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47. IODINE FLUOROSULFATES

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IODINE FLUOROSULFATES

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ABSTRACT

Iodine (I) fluorosulfate ($IOSO_2F$) and triiodine fluorosulfate (I_3OSO_2F) have been prepared by the reaction of iodine with peroxydisulfuryl difluoride ($S_2O_6F_2$). Their solutions in fluorosulfuric acid have the colors and spectra characteristic of the I^+ and I_3^+ ions, respectively. Dichlorofluorosulfatoiodine (ICl_2OSO_2F) has been produced from chlorine and $IOSO_2F$. Iodine (III) fluorosulfate decomposes slowly when under vacuum at about 80° to 90° to give iodine (I) fluorosulfate, which remains with the unreacted $I(OSO_2F)_3$, and the volatile products SO_3, $IF_3(OSO_2F)_2$ and an unidentified substance which may be $I(OSO_2F)_5$.

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Peroxydisulfuryldifluorid[1] is a very convenient starting material for the preparation of halogen fluorosulfates using the following route: $X_2 + nS_2O_6F_2 = 2X(OSO_2F)_n$, in which n = 1 or 3. The following compounds have been prepared and characterized: $FOSO_2F$,[2] $ClOSO_2F$,[3] $BrOSO_2F$,[4] $Br(OSO_2F)_3$,[4] and $I(OSO_2F)_3$,[4]. Another compound, $IF_3(OSO_2F)_2$ was prepared by allowing I_2 to react with $FOSO_2F$.[5] Some evidence was obtained for the possible existence of lower fluorosulfates.[4] Reactions using iodine in an excess over that required for $I(OSO_2F)$ yielded green to black liquids or brown solids of various compositions. The excess iodine appeared to be chemically bound since it could not be removed by distillation or by extraction with perfluoromethylcyclohexane. The reaction of ICl with an excess of $S_2O_6F_2$ finally gave $I(OSO_2F)_3$ after an orange-red colored intermediate was observed.[6] The reaction of CF_3I with $S_2O_6F_2$ produced CF_3OSO_2F and a mixture of iodine fluorosulfates.[7]

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[1] F.B. Dudley, and G.H. Cady, J. Am. Chem. Soc. 79, 513 (1957).

[2] J.F. Roberts, and G.H. Cady, J. Am. Chem. Soc. 81, 4166 (1959).

[3] W.P. Gilbreath, and G.H. Cady, Inorg. Chem. 2, 496 (1963).

[4] J.E. Roberts, and G.H. Cady, J. Am. Chem. Soc. 82, 352 (1960).

[5] J.E. Roberts, and G.H. Cady, J. Am. Chem. Soc. 32, 354 (1960).

[6] J.M. Shreeve, and G.H. Cady, J. Am. Chem. Soc. 83, 452 (1961).

[7] M. Lustig, Ph.D. Thesis, University of Washington, 1962.

In the above processes $S_2O_6F_2$ reacted as a pseudohalogen. This type of behavior also has occurred in reactions of $S_2O_6F_2$ with chlorides to give free Cl_2 and fluorosulfates.[6,8] Just as Cl_2 adds across a carbon-carbon double bond to give a dichloride, $S_2O_6F_2$ adds to give a difluorosulfate.[6] The formation of halogen fluorosulfates may therefore be considered as analogous to the formation of interhalogen compounds. As in the preparation of I Cl,[9] where stoichiometric amounts are allowed to react, the compound $IOSO_2F$ has now been produced by the reaction of equimolar amounts of the reagents. $S_2O_6F_2$ of high purity was distilled from a calibrated trap of small internal diameter onto a weighed equimolar amount of iodine. As the material warmed to room temperature, a reaction occurred. This method permitted one to add $S_2O_6F_2$ in an amount within 4 mg of that desired (less than 0.5% deviation from the theoretical value). In order to avoid interference by the reaction of stopcock grease with $S_2O_6F_2$, a sealed reactor with a breakseal attachment was used. The crude product obtained in this manner had a broad melting range from 35 to 65°, indicating the presence of some unreacted iodine and $I(SO_3F)_3$. To get a complete conversion to $IOSO_3F$, the mixture

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[8] M. Lustig, and G.H. Cady, Inorg. Chem. 1, 714 (1962).

[9] J. Cornog, and R.A. Karges, J. Am. Chem. Soc. 54, 1882 (1932).

was heated for one hour at about 60°. The resulting product was a dark brown to black liquid, which solidified to a black solid. After storing a sample in a sealed tube at room temperature for two weeks or more, small glistening black crystals could be seen. These had a sharp melting point of 51.5°. No $S_2O_6F_2$ and only a trace of SiF_4 could be recovered by pumping at room temperature, indicating a complete reaction and negligible attack upon the glass vessel. The substance was very hygroscopic and reacted as a strong oxidizing agent. When it was dissolved in CCl_4, $CHCl_3$ or $CFCl_3$, chlorine was liberated together with $COCl_2$, CO_2 and $S_2O_5F_2$. The brown solution in CCl_4 absorbed light in the visible region at 4640 Å, the exact position for I Cl.[10] The results indicate the following reactions:

$$2IOSO_2F + CCl_4 = 2ICl + S_2O_5F_2 + COCl_2$$

$$4IOSO_2F + CCl_4 = 4ICl + 2S_2O_5F_2 + CO_2$$

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[10] A.E. Gillam, and R.A. Morton, Pr. Roy. Soc. A 124, 610 (1929).

Attempts to prepare an addition compound with pyridine resulted in a pale yellow solid, which decomposed quickly to a brown oil. The preparation of $[I(py)_2^+]SO_3F$ by Schmidt and Meinert[11] using $Ag\ SO_3F$ and I_2 in CH_3CN as solvent and in the presence of pyridine also yielded an unstable product.[11]

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[11] H. Schmidt and H. Meinert, Angew. Ch. 71, 126 (1959).

To substantiate the character of $IOSO_2F$ as a true I(I)-compound, spectroscopic measurements were made using fluorosulfuric acid as a solvent. This liquid was not attacked by $IOSO_2F$ and it did not oxidize I_2 to I^+ (see evidence in Table II). It has been reported to dissolve ICl giving a blue color[12] but no spectrum was observed.

The existence of I^+-cations in solution has recently been established by measuring the ultraviolet and visible spectra, the magnetic susceptibility and the conductivity of suitable solutes in 65% Oleum as a solvent (where SO_3 acts as oxidizing agent).[12 to 17] The I^+ ion has also been produced by dissolving a little iodine in IF_5 [18] under certain conditions.

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[12] J. Arotsky, H.C. Mishra, and M.C.R. Symons, J. Chem. Soc. 1951, 12.

[13] M.C.R. Symons, J. Chem. Soc. 1957, 387.

[14] M.C.R. Symons, J. Chem. Soc. 1957, 2186.

[15] T. M. Connor, and M.C.R. Symons, J. Chem. Soc. 1959, 963.

[16] J. Arotsky, H.C. Mishra, and M.C.R. Symons, J. Chem. Soc. 1962, 2582.

[17] J. Arotsky, and M.C.R. Symons, Quart. Rev. XVI, 282 (1962).

[18] E.E. Aynsley, N.N. Greenwood, and D.H. Wharmby, J. Chem. Soc. 1963, 5369.

The compound $IOSO_2F$, dissolved readily in fluorosulfuric acid giving a blue color. (If the sample had become partially hydrolyzed, a green solution was obtained due to the presence of some I_3^+ ions.) The absorption curve shown in Fig. 1 had maxima at 6380 Å (1.567×10^4 cm^{-1}), 4840 Å (2.066×10^4 cm^{-1}) and 4040 Å (2.475×10^4 cm^{-1}), with optical densities of 1.10, 0.35, and 0.403, respectively. These results are compared in Table I with those found by others in oleum and IF_5.

Table I

Spectra of Solutions Containing I^+

Solvent	Solute	Absorption maxima, Å			Reference
65% Oleum	I_2/SO_3	6400	5000	4100	12
65% Oleum	I Cl	6400	5000	4100	12
Oleum	I_2/SO_3	6480	5070	4130	18
IF_5	I_2	6410	5080	4180	18
IF_5	I Cl	6450	5150	4200	18
HSO_3F	$IOSO_2F$	6380	4840	4040	

A comparison shows that the absorption maxima in HSO_3F occur at somewhat lower wavelengths than in oleum. This must be due to the solvent since the shape of all curves and the relative optical densities agree.

The existence of I^+ cations in solution suggested the possibility that $IOSO_2F$ in the solid state might have an ionic lattice. The compound was found to be diamagnetic, however, thereby suggesting covalent bonding.

The former observation that it is very difficult to remove an excess of I_2 over that required to give $IOSO_2F$[4] indicated that another lower iodine fluorosulfate, perhaps of the composition I_3OSO_2F, might exist. The existence of I_3^+ cations together with I_5^+ was at first postulated by I. Masson,[19] when he dissolved I_2 and I_2O_5 in sulfuric acid and obtained a brown solution.

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[19] I. Masson, J. Chem. Soc. 1938, 1708.

Reports of materials which may have contained a positive I_3 group go back to 1862, when Lenssen and Loewenthal[20] observed a brown 1:1 addition product of I_2 and "IOH" in acidic aqueous solution formulated as "I_3OH". These results were confirmed by others.[21]

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[20] E. Lenssen, and J. Loewenthal, J. Prakt. Chem. 86, 219 (1862).

[21] A. Skrabal, and F. Buchta, Chem. Ztg. 33, 1194 (1909).

Spectrometric measurements by Symons, et al.[16] led to the assignment of absorption maxima at 4600 Å and 2900Å for the I_3^+ cation in H_2SO_4 and an additional shoulder in the 3300 Å region for the I_5^+ cation. There were no reports of the isolation of I_3^+ or I_5^+ containing species.

The compound I_3OSO_2F has now been prepared using the type of procedure described above for $IOSO_2F$. Only a small excess of I_2 over that stoichiometrically required was used and the reaction was run in the presence of dry air at one atmosphere pressure. After standing for 12 hours at room temperature the reactor was heated in a water bath. At temperatures somewhat above 60° a black liquid, presumably $IOSO_2F$, and a dark solid were present. At 85° a reaction occurred and the liquid phase disappeared. Big lumps of a brown-black solid were formed. By cooling down to liquid O_2 temperature, the solid lumps broke up to a fine brown-black powder which melted at 92° with decomposition liberating I_2.

Excess iodine was removed from the black powder by pumping at room temperature. Only a trace of $S_2O_5F_2$ was found in the volatile fraction. The composition of the solid corresponded to the formula I_3OSO_2F. The compound when dissolved in HSO_3F gave the spectrum shown in Fig. 2. Surprisingly, I_2 dissolved in HSO_3F showed almost the same spectrum. By contrast, iodine in 96% H_2SO_4 showed a single absorption maximum corresponding to I_2 while I_3OSO_2F gave essentially the same spectrum as in HSO_3F. The results are given in Table II.

Table II

Absorption Spectra Due to I_3^+

Solvent	Solute	Absorption maxima, Å		Optical Density	
HSO_3F	I_3OSO_2F	4670	2970	0.350	0.805
HSO_3F	I_2	4740	2970	0.324	0.692
96% H_2SO_4	I_3OSO_2F	4620	2900	0.335	0.705
96% H_2SO_4	I_2	5020		0.230	
H_2SO_4	I_3^+(Ref. 16)	4600	2900		

These results indicate that I_3OSO_2F gave the I_3^+ ion in fluorosulfuric and in sulfuric acids. No I^+ was detected. The solution of I_2 in HSO_3F also contained I_3^+.

I_3OSO_2F was found to be extremely hygroscopic and iodine crystals were formed at once on the surface by leaving the substance in open air. The fact that all iodine in excess over that required for I_3OSO_2F could be distilled off easily left little hope for the possible preparation of I_5OSO_2F.

The reaction of iodine with $S_2O_6F_2$ in a ratio of 1:2 produced a dark green viscous liquid, probably a mixture of $I(OSO_2F)_3$ and $IOSO_2F$. All attempts to crystallize this product failed. By cooling to liquid O_2 temperature a dark green glass was formed. The above observations together with those of Roberts and Cady[4] show that $S_2O_6F_2$ and iodine react completely in proportions ranging from 1:3 to :1 to form iodine fluorosulfates. Pure $IOSO_2F$ could therefore only be obtained by reacting equimolar amounts of the reagents.

The reaction of chlorine, in excess, with $IOSO_2F$ gave the compound ICl_2OSO_2F an orange-red substance of less than 100% purity which was not completely solid at 25° after distilling of the excess of Cl_2. Upon warming, the last of the solid melted between 34-35°. Two other compounds ICl_2SbCl_6 and ICl_2AlCl_4,[22] are known to contain the ICl_2 group. Attempts to prove the existence of ICl_2^+ cations in solution have failed; the structure was determined by X-ray diffraction.[23]

When $I(OSO_2F)_3$ was heated to 114° at 3 cm pressure by Roberts and Cady[4] decomposition was noted with formation of a green liquid (approximating in composition $IOSO_2F$) and a volatile product reported to be $S_2O_6F_2$. This decomposition reaction has now been studied in greater detail and the conclusions differ somewhat from those of Roberts and Cady. A color change to green occurred even at 65° within one hour. Even by leaving solid $I(OSO_2F)_3$ at room temperature for 48 hours the solid started to melt and a little color change was noticed. In no case was $S_2O_6F_2$ obtained as a decomposition product. Instead, the colorless

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[22] C.G. Vonk, and E.H. Wiebenga, Rec. trav. chim. <u>78</u>, 913 (1959).

[23] C.G. Vonk, and E.H. Wiebenga, Acta Cryst. <u>12</u>, 859 (1959).

volatile product was found to be a mixture of sulfur trioxide with the previously reported[5] compound $IF_3(OSO_2F)_2$. A small amount of an unidentified white solid was also present in the mixture. The general reaction can therefore be considered to be essentially the disproportionation shown by the equation:

$$2I(OSO_2F)_3 = IOSO_2F + IF_3(OSO_2F)_2 + 3SO_3$$

The compound $IF_3(OSO_2F)_2$ proved to be slightly volatile at room temperature and even at -10° and 10^{-2} mm pressure. It could very slowly be distilled away from the white solid. The latter was only obtained in quantities of 50 to 100 mg. A good identification was not successfully made. A sulfur and iodine determination suggested a composition close to $I(OSO_2F)_5$.

The residual $IOSO_2F$ obtained by the above disproportionation dissolved to give a blue-green color in HSO_3F. Incomplete crystallization at 25° also indicated an impure product.

Further evidence for a disproportionation of I(III) to I(I) and I(V) was found when the visible and ultraviolet spectrum in HSO_3F was measured. $I(OSO_2F)_3$ dissolved readily in HSO_3F giving a yellow color. The change in the absorption spectrum is given in Fig. 3. Curve 1 shows the spectrum obtained after approximately 1/2 hour. Absorption maxima are only ill-formed in the 6000 region and also in the 4000 and 3000 region.

After 36 hours the color had changed to blue-green (curve 2) and after another 24 hours to blue (curve 3). The results are listed in Table III.

Table III

Aging of $I(OSO_2F)_3$ in $HOSO_2F$

Time	Absorption/maxima, (Å)			Optical Densities		
1/2 hour	6300	3800	3200	0.130	0.175	0.280
36 hour	6380	4800	3950	0.545	0.210	0.253
60 hour	6380	4820	3980	0.785	0.280	0.310

The curves indicate that I^+ cation was formed in solution. Since the possibility of reduction of I (III) could be excluded, the formation of I^+ must have resulted from disproportionation. A reason to doubt that the weak maxima for $I(OSO_2F)_3$ at ~ 3800 Å and ~ 3200 Å were due to the I^{3+} ion is that the ionization potential is very large to obtain the $5s^2\ 5p^2$ configuration.[16] The disproportionation I(III) to I(I) and I(V) in sulfuric acid has already been discussed by Masson and Argument.[24]

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[24] I. Masson and Argument, J. Chem. Soc. 1938, 1702.

It has been stated above that $IOSO_2F$ reacted with carbon tetrachloride. Iodine (III) fluorosulfate also reacted when dissolved in carbon tetrachloride and the solution exhibited the absorption maxima of ICl_3 at 6400 and 3300 Å.[23] The infrared spectrum of the gaseous product showed the presence of CO_2, $COCl_2$

and $S_2O_5F_2$. The evidence suggested the reactions:

$$4I(OSO_2F)_3 + 3CCl_4 = 4ICl_3 + 6S_2O_5F_2 + 3CO_2$$

or $$4I(OSO_2F)_3 + 6CCl_4 = 4ICl_3 + 6S_2O_5F_2 + 6COCl_2$$

The F^{19} nmr spectrum of $I(OSO_2F)_3$ was found to consist of only one sharp peak which means either that bridging fluorosulfate groups were absent or that a rapid exchange occurred.

In addition to the process involving pyrolysis of $I(OSO_2F)_3$, two other unsuccessful attempts were made to prepare iodine pentafluorosulfate. One method was the reaction of iodine with $S_2O_6F_2$ in a 1:7 ratio at temperatures between 90° and 130° and the other was the reaction of $IF_3(OSO_2F)_2$ with an excess of SO_3 at 55°.

EXPERIMENTAL

The compounds $S_2O_6F_2$ and SO_3F_2 were prepared from sulfur trioxide and fluorine by previously described methods.[6,25] A reference sample of $IF_3(OSO_2F)_2$ was prepared by the reaction of $I(OSO_2F)_3$ with $FOSO_2F$ as described by W. P. Gilbreath.[26] The

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[25] F. B. Dudley, G. H. Cady, and D. F. Eggers, J. Am. Chem. Soc., 78, 290 (1956).

[26] W. P. Gilbreath, Ph.D. Thesis, University of Washington, 1962.

product was purified by repeated vacuum distillation. Technical grade fluorosulfuric acid was purified by distillation in apparatus like that of R. C. Thompson.[27] The acid had at 3200 Å a small absorption of optical density 0.285. The spectrum was run against air. Iodine (III) fluorosulfate was prepared by the reaction of an excess of $S_2O_6F_2$ with I_2^4. All other materials were of reagent grade.

Infrared spectra were studied using a Perkin-Elmer Model 21 infrared Spectrometer with a sodium chloride prism. Gaseous samples were contained in a 10 cm Monel metal cell, sealed with Teflon-O-rings and equipped with silver chloride windows. Nuclear magnetic resonance spectra were obtained through the use of a Varian Model 4311B Spectrometer with a 40 megacycle oscillator. UV and visible spectra were obtained with a Cary Model 14 Spectrometer. Glass stoppered quartz cells with 10 mm and 20 mm path length were used. All samples for measurements were dissolved and poured into the cells in a dry box. The cells were cleaned by repeated preliminary washing with the solution to be tested. All HSO_3F was distilled immediately before use. When observing spectra of solutions two matched cells were used, one containing the solution and one the pure solvent. The observed absorption was, therefore, due to the solute but not the solvent.

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[27] R. C. Thompson, Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada, 1962.

Iodine was determined by titration with sodium thiosulfate solution or by the Volhard method following reduction to I^- by hydrazine and boiling off the excess hydrazine. Chlorine was determined by Volhard's method and sulfur as barium sulfate.

Iodine (I) Fluorosulfate: A Pyrex glass reaction vessel, consisting of a 25 ml flask with a 15 cm neck ending at a 19/38 inner ground joint was used. The flask also had a side arm with a breakseal attachment. Iodine was added and the flask was connected to a vacuum line by the ground joint. After removal of air and water vapor by evacuation the iodine was weighed. In one typical experiment for which data will be given here the iodine weighed 645.8 mg. Peroxydifulfuryl difluoride, $S_2O_6F_2$, (506.3 mg) was distilled into the flask from a calibrated trap having an internal diameter of 3 mm. The volume of liquid in the trap was measured frequently by a graph paper scale, and finally the amount of reagent added was determined precisely by weighing. The evacuated reactor was then sealed off and allowed to stand at room temperature for at least eight hours. A black solid was formed. The product was then heated in a water bath at 60° and left for an hour while shaking from time to time. At this temperature the material was a dark colored liquid which as a thin film had at first a green to brown color. During the course of the heating period the color became very dark brown, almost black. By cooling to room temperature, the compound solidified at once. After standing two weeks glittering crystals had formed. While pumping on it at room temperature, the compound's weight remained almost constant. Final weight of the product: 1148.0 mg.

The solid melted sharply at 51.5° under vacuum. By heating at 100° in high vacuum the $IOSO_2F$ did not boil, but a continued slow evolution of SiF_4 indicated a wall reaction. The solid dissolved readily in CCl_4 and $CHCl_3$, being less soluble in the latter, to give brown colored solutions. UV absorption maxima at 4640 Å and the production of $S_2O_5F_2$, CO_2 and $COCl_2$ indicated solvent interaction. An iodometric titration of the solid using sodium thiosulfate gave a value of 1.990 oxidizing equivalents per mole of $IOSO_2F$, corresponding to an oxidation state of 0.995 for iodine in the compound. I found by Volhard method 55.9%; calculated, 56.16%.

Triiodine Fluorosulfate, (I_3OSO_2F): Iodine (1.2619 g) and $S_2O_6F_2$ (0.2958 g) at a molar ratio of 3.328:1 were allowed to react in a vessel like that described above. An atmosphere of dry air was present to reduce the evaporation of iodine from the reacting mixture. After warming to room temperature, a black-brown solid was formed. By heating to 60°, a part of the material melted to a black liquid. Solid material, probably unreacted iodine, remained. When the temperature was raised slowly, at 85° the liquid and solid reacted quite vigorously, with some evaporation of iodine forming big lumps of a dark brown solid. By cooling to liquid oxygen temperature, the lumps broke up into a very fine powder. Excess iodine was removed by pumping at room temperature for 12 hours. The volatile product contained only traces of $S_2O_5F_2$ and SiF_4. After reaching constant weight the solid weighed 1.4305 g (calculated for I_3OSO_2F, 1.4330 g). The solid melted at 92° in a sealed tube but with slow decomposition liberating iodine. It was extremely hygroscopic and hydrolysis by water vapor produced glistening crystals of iodine on the surface of the solid. It dissolved in 96% H_2SO_4 very readily to give a dark brown **solution**.

Dichlorofluorosulfatoiodine (III): 1.4241 g of $IOSO_2F$ was transferred to a trap. The trap was chilled and approximately 5 ml of liquid chlorine was added by distillation. The mixture was then held at -30° in a trichloroethylene bath and stirred with a magnetic stirrer. A yellow solid formed. After 8 hours the black color of $IOSO_2F$ had disappeared completely. The mixture was then warmed to room temperature while allowing the excess chlorine to distil away. The last of the free chlorine was removed by pumping for 10 minutes. The remaining product changed in color to orange, and parts of it melted to an orange-red oil. The last solid melted between 34-35°. Upon cooling to 25° most of the material froze. By cooling long needle-like crystals were formed. The material dissolved in water forming a yellow solution.

I found 43.29%, calculated for ICl_2SO_3F, 42.75%; Cl found 23.45%, calc. 23.88%; S found 11.13%, calc. 10.81%. Total weight 1.8803 g; calculated 1.8710 g.

An equimolar mixture of iodine (I) and iodine (III) fluorosulfates was produced by the reaction of 0.6677 g of iodine with 1.0396 g of $S_2O_6F_2$ at room temperature but with final heating at 60° for an hour. The product was a viscous dark green oil which was liquid at 20° and gave only a single peak in its nmr spectrum.

Pyrolysis of $I(OSO_2F)_3$: 6.55 g of $I(OSO_2F)_3$ was decomposed in a closed system under vacuum and at a temperature between 80° to 90° over a period of 120 hours. The color changed from yellow through light green to dark green to black. The volatile fraction distilled away and condensed in a trap at -183°. The decomposition was found to occur, but only very slowly, at 50°. The black residue dissolved in fluorosulfuric acid giving a blue-green color, indicating an impure sample of $IOSO_2F$. The volatile fraction contained sulfur trioxide and two volatile I(V) compounds, one of which was a colorless liquid at 25° and one a white solid, the latter being present only in small amount. The sulfur trioxide was distilled off under high vacuum at -20° to 0° over 20 hours. The liquid iodine (V) compound then distilled over at 10° over a period of 2 or 3 days leaving most of the white solid behind. By distillation at 10° the white solid could be only partially retained; to get a good separation, the distillation had to be repeated 4 times. Analysis of the white solid: Iodine, 19.57 % and sulfur 25.61 %. Calculated for $I(OSO_2F)_5$: I_2 = 20.395, sulfur 25.77. Although this indicates that the solid may have been $I(OSO_2F)_5$, the evidence does not constitute a proof of the existence of the compound. More work is needed. After 5 distillations, 1.5586 g of the colorless liquid was obtained. Iodine found 34.05%, calc. for $IF_3(SO_3F)_2$, 33.22%. The compound was distilled into an nmr tube. The F^{19} nmr spectrum at 40 megacycles like that of Roberts and Cady[5] consisted of a sharp signal for fluorine, bound to sulfur and a broad signal, caused by fluorine attached to iodine. The separation was 31.8 ppm contrasted to 30.6 for Roberts and Cady[5], and relative areas under the peaks in the spectrum were about 3.8 to 2 as compared to 4.5 to 2 found by Roberts and Cady[5]. The broad fluorine signal was resolved at approximately -10° into two different peaks of a separation of 152 cps and a ratio of the areas of 1:2. At approximately 40° the peak for fluorine attached to iodine was more sharp than at 25°.

Attempts to Prepare $I(OSO_2F)_5$. Unsuccessful attempts were made by two methods to prepare iodine (V) fluorosulfate. In one procedure iodine was allowed to react with $S_2O_6F_2$ in relative proportions of about 1 to 7 at 95°, 115° or 130°. Oxygen and $S_2O_5F_2$ were found as products. After removal of the volatile substances, a yellow material remained in which the oxidation state of iodine was close to 5 and the ratio of fluorosulfate to iodine (as shown by the ratio, weight of product to weight of iodine) was from 2:1 to 3:1. When the reaction occurred at 60°

in an nmr tube, even after 72 hours the principal product was $I(OSO_2F)_3$ and the excess $S_2O_6F_2$ had not decomposed. In the second procedure a mixture of sulfur trioxide with $IF_3(OSC_2F)_2$ in a molar ratio of 7 to 1 was held at 50 to 55° for several hours. A yellow oil was produced in which the oxidation state of iodine was 5 but the weight was much less than for iodine (V) fluorosulfate. The products included $S_2O_5F_2$ and $S_3O_8F_2$ (identified by infrared spectra). When the reactants were held together in an nmr tube for eight days the final spectrum indicated that a part of the fluorine originally bound to iodine had been removed but that the number of SO_3F groups attached to iodine had not increased. Probably an iodine (V) oxyfluorosulfate was formed.

Acknowledgements

The authors appreciate the assistance of B. J. Nist for running nmr spectra and thank Professor Howard Clark of the University of British Columbia for his assistance in using a Gouy balance at that institution.

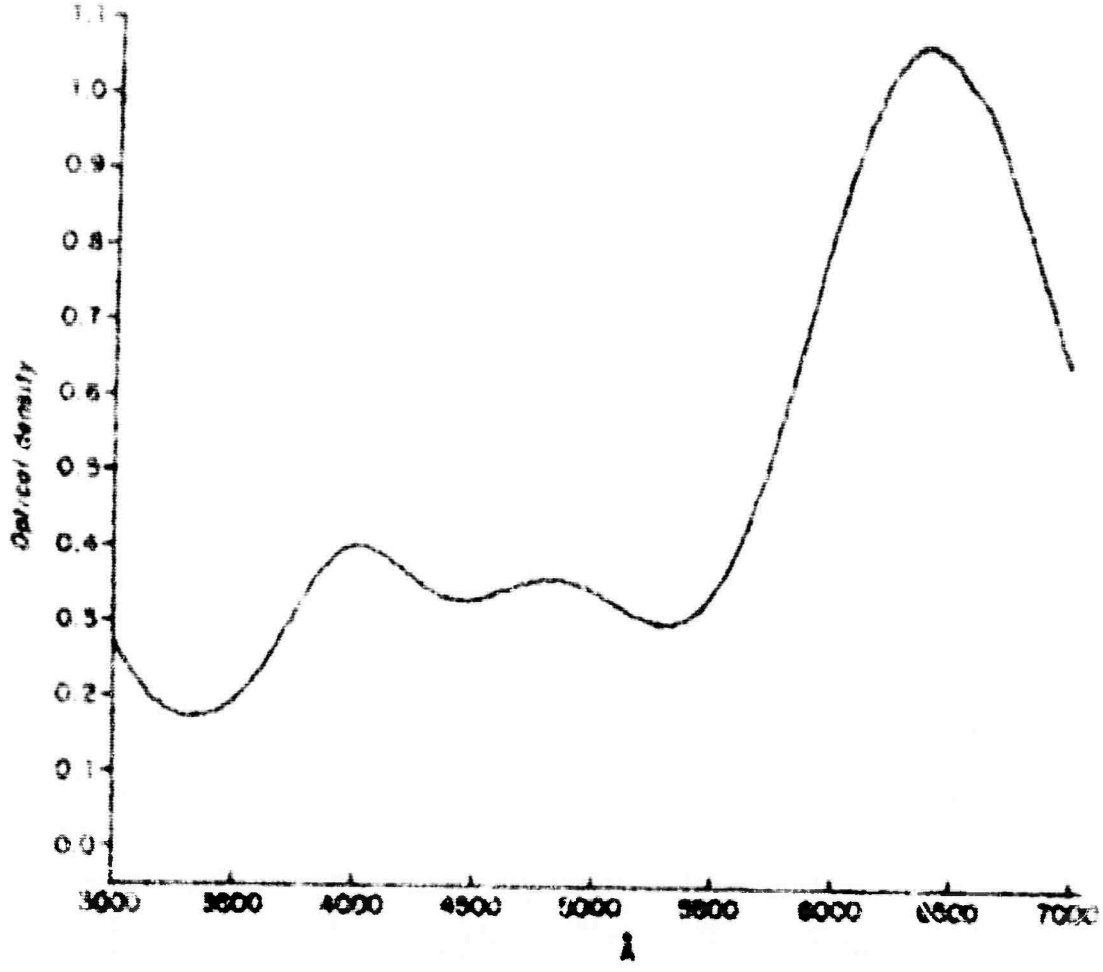

Fig. 1. Absorption spectrum of $IOSO_2F$ dissolved in fluorosulfuric acid.

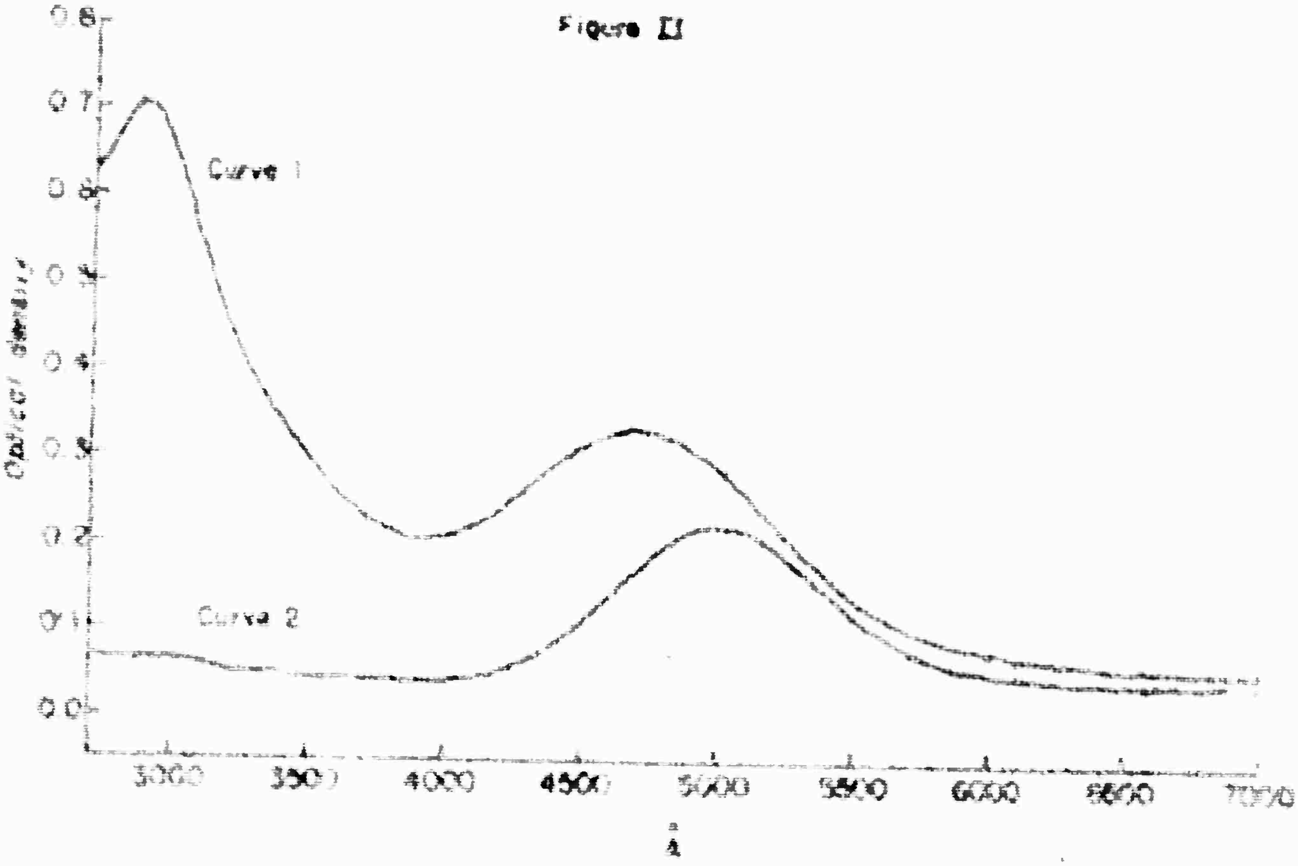

Fig. 2. Curve 1 is the absorption spectrum of I_3OSO_2F dissolved in fluorosulfuric acid. Curve 2 is the spectrum of I_2 in 96% sulfuric acid.

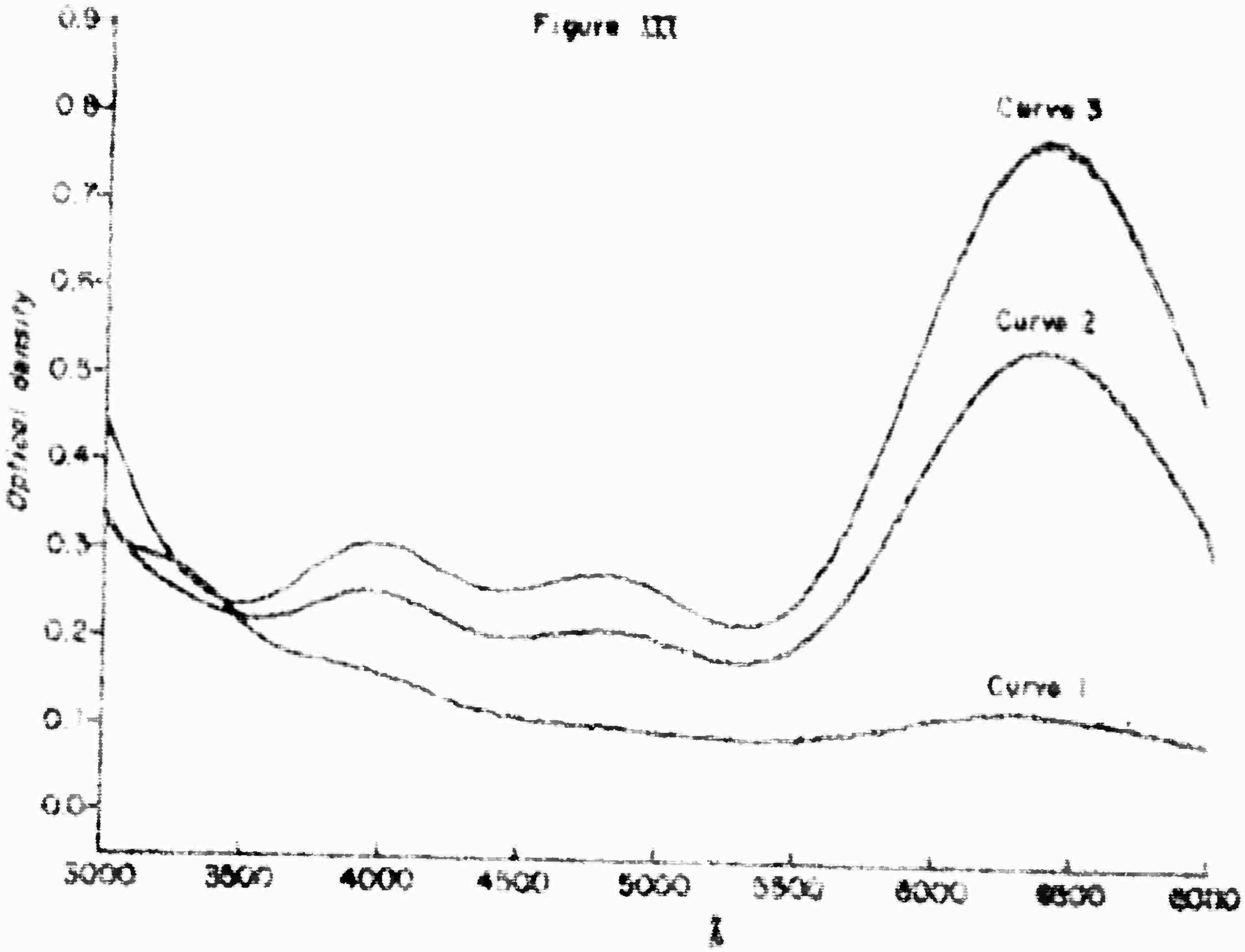

Fig. 3. Absorption spectrum of solution made by dissolving $I(OSO_2F)_3$ in fluorosulfuric acid at room temperature. Curve 1: after one-half hour. Curve 2: after 36 hours. Curve 3: after 60 hours. The change results from disproportionation of I(III) to give I(V) and I(I).

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IODYL FLUOROSULFATE

by Friedhelm Aubke*, George H. Cady and C.H.L. Kennard

Only a few inorganic compounds are known which contain the IO_2 group. Muir[1] prepared an addition compound, $I_2O_5 \cdot 2SO_3$, which was later formulated as $(IO_2)_2 S_2O_7$[2] and presumed to contain the cation IO_2^+. However, recent work of Gillespie and Senior[3] on solutions of HIO_3 in H_2SO_4 gave no evidence for IO_2^+ cations. Conductometric and cryoscopic measurements indicated that IO_2HSO_4 was present in a solvated and polymeric form. Iodyl fluoride[4,5] has been reported[6] not to combine with sulfur trioxide to form iodyl fluorosulfate.

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[1] M. P. P. Muir, J. Chem. Soc., 95, 656 (1909).

[2] H. A. Lehmann and H. Hesselbarth, Z. Anorg. Allgem. Chem., 299, 51 (1959).

[3] R. J. Gillespie and J. B. Senior, Inorg. Chem. 3, 440 (1964).

[4] E. E. Aynsley, R. Nichols and P. L. Robinson, J. Chem. Soc., 623 (1953).

[5] M. Schmeisser and K. Lang, Angew. Chem., 67, 156 (1955).

[6] E. E. Aynsley and S. Sampath, J. Chem. Soc., 3099 (1959).

Peroxydisulfuryl difluoride[7], a substance known to be a good reagent for preparing fluorosulfates[8,9] has now been used to prepare iodyl fluorosulfate from iodine pentoxide. The iodine pentoxide was first dried at 150°, pulverized and placed in a flat bottom reaction flask containing a Teflon coated stirring bar. The flask had a side arm ending at a break-seal and a neck ending at a ground joint by which it could be attached to a vacuum line. A large excess of peroxydisulfuryl difluoride, $S_2O_6F_2$, was transferred to the flask by distillation, then the neck of the flask was sealed shut while the vessel was cold and evacuated. The flask was then allowed to stand at room temperature for a week. During the first part of this period the formation of bubbles of a gas (later shown to be oxygen) was observed. After the formation of bubbles had stopped, the vessel was held at 65° for two hours while stirring. As the reaction occurred, the white I_2O_5 disappeared and was replaced by a solid powder having a light yellow color. Finally the reactor was attached to the vacuum line through the side arm and the excess of $S_2O_6F_2$ was distilled away through the break-seal into an evacuated cold trap. From 1.1056g of I_2O_5 the weight of the solid product obtained was 1.6995g. (Theoretical

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[7] F. B. Dudley and G. H. Cady, J. Am. Chem. Soc., 79, 513 (1957).

[8] J. E. Roberts and G. H. Cady, ibid, 82, 353 (1960).

[9] J. M. Shreeve and G. H. Cady, ibid, 83, 4521 (1961).

for IO_2SO_3F, 1.7080g.) The oxidation state of iodine in the compound was found to be five (5.04 observed) as shown by a Volhard determination of iodine and an iodometric determination of the oxidizing capacity.

Found: I, 48.9% ; S, 12.8% .

Theoretical for IO_2SO_3F: I, 49.19% ; S, 12.43% .

The reaction involved in the preparation was $I_2O_5 + S_2O_6F_2 = 2IO_2SO_3F + \frac{1}{2} O_2$.

The IO_2SO_3F was a pale yellow, very hygroscopic powder which was stable up to 100°. At 120° it reacted slowly with the glass container producing SiF_4, SO_3 and a colorless oil (probably $IF_3(SO_3F)_2$) containing 32.6% I. (Theoretical for $IF_3(SO_3F)_2$, 32.2%.) The above products distilled away under vacuum as the reaction occurred. A bright yellow material remained behind in the reactor.

Iodyl fluorosulfate reacted with the solvent when dissolved in $CFCl_3$, $CHCl_3$ or CCl_4. Chlorine was produced even at room temperature and the color changed from yellow to orange to red. The resulting solution had absorption maxima at 4600 and 3300 Å corresponding to ICl and Cl_2. An infrared spectrum of the volatile products indicated $S_2O_5F_2$, $COCl_2$ and CO_2. This behavior with the above solvents resembles that of ISO_3F and $I(SO_3F)_3$.[10] Iodyl fluorosulfate was substantially insoluble in fluorosulfuric acid but it dissolved readily with hydrolysis in water, the iodine remaining in the (V) oxidation state.

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[10] F. Aubke and G. H. Cady, This Journal

Finely crushed IO_2SO_3F was packed into a 0.5 mm Lindemann glass capillary inside a dry box. The tube was sealed with halcarbon wax and after removal from the dry-box was mounted in a large standard Philips powder camera (radius = 57.2956 mm) having the conventional Straumanis arrangement. After a twelve-hour exposure using nickel filtered copper X-radiation (λ_{K_α} = 1.54178 Å), over forty nine lines were observed and measured to within 0.05 mm. A second exposure of two hours was also made. The camera was calibrated with a thirty-minute exposure of a standard (sodium chloride, a = 5.63874 Å). Calculations showed the camera to have an effective radius of 57.208 ± 0.027 mm. Using the now calibrated IO_2SO_3F intense lines in the two-hour exposure, the twelve-hour exposure powder spectrum was measured and the radius correction applied. The results are listed in Table I. A sample of solid I_2O_5 gave a different powder spectrum and agreed with ASTM Inorganic X-ray Powder File 1962, p. 99, No. 1-0692.

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TABLE I

d Spacings From Lines in X-ray Powder Photograph

Å	Intensity	Å	Intensity	Å	Intensity	Å	Intensity
8.031	M	2.596	L	1.785	M	1.351	L
6.501	H	2.532	L	1.737	L	1.331	L
5.238	M	2.376	L	1.710	L	1.296	L
4.108	L	2.335	L	1.673	L	1.268	L
4.016	M	2.256	L	1.629	L	1.248	L
3.556	H	2.153	L	1.593	L	1.218	L
3.262	L	2.124	M	1.566	L	1.205	L
3.127	L	2.064	L	1.561	L	1.190	L
2.917	L	1.974	L	1.528	L	1.163	L
2.827	L	1.934	L	1.482	L	1.141	L
2.694	M	1.893	L	1.457	L	1.134	L
2.663	L	1.815	L	1.423	L	1.128	L
						1.078	L

H = High intensity

M = Medium intensity

L = Light intensity