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The Iodine–Peroxydisulfuryl Difluoride System

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Melting points for the system I_2–$S_2O_6F_2$ confirm the previously known solid compounds $I(SO_3F)_3$, ISO_3F, and I_3SO_3F. A new compound, I_7SO_3F, is also established. High viscosity over most of the range of composition indicates polymerization in the liquid state.

Introduction

The existence of yellow $I(SO_3F)_3$ was established by Roberts and Cady[1] by allowing an excess of peroxydisulfuryl difluoride, $S_2O_6F_2$, to react with iodine. Evidence was also obtained for fluorosulfates of iodine in oxidation states below three. Two solid and black compounds of this type, ISO_3F and I_3SO_3F, were later prepared by Aubke and Cady[2] by using reaction temperatures of 60 and 85°, respectively. Roberts and Cady had obtained complete conversion of iodine to $I(SO_3F)_3$ by the action of $S_2O_6F_2$ in excess at room temperature but had not obtained complete reaction when an excess of iodine was used. Higher temperature was needed.

Symons[3–7] and his coworkers have accumulated considerable evidence for the ions I^+, I_3^+, and I_5^+ in oleum as a solvent. The latter two ions give solutions having a brown color. I^+ is reported to be blue. Gillespie and his coworkers have obtained good evidence, however, that the blue color is due to I_2^+ rather than I^+. The reaction of $S_2O_6F_2$ with I_2 in fluorosulfuric acid has been used by Gillespie and Milne[8] to produce I_2^+, I_3^+, and I_5^+ ions. Evidence for these species and for the absence of I^+ is good. The I_2^+ ion in fluorosulfuric acid has been shown by Gillespie, Milne, and Morton[9] to dimerize at about $-40°$ and below, to give red-brown I_4^{2+}. Gillespie and Malhotra[10] have shown that the blue species in oleum or disulfuric acid is I_2^+ rather than I^+. Gillespie and Milne[11] have confirmed the finding[1,2] that the action of $S_2O_6F_2$ in excess upon I_2 gives $I(SO_3F)_3$ but not the higher fluorosulfate, $I(SO_3F)_5$.

Since studies of solutions establish the existence of I_2^+ and I_5^+ ions, for which no corresponding fluorosulfates have been reported, investigation of the complete I_2–$S_2O_6F_2$ system is desirable.

Experimental Section

Materials.—Iodine of analytical grade was held under vacuum while being in part evaporated away to remove possible volatile impurities. The remaining solid was used without further purification. Peroxydisulfuryl difluoride, $S_2O_6F_2$, was prepared by the method of Dudley and Cady[12] as described by Shreeve and Cady.[13] It was refined by being passed as a vapor under vacuum through traps at $-78°$ and $-183°$. The material collected at $-78°$ was then condensed as a solid in the upper portion of a glass trap having a sealed sintered disk near the bottom. As the trap was allowed to warm slowly, the solid began to melt and the resulting liquid passed through the disk and was then removed from the bottom of the trap through a capillary tube. A slow stream of dry nitrogen passed through the trap and carried the liquid out through the capillary. As the temperature of the bath surrounding the trap slowly rose from -56 to $-51.5°$, a substantial fraction of the material melted and was removed. Material remaining as solid when the bath reached $-51.5°$ was transferred to a storage vessel equipped with a glass valve having a Teflon stem. This refined sample was later found to contain some $S_2O_5F_2$ as an impurity. It will be shown later that this contaminant could be removed after allowing the product to react with iodine.

Determination of Melting Points.—The melting points of I_2 and of $S_2O_6F_2$ were determined using several grams of solid contained in a closed glass vessel equipped with a well holding a copper–constantan thermocouple which had been carefully calibrated at the condensing temperature of steam and the subliming temperature of carbon dioxide. The material was observed while being shaken as the temperature rose slowly. The sample of iodine melted sharply with the last crystals melting at $113.6 \pm 0.1°$. This agreed with the value of Frederick and Hildebrand,[14] indicating the material to be pure. Peroxydisulfuryl difluoride appeared to start melting at $-54°$ and to be about half melted at $-53.4°$. It became completely liquid at $-52.7°$. From this evidence it appears that the sample was not 100% pure and that pure $S_2O_6F_2$ would have a melting point close to $-52.0°$. This value should be regarded as better than that ($-55.4°$) reported by Dudley and Cady.[12]

An attempt was made to study the system by use of cooling curves. This was found to be an unsatisfactory procedure, because of large supercooling before onset of freezing. Nearly all of the satisfactory temperatures were obtained by slowly warming the sample while held in a closed glass vessel immersed in a bath of liquid. The sample was shaken by hand, and the temperature of the bath at the time of disappearance of the last crystals was taken as the melting point. Temperatures were taken with a thermometer calibrated against the copper–constantan thermocouple. The rate of warming the sample near its melting point was normally about 0.1°/min. At least two measurements of the melting point were made for each composition. Since this was a difficult system to study, the temperatures given in Table I are probably not accurate to the nearest 0.1° as suggested by the data. For example, irregular variations reported over the mole fraction range from about 0.83 to 0.95 are probably due to experimental error. There does, however, appear to be a real decrease of about 1.5° over this range.

Since the liquid mixtures of mole fraction below about 0.73 were opaque and substantially black in color, it was difficult to observe crystals when only a few were present. The procedure employed was to tip the vessel onto its side in the bath and slowly bring it back to upright position. As the liquid flowed along the wall the crystals could be seen.

Samples having a mole fraction of $S_2O_6F_2$ below 0.73 were held at 90–94° for 1 hr before being chilled to obtain crystals. Those

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TABLE I

MELTING POINTS OF THE SYSTEM I_2–$S_2O_6F_2$

Mole fraction of $S_2O_6F_2$	Mp, °C	Mole fraction of $S_2O_6F_2$	Mp, °C	Mole fraction of $S_2O_6F_2$	Mp, °C
0.0000	113.6	0.337	78.5	0.758	33.3
0.0172	110.8	0.354	68.5	0.765	31.0
0.0362	108.4	0.374	54.2	0.776	28.8
0.0495	106.0	0.389	40.1	0.795	25.2
0.0788	99.1	0.404	36.6	0.793	25.0
0.0947	93.5	0.421	26.5	0.803	22.3
0.111	89.7	0.434	32.7	0.812	20.9
0.119	90.2	0.452	39.6	0.833	17.8
0.125	90.5	0.472	45.6	0.835	17.9
0.131	90.3	0.485	48.7	0.852	17.7
0.137	90.2	0.499	50.2	0.872	17.8
0.147	89.7	0.515	49.8	0.874	16.0
0.157	88.5	0.529	48.4	0.877	17.9
0.159	86.3	0.567	39.9	0.889	15.7
0.177	84.3	0.574	38.4	0.897	17.8
0.184	84.1	0.617	26.9	0.905	15.5
0.193	87.7	0.627	22.8	0.924	15.4
0.209	94.5	0.645	18.5	0.925	16.8
0.229	99.1	0.683	14.3	0.952	17.0
0.244	101.3	0.700	20.9	0.966	15.9
0.250	101.5	0.703	20.5	0.975	7.9
0.261	101.2	0.724	26.9	0.987	1.0
0.276	99.2	0.737	32.4	0.997	−10.8
0.311	91.8	0.746	32.7	0.998	−23.0
0.326	85.6	0.753	33.7	1.00	(−52.0)

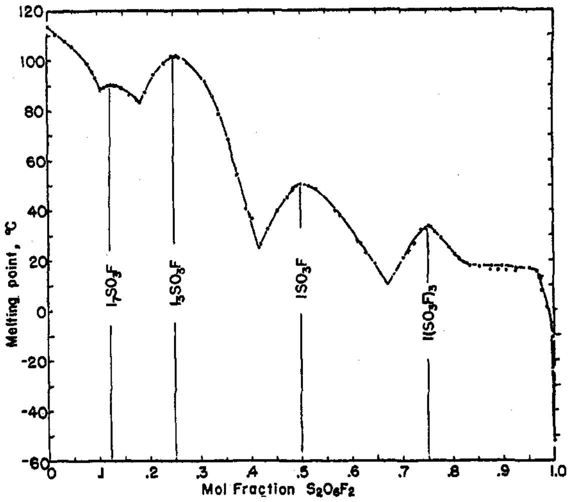

Figure 1.—The system I_2–$S_2O_6F_2$.

samples having melting points above 94° were held at temperatures just above their melting points. This treatment allowed all of the iodine to react. Since $I(SO_3F)_3$ can be formed readily at room temperature and since it is known to decompose when heated,[2] samples of mole fraction above 0.73 were first held at 30° for 30 min and after that were stored at −78° and only allowed to become warm when their melting points were being determined.

Preparation of Samples.—Iodine and $S_2O_6F_2$ were handled on a vacuum line and were distilled into a 70-ml glass bulb used for observing melting points. The bulb could be closed by a Fischer and Porter Lab Crest valve having a Teflon stem, and the amounts of the materials were established by weighing the bulb. Most of the range of composition was covered by starting with a weighed portion of iodine (about 3 g for example) and later adding $S_2O_6F_2$ in increments with a determination of melting point after each addition. Most of the samples had total volumes of about 1–4 ml. Over the range of mole fraction from about 0.1 to 0.8 the liquids were very viscous and in many cases the formation and growth of crystals was slow. In Figure 1, no points are shown near the eutectic at mole fraction 0.669. Mixtures near this composition could not be persuaded to crystallize.

As increasing numbers of increments of $S_2O_6F_2$ were added, it became apparent that a small amount of a volatile material was building up in the glass bulb. With the sample of iodine fluorosulfate in frozen condition one could see a small amount of colorless fluid liquid on the solid. With the bulb at −183°, no material could be removed by vacuum pumping. This indicated the absence of O_2. When the bulb was then held at 0°, the colorless volatile liquid could be easily distilled away. Several tests showed it to have a weight of about 1.5% of that of the $S_2O_6F_2$ consumed. The infrared spectrum of the material was that of $S_2O_5F_2$. Since no oxygen was produced, it is apparent that this material was present in the $S_2O_6F_2$ as an impurity. It became a routine part of the procedure to remove the $S_2O_5F_2$ after adding $S_2O_6F_2$ and allowing it to react. The weight of $S_2O_5F_2$ so removed was not counted as a part of the $S_2O_6F_2$ present in the system. It was found that the presence of a small amount of $S_2O_5F_2$ had very little effect upon the melting points of iodine fluorosulfates and their mixtures, presumably because the $S_2O_5F_2$ was mostly present in the vapor phase.

^{19}F Nmr Spectra.—Nmr spectra of liquid mixtures were observed using a Varian HR 60 spectrometer operating at 56.4 MHz. Samples which were liquid at room temperature were studied at this temperature. Those which were solid at room temperature were run at 110°. Fluorotrichloromethane was used as an external standard.

Results

Melting Points.—Table I gives the observed melting points. These are represented in Figure 1. A summary of eutectic points and of melting points of substances is given in Table II. Eutectic temperatures are estimated to the nearest degree. The only new compound in the list is I_7SO_3F. Melting points given for the other compounds probably are more nearly correct than those reported previously.

TABLE II

MELTING POINTS AND EUTECTIC POINTS

Substance	Mp, °C	Eutectic, °C	Mole fraction of $S_2O_6F_2$
I_2	113.6	89	0.107
I_7SO_3F	90.5	83	0.181
I_3SO_3F	101.5	21	0.414
ISO_3F	50.2	8	0.669
$I(SO_3F)_3$	33.7	−52	0.999
$S_2O_6F_2$	−52.0		

^{19}F Nmr Spectra.—Chemical shifts for liquids of various compositions are given in Table III. At mole fractions of $S_2O_6F_2$ greater than 0.75, two sharp peaks were observed. One at about −39 ppm was due to $S_2O_6F_2$. The other at about −46 ppm was due to iodine(III) fluorosulfate. The chemical shift for supercooled pure iodine(III) fluorosulfate was −46.4 ppm both at room temperature and at 0°. No peak was observed at −78°. For mole fractions of $S_2O_6F_2$ of 0.753 and below, only a single peak was present and it was rather broad. The chemical shift was dependent upon concentration.

TABLE III

^{19}F NMR SPECTRA OF MIXTURES MADE FROM I_2 AND $S_2O_6F_2$

Mole fraction of $S_2O_6F_2$	Chemical shift, ppm (from external $CFCl_3$)	Mole fraction of $S_2O_6F_2$	Chemical shift, ppm
At room temperature		At about 110°	
0.753	−46.4	0.664	−47.5
0.774	−46.3, −39.4	0.493	−45.7
0.810	−46.3, −39.1	0.467	−45.4
0.876	−45.4, −38.8	0.267	−41.0
0.908	−45.3, −38.7	0.133	−45.3
1.00	−38.5		

Magnetic Measurements.—Some of the samples for the above nmr spectra were also used to learn whether the materials were paramagnetic. Additional similar samples were also employed so that mixtures having the following mole fractions were studied at room temperature: 0.664, 0.580, 0.493, 0.463 0.413, 0.328, 0.283, 0.267, 0.179, and 0.133. All of these materials were slightly repelled by a magnet. None were paramagnetic.

Infrared Spectra.—Infrared spectra were observed for the thin films of samples held between windows of the following materials: AgCl, NaCl, KBr, polyethylene, and BaF_2. In general, the spectra were not regarded as satisfactory, principally because of the high reactivity of the iodine fluorosulfates. Results are reported in the Ph.D. thesis of Chung.[15] For frequencies above about 800 cm^{-1}, the cutoff limit, spectra obtained with BaF_2 windows were good. Data for supercooled samples of liquid $I(SO_3F)_3$ and ISO_3F at room temperature are given in Table IV.

TABLE IV

INFRARED BANDS FOR LIQUID ISO_3F AND $I(SO_3F)_3$ USING BaF_2 WINDOWS

Frequency,[a] cm^{-1}		
For ISO_3F	For $I(SO_3F)_3$	Assignment
1395	1390 s, br	SO_3 asym str
1200	1195 s, br	SO_3 sym str
960	985 m	
800–880	895 br	SF str

[a] Key: s, strong; br, broad; m, medium; str, stretching.

Discussion

The maxima in Figure 1 confirm the existence of $I(SO_3F)_3$, ISO_3F, and I_3SO_3F which have been reported previously. A new compound, I_7SO_3F, also is indicated. There is no evidence for a solid of the composition, I_2SO_3F. Since all samples in the range of mole fractions from 0.133 to 0.664 were diamagnetic, one can conclude that molecular or ionic species containing unpaired electrons were absent. If I_2^+ were present, one would expect it to be paramagnetic and to have its maximum concentration at a mole fraction of $S_2O_6F_2$ of about 0.33. The fact that this species was not present, should not be interpreted to mean that I_2^+ ion does not exist in oleum or other suitable solvent. Species present in the I_2–$S_2O_7F_2$ system probably are covalent, therefore it is not surprising that the ion I_2^+ is absent.

Infrared spectra of ISO_3F and $I(SO_3F)_3$ are similar to those of other covalent fluorosulfates but differ from the spectrum of SO_3F^- found in KSO_3F.[16]

Liquid iodine has a much lower viscosity than the iodine fluorosulfates. Upon the addition of $S_2O_6F_2$ to I_2, the viscosity increased and became very high as the mole fraction of $S_2O_6F_2$ approached 0.33. It remained very high for liquids of mole fraction through 0.75 and then decreased as more $S_2O_6F_2$ was added. Liquid $S_2O_6F_2$ has low viscosity. For all samples, the viscosity decreased with rising temperature. Samples having mole fractions below about 0.80 when existing as liquids at 25° had the consistency of cold honey. It is probable that the high viscosities were caused by polymerization of the iodine fluorosulfates. Carter, Jones, and Aubke[17] have studied Raman spectra of $I(SO_3F)_3$ and $Br(SO_3F)_3$ and have interpreted the spectra to be indicative of polymerization of the compounds, probably by bridging through fluorosulfate groups.

Freezing points of the most dilute solutions of $S_2O_6F_2$ in I_2 may be used to obtain an approximate molecular weight of the solute by using a freezing point lowering constant of 20.3° per mole of solute in 1000 g of iodine. The constant corresponds to the heat of fusion of iodine of 3740 cal/mol reported by Frederick and Hildebrand.[14] The point at mole fraction 0.0172 corresponds to molecular weight 99 while that at mole fraction 0.0362 corresponds to a molecular weight of 114. While these values should not be regarded as precise, it is clear that each mole of $S_2O_6F_2$ (mol wt 198) has given rise to 2 mol of solute. The dissolved species contains one fluorosulfate group per molecule.

The vapor phase above iodine at its melting point has an intense violet color due to I_2 molecules. The dilute solutions of $S_2O_6F_2$ in I_2 also are in equilibrium with violet vapor. As the mole fraction of $S_2O_6F_2$ is increased, the intensity of the violet color decreases but is still easily observed above liquid I_7SO_3F. By the time that the composition of I_3SO_3F is reached, the violet color (at the melting point) has essentially vanished. These observations are consistent with the experience of Aubke[2] who allowed an excess of I_2 to react with $S_2O_6F_2$ at 85° and later pumped away I_2 vapor at room temperature until the solid reached a constant weight corresponding to I_3SO_3F. Apparently he was able to pump I_2 away from I_7SO_3F, but not from I_3SO_3F.

From mole fraction 0.83–0.95 the melting point changed very little. This suggested the possible presence of two liquid phases. Mixtures in this range were examined with great care and none of those persons who looked could see two liquids. The progressive change in viscosity of the liquid mixture as a whole over this range also indicated only one liquid phase. The authors are convinced that only one liquid phase was present. The solid which formed upon cooling the solutions in this range of composition consisted of rather large yellow crystals. To confirm the evidence of Figure 1, that they were crystals of $I(SO_3F)_3$, a mixture having mole fraction 0.895 was allowed to partially crystallize. The liquid was then removed from the solid by filtering with a centrifugal filter under anhydrous conditions. Analysis of the resulting crystals (somewhat contaminated with the liquid phase) showed them to be $I(SO_3F)_3$. *Anal.* Calcd for $I(SO_3F)_3$: I, 29.9; S, 22.6; F, 13.4. Found: I, 28.9; S, 23.6; F, 13.6.

Over the range of composition from mole fraction 0.83 to 0.95 the fluidity increased as the concentration of $S_2O_6F_2$ increased. Depolymerization of iodine(III) fluorosulfate must have occurred as the proportion of $S_2O_6F_2$ increased. In spite of this, the activity of the molecular species present in solid iodine(III) fluorosulfate must not have changed much with concentration, because the melting point was almost constant. The following explanation may possibly account for this behavior. (1) Solid iodine(III) fluorosulfate may consist of small molecules, possibly $I_2(SO_3F)_6$. (Solid ICl_3 is reported to be a dimer.[18]) (2) Over the range from mole fraction 0.83 to 0.95 the

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[15] C. Chung, Thesis, University of Washington, Seattle, Wash., 1971.

[16] J. Gobeau and J. B. Milne, *Can. J. Chem.*, **45**, 2321 (1967).

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activity of $I_2(SO_3F)_6$ in the liquid phase remains essentially constant as dilution causes the higher polymer(s) to dissociate.

$I(SO_3F)_3$ is yellow in both the solid and liquid states. The sample of mole fraction 0.746 was green. Samples of smaller mole fraction appeared in bulk to be black, but thin films showed some green color down to mole fraction 0.53. Below this concentration, thin films were dark brown.

Over much of the range of composition the liquid had little tendency to wet the glass container. A film might flow from the wall completely or it might leave isolated drops of liquid.

Since the reaction of I_2 with $I(SO_3F)_3$ or ISO_3F is slow at room temperature and since many samples were heated to obtain complete reaction, it seems likely that subsequent cooling to obtain melting points carried the materials to temperatures low enough to prevent existence of true equilibrium among molecular species at some of the observed melting points. It is not certain that this was the case, however, and it seems likely that the observed melting ponts were close to those which would have been obtained at true equilibrium. Nmr spectra taken at 110° contained only one line, thereby indicating a rather rapid exchange among molecular species at this temperature. The line was rather broad.

Materials listed in Table I at mole fractions 0.131, 0.250, 0.499, and 0.753 had compositions close to those of the iodine fluorosulfates listed in Table II. In each case the observed range of melting for these samples was about 1.5° with most of the material melting close to the indicated melting point. Compositions of eutectic mixtures and the corresponding eutectic temperatures given in Table II were taken from the graph of melting point *vs.* composition (Figure 1). For each of the first three eutectics the onset of melting of mixtures of nearby composition was observed to be close to the temperature given in Table II. The eutectic point listed as −52° really was not observed. From the data of Table I, it appears that the mole fraction of $S_2O_6F_2$ at the eutectic point was 0.999 or more. The eutectic temperature must be only slightly below the melting point of pure $S_2O_6F_2$, which is listed as −52.0°, the value discussed above in the Experimental Section.

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Chemistry of Bis(fluoroformyl) Peroxide. Isomerization and Disproportionation

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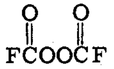
Bis(fluoroformyl) peroxide was shown to isomerize to the ozonide of the unknown difluoroketene. The isomerization was effected at low temperature with either activated KF or trimethylamine and was shown to be reversible. Strong bases, such as CsF and trimethylamine, also catalyzed the disproportionation of $C_2F_2O_4$ to bis(trifluoromethyl) bis(peroxy)carbonate, $(CF_3OO)_2CO$, and trifluoromethyl fluoroformyl peroxide, CF_3OOCOF. These reactions constitute new syntheses for these compounds. Fragmentation patterns are reported for all peroxides studied in this work as well as infrared data.

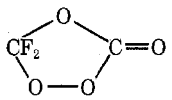
Introduction

Much of the chemistry of bis(fluoroformyl) peroxide (I)[1] has been devoted to the elucidation of its reaction chemistry as a radical source.[2-5] One of the more interesting of these reactions was the complex, low-yield reactions of I with difluorodiazone to give fluoroformyl perfluoromethyl peroxide.[5] As part of a study of acyl fluorides we were interested in both the conversion of the —C(O) F moiety to the CF_3O group and the reactions of I with Lewis bases. Indeed, the action of bases such as alkali fluorides on I have given two distinct sets of products depending on the strength of the base. With a weak base such as KF, I is converted to the ozonide of difluoroketene, 3,3-difluoro-2,4,5-trioxacyclopentanone (II). Strong bases, such as CsF, cause the peroxide (I) to disproportionate in high yields to peroxide III and to bis(trifluoromethyl) bis(peroxy)carbonate (IV).



$F\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}F$

I



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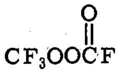
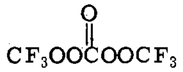


$CF_3OO\overset{\overset{O}{\|}}{C}F$

III



$CF_3OO\overset{\overset{O}{\|}}{C}OOCF_3$

IV

Experimental Section

Apparatus and Materials.—Reactions were conducted in stainless steel cylinders and the products were separated and purified using a stainless steel–Teflon FEP vacuum line. Pressures were measured by means of a Heise Bourdon tube pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained using a Varian Associates high-resolution nmr spectrometer

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