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Iodine Fluorosulfates

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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 $I(OSO_2F)_5$.

Peroxydisulfuryl difluoride[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 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]

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 ICl,[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 break-seal 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 was heated for 1 hr. 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 2 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 ICl.[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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[1] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).
[2] J. E. Roberts and G. H. Cady, *ibid.*, **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, *ibid.*, **82**, 354 (1960).
[6] J. M. Shreeve and G. H. Cady, *ibid.*, **83**, 452 (1961).
[7] M. Lustig, Ph.D. Thesis, University of Washington, 1962.
[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).
[10] A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.* (London), **A124**, 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 $AgSO_3F$ and I_2 in CH_3CN as solvent and in the presence of pyridine also yielded an unstable product.[11]

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 an oxidizing agent).[12–17] The I^+ ion has also been produced by dissolving a little iodine in IF_5,[18] under certain conditions.

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 Figure 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.

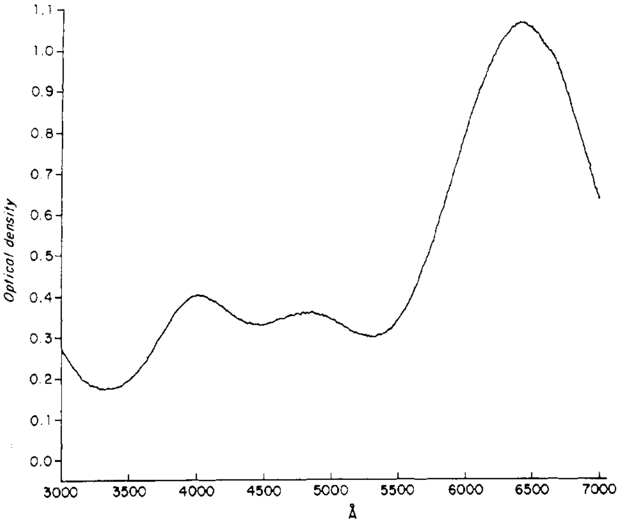

Figure 1.—Absorption spectrum of $IOSO_2F$ dissolved in fluorosulfuric acid.

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

TABLE I

SPECTRA OF SOLUTIONS CONTAINING I^+

Solvent	Solute	Absorption maxima, Å.			Ref.
65% oleum	I_2–SO_3	6400	5000	4100	12
65% oleum	ICl	6400	5000	3100	12
Oleum	I_2–SO_3	6480	5070	4130	18
IF_5	I_2	6410	5080	4180	18
IF_5	ICl	6450	5150	4200	18
HSO_3F	$IOSO_2F$	6380	4840	4040	

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 Masson,[19] when he dissolved I_2 and I_2O_5 in sulfuric acid and obtained a brown solution. 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] Spectrometric measurements by Symons, *et al.*,[16] led to the assignment of absorption maxima at 4600 and 2900 Å. 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 1 atm. pressure. After standing for 12 hr. 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 in dilute solution in fluorosulfuric acid in a cell of 1 cm. length gave the spectrum shown in Figure 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

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(11) H. Schmidt and H. Meinert, *Angew. Chem.*, **71**, 126 (1959).

(12) J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 12 (1951).

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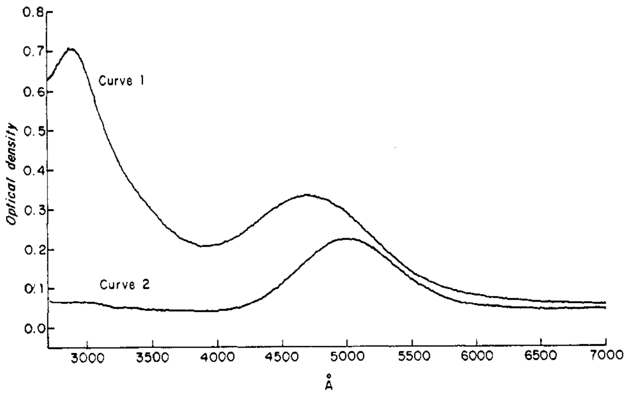

Figure 2.—Curve 1 is the absorption spectrum of I_3OSO_2F dissolved in fluorosulfuric acid. Curve 2 is the spectrum of I_2 in 96% sulfuric acid.

same spectrum as in HSO_3F. The results are given in Table II.

TABLE II

ABSORPTION SPECTRA DUE TO I_3^+

Solvent	Solute	λ, mμ	log (I_0/I)	λ, mμ	log (I_0/I)
HSO_3F	I_3OSO_2F	467	0.350	297	0.805
HSO_3F	I_2	474	0.324	297	0.692
96% H_2SO_4	I_3OSO_2F	462	0.335	290	0.705
96% H_2SO_4	I_2	502	0.230		
H_2SO_4	I_3^+ (ref. 16)	460		290	

These results indicate that I_3OSO_2F gave the I_3^+ ion in fluorosulfuric and 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 3:1 to form iodine fluorosulfates. Pure $IOSO_2F$ could therefore only be obtained by reaction of 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 off the excess of Cl_2. Upon warming, the last of the solid melted between 34 and 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 1 hr. Even by leaving solid $I(OSO_2F)_3$ at room temperature for 48 hr. 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 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.

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} n.m.r. 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.[6,24] A

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

[23] C. G. Vonk and E. H. Wiebenga, *Acta Cryst.*, **12**, 859 (1959).

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

reference sample of $IF_3(OSO_2F)_2$ was prepared by the reaction of $I(OSO_2F)_3$ with $FOSO_2F$ as described by Gilbreath.[25] The product was purified by repeated vacuum distillation. Technical grade fluorosulfuric acid was purified by distillation in apparatus like that of Thompson.[26] 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-Mc. oscillator. Ultraviolet and visible spectra were obtained with a Cary Model 14 spectrometer. Glass-stoppered quartz cells with 10 and 20 mm. path length were used. All samples for measurements were dissolved and poured into the cells in a drybox. 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.

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 break-seal 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. Peroxydisulfuryl 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 8 hr. A black solid was formed. The product was then heated in a water bath at 60° and left for 1 hr. 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 2 weeks glittering crystals had formed. While pumping on it at room temperature, the compound's weight remained almost constant. The final weight of the product was 1148.0 mg.

The solid melted sharply at 51.5° under vacuum. By heating at 100° under 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 solutions. Ultraviolet 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. *Anal.* Calcd.: I, 56.16. Found: I (Volhard method), 55.9.

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 hr. 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 was dissolved in 96% H_2SO_4 very readily to give a dark brown solution.

Dichlorofluorosulfatoiodine(III).—$IOSO_2F$ (1.4241 g.) 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 −50° in a trichloroethylene bath and stirred with a magnetic stirrer. A yellow solid formed. After 8 hr. 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 min. The remaining product changed in color to orange, and parts of it melted to an orange-red oil. The last solid melted between 34 and 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. *Anal.* Calcd. for ICl_2SO_3F: Cl, 23.88; I, 42.75; S, 10.81; total wt., 1.8710 g. Found: Cl, 23.45; I, 43.29; S, 11.13; total wt., 1.8803 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 1 hr. The product was a viscous dark green oil which was liquid at 20° and gave only a single peak in its n.m.r. spectrum.

Pyrolysis of $I(OSO_2F)_3$.—$I(OSO_2F)_3$ (6.55 g.) was decomposed in a closed system under vacuum and at a temperature between 80 to 90° over a period of 120 hr. 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 hr. 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 four times. *Anal.* Calcd. for $I(OSO_2F)_5$: I, 20.395; S, 25.77. Found: I, 19.57; S, 25.61. 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 five distillations, 1.5586 g. of the colorless liquid was obtained. *Anal.* Calcd. for $IF_3(SO_3F)_3$: I, 33.22. Found: I, 34.05. The compound was distilled into an n.m.r. tube. The F^{19} n.m.r. spectrum at 40 Mc. 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 p.p.m. contrasted to 30.6 p.p.m. 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 c.p.s. and a ratio of the areas of 1:2. At approximately 40° the peak for fluorine attached to iodine was sharper than at 25°.

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(25) W. P. Gilbreath, Ph.D. Thesis, University of Washington, 1962.

(26) R. C. Thompson, Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada, 1962.

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 n.m.r. tube, even after 72 hr. 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 $IF_3(OSO_2F)_2$ 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 n.m.r. tube for 8 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.

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The Reaction of Diphenylchlorophosphine with Ammonia-Free Chloramine

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The reaction of diphenylchlorophosphine with ammonia-free chloramine in diethyl ether yields $(C_6H_5)_2P(NH_2)(Cl)NHP(Cl)_2(C_6H_5)_2$. When this compound is pyrolyzed $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$ are formed in high yield. Hydrolysis gives $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$ and $(C_6H_5)_2P(O)NP(Cl)(C_6H_5)_2$. Ammonolysis gives the known compound $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$.

In a previous paper[1] the reaction of diphenylchlorophosphine with a gaseous mixture of chloramine and excess ammonia was described. Since the postulated course of this reaction involved ammonolysis of the halophosphine, followed by addition of the chloramine to the aminophosphine, and the subsequent condensation to the phosphonitrile by loss of ammonium chloride, it was considered of interest to study the reaction of diphenylchlorophosphine with chloramine in the absence of ammonia and to compare the intermediates and final products obtained with those obtained when the presence of ammonia brings about ammonolysis of the phosphorus–halogen bond. Furthermore, the complete absence of ammonia or other strong base in the system should make it possible to draw interesting implications concerning the nature of the chloramination reaction.

Experimental

Materials.—Diphenylchlorophosphine, obtained from the Victor Chemical Works, was redistilled under vacuum immediately before use.

The gaseous mixture of chloramine and excess ammonia was produced by the gas phase reaction of chlorine with an excess of ammonia in a generator of the type described by Sisler and Omietanski[2] and was freed of ammonia using anhydrous copper sulfate, as described below.

All solvents were redistilled and kept over an appropriate drying agent, usually calcium hydride.

Handling operations were carried out in either a drybox or a dry polyethylene bag, under an atmosphere of dry nitrogen. All reaction apparatus was flushed with dry nitrogen before use.

Elementary analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Nitrogen and chlorine analyses were also checked by the authors. All melting points are uncorrected.

Preparation of Anhydrous Ammonia-Free Chloramine Solutions.—A gaseous mixture of chloramine and ammonia, produced by the gas phase reaction of chlorine with an excess of ammonia,[3] was introduced into the solvent, cooled in an ice–salt bath, until approximately the desired concentration of chloramine was obtained. The solution was warmed to room temperature to decrease the ammonia content and then passed through a column of anhydrous copper sulfate. The copper sulfate had previously been dried at over 500° and the column dimensions were chosen with regard to the volume of solutions used, a column approximately 2 in. in diameter and 3 in. long being sufficient for 250 ml. of solution using a flow rate of about 50 ml./min. or greater. The fast flow rate is desirable since the chloramine slowly reacts with the copper sulfate. This is shown by the observation of a green color in the column below the deep blue region of ammonia absorption, by the evolution of a colorless, odorless gas, presumably nitrogen, and by a decrease in the chloramine content of the solution during its passage through the column.

The absence of ammonia in the effluent solution was shown by extracting samples of that solution with water and measuring the pH of the aqueous extract. In each case pH values between 6.5 and 7.0 were obtained.

The chloramine solutions were allowed to stand over Linde Molecular Sieve; Type 4A was used since this absorbs water but not ammonia or chloramine. The solutions were sampled at regular time intervals. The chloramine content was determined by pipetting a 10-ml. sample into a mixture of 25 ml. of acidified potassium iodide solution and 10 ml. of chloroform. The mixture was then titrated with standard sodium thiosulfate solution, with vigorous shaking, until the color in the chloroform layer was discharged. In all solvents tried (diethyl ether, benzene, and tetrachloroethane) the concentration of chloramine decreased with time. Data for a typical experiment in diethyl

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[1] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

[2] H. H. Sisler and G. Omietanski, *Inorg. Syn.*, **5**, 91 (1957).

[3] H. H. Sisler and R. Mattair, *J. Am. Chem. Soc.*, **73**, 1619 (1951).