIO_4$ in anhydrous HF contain $HOIF_4O$ and the report by Engelbrecht and co-workers[6,7] that $HOIF_4O$ interacts with alkali-metal fluorides to form $IF_4O_2^-$ salts. Consequently, the above equilibrium reaction involves at least two reactions, the first being

$$IO_4^- + 6HF \underset{-HF}{\overset{+HF}{\rightleftharpoons}} HOIF_4O + HF_2^- + 2H_2O$$

and, upon HF and H_2O removal, the second being

$$HOIF_4O + CsHF_2 \underset{+HF}{\overset{-HF}{\rightleftharpoons}} CsIF_4O_2 + 2HF$$

The intermediate formation and the slight volatility of $HOIF_4O$ also explain why in some of our $CsIF_4O_2$ preparations, when the HF was rapidly pumped off at elevated temperature, a weight loss accompanied by some $CsHF_2$ formation was observed.

The above synthesis of $CsIF_4O_2$ from $CsIO_4$ and HF appears more convenient than the previously reported methods involving either the difficult to obtain IF_3O_2 as a starting material or the isolation and recrystallization of $MIF_4O_2{\cdot}2IF_5$ from IF_5, followed by its pyrolysis. However, the latter method produces almost exclusively the trans isomer and might be the

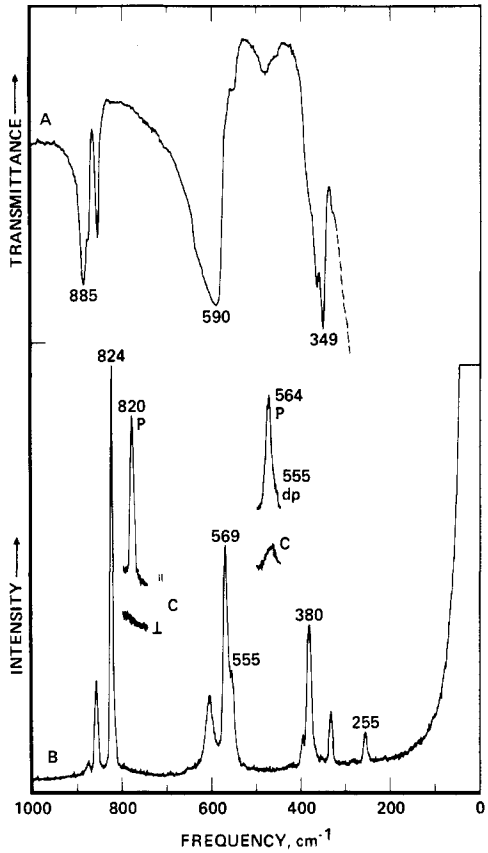

Figure 1. Vibrational spectra of a $CsIF_4O_2$ sample containing mainly *trans*-$IF_4O_2^-$ (bands marked by their frequency values) and smaller amounts of *cis*-$IF_4O_2^-$. Trace A is an infrared spectrum of the solid as a dry powder pressed between AgCl disks; the broken line indicates absorption due to the window material. Trace B is a Raman spectrum of the solid. Inserts C are Raman bands of the CH_3CN solution, recorded with parallel and perpendicular polarization.

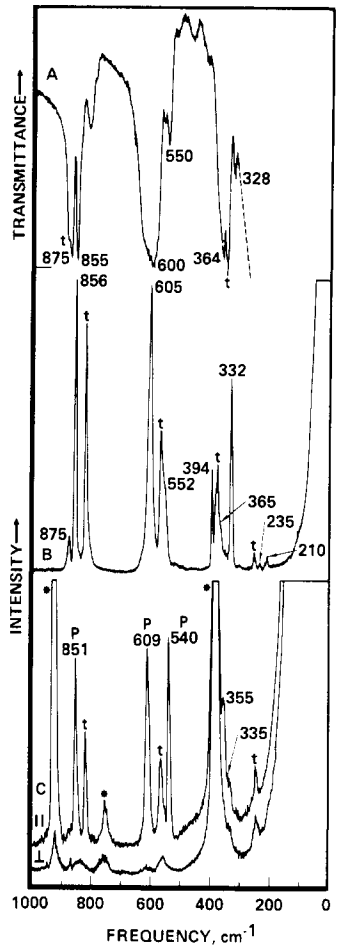

Figure 2. Vibrational spectra of a $CsIF_4O_2$ sample containing mainly *cis*-$IF_4O_2^-$ (bands marked by frequency values) and smaller amounts of *trans*-$IF_4O_2^-$ (marked by t). Trace A is an infrared spectrum of the solid as a dry powder pressed between AgCl disks. The weak bands at 815 and 470 cm^{-1} probably do not belong to $IF_4O_2^-$. Trace B is a Raman spectrum of the solid. Traces C are Raman spectra of a CH_3CN solution. Solvent bands are marked by an asterisk.

preferred method if pure *trans*-$IF_4O_2^-$ is desired. The fact that the cis–trans isomer ratio strongly depends on the nature of the reactants suggests that this ratio is kinetically and not thermodynamically controlled. This conclusion is in excellent agreement with those reached by Toetsch and Sladky for the closely related $TeF_4(OH)_2$ system.[21b]

An alternate method for the formation of $CsIF_4O_2$ involves the reaction of $CsIO_4$ with BrF_5. The main reaction can be described by

$$CsIO_4 + 2BrF_5 \rightarrow CsIF_4O_2 + 2BrF_3O$$

This reaction is analogous to that[10] previously reported for $KIO_4 + IF_5$, i.e.

$$KIO_4 + 2IF_5 \rightarrow KIF_4O_2 + 2IF_3O$$

and produces almost entirely the trans isomer. Compared to the IF_5 reaction, the BrF_5 reaction offers the advantage that the BrF_3O and BrF_3 byproducts are volatile and can easily be pumped off. However, the resulting product was contaminated by nonvolatile $CsBrF_4$, which could not be readily separated from the $CsIF_4O_2$.

The reactions of $CsIO_4$ with chlorine fluorides were also briefly studied. With ClF_5, *trans*-$CsIF_4O_2$ was formed in low conversion according to

$$CsIO_4 + ClF_5 \rightarrow CsIF_4O_2 + FClO_2$$

Attempts to achieve higher conversions by the use of longer reaction times failed due to the formation of $CsIF_8$ as the main product and of $CsIF_4O$ as a minor product.

When ClF_5 was replaced by the more reactive ClF_3, complete conversion of the $CsIO_4$ was obtained; however, all the oxygens in IO_4^- were exchanged for fluorine, and the solid product consisted of a mixture of $CsIF_6 \cdot 2IF_5$[22] and $CsClF_4$.[23] Based on the observed material balance, the following reaction occurred:

$$3CsIO_4 + 11ClF_3 \rightarrow 6FClO_2 + 3ClF + 2CsClF_4 + CsIF_6 \cdot 2IF_5$$

The formation of ClF and of half of the $FClO_2$ can be readily explained by the well-known[24] disproportionation of the expected unstable FClO intermediate:

$$2FClO \rightarrow FClO_2 + ClF$$

The fluorination of $CsIO_4$ by elemental fluorine at temperatures up to 60 °C in a static system was also studied. The main products were $CsIF_8$ and $CsIF_6$, with $CsIF_4O$ and *cis*- and *trans*-$CsIF_4O_2$ as minor products.

In view of the fact that the fluorination reactions of $CsIO_4$ with ClF_5, BrF_5, ClF_3, or F_2 do not result in pure compounds, they are less attractive synthetic methods for the preparation of $CsIF_4O_2$.

Vibrational Spectra of $CsIF_4O_2$. The vibrational spectra of solid $CsIF_4O_2$ were recorded for samples that differed in their cis and trans isomer content. The observed spectra are given

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(23) Christe, K. O.; Sawodny, W. *Z. Anorg. Allg. Chem.* **1970**, *374*, 306.
(24) Cooper, T. D.; Dost, F. N.; Wang, C. H. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3564.

Table I. Vibrational Spectra of *trans*-$IF_4O_2^-$ and Their Assignments in Point Group D_{4h} Compared to Those of Closely Related Molecules

obsd freq, cm^{-1}, and rel intens												
trans-$CsIF_4O_2$												
solid		CH_3CN soln	IF_4O^-,[c] solid		IF_4^-,[d] solid		IF_5O,[e] gas		IF_5,[f] gas		assignt for $IF_4O_2^-$ in D_{4h}	approx description of mode
IR	Raman[a]	Raman[a]	IR	Raman	IR	Raman	IR	Raman	IR	Raman		
...	569 (5.5)	564 (7) p	540 sh	540 (5.8)	...	522 (10)	640 s	640 vs, p		616 vs, p	A_{1g}	ν_1 $\nu_s(IF_4)$ in phase
	824 (10)	820 (10) p			...	...			...	...	ν_2	$\nu_s(IO_2)$
885 s	...	...	885 s	887 (10)	...	...	927 vs	927 s, p	...	...		
349 s	...	...	279 ms	283 (0.3)	271 ms	...	363 m		318 m	318 m, p	A_{2u} ν_3	$\nu_{as}(IO_2)$
											ν_4	$\delta_{umbrella}(IF_4)$
...	555 (2)	555 (2) dp		478 (2.3)	...	455 (7.2)		647 s, dp		604 m	B_{1g} ν_5	$\nu_s(IF_4)$ out of phase
...	255 (0.7)	248 (2.5) dp		224 (0.5)	...	195 (0+)	...	330 w	...	276 w	B_{2g} ν_6	$\delta_s(IF_4)$ in plane
...	...	...	...	...	...	...			...	...	B_{2u} ν_7	$\delta_{as}(IF_4)$ out of plane
...	380 (3.5)	*b*	366 mw	368 (1)	...	...	372 s	375 m, dp	...	...	E_g ν_8	δOIF_4O
590 vs, br	...	...	480 vs		448 vs	...	710 vs	712 w, dp	640 vs	631 w	E_u ν_9	$\nu_{as}(IF_4)$
			...	...	...	...	...	...	...	...	ν_{10}	$\delta_{sciss}(IO_2)$
				140 (0+)			205 vw	208 vw, dp	...	~200 w	ν_{11}	$\delta_{as}(IF_4)$ in plane

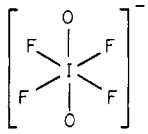
[a] Uncorrected Raman intensities (peak heights). [b] Obscured by solvent band. [c] Data from ref 26. [d] Data from ref 25. [e] Data from ref 14 and 29. [f] Data from ref 27 and 28.

Table II. Vibrational Spectra of *cis*-$IF_4O_2^-$

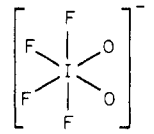
obsd freq, cm^{-1}, and rel intens[a]				
solid		CH_3CN soln	assignt for point group C_{2v}	approx description of mode
IR	Raman	Raman		
875 vs	875	870 sh	ν_{12} (B_2)	$\nu_{as}(IO_2)$
855 vs	856 (10)	851 (9) p	ν_1 (A_1)	$\nu_s(IO_2)$
600 vs, br			ν_9 (B_1)	$\nu_{as}(IF_2)_{ax}$, $\nu_{as}(IF_2)_{eq}$
600 vs, br	605 (9.8)	609 (10) p	ν_2 (A_1)	$\nu_s(IF_2)_{eq}$
550 mw	552 sh	540 (10) p	ν_3 (A_1)	$\nu_s(IF_2)_{ax}$
395 sh	394 (3.4)		ν_4 (A_1)	$\delta_{sciss}(IO_2)$
364 s	365 sh	355 sh		
328 mw	332 (6.5)	335 sh		
	235 (0.2)			
	210 (0.5)			

[a] Uncorrected Raman intensities (peak height).

in Figures 1 and 2, and the observed frequencies and their assignments in point group D_{4h} and C_{2v}



D_{4h}, trans



C_{2v}, cis

are summarized in Tables I and II, respectively. The bands belonging to the trans isomer could be readily distinguished from those of the cis isomer due to the fact that only the trans isomer has a center of symmetry, which causes the infrared and Raman bands to be mutually exclusive. Furthermore, the ^{19}F NMR spectrum (see below) clearly distinguished the trans from the cis isomer and established which isomer was more abundant in a given sample.

Assignments and Normal-Coordinate Analysis for *trans*-$IF_4O_2^-$. The *trans*-$IF_4O_2^-$ anion of symmetry D_{4h} should possess 11 fundamental modes classified as $2\ A_{1g} + 2\ A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3\ E_u$. Of these, the A_{1g}, B_{1g}, B_{2g}, and E_g modes should be Raman active only and the A_{2u} and E_u modes should be infrared active only, whereas the B_{2u} mode should be inactive in both spectra. Of the 10 active modes, all five Raman-active modes and three out of the five infrared-active modes have been observed and can be readily assigned on the basis of their activity, polarization data, and comparison with the closely related species IF_4^-,[25] IF_4O^-,[26] IF_5,[27,28] and IF_5O[14,29] (see Table I). The correctness of these assignments was confirmed by a normal-coordinate analysis using the symmetry coordinates and G matrix elements previously published[30] by Beattie and co-workers. The bond distances were estimated to be $r_{IF} = 1.92$ Å and $d_{IO} = 1.72$ Å, on the basis of the known structures and stretching frequencies of the related IF_5O[14,29,31] and IF_5[27,28,32] molecules and the IF_4O^- anion.[26,33] The force constants of the B_{1g}, B_{2g}, and E_g species are uniquely determined. In the A_{1g} block, the G_{12} element is zero, and therefore F_{12} can be ignored. For the A_{2u} block, the extremal solution[34] F_{44} = minimum was used, which has previously been shown[25] for the closely related IF_4^- anion

(25) Christe, K. O.; Naumann, D. *Inorg. Chem.* **1973**, *12*, 59.
(26) Christe, K. O.; Wilson, R. D.; Curtis, E. C.; Sawodny, W., Kuhlmann, W. *Inorg. Chem.* **1978**, *17*, 533.
(27) Begun, G. M.; Fletcher, W. H.; Smith, D. F. *J. Chem. Phys.* **1965**, *42*, 2236.
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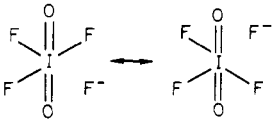
(33) Ryan, R. R.; Asprey, L. B. *Acta Crystallogr., Sect. B* **1972**, *B28*, 979.
(34) Sawodny, W. *J. Mol. Spectrosc.* **1969**, 30, 56.

Table III. Symmetry Force Constants[a] of *trans*-$IF_4O_2^-$

A_{1g}	ν_1	569	$F_{11} = f_r + 2f_{rr} + f_{rr}'$	3.623
	ν_2	824	$F_{22} = f_\alpha + f_{\alpha\alpha}$	6.400
A_{2u}	ν_3	885	$F_{33} = f_d - f_{dd}$	5.903
	ν_4	349	$F_{44} = f_\beta + 2f_{\beta\beta} + f_{\beta\beta}' - f_{\beta\beta}'' - 2f_{\beta\beta}^\circ - f_{\beta\beta}^\dagger$	1.700
			$F_{34} = 2f_{d\beta} - 2f_{d\beta}'$	−0.036
B_{1g}	ν_5	555	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	3.447
B_{2g}	ν_6	255	$F_{66} = f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}'$	0.671
B_{2u}	ν_7		$F_{77} = f_\beta - 2f_{\beta\beta} + f_{\beta\beta}' - f_{\beta\beta}'' + 2f_{\beta\beta}^\circ - f_{\beta\beta}^\dagger$	
E_g	ν_8	380	$F_{88} = f_\beta - f_{\beta\beta}' - f_{\beta\beta}'' + f_{\beta\beta}^\dagger$	1.201
E_u	ν_9	590	$F_{99} = f_r - f_{rr}'$	2.998

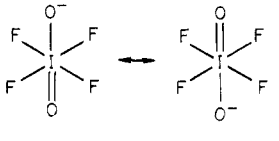
[a] stretching constants in mdyn/A, deformation constants in mdyn A/rad², and stretch–bend interaction constants in mdyn/rad.

to be an excellent approximation to a general valence force field for these weakly coupled systems. For the E_u block, only the frequency value of the stretching mode is experimentally known. A comparison with the force field of the related IF_4^- anion[25] showed that, due to the heavy iodine central atom, the approximation $F_{99} = \lambda_9/G_{99}$ yields an almost exact value for the stretching force constant in the E_u block and was therefore used for $IF_4O_2^-$. The resulting force field is listed in Table III and strongly supports our assignments. Table IV gives a comparison of the internal stretching force constants of *trans*-$IF_4O_2^-$ with those of the closely related species IF_4^-,[25] IF_4O^-,[26] IF_5,[35] IF_5O,[29] and IF_6^+.[36] As previously discussed[37] for chlorine oxyfluorides, the IF stretching force constants increase in the sequence anions < neutral molecules < cations and within a given group with increasing oxidation state of the iodine central atom. The IO stretching force constants are in the range expected for I=O double bonds and demonstrate that, even in the anions, the formal negative charge is located mainly on the more electronegative fluorine ligands rather than on the oxygen ligand. Consequently, contributions from resonance structures such as I and II are more important



I II

than those from III and IV to explain the bonding in $IF_4O_2^-$.



III IV

Resonance structures such as I and II also account for the decrease of the IF stretching force constants with increasing formal negative charges and also with decreasing oxidation state of the central atom. Both effects increase the $I^{\delta+}-F^{\delta-}$ polarity of the IF bonds, thereby causing the bonds to become more ionic, longer, and therefore weaker. This weakening of the IF bonds can be very significant as is demonstrated by the low value of f_r in IF_4^-, which is only 41% of that in IF_6^+. The fact that the IO stretching force constant drops from IF_4O^- (6.56 mdyn/Å) toward $IF_4O_2^-$ (6.15 mdyn/Å), in spite of an increase in the oxidation state of the iodine atom, is interesting and parallels the trends previously noted[37] for chlorine oxyfluorides, i.e., the electron-releasing effect of oxygen ligands in highly electronegative compounds.

Assignments for *cis*-$IF_4O_2^-$. Our assignments for *cis*-$IF_4O_2^-$ have been limited to the stretching modes because only 10 of the 15 fundamentals expected for point group C_{2v} have been observed and because no reliable assignments have been published for similar XF_4O_2 species. The assignment of the two IO_2 stretching modes is straightforward on the basis of their high frequencies, relative intensities, and the previously published ^{18}O spectra.[9] The symmetric IF_2 axial and the symmetric IF_2 equatorial stretches must belong to the two intense polarized Raman bands at 540 and 609 cm^{-1}, respectively, with the axial mode resulting in a weak and the equatorial mode resulting in a strong infrared counterpart. The antisymmetric axial and the antisymmetric equatorial IF_2 stretches should both be very intense in the infrared spectrum and therefore are assumed to coincide at about 600 cm^{-1}, resulting in a very strong, broad band.

Comparison with Previous $IF_4O_2^-$ Assignments. Disregarding some solvent-induced shifts, we find the above assignments for *cis*-$IF_4O_2^-$ agree well with those previously reported[9] by Selig and Elgad for an aqueous solution. The only minor discrepancy is the assignment of the antisymmetric axial IF_2 stretch. For *trans*-$IF_4O_2^-$, the assignments proposed by Gillespie and Krasznai for six of the modes have been revised for three of them. The vibrational spectra reported by Carter et al.[8] show that their sample contained mainly *trans*-$IF_4O_2^-$ but was incorrectly interpreted in terms of the cis isomer.

^{19}F NMR Spectra of $IF_4O_2^-$ and $HOIF_4O$. The presence and the relative amounts of *cis*- and of *trans*-$IF_4O_2^-$ in the above samples were verified by ^{19}F NMR spectroscopy. The spectra were recorded in CH_3CN solution at −70 °C and showed a narrow singlet at ϕ 65.1 for the trans isomer and a broader A_2B_2 pattern at ϕ 66.0 and 112.8 with J_{FF} = 204 Hz for the cis isomer. The observed shifts and coupling constant are in fair agreement with the value previously reported for solutions in CH_3CN (trans ϕ 62.0),[10] IF_5 [cis ϕ 68.5, 102.1 (J_{FF} = 202 Hz); trans ϕ 70.6], and aqueous HF [cis ϕ 64, 105 (J_{FF} = 196 Hz)].[9]

Solutions of $CsIF_4O_2$ in anhydrous HF at −75 °C resulted in a sharp singlet at ϕ 62.0 and a broadened A_2B_2 pattern at ϕ 61.8 and 85.9 with J_{FF} = 220 Hz. At room temperature, the A_2B_2 pattern was broadened to the extent that it could barely be detected. Although these spectra are similar to those of $IF_4O_2^-$, it was conclusively shown (see below) by Raman spectroscopy that they are due to *cis*- and *trans*-$HOIF_4O$ and not to $IF_4O_2^-$. This finding is in excellent agreement with the conclusion[9] reached by Selig and Elgad that their signals 1 and 2 observed for solutions of $NaIO_4$ in HF are due to *cis*- and *trans*-$HOIF_4O$. The observed chemical shifts and coupling constant are in fair agreement with previous reports,[6,7,9,10] considering the different solvents and conditions used for recording the spectra. The coupling constant of 21 Hz previously reported by Gillespie and Krasznai[10] appears to be a typographical error.

Synthesis and Properties of $HOIF_4O$. The above described experiments involving $CsIF_4O_2$ in HF solutions indicate the existence of the equilibrium

$$CsIF_4O_2 + 2HF \underset{-HF}{\overset{+HF}{\rightleftharpoons}} CsHF_2 + HOIF_4O$$

which, in the presence of a large excess of HF, is shifted all the way to the right side. In view of the lack of a convenient synthesis of $HOIF_4O$,[6,7] this reaction was utilized to prepare $HOIF_4O$. Since during HF removal the above equilibrium is shifted back to the left, the $CsHF_2$ was converted into an insoluble BiF_6^- salt according to

$$CsHF_2 + BiF_5 \xrightarrow{HF} CsBiF_6\downarrow$$

which can be filtered off at −78 °C. The resulting mixture

(35) Christe, K. O.; Curtis, E. C.; Wilson, R. D. *J. Inorg. Nucl. Chem. Suppl.* **1976**, 437.
(36) Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1967**, *6*, 1783.
(37) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 331.

Table IV. Stretching Force Constants (mdyn/Å) of *trans*-$IF_4O_2^-$ Compared to Those of Similar Molecules and Ions

	anions			molecules		cation
	IF_4^- (+III)[a]	IF_4O^- (+V)[b]	$IF_4O_2^-$ (+VII)	IF_5 (+V)[c]	IF_5O (+VII)[d]	IF_6^+ (+VII)[e]
f_r(IF)	2.22	2.46	3.27	3.77	4.42	5.42
f_{rr}	0.18	0.16	0.04	0.04	0.00	−0.07
$f_{rr'}$	0.47	0.45	0.27	0.38	0.18	0.19
f_d(IO)		6.56	6.15		6.99	
f_{dd}			0.25			

[a] Data from ref 25; iodine oxidation state in parentheses for all species. [b] Data from ref 26. [c] Data from ref 35. [d] Data from ref 29. [e] Data from ref 36.

of $HOIF_4O$ and HF can be easily separated by fractional condensation or distillation.

The ^{19}F NMR spectrum of $HOIF_4O$ in HF solution was recorded at −78 °C and was identical with that of the product obtained by dissolving $CsIF_4O_2$ in HF (see above). The ratio of cis to trans isomer in the $HOIF_4O$ sample appeared to be similar to that in the $CsIF_4O_2$ starting material. It should be pointed out that at room temperature the signal due to the cis isomer can be so broad that it is difficult to detect, thereby giving the false impression of dealing with samples containing exclusively the trans isomer.

The Raman spectra of liquid $HOIF_4O$ showed some variation. Freshly prepared samples and HF solutions exhibited spectra similar to that of trace A of Figure 3. After the solutions were allowed to stand, the 872 cm^{-1} band decreased in intensity and bands at 828 and 799 cm^{-1} started to grow. In addition the bands in the 600–700 cm^{-1} region became broader and shifted to slightly lower frequencies, as shown by trace B of Figure 3. On the basis of its ^{19}F NMR spectrum, a sample of $HOIF_4O$ in HF solution, which showed a Raman spectrum very similar to that of trace A of Figure 3, consisted mainly of the cis isomer. Whether the change from Raman spectrum A to spectrum B involves a change in the isomer ratio or is caused by association effects was not clearly established.

Synthesis of $FOIF_4O$. Previous studies have shown that unstable NF_4^+ salts containing oxyanions such as ClO_4^-[3] or SO_3F^-[4] can be prepared by metathesis in anhydrous HF solution according to

$$NF_4SbF_6 + CsXO_4 \xrightarrow{HF} CsSbF_6\downarrow + NF_4XO_4$$

Thermal decomposition of these NF_4^+ salts provided a new high-yield synthetic route to hypofluorites.[3,4] Since no examples of iodine hypofluorites had previously been known, it was interesting to examine the applicability of this method to periodates.

Since the IO_4^- anion is fluorinated to $IF_4O_2^-$ in anhydrous HF, as shown by the above studies and the previous report by Selig and Elgad,[9] the metathetical reaction of IO_4^- itself could not be studied. However, when IO_4^- was replaced by $IF_4O_2^-$, the following metathetical reaction occurred:

$$NF_4SbF_6 + CsIF_4O_2 \xrightarrow[-78\ °C]{HF} CsSbF_6\downarrow + HOIF_4O + NF_4HF_2$$

The $CsSbF_6$ precipitate could be easily filtered off at −78 °C, and Raman and ^{19}F NMR spectroscopy of the filtrate showed the presence of NF_4^+[38] and $HOIF_4O$ (see above) with no evidence for the $IF_4O_2^-$ anion. This is in agreement with the above results for $CsIF_4O_2$, which demonstrated that MIF_4O_2 salts undergo solvolysis in anhydrous HF according to

$$MIF_4O_2 + 2HF \rightarrow MHF_2 + HOIF_4O$$

Raman and ^{19}F NMR spectra showed that these NF_4HF_2–$HOIF_4O$-containing HF solutions are unstable at room temperature and slowly decompose to NF_3[39,40] and a new compound identified (see below) as a mixture of *cis*- and *trans*-$FOIF_4O$. At the same time, the relative intensities of the NF_4^+ and $HOIF_4O$ signals decreased accordingly. When the HF solvent was pumped off at −30 °C from a freshly prepared NF_4HF_2–$HOIF_4O$ solution, a white solid residue was obtained. The low-temperature Raman spectrum of this solid showed the presence of the NF_4^+ cation, but the remaining bands were too broad to permit a positive distinction among $IF_4O_2^-$, $HOIF_4O$, and possibly some $HF_2^-\cdot nHF$.[3] The new compound $FOIF_4O$ was obtained in high yield by decomposing at room temperature this thermally unstable solid, with the byproduct being NF_3. Since the same products were obtained from HF solutions that, on the basis of their ^{19}F NMR and Raman spectra, contained only $HOIF_4O$ but not $IF_4O_2^-$, it appears

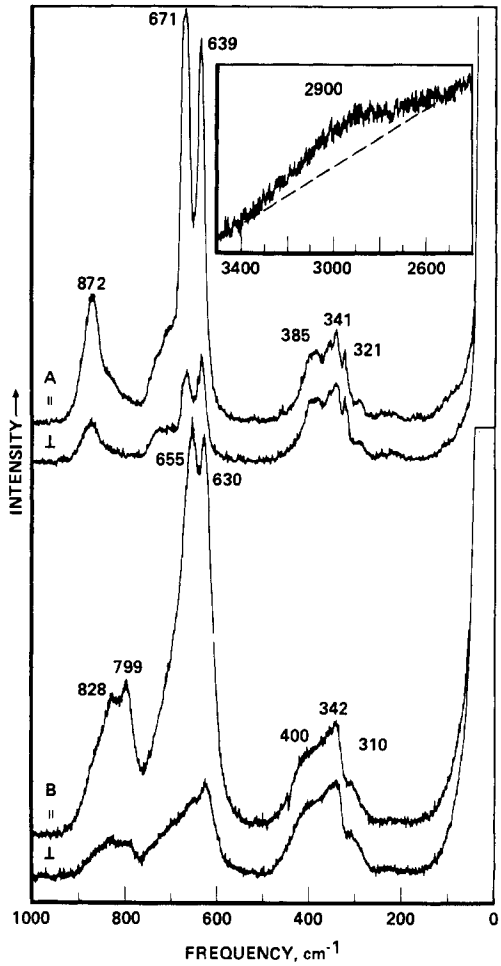


Figure 3. Raman spectra of liquid $HOIF_4O$, recorded in Teflon FEP tubes at room temperature.

(38) Christe, K. O.; Guertin, J. P.; Pavlath, A. E.; Sawodny, W. *Inorg. Chem.* **1967**, *6*, 533.

(39) Rose, W. B.; Nebgen, J. W.; Metz, F. I. *Rev. Sci. Instrum.* **1966**, *37*, 238.

(40) Shamir, J.; Hyman, H. H. *Spectrochim. Acta, Part A* **1967**, *23A*, 1899.

that $FOIF_4O$ is formed by fluorination of $HOIF_4O$ by either NF_4^+ or nascent fluorine formed during the thermal decomposition of the marginally stable $NF_4^+HF_2^-\cdot nHF$.[3] Consequently, it was interesting to investigate whether $FOIF_4O$ could also be obtained by the fluorination of $HOIF_4O$ with elemental fluorine. However, fluorination reactions carried out at 25 °C with the use of either neat or HF solutions of $HOIF_4O$, 2 atm of F_2 pressure, and a shaker for agitation did not result in any fluorination of $HOIF_4O$, and only unchanged starting materials were recovered.

Since the fluorination reactions of alkali-metal salts such as $CsSF_5O$, $CsCF_3O$, $CsClO_4$, or KNO_3 with elemental fluorine yield the corresponding hypofluorites,[1] it was interesting to study the analogous fluorination reaction of $CsIF_4O_2$. In static systems up to 60 °C slow reactions between $CsIF_4O_2$ and F_2 were observed, producing IF_5O in low yield as the only volatile product. Since IF_5O is the primary decomposition product of $FOIF_4O$ (see below), the intermediate formation of some $FOIF_4O$ in this reaction cannot be ruled out. Similarly, the fluorination of $CsIO_4$ with F_2 under comparable conditions produced small amounts of IF_5O as the only volatile product. The Raman spectra of the solid residues from both reaction systems showed the presence of $CsIF_8$,[41] $CsIF_6$,[22] *cis*- and *trans*-$CsIF_4O_2$, and $CsIF_4O$.[26] The low reactivity of the I=O double bond in IF_5O was further demonstrated by separate experiments, showing that F_2 is not added across the I=O double bond, even in the presence of CsF as a catalyst, at temperature between −196 and +25 °C with the use of an excess of F_2.

Properties of $FOIF_4O$. As shown by NMR and vibrational spectroscopy (see below), $FOIF_4O$ exists in the form of two isomers, one in which the two oxygens are cis and one in which they are trans to each other. Attempts were unsuccessful to separate the two isomers by gas chromatography at 25 °C using a 30-ft, $^3/_{16}$-in. o.d. stainless-steel column containing 50% Halocarbon oil No. 4-11V on Kel-F 300 (70–80 mesh).[42] Consequently, the physical properties could only be determined for a mixture of both isomers. On the basis of their ^{19}F NMR peak areas, the ratio of cis to trans isomers in the sample used for the physical property measurements was 1.92:1. $FOIF_4O$ is colorless as a gas, pale yellow as a liquid, and white in the solid state. The given sample melted at −33.1 °C. Vapor pressures were fitted by the method of least squares to the equation

$$\log [P\ (\text{mm})] = 7.62925 - 1432.0/[T\ (\text{K})]$$

the index of correlation being 0.99991. The extrapolated boiling point is 28.37 °C. Measured vapor pressures at the noted temperatures are as follows [T (°C), P (mm)]: −45.3, 22; −33.1, 47; −23.0, 80; −13.7, 129; 0, 244. The latent heat of vaporization of $FOIF_4O$ is 6.55 kcal/mol and the derived Trouton constant is 21.73, indicating little association in the liquid phase. This is in agreement with the relatively low boiling point and the small changes between the vibrational spectra of the gas and the liquid (see below). The molecular weight was determined from the vapor density and found to be 254.5 (calcd for $FOIF_4O$ 253.9). The good agreement indicates little or no association in the gas phase at the pressure used ($P \sim 1$ atm).

$FOIF_4O$ is marginally stable at room temperature and can be handled in well-passivated metal and Teflon equipment without rapid decomposition. The fact that IF_5O was frequently observed as an impurity in the vibrational and NMR spectra suggests the primary decomposition mode

$$FOIF_4O \rightarrow IF_5O + {}^1/_2O_2$$

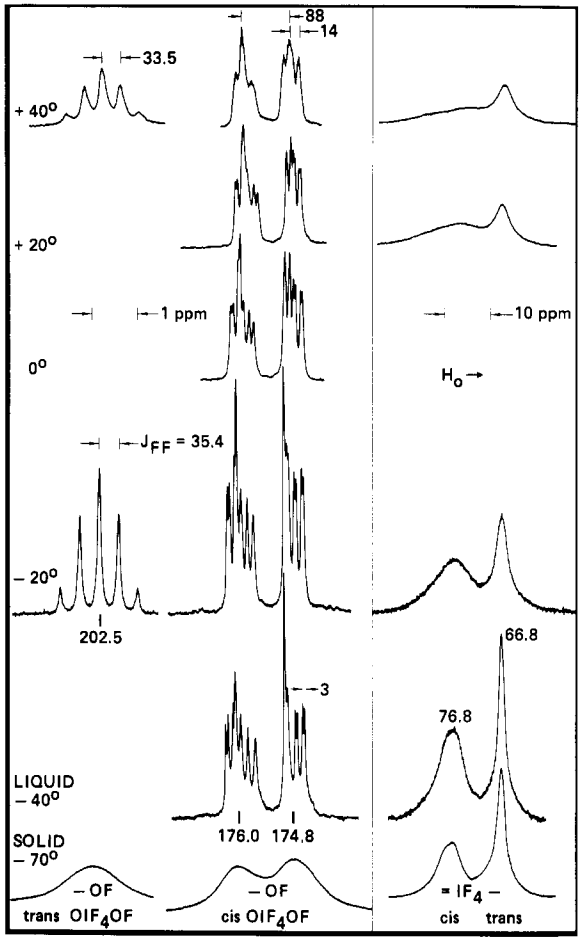
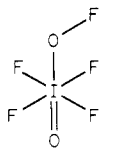


Figure 4. ^{19}F NMR spectra of *cis*- and *trans*-$FOIF_4O$ recorded at different temperatures. The signals due to the O–F fluorines are given at a 10 times wider scale than those due to fluorines on iodine. Positive shifts are downfield from the external $CFCl_3$ standard.

When a sample of $FOIF_4O$ has heated in a stainless-steel cylinder to 120 °C for 388 h, decomposition to IF_5 and O_2 was observed. This is not surprising in view of a previous report[13] that IF_5O readily decomposed to IF_5 and O_2. As expected for a hexacoordinated iodine species, $FOIF_4O$ is neither a good fluoride ion acceptor nor a good donor. Thus, it does not form stable adducts at room temperature with either the strong Lewis acid SbF_5 or the strong Lewis base CsF. Attempts to add $FOIF_4O$ across the C=C double bond in C_2F_4 were unsuccessful. Fluorination and oxygenation of C_2F_4 occurred with COF_2, CF_3CFO, and C_2F_6 being the principal reaction products.

^{19}F NMR Spectra of $FOIF_4O$. The ^{19}F NMR spectra of $FOIF_4O$ were recorded for the neat material and HF solutions and were essentially identical. The spectra of the neat liquid and solid are shown in Figure 4, together with the observed chemical shifts and coupling constants. Peak-area measurements showed that the 202 and 67 ppm signals belong to an AX_4 and the 176, 175, and 77 ppm signals to an A_2BCX system. The AX_4 system is readily assigned to the trans isomer



The chemical shift of 66.8 ppm of the four equatorial fluorines is almost identical with that in IF_5O (68.5 ppm for neat IF_5O at −20 °C), and that of 202.5 ppm of the fluorine on oxygen

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(42) Dayan, V. H.; Neale, C. B. *Adv. Chem. Ser.* **1966**, *No. 54*, 223.

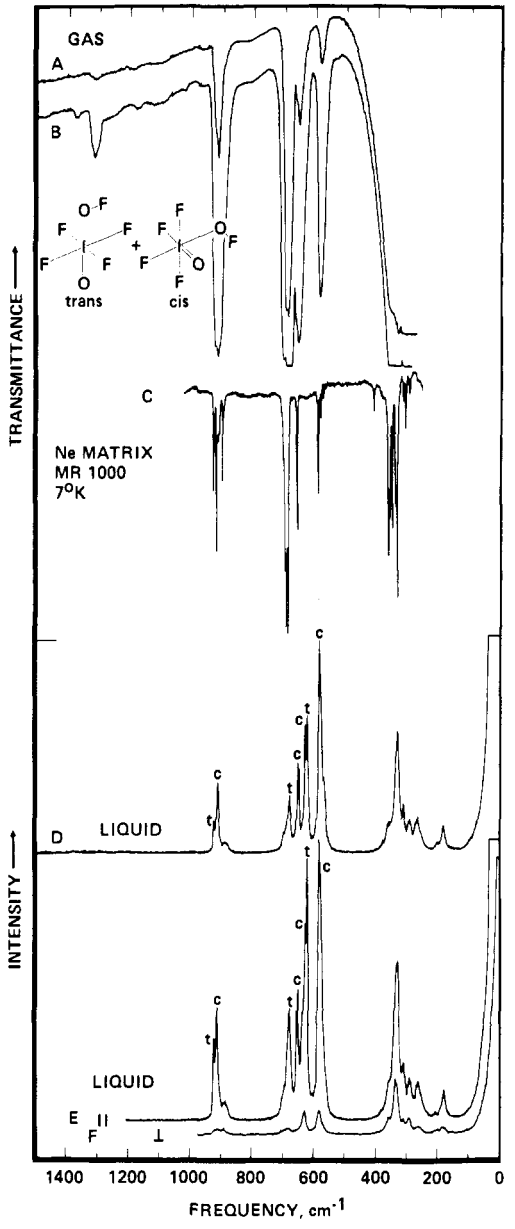

Figure 5. Vibrational spectra of a mixture of *cis*- and *trans*-$FOIF_4O$ in a ratio of about 1.9:1. Traces A and B are infrared spectra of the gas, recorded at pressures of 10 and 95 mm, respectively, in a 5-cm path length cell equipped with AgCl windows. Most of the absorption below 400 cm^{-1} is due to the window material. Trace C is an infrared spectrum of $FOIF_4O$ isolated in a neon matrix [mole ratio (MR) 1000:1] and recorded at 6 K. Traces D–F are Raman spectra of liquid $FOIF_4O$ recorded in 4-mm o.d. quartz tubes at −20 °C for two samples containing somewhat different ratios of cis (c) to trans (t) isomers, with the incident polarization parallel and perpendicular.

is similar to those of other hypofluorites such as O_3ClOF (219 ppm),[43] SF_5OF (189 ppm),[44] or *trans*-$SeF_4(OF)_2$ (179 ppm).[45] The fluorine–fluorine coupling constant, J_{FF} = 34 Hz, is in good agreement with the value of 27 Hz previously reported for the coupling constant of the four equatorial fluorines to the two hypofluorite fluorines in *trans*-$SeF_4(OF)_2$.[45] The broadened fluorine on iodine resonance and the lack of observable fine structure of $FOIF_4O$ is attributed to unresolved IF coupling ($I_I = {}^5/_2$) due to decreased quadrupole relaxation caused by the approximately spherically symmetric electric

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(45) Smith, J. E.; Cady, G. H. *Inorg. Chem.* **1970**, *9*, 1293.

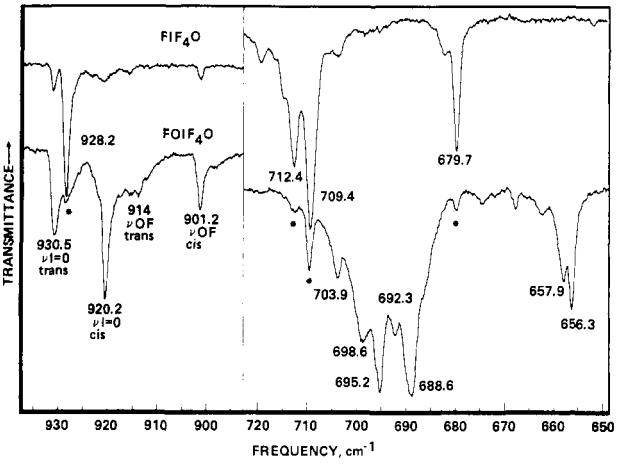


Figure 6. Infrared spectra of IF_5O and $FOIF_4O$ in a Ne matrix (MR 1000:1) at 6 K recorded at 20-fold scale expansion. The bands due to IF_5O in the $FOIF_4O$ spectrum are marked by an asterisk.

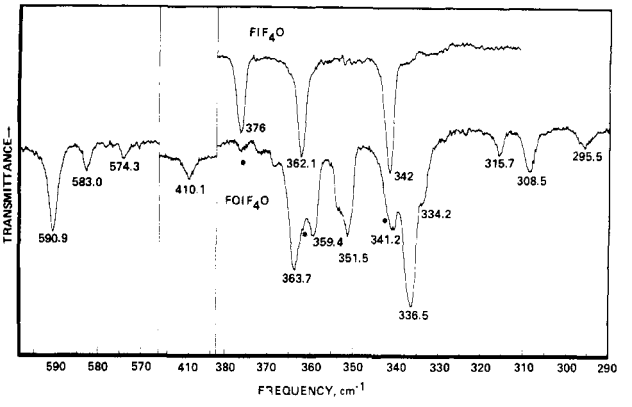
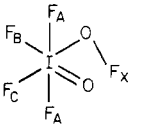


Figure 7. Infrared spectra of IF_5O and $FOIF_4O$ in a Ne matrix (MR 1000:1).

field about the iodine.[6] The A_2BCX system is assigned to the cis isomer



and also shows an unresolved IF signal (at about 77 ppm) and a resolved hypofluorite signal (at about 202 ppm), which exhibits a pronounced temperature dependence. At 40 °C, the OF signal approximates a first-order doublet (J = 88Hz) of triplets (J = 14Hz). Since coupling should be stronger to the cis fluorines than to the trans fluorine,[44] this spectrum could then be interpreted as being due to the cis isomer with free rotation around the I—O single bond and J_{BX} = 88 Hz, J_{AX} = 14 Hz, and J_{CX} being too small to be resolved. When the solution is cooled, the line width becomes smaller and the CX coupling becomes observable. As can be seen from Figure 4, the spectrum exhibits pronounced second-order effects, and a computer-aided analysis will be required to obtain precise coupling constants. The fact that the unresolved fluorine on iodine signal has a significantly larger line width for the cis than for the trans isomer is not surprising because the cis isomer possesses three similar but nevertheless nonequivalent types of fluorine on iodine.

Vibrational Spectra of $FOIF_4O$ and IF_5O. The infrared spectra of the gas and of the neon matrix isolated solid and the Raman spectra of liquid and solid $FOIF_4O$ were recorded (see Figures 5–7), and the observed frequencies are summa-

Table V. Vibrational Spectra of $FOIF_4O$[a]

obsd freq, cm^{-1}, and rel intens[b]				
IR		Raman		tentative assignts to to cis and trans isomers
gas	Ne matrix	liquid, −20 °C	solid, −80 °C	
1375 vw				2 × 688
1315 w				2 × 655
	930.5 m	926 (2.9) p	924 (1.7)	$\nu(I{=}O)_{trans}$
916 s	920.2 ms	916 (4) p	914 (3.6)	$\nu(I{=}O)_{cis}$
	914 mw	890 (0.6) p	891 (0.4)	$\nu(OF)_{trans}$
900 sh	901.2 m			$\nu(OF)_{cis}$
701 sh	703.9 m			
	698.6 s			
693 vs	695.2 vs	695 sh	690 sh	$\nu_{as}(IF_4)_{trans}$
	692.3 m			$\nu_{as}(IF_2)_{ax,cis}$
688 vs	688.6 vs	680 (3.9) p	679 (3.3)	$\nu(I{-}O)_{trans}$
	686 sh			
	657.9 m			
653 s	656.3 ms	654 (4.5) p	652 (2.9)	$\nu(I{-}O)_{cis}$
		631 (6) p	630 (5)	$\nu_s(IF_2)_{ax,cis}$
		624 (9.2) p	622 (6.8)	$\nu_s(IF_4)_{trans}$
584 ms	590.9 ms	585 (10) p	586 (10)	$\nu_s(IF_2)_{eq,cis}$ and
	583.0 mw	575 sh	577 (4)	$\nu_{as}(IF_2)_{eq,cis}$
	574.3 w		570 sh	
	410.1 mw			
	363.7 ms			
	359.4 m	360 sh	358 (1)	
	353.5 sh			
	351.5 ms			
	341.2 m	340 sh		
335 s	336.5 vs			
	334.2 sh	334 (5.4) p	333 (4)	
	315.7 mw			
	308.5 m	311 (0.4) p	311 (0.4)	
	295.5 mw			
		291 (0.7)	291 (1)	
		264 (1) p	263 (0.8)	
		205 (0.1)	203 (0+)	
		182 (0.9) p	183 (0.6)	

[a] Mixture of cis and trans isomers. [b] Uncorrected Raman intensities based on trace E of Figure 5.

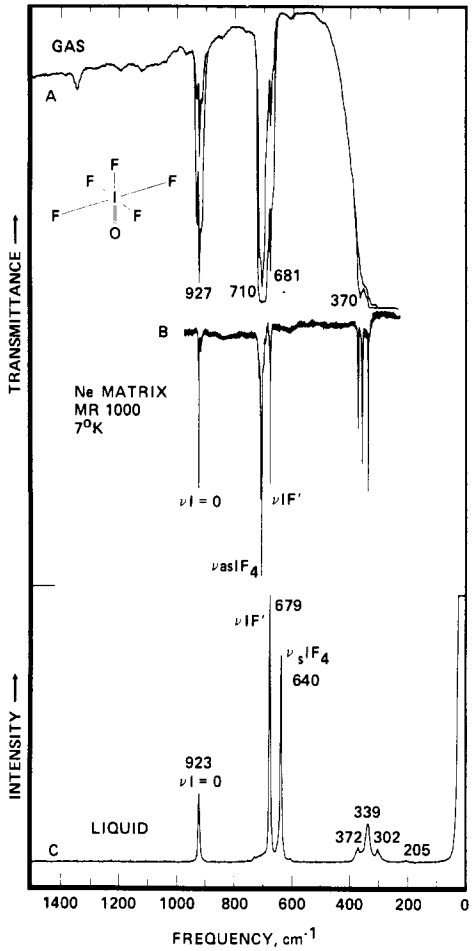


Figure 8. Vibrational spectra of IF_5O. Trace A is infrared spectra of the gas, trace B is an infrared spectrum in a Ne matrix, and trace C is a Raman spectrum of the liquid. All were recorded under conditions identical with those of Figure 5.

rized in Table V. The studied samples were mixtures of *cis*- and *trans*-$FOIF_4O$ with a cis:trans ratio of about 1.9 based on the NMR spectra and, in the matrix study, also contained a small amount of IF_5O, formed during manipulation of the sample. Since the vibrational spectra of *cis*- and *trans*-$FOIF_4O$ and of IF_5O (see Figure 8) are all very similar, the gas-phase infrared spectra are only of limited value for distinguishing the three compounds. However, the Raman spectra of the liquid and solid and particularly the infrared spectra of the matrix-isolated samples definitely confirm the presence of the two $FOIF_4O$ isomers established by the ^{19}F NMR study. Some distinction of the cis from the trans isomer bands was possible from a comparison of spectra of samples having different cis to trans ratios (see for example traces D and E of Figure 5).

Tentative assignments for the stretching modes of *cis*- and *trans*-$FOIF_4O$ are given in Table V and were made by comparison with those established for IF_5O[14,29] and $IF_4O_2^-$ (see above), relying mainly on the observed relative infrared and Raman intensities.

The vibrational spectra observed for IF_5O are in excellent agreement with those previously reported,[14,29] except for the fact that our spectra do not show a strong infrared band at 640 cm^{-1}. As previously suggested,[29] this band is due to IF_5, the principal decomposition product of IF_5O.

Mass Spectra. The recording of the mass spectrum of $FOIF_4O$ presented difficulties due to reaction of the compound with the inlet system, resulting in the formation of some IF_5O. Furthermore, I_2 has almost the same mass (253.8) as the parent $FOIF_4O$ (253.9) thus making a distinction of the two molecules difficult. These problems were overcome by recording the spectra of pure IF_5O under the same conditions and subtracting the IF_5O pattern from that of the $FOIF_4O$-containing sample. The interference from I_2 was eliminated by recording spectra of 1:1 mixtures of ClF_3 and $FOIF_4O$. The ClF_3 oxidized I_2 rapidly to iodine fluorides but did not appear to interact with $FOIF_4O$. The mass cracking pattern obtained in this manner for $FOIF_4O$ is listed in Table VI and agrees with the expectations[46] for a hypofluorite. The I–OF single bond is readily broken to yield an intense IF_4O^+ fragment, which can undergo additional oxygen and/or fluorine loss.

Table VI. Mass Spectrum[a] of a Mixture of *cis*- and *trans*-$FOIF_4O$

m/e	rel intens	ion	*m/e*	rel intens	ion
219	72	IF_4O^+	165	18	IF_2^+
203	100	IF_4^+	162	38	IOF^+
200	32	IF_3O^+	146	15	IF^+
184	18	IF_3^+	143	7	IO^+
181	73	IF_2O^+	127	38	I^+
178	1	IO_2F^+			

[a] Recorded with an ionization potential of 70 eV, with the use of a 1:1 mixture of $FOIF_4O$ and ClF_3. Peaks due to ClF_3 and IF_5O have been subtracted from the pattern.

Synthesis of $ClOIF_4O$. Since $FOIF_4O$ was found to be stable, the synthesis of the analogous hypochlorite, $ClOIF_4O$, appeared feasible. Using $CsIF_4O_2$ and $ClOSO_2F$, a generally

(46) Huston, J. L.; Studier, M. H. *J. Fluorine Chem.* **1979**, *13*, 235.

useful reagent for the syntheses of hypochlorites,[47] the synthesis of $ClOIF_4O$ was accomplished according to

$$CsIF_4O_2 + ClOSO_2F \xrightarrow{-78\ °C} CsSO_3F + ClOIF_4O$$

The resulting $ClOIF_4O$ appears to be highly reactive, difficult to handle, and thermally unstable. Consequently, the compound could not be well characterized. The main evidence for its existence is the infrared spectrum of the gas, which is similar to that of $FOIF_4O$ except that the O—F stretch is replaced by a band at 763 cm^{-1}, characteristic of an O—Cl stretch,[47] and the I=O, IF, and I—O stretching modes are shifted to slightly lower frequencies. The compound decomposes to IF_5, and attempts to add it across the C=C double bond of C_2F_4 did not result in stable adducts.

Conclusion. Although the isolation of NF_4^+ salts of either IO_4^- or $IF_4O_2^-$ was not possible, solutions containing NF_4^+ and $HOIF_4O$ were found to decompose to produce $FOIF_4O$ in high yield. This is in marked contrast to the similar syntheses of $FOClO_3$ and $FOSO_2F$ where the corresponding $NF_4^+ClO_4^-$[3] and $NF_4^+SO_3F^-$[4] salts were shown to be the actual intermediates. $FOIF_4O$ is the first known example of an iodine hypofluorite and exists as cis and trans isomers. It is a stable compound and was thoroughly characterized. The analogous hypochlorite, $ClOIF_4O$, was also prepared for the first time but, as expected, is considerably less stable than $FOIF_4O$. The reaction of $CsIO_4$ with HF was found to be a convenient synthesis of $CsIF_4O_2$, which, by reaction with BiF_5 in HF, can readily be converted into $HOIF_4O$, thus providing easy access to tetrafluoroperiodates. The bonding in *trans*-$IF_4O_2^-$ was studied by vibrational spectroscopy, and the results of a normal-coordinate analysis are in excellent agreement with the trends previously established[37] for chlorine oxyfluorides.

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Registry No. *trans*-$CsIF_4O_2$, 77224-44-3; *cis*-$CsIF_4O_2$, 55188-51-7; *trans*-$HOIF_4O$, 25685-16-9; *cis*-$HOIF_4O$, 25685-15-8; *trans*-$FOIF_4O$, 72151-31-6; *cis*-$FOIF_4O$, 72123-55-8; $ClOIF_4O$, 77224-34-1; $CsIO_4$, 13478-04-1; HF, 7664-39-3; BrF_5, 7789-30-2; ClF_3, 7790-91-2; ClF_5, 13637-63-3; F_2, 7782-41-4; BiF_5, 7787-62-4; NF_4SbF_6, 16871-76-4; $ClSO_3F$, 13997-90-5; IF_5O, 16056-61-4.

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Oxidation by Aqueous Fluoroxysulfate: Catalysis by Silver(I)[1a]

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The oxidations of the ions Cr^{3+}, Co^{2+}, and VO^{2+} by the fluoroxysulfate ion, SO_4F^-, in aqueous solution are catalyzed by Ag^+. The rate-determining step for all three catalyzed reactions is the bimolecular oxidation of Ag^+ by SO_4F^-, which has a rate constant of $(1.3 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$ at 17 °C. Activation parameters for this reaction are $\Delta H^* = 6.1 \pm 0.5$ kcal/mol and $\Delta S = -23 \pm 2$ cal/(mol deg). In the absence of Ag^+, Co^{2+} and VO^{2+} react very slowly with SO_4F^-, while Cr^{3+} does not react at all. Despite its high thermodynamic oxidizing power, the fluoroxysulfate ion acts as a very selective oxidant.

Introduction

The fluoroxysulfate ion, SO_4F^-, is the only known ionic hypofluorite.[2] It is also one of the most powerful of all aqueous oxidants, with a standard electrode potential of 2.46 V.[3] The rubidium and cesium fluoroxysulfates are rather easily made and are sufficiently stable that they can be conveniently stored prior to use. These salts are therefore very suitable substances with which to explore and take advantage of the chemical properties of a hypofluorite, which we may expect to act as a vigorous oxidizing and fluorinating agent.

In the course of our initial survey of the reaction chemistry of aqueous fluoroxysulfate,[2,4] we have observed that SO_4F^- readily oxidizes most reducing substrates. However, some reducing agents such as Cr^{3+} are not oxidized at all, while others such as Mn^{2+}, Ce^{3+}, Co^{2+}, and VO^{2+} react rather sluggishly. On the other hand, Ag^+ is very rapidly oxidized by SO_4F^-, and since higher oxidation states of silver are known to be powerful oxidants, it appeared to us that Ag^+ should catalyze oxidation by SO_4F^- and might thereby extend the application of the latter as an oxidizing agent. We have found that such catalysis does indeed take place, and we have undertaken to study the Ag^+-catalyzed reactions of SO_4F^- with Cr^{3+}, Co^{2+}, and VO^{2+}. For the sake of comparison, we have also examined the slow uncatalyzed reactions of SO_4F^- with Co^{2+} and VO^{2+}.

Experimental Section

Materials. Cesium fluoroxysulfate was prepared and purified by techniques described previously.[2,4] Solutions of $VO(ClO_4)_2$ in 1 M $HClO_4$ were prepared from commercial vanadyl sulfate by ion exchange. Stock solutions of lower acidity were obtained by partial neutralization of the acid with lithium carbonate. Zinc perchlorate was prepared by the reaction of Johnson-Matthey high-purity ZnO with $HClO_4$, followed by two recrystallizations. Other starting materials such as G. F. Smith $Zn(ClO_4)_2$, reagent grade ZnO, and reagent grade Zn metal resulted in $Zn(ClO_4)_2$ solutions containing impurities that rapidly reduced or decomposed fluoroxysulfate. The preparations of $Co(ClO_4)_2$, $Cr(ClO_4)_3$, and $LiClO_4$ have been described elsewhere.[5] Other materials were commercial products of reagent grade. Deionized water was distilled before use first from acid dichromate and then from alkaline permanganate.

Solutions of HSO_5^- in which the terminal peroxide oxygen was enriched in ^{18}O were prepared by allowing cesium fluoroxysulfate to decompose in a 1 M $HClO_4$ solution that was enriched in ^{18}O. The hydrogen peroxide formed was decomposed by addition of a stoichiometric amount of Ce(IV). The yield of peroxymonosulfate in 1 M $HClO_4$ was of the order of 40% of the fluoroxysulfate. This is considerably higher than the yield obtained at lower acidity.[4]

Analytical Procedures. Solutions of Co^{2+}, Co^{3+}, VO^{2+}, VO_2^+, and $HCrO_4^-$ were analyzed spectrophotometrically, with use of extinction

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