TRIFLUOROMETHANESULFONATES OF IODINE

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Abstract

The investigation of iodine trifluoromethanesulfonates was initiated by the synthesis of $I(SO_3CF_3)_3$ via the reaction:

$$I_2 + 6HSO_3CF_3 + 3S_2O_6F_2 \xrightarrow{HSO_3CF_3} 2I(SO_3CF_3)_3 + 6HSO_3F$$

Isolation of iodine(III) tristrifluoromethanesulfonate was possible because of the very low solubility of the compounds in the acid mixture. The yellow white solid proved to be free of fluorosulfate.

The compound was used subsequently in the synthesis of salts of the general formula,

$M^I[I(SO_3CF_3)_4]$, with M^I = K, Rb, or Cs, using HSO_3CF_3

as the reaction medium. Alternate routes to the tetrakis (trifluoromethanesulfonate) iodate(III) compounds were also realized.

Reduction of $I(SO_3CF_3)_3$ by an equimolar amount of I_2 at elevated temperature in a sealed tube resulted in the formation of iodine(I) trifluoromethanesulfonate. Poly iodine compounds of the type $I_nSO_3CF_3$ with n = 3,5 or 7 could not be obtained.

The addition of Br_2 to ISO_3CF_3 resulted in the formation of the dibromoiodonium trifluoromethanesulfonate, $IBr_2SO_3CF_3$. Other triatomic interhalogen polyhalogen cations such as ICl_2^+ or I_3^+ could only be produced in solutions of HSO_3CF_3. The solvolysis of ISO_3CF_3 in HSO_3CF_3 was found to lead to blue solutions containing the I_2^+ cation.

Attempts to prepare abromine(III) trifluoromethanesulfonate via three different routes, solvolysis of $BrSO_3F$ in HSO_3CF_3, solvolysis of BrF_3 in HSO_3CF_3 and oxidation of Br_2 in HSO_3CF_3 with $S_2O_6F_2$, were unsuccessful. The usual result was a violent detonation of the reaction mixture.

The synthesis of iodyl trifluoromethanesulfonate, $IO_2SO_3CF_3$, was effected by reacting HI_3O_8 and HSO_3CF_3. Similarly iodosyl trifluoromethanesulfonate was obtained from I_2 and HI_3O_8 in HSO_3CF_3. Based on the results of vibrational spectroscopy, $IOSO_3CF_3$ is thought to be made up of discrete IO units bridged by SO_3CF_3 groups.

Structural studies based on infrared and Raman spectroscopy were undertaken on all the products mentioned. In addition the previously synthesized compound $CF_3SO_3CF_3$ was also studied as an example of a monodentate SO_3CF_3 group.

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Acknowledgements

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I. Introduction

From a first year general chemistry text the following description of the halogens is taken[1]:

> "The halogen atoms all have seven electrons in their outer shell and are followed, in each case, in the periodic table by a noble gas. Consequently their most stable oxidation number is -1. All the halogens except fluorine are known to exist in several oxidation states."

This preliminary definition is followed by a descriptive chemistry of the halogens which is exclusively the chemistry of the halides, X^-. Most first year chemistry students when asked to describe the chemistry of the halogens respond with a description of halide chemistry. Very few are aware of the positive character which all halogens except fluorine can and do display. Since the compounds synthesized here are all cationic halogen compounds, a short introduction of the subject is in order.

Cationic halogen compounds are ones in which the halogen X can be considered to have a positive oxidation number, either 1, 3, 5 or 7 and to occupy formally a cationic position. An example is chlorine nitrate, $ClNO_3$, where in analogy to potassium nitrate KNO_3 the chlorine occupies the cationic position. In general the halogen will not exist as a true cation as found in an ionic compound but rather it will be the positively polarized part of a covalent molecule of general formula $\overset{\delta+}{X}-\overset{\delta-}{Y}$ or in the example $\overset{\delta+}{Cl}-\overset{\delta-}{ONO_2}$ rather than $K^+ NO_3^-$. There are several important consequences of this covalent nature of cationic halogen compounds which may result:

a) The compounds may be volatile, in particular when the halogen is chlorine.

b) The symmetry of the "anion" may be reduced (e.g. for NO_3^- D_{3h} to C_{2v} or even lower)

c) hydrolysis of the compound will be complex resulting in more than just simple ion formation.

$$\text{e.g. } NaNO_3 \xrightarrow{H_2O} Na^+ (solv) + NO_3^- (solv) \quad (1)$$

$$ClNO_3 \xrightarrow{H_2O} 2H^+ (solv) + NO_3^- ClO^- \quad (2)$$

The halogen most likely to form cationic halogen compounds is iodine (with the possible exception of astatine*). This is apparent from the electronegativities of the halogens listed in table 1. On purely electronegativity grounds positively polarized iodine is expected for bonds with the following: the halogens Br, Cl and F; the chalcogenides Se, S and O; the group V element N and the group IV element C. For bromine and chlorine only F, O and N remain as potential partners. Fluorine, as expected from its electronegativity has not been found to form any cationic halogen compounds.

In spite of a wide array of possible anion sources in practice only oxygen, the halogens themselves, and a to a limited extent nitrogen have been found to produce binary cationic halogen compounds. The compounds are the interhalogens, halogen oxides, and halogen nitrides. Only the first two categories will be discussed.

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*Astatine should have a greater cationic tendency than Iodine, however, its very short half life, only 8.3 hours for the most stable isotope, has prevented any detailed chemical investigation.

TABLE 1

Allred-Rochow Electronegativities* for selected Elements

Group	IV A	V A	VI A	VII A
	C	N	O	F
	2.50	3.07	3.50	4.10
		P	S	Cl
		2.06	2.44	2.83
			Se	Br
			2.48	2.74
				I
				2.21

*Values taken from: J. Inorg. Nucl. Chem., 5, 264 (1958).

A. The interhalogens

The general formula for any interhalogen is XY_n when Y is always the lighter halogen and n is odd, either 1, 3, 5 or 7. In all, 13 interhalogens are known to be stable and are listed in table 2. Note that fluorine only acts as the Y group. The majority of interhalogen compounds are halogen fluorides. Iodine is the cationic halogen for the largest number of interhalogens and it exhibits its highest oxidation number, +7 with fluorine. All these are expected from the electronegativity arguments.

The thermal stability of the diatomic interhalogens, XY, is due to a combination of two main factors. First there is the intrinsic bond energy of the X-Y bond. This can be estimated from the standard free energies $\Delta G°$ given in table 2. Second there is the tendency for XY to undergo disproportionation into nX_2 and $XY_{(2n+1)}$. This tendency is apparent from the ΔG of reaction and is indicated by an increased $\Delta G°$ of the products. From thermodynamic data and measured or estimated bond energy values accumulated by Wiebenga et al.[2] it can be seen that, although the bond energies for XY were less for the lighter cationic, X, halogens, the corresponding XY_3 and XY_5 compounds were also much less stable. For the diatomic fluorides formed from the heavier halogens, i.e. IF, the greater stability of IF_5 and IF_7 effectively nullified the stability factor of the high bond energy for IF.

$$5IF \rightleftharpoons 2I_2 + IF_5 \qquad \Delta G^\circ_{298} = -39.8 \text{ Kcal} \qquad (3)$$

$$7IF \rightleftharpoons 3I_2 + IF_7 \qquad \Delta G^\circ_{298} = +28.4 \text{ Kcal} \qquad (4)$$

TABLE 2

$\Delta G^\circ_{f_{298}}$ (Kcal/mole) for the Interhalogens[2]

X	XY	ΔG°	XY_3	ΔG°	XY_5	ΔG°	XY_7	ΔG°
Cl	$ClF_{(g)}$	-13.4	$ClF_3(g)$	-38.8	$ClF_5(g)$	-	-	-
Br	$BrF_{(g)}$	-14.7	$BrF_3(l)$	-75	$BrF_5(l)$	-127.5	-	-
	$BrCl_{(g)}$	-3.46	-	-	-	-	-	-
I	$IF_{(g)}$	-22.7	IF_3	-	$IF_5(l)$	-205.3	$IF_{7(g)}$	-224.3
	$ICl_{(s)}$	-7.67	$ICl_3(s)$	-21.1	-	-	-	-
	$IBr_{(s)}$	-	-	-	-	-	-	-

As a result, while the order of stability for the binary interhalogens with respect to the elements is IF > BrF > ClF > ICl > IBr > BrCl, iodine monofluoride which has supposedly the most stable bond has been detected only in flames where iodine is brought into contact with fluorine. That is at high temperatures where I-F bonds are cleaved quite readily and the disproportionation reactions mentioned above do not occur irreversibly.

B. Polyhalides and Positive Polyhalogen Complexes

Interhalogens are closely related to two kinds of ions; the polyhalide anions, and the polyhalogen cations.

An interhalogen such as BrF_3 can act as a halide ion acceptor to form a polyhalide anion, BrF_4^-, or a halide ion donor to form a polyhalogen cation, BrF_2^+ according to

$$BrF_2^+ SbF_6^- \xleftarrow{\text{excess } SbF_5} BrF_3 \xrightarrow{KF} K^+BrF_4^- \qquad (5)$$

Except for short lived radicals such as Cl_2^- and FCl^- [3] polyhalogen anions are diamagnetic and thus contain generally an odd number of atoms. In the exceptions, the even polyhalides i.e. CsI_4 the observed diamagnetism indicates that at least two empirical units make up the real formula. This has been confirmed by X-ray diffraction studies[4]. The chemistry, structure, and bonding of polyhalide anions has been reviewed recently by Popov[5] and shall not be discussed further.

Polyhalogen cations, as shown by the above example (eq. 5), may be formed from the neutral interhalogens on interaction with strong Lewis acids such as SbF_5 or $AlCl_3$ effecting halide ion transfer from the neutral interhalogen. Recently[6] some fluorosulfates with triatomic

cations of the type IX_2^+ or I_2X^+ (with X = Cl or Br), have been reported, suggesting an alternate route to inter- and polyhalogen cationic compounds. Details will be discussed later.

A word of caution is necessary regarding the use of the term "cation" in referring to these inter- and poly-halogen compounds. From the bond distances for ICl_2-$SbCl_6$ [7] given in figure 1 it can be seen that the use of the term cation for the ICl_2 moiety is somewhat misleading because appreciable anion-cation interaction is present. In this case the interaction involved chlorine bridges which result in a distorted anion and a polymeric structure. The true structure is somewhere between a genuine ionic solid and a two dimensional polymer. Anion cation interactions of varying degrees have been found for all compounds of this type. They are most easily detected by X-ray structure analysis[8] but are also apparent from vibrational spectral analysis[9] or from N.Q.R. studies[10]. The observed anion-cation interaction in the solid state may be broken up by dissolving the compound in strong protonic acids. e.g.:

$$BrF_2\,SbF_6 \xrightarrow{HSO_3F} BrF_2^+(solv) + SbF_6^-(solv) \qquad (6)$$

In summary, whereas monoatomic halogen cations of the type X^+ are nonexistent, polyhalogen or interhalogen cations X_n^+ or XY_n^+ do exist. However, some degree of anionic-cationic association in the solid state and stabilization by suitable strong protonic acids in solution is necessary for their existence.

An additional group of compounds exist where a positively charged halogen is stabilized by Lewis bases[11] such as pyridine or quinoline.

The Structure of $[ICl_2^+][SbCl_6^-]$

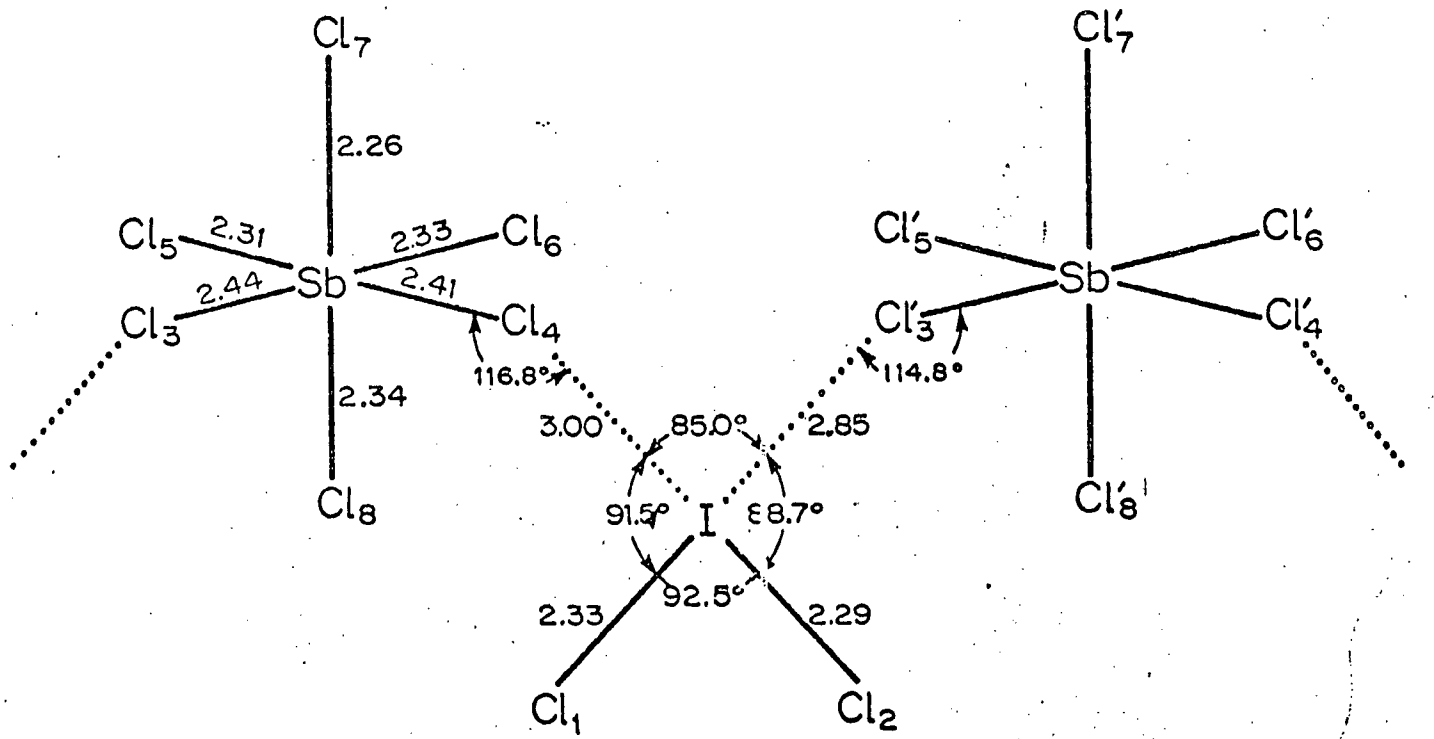


Figure 1

These compounds, commonly called stabilized halogen compounds are obtained by reaction such as

$$I_2 + AgNO_3 + 2py \xrightarrow{C_2H_5OH} AgI + [I(py)_2]^+ [NO_3] \qquad (7)$$

where the driving force of the reaction is the formation of the insoluble silver salt. They are mentioned here for the sake of completeness.

C. Halogen Oxyacid Compounds

Of greater relevance to this study are halogen oxy derivatives of oxyacids such as $IO(NO_3)$[12]. They have been known for a long time and were commonly referred to as basic salts[13]. For example, as shown recently by T. Kikindai[14] the interaction product between fuming nitric acid and I_2 is best regarded as $IONO_3$. This compound was originally obtained by M. Millon[12].

The oxides of iodine I_2O_4 and I_2O_5 have long been forumlated as iodosyl and iodyl iodates. These and related compounds such as the iodosyl derivatives of H_2SO_4 and H_2SeO_4 are well studied.

Although bromine oxygen analogues to IO and IO_2 compounds appear to be thermally unstable, some chlorine oxygen compounds containing the chloryl group, ClO_2 are known. Compounds such as ClO_2SO_3F[15] and $(ClO_2)_2S_3O_{10}$ [16], in marked contrast to the highly polymeric IO_2 compounds, are found to be soluble in strong acids, and produce quantitatively the chloronium cation ClO_2^+.

Generally iodine (III) compounds as well as iodyl, IO_2, and iodosyl, IO, compounds are formed by a number of strong to medium strong acids such as the monobasic oxyacids, HO_2CCF_3 and HNO_3 and including dibasic acids like H_2SO_4 and H_2SeO_4 and even tribasic H_3PO_4.

As can be seen from table 3, the formation of Br(I) and Br(III) and Cl(I) oxyacid derivatives are restricted to relatively strong monobasic acids. Finally, only one stable I(I) derivative, ISO_3F, has been made. It seems that in analogy to the disproportionation of IF into IF_5 and I_2 in equation (3) that the I(III) compounds are thermodynamically favoured.

There is a rich chemistry of positive halogens. Of the halogens, iodine has the most extensive chemistry including binary oxyacid derivatives. The occurrence of cationic halogen compounds appears to be connected with the acid strength of the given oxyacid. A brief discussion of HSO_3CF_3, the acid used in this work, follows.

D. Trifluoromethanesulfonic Acid and its Derivatives

Trifluoromethanesulfonic acid is a strong monobasic protonic acid. It was originally prepared in 1954[17] by the oxidation of bis (trifluoromethylthio) mercury and purified by treatment of barium bis trifluoromethanesulfonate with fuming sulfuric acid. This method is not practicable for producing large quantities. HSO_3CF_3 is now manufactured commercially by the electrofluorination of CH_3SO_2Cl and distributed as Fluorochemical Acid by the Minnesota Mining and Manufacturing Company. In respect to acid strength trifluoromethanesulfonic acid has been claimed to be the strongest monobasic acid known[14] based on the conductivities of various acids in acetic acid. On the other hand, HSO_3CF_3 reacts with organotin compounds in much the same manner as HSO_3F[18]. The resulting organotinsulfonates are isostructural

TABLE 3

Cationic Compounds of Oxyacids

Acids H_nY	Groups	Compounds formed by Oxyacids and Halogens
CH_3COOH	1	Group 1 IY_3
CF_3COOH	1	IOY
H_2SO_4	1	IO_2Y
H_3PO_4	1	
H_2SeO_4	1	Group 2 ClY
H_2TeO_4	1	BrY
$HOTeF_5$	1 2	BrY_3
$HOSeF_5$	1 2	
HNO_3	1 2	Group 3 IY
$HClO_4$	1 2	I_3Y
HSO_3F	1 2 3	IX_2Y (X=Cl or Br)

and have completely identical ^{119}Sn Mossbauer parameters. It, therefore, seems reasonable to assume HSO_3CF_3 is as strong an acid as HSO_3F or $HClO_4$. Some physical properties of HSO_3CF_3 would indicate this. A brief review of the chemistry of HSO_3CF_3 up to 1965 has been given by Senning[19].

No detailed structural studies (e.g. X-ray diffraction) of trifluoromethanesulfonic acid derivatives have been undertaken. However, there are two infrared and Raman studies involving normal coordinate analyses and force field calculations on the $SO_3CF_3^-$ anion[20,21]. The problem of assigning bands is complicated by a near coincidence of CF_3 and SO_3 vibrational modes and extensive vibrational mixing of modes. The proposed assignments in the two studies differ widely.

The trifluoromethanesulfonate group can act as a monodentate, bidentate, or even tridentate ligand through oxygen. In the alkali metal salts the SO_3CF_3 group is an anion $SO_3CF_3^-$ while in the titanium chloro salts it acts as a bidentate ligand in $TiCl_2(SO_3CF_3)_2$ or a tridentate ligand in $TiCl_3SO_3CF_3$ [22]. In a manner similar to the fluorosulfates of titaniam and tin[22,23] the trifluoromethanesulfonates have bidentate or tridentate SO_3CF_3 groups which act as bridging ligands rather than as chelating groups.

In organic chemistry the acid strength of HSO_3CF_3 is utilized in situations where perchloric acid has been used. In this respect trifluoromethanesulfonic acid is of comparable strength but is not nearly such a strong oxidizer and its use reduces hazards. Two examples of this use are; first, the use of HSO_3CF_3 as a titrant in glacial

acetic acid solution[24] and second, as a replacement for $HClO_4$ when a strongly acidic media is required. In organic syntheses the SO_3CF_3 group is a good leaving group, and in electrochemistry the weakly co-ordinating properties of the $SO_3CF_3^-$ ion make it a good alternative to the perchlorate ion as a support electrolyte.

That trifluoromethanesulfonic acid has been investigated because of its similarity to other strong acids, at least in part, is borne out by several authors who have used the properties of HSO_3F [25,26], $HClO_4$ [24] and H_2SO_4 [27] to argue the feasability of HSO_3CF_3. However, even when the similarity of HSO_3CF_3 to other strong acids is the reason for its investigation, it is the unique characteristics of the acid which are most important. For example, as a strong acid media instead of $HClO_4$, it is the oxidative stability of HSO_3CF_3 which is so valuable, while in titrations in acetic acid the non formation of gels with potassium hydrogen phthalate is important.

Trifluoromethanesulfonic acid fumes on contact with air and reacts with moisture to form a stable monohydrate, $HSO_3CF_3 \cdot H_2O$ which melts at 30°C. The formation of this hydrate necessitates the use of a dry box to handle the acid. The formation of the monohydrate has on occasion proved useful. When water is generated in a reaction, the acid effectively removes the water from the reaction. For all normal uses HSO_3CF_3 can be handled in the same manner as HSO_3F [28].

Finally, a word about the naming of HSO_3CF_3. The original synthesis calls the acid trifluoromethane-sulfonic acid. From the point of view of inorganic nomenclature an argument can be made

for trifluoromethylsulfuric acid. Various other permutations exist in the literature. There is even a proposal that salts of HSO_3CF_3 be called "triflats" for the sake of brevity. In this thesis, however, the acid will be called trifluoromethanesulfonic acid and derivatives of it trifluoromethanesulfonates. The main reason for this decision is to avoid confusion and promote clarity. As for choosing the organic name over the inorganic name no real reason exists but the terminology used is that most common in the literature.

II. Experimental

A. Chemicals

1. Reagents

Except for peroxydisulfuryldifluoride, $Rb[I(SO_3F)_4]$ and cesium trifluoromethanesulfonate all the reagents used in the synthesis of the various iodine trifluoromethanesulfonates were either available commercially, or else were trifluoromethanesulfonates, where the synthesis is the subject of this thesis.

a. Commercial

i) Elemental iodine was supplied by the Fisher Scientific Company (resublimed) and 99% pure. No further purification was undertaken.

ii) Elemental fluorine, 98% pure, used in the preparation of $S_2O_6F_2$ was obtained from Allied Chemical Corporation, and passed through a sodium fluoride, NaF, metal trap to remove hydrogen fluoride, HF. No attempt was made to remove other impurities commonly present in the F_2 such as O_2, N_2 or OF_2 since they do not enter into the reaction between SO_3 and F_2. A high pressure Autoclave Engineering Valve and Crosby high pressure gauge regulated the flow of F_2 from the cylinder.

iii) Elemental bromine, 99% pure, was supplied by British Drug House. It was stored over P_2O_5 and KBr and used without further purification.

iv) Elemental chlorine, 99.5% pure, was supplied by Matheson of Canada Ltd. It was dried by passing the gas through two 96% H_2SO_4 traps and finally through a P_2O_5 tube. No attempt was made to remove O_2 or N_2 or other impurities.

v) Sulfur trioxide was purchased from Baker and Adamson, Allied Chemical Corporation, as "Sulfan" (stabilized SO_3) and used without purification.

vi) Iodine pentoxide was obtained from Fisher Scientific Company (purity 99%). However, based on the infrared spectrum of the coupound it was HI_3O_8[29] and not I_2O_5. It was used as such without any attempt to purify it.

vii) Iodic Acid, HIO_3, was obtained from British Drug House at a purity of 97.5%. Again it was found to be HI_3O_8[29]. It was used without purification.

viii) Potassium iodide, 99% pure, was obtained from Fisher Scientific Company and used without further purification.

ix) Rubidium iodide, 99% pure, was obtained from Alfa Inorganics Ltd. and used without further purification.

x) Cesium chloride, 99.9% pure, was obtained from British Drug House and used without further purification.

xi) Trifluoromethanesulfonic acid, HSO_3CF_3, was obtained from the Minnesota Mining and Manufacturing Company as "Fluorochemical Acid" and the purity was not given. It was purified by distillation under reduced pressure.

xii) Fluorosulfuric Acid, HSO_3F, (technical grade) was supplied by Allied Chemical Corp. and was purified by double distillation under dry nitrogen at atmospheric pressure[30].

b. Prepared

i) Peroxydisulfuryldifluoride, $S_2O_6F_2$, was prepared in 500 g. quantities in a modified version of a general method reported by

Shreeve and Cady[31]. After having passed through a NaF trap, F_2 was mixed with dry N_2 and SO_3 (sulfan) in a silver(II) fluoride catalytic furnace reactor Fig. 2. The reaction temperature was 180°C and the $S_2O_6F_2$ generated was condensed out at -78°C in dry ice traps. Any unreacted SO_3 was removed by extraction with Oleum, concentrated H_2SO_4 and later purified by fractional distillation to yield pure $S_2O_6F_2$ as indicated by ^{19}F N.M.R. and infrared spectroscopy.

ii) Rubidium tetrakis-fluorosulfate iodate(III), $Rb[I(SO_3F)_4]$ was synthesized from RbI and $S_2O_6F_2$ in analogy to the reported synthesis of the potassium salt by Lustig and Cady[32]. An excess of $S_2O_6F_2$ was distilled onto RbI and after several hours the excess $S_2O_6F_2$ was removed leaving the $Rb[I(SO_3F)_4]$ as a white solid. No purification of the product was necessary. The reaction was followed by weight.

iii) Cesium trifluoromethanesulfonate, $CsSO_3CF_3$, was obtained from CsCl and HSO_3CF_3. An excess of HSO_3CF was added to CsCl in a two part reactor and after several hours the excess acid was removed leaving the $CsSO_3CF_3$ behind. The reaction was followed by weight.

iv) Iodine trisfluorosulfate $I(SO_3F)_3$ was synthesized from I_2 and $S_2O_6F_2$ by the method of Roberts and Cady[33]. An excess of $S_2O_6F_2$ was distilled onto I_2 and the mixture was allowed to warm to room temperature. Heat was evolved and a greenish liquid was formed. Eventually, after leaving the reaction overnight, the liquid became light yellow indicating a complete reaction. The excess $S_2O_6F_2$ was removed in vacuo and the product used without further purification. The reaction was followed by weight.

2. Products

a. Iodine(III) and Iodine(I) Trifluoromethanesulfonates.

i) Iodine tristrifluoromethanesulfonate $I(SO_3CF_3)_3$ I_2 (0.958 g. 3.78 mmol.) was suspended in 29 g. of HSO_3CF_3 in a two part reactor. Then 2.453 g. (12.38 mmol.) of $S_2O_6F_2$ was added by vacuum distillation from a calibrated trap. The mixture was allowed to warm to room temperature and shaken manually from time to time. The colour was initially brown and then changed to blue and blue green. After 20-30 minutes the colour had changed to a light yellow and a precipitate had begun to form. The volatile products were removed in vacuo and 4.307 g. of $I(SO_3CF_3)_3$ was obtained.

ii) An alternate route to $I(SO_3CF_3)_3$ via $I(SO_3F)_3$. 12 grams of HSO_3F was distilled onto 2.9654 g. of $I(SO_3F)_3$ in a two part reactor The reactor was evacuated and introduced into the dry box where approximately 8 grams of HSO_3CF_3 was added. A yellow precipitate was formed immediately. Volatile components were removed and 3.8279 g. of $I(SO_3CF_3)_3$ were obtained.

iii) Iodine(I) trifluoromethanesulfonate, ISO_3CF_3; in a typical preparation 0.982 g. (1.72 mmol.) of $I(SO_3CF_3)_3$ and .460 g. (1.80 mmol.) of I_2, both finely ground, were combined in a thick walled pyrex glass tube. After flame sealing the reaction the tube containing one atmosphere of dry nitrogen was completely immersed in an oil bath at 135°C. Both reactants melted to a viscous dark brown liquid. No appreciable quantities of I_2 vapour could be detected visually. The temperature of the oil bath was raised to 145°C and the reaction left in it for one hour. After cooling slowly the product solidified

to a black brown cake. Attempts to perform the reaction at higher temperatures resulted in decomposition with the formation of I_2 and a clear colourless liquid. The reactor was broken open in the dry box and the contents transfered to a two part reactor. To ensure complete reaction, the powder was melted at 130°-135°C and then allowed to anneal slowly. All volatiles were removed by vacuum distillation and the product was stored in the dry box.

b. Alkali metal tetrakis trifluoromethanesulfonate iodate(III) salts.

i) $K[I(SO_3CF_3)_4]$; KI (0.239 g.) in a two part reactor was dissolved in 19 g. of HSO_3CF_3 and oxidized by .607 g. of $S_2O_6F_2$. The mixture was treated in the same way as described for $I(SO_3CF_3)_3$ in section (IIA2ai). White to slightly yellowish crystals began to form only after the volume of the liquid had been considerably decreased. A solid (1.170 g.) identified as $K[I(SO_3CF_3)_4]$ was obtained.

ii) $Rb[I(SO_3CF_3)_4]$; $Rb[I(SO_3F)_4]$ (0.892 g.) was dissolved in 10 g. of HSO_3CF_3. After removal of all the volatiles 1.071 g. of $Rb[I(SO_3CF_3)_4]$ was obtained as a white solid.

iii) $Cs[I(SO_3CF_2)_4]$; $CsSO_3CF_3$ (0.245 g.) was dissolved in 10.7 g. of HSO_3CF_3 and 0.472 g. of $I(SO_3CF_3)_3$ was added. A clear yellow solution formed from which $Cs[I(SO_3CF_3)_4]$ crystallized out as a white solid.

c. Iodyl and Iodosyl trifluoromethanesulfonate $IO_2SO_3CF_3$ and $IOSO_3CF_3$

i) Iodyl trifluoromethanesulfonate, $IO_2SO_3CF_3$; HI_3O_8 (1.2211 g.) and 20 g. of HSO_3CF_3 were stirred together in a two part pyrex reactor with a magnetic stirrer for two and a half days. The solid appeared to be ~~different~~ changed but at no time was all solid dissolved. Upon removal

of all liquid by filtration the white solid product was dried under vacuum.

ii) Iodosyl trifluoromethanesulfonate, $IOSO_3CF_3$; HI_3O_8 (.6017 g.) and I_2 (.3050 g.) were combined with 20 g. of HSO_3CF_3 in a two part reactor containing a magnetic stirrer. The mixture was stirred for one week and the liquid removed by filtration. The solid product, which was contaminated with small amounts of iodine was washed with HSO_3CF_3. The yellow solid $IOSO_3CF_3$ was further dried in vacuo removing the final traces of I_2.

d. Dihalo iodine trifluoromethanesulfonate

i) IBr_2SO_3CF; ISO_3CF_3 (1.2447 g.) was placed in an evacuated two part reactor connected with a glass T to a storage vessel of Br_2 at room temperature. Bromine vapour was admitted to the evacuated 2 part reactor. A reaction between the Br_2 and the ISO_3CF_3 took place and was followed by weight. The final product $IBr_2SO_3CF_3$ (1.9305 g.) was carefully dried in vacuo to remove excess Br_2.

ii) $ICl_2SO_3CF_3$; ISO_3CF_3 (0.2897 g.) was placed in a one piece glass reactor and with the reactor at -196°C (cooled in liquid nitrogen) approximately 10 mls of chlorine was added by vacuum transfer. The reaction mixture was kept at -78°C in a dry ice trichloroethylene slush bath. Periodically the reactor was shaken to promote reaction. While the reactor was still at -78°C the excess chlorine was removed in vacuo. Upon warming to room temperature, the orange solid obtained liquified and turned yellow decomposing into $(ICl_3)_2$.

iii) $I_3SO_3CF_3$;attempts to synthesize $I_3SO_3CF_3$ were made in strict analogy to the successful synthesis of I_3SO_3F (34) and the

synthesis of ISO_3CF_3 described in this study. Only incomplete uptake of I_2 could be accomplished at the high temperature ∿140°C needed to maintain the reactants in the molten state.

B. Apparatus

1. Vacuum Lines

Standard high vacuum techniques were employed with all the compounds described because of their reactivity toward oxygen and water vapour. In order to achieve and maintain the vacuum necessary a Welch Duo-Seal pump Model 1400, was used, capable of maintaining a vacuum of .001 torr. The pump was connected to the line through a liquid nitrogen cold trap to prevent any volatile materials from being drawn through the pump.

a. Glass line

The main manifold of the glass line was constructed of Pyrex tubing 600 mm. long and 20 mm. in diameter, sealed off at one end and connected to the cold trap and manometer by a Fischer and Porter 4 mm. glass and teflon stopcock and a B19 ground glass cone and socket joint. Four additional Fischer and Porter stopcocks served as inlets to the manifold for attaching reactors and other apparatus via B10 ground glass cone and socket joints. Pressures in the manifold were measured with a mercury manometer which was attached to the main line by a Kontes stopcock and a B10 cone and socket joint.

b. Monel Metal Line

In the attempted preparation of $Br(SO_3CF_3)_3$, where the reagent

BrF_3 is known to attack glass, a monel metal line was used. This line is a standard metal vacuum line and has been previously described in the M.Sc. thesis of Larry Levchuck [68].

2. Metal Fluorine Line

For the preparation of $S_2O_6F_2$ it was necessary to use a system suitable for flow reactions. The fluorine line used consisted basically of a skeleton of copper tubing and Whitey, Hoke, and Autoclave Engineering valves. The valves were supplied by Whitey Research Tool Co., Oakland, California; Hoke Inc., Criskill, New Jersey; and Autoclave Engineering Inc., Erie, Pennsylvania respectively. Fluorine was introduced through a NaF trap which could be regenerated by heating electrically to remove any HF which became absorbed in it. The fluorine could then be mixed with dry nitrogen or used undiluted and led directly into a catalytic reactor furnace. Another inlet to the furnace permitted the addition of SO_3 gas. This system is shown schematically in figure 2.

3. Dry Atmosphere Box

All manipulation of solid air sensitive materials and all additions of HSO_3CF_3 were carried out in a Vacuum Atmosphere Corporation "Dri Lab" Model No. HE-43-2, filled with purified dry nitrogen and equipped with "Dri Train" Model No. HE-93B. In order to make quantitative additions in the dry box a Mettler P160 top loading balance was used.

4. Reactors

a. Two Part Glass Reactor

For the most part reactions were carried out in a two part

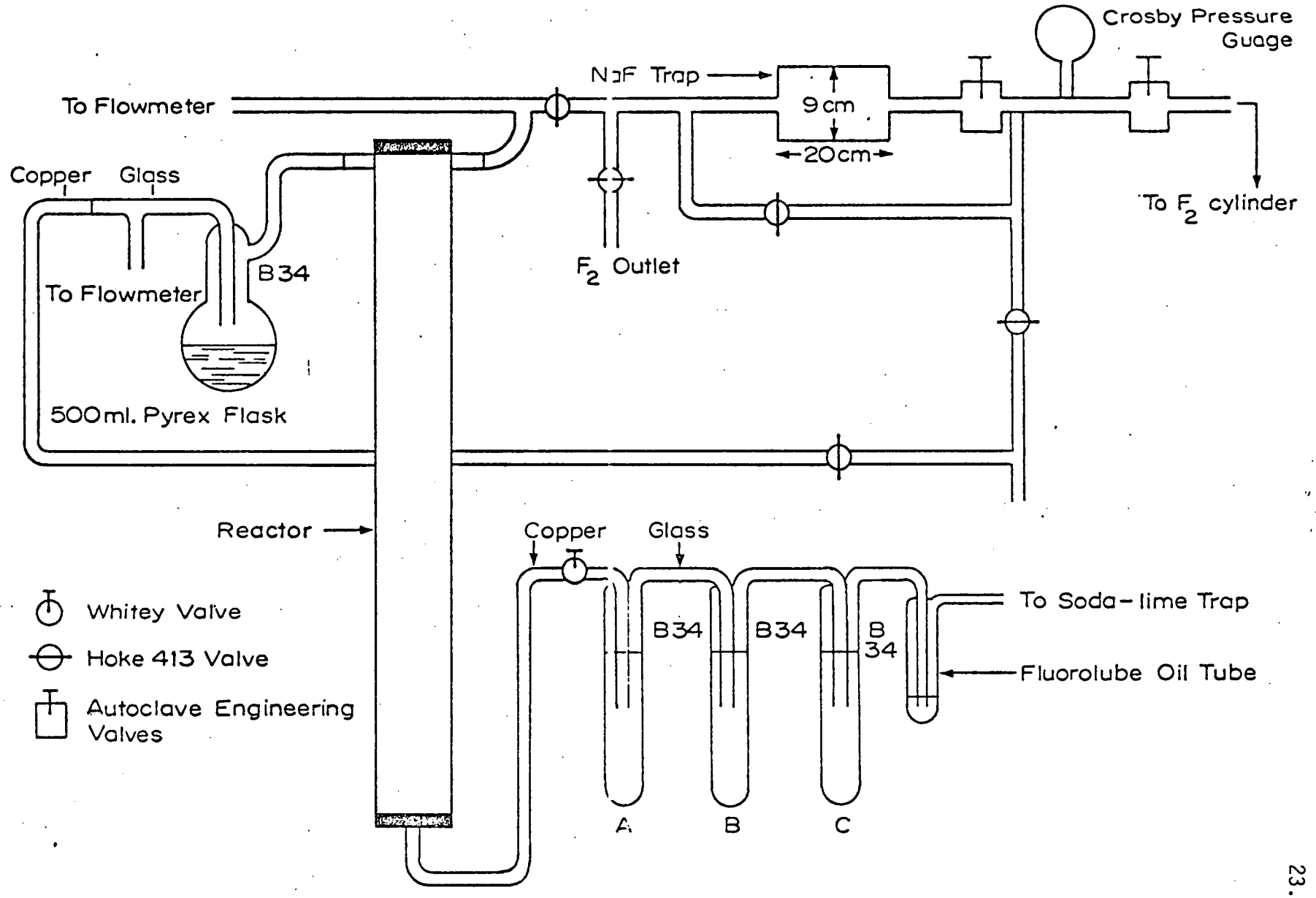


Fig. 2. Apparatus for the Preparation of $S_2O_6F_2$

pyrex glass reactor. The reaction flask was a 50 ml. round bottom flask with a B19 cone top. The reactor top consisted of a Teflon stem stopcock (Fischer and Porter, or Kontes) joining in line a B19 socket, to be fitted to the flask, and a B10 cone, for attachment to the glass vacuum line.

b. One Part Glass Reactor.

In the attempted synthesis of $ICl_2SO_3CF_3$ and in purifying ISO_3CF_3 a one part pyrex glass reactor was used. This consisted of a pyrex tube 20 mm diameter sealed at one end with a Teflon stopcock at the other. In the attempt to prepare $Br(SO_3CF_3)_3$ a similar reactor utilizing a quartz reactor and a graded quartz glass seal was used.

c. Thick Walled Glass Tube Reactor

In the preparation of ISO_3CF_3 where I_2 and $I(SO_3CF_3)_3$ are combined at 145°C high pressures were possible. For this reaction then a thick-walled Pyrex tube of 20 mm outer diameter sealed at one end and with a constriction near the other end which had a B19 cone on it was used. The two solids were introduced via glass funnels whose stems protruded beyond the constriction. The reactor was fitted via the B19 cone, with a P_2O_5 drying tube to prevent the entrance of moisture when the tube was sealed with a flame in the air.

d. Two part Monel reactor

As mentioned above, when BrF_3 was used as a reagent glass apparatus had to be avoided. When large quantities of BrF_3 were handled for long periods at elevated temperatures the quartz reactor

described above was not suitable and a two part monel metal reactor was used. A suitable monel reactor consisted of a cylindrical metal pot of about 100 m. capacity which was connected with six bolts to a lid equipped with a Hoke valve (#431). A vacuum tight seal was achieved with a teflon ring inserted into a groove between the pot and the lid. This reactor could be attached directly to the metal line using Swagelok connections.

The two types of glass reactors described above are shown in figure 3 and the metal reactor in figure 4.

5. Miscellaneous

a. Vacuum Filtration Apparatus

A pyrex device, similar to the one described by Shriver (35), designed to separate liquids from solids by filtration under partial vacuum was also used. The apparatus consisted of a 25 mm. outer diameter glass tube in which a medium coarseness glass frit was set about one third from the bottom. The top of the tube ended in a B19 socket for connecting a reaction flask from a two part glass reactor and at the bottom was a B19 cone for attaching a 250 ml round bottom flask with a B19 socket. Below the glass frit a side arm outlet connected to a 4mm bore greased stopcock and a B10 cone. This allowed attachment to the glass vacuum manifold. The overall length of the apparatus without the flasks is 350 mm.

b. Lubricating grease

All ground glass joints described in the preceding sections were lubricated with a low volatility grease designed to be inert

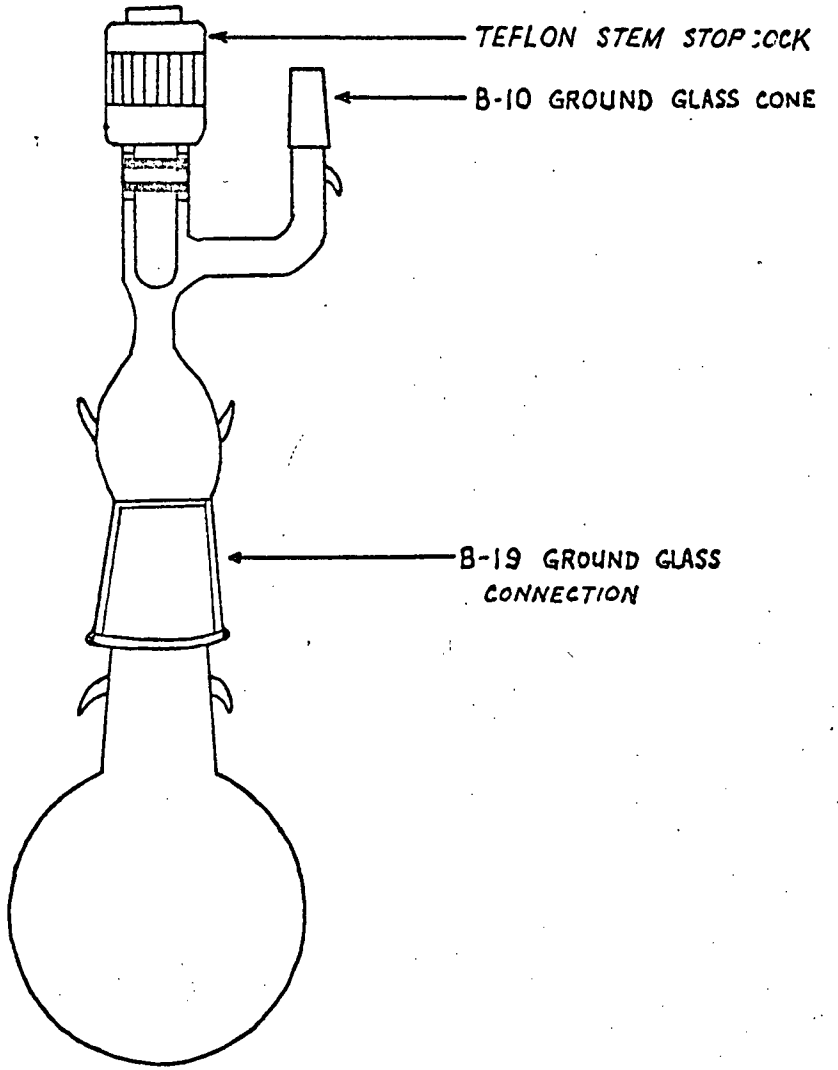
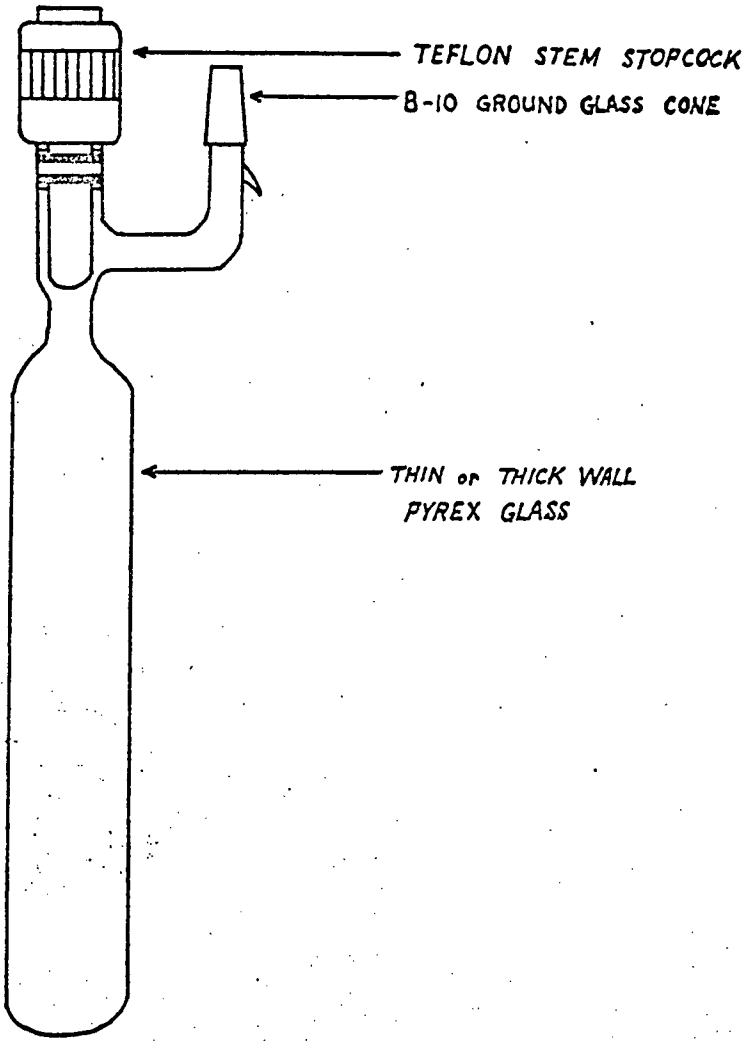


FIGURE 3. TWO-PART GLASS REACTOR



1 ONE PIECE GLASS REACTOR

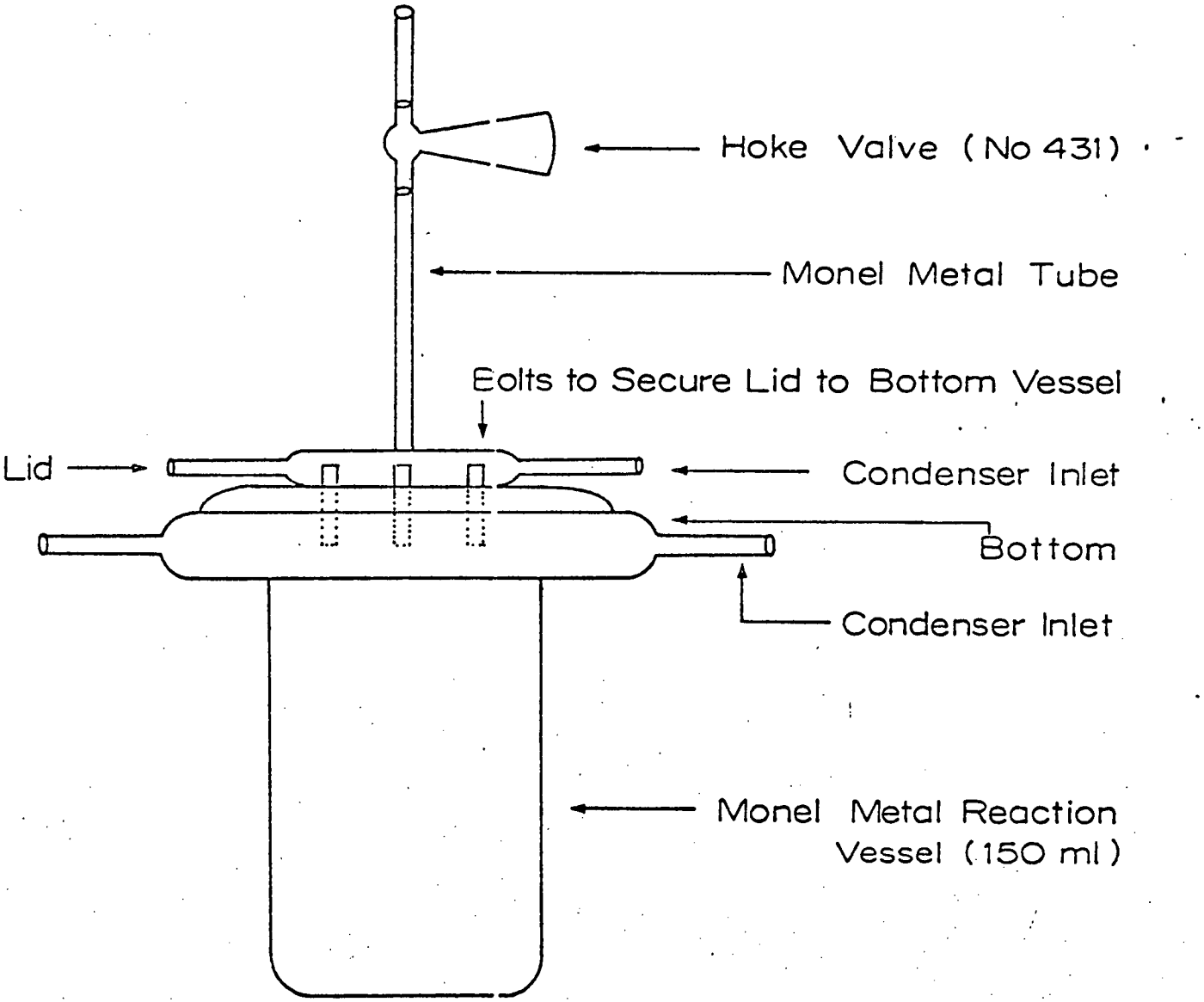


Fig. 4 Monel Metal 2-Part Reaction Vessel (Front View)

to fluoro acids and to maintain leakproof connections under vacuum. The grease was supplied by Hooker Chemical Company, Fairlawn, New Jersey, as Fluorolube grease GR-90 distributed by Fisher Scientific Company.

c. Analyses

All elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Elbach, West Germany.

C. Spectrophotometers

1. Infrared Spectrometer

Infrared spectrographs were recorded using a Perkin Elmer Model 457 Grating Infrared Spectrophotometer in the range 4000-250 cm^{-1}. Samples were genreally run neat between two salt windows. Due to the high reactivity of all samples there was no suitable mulling agent. Because of the high reactivity of the samples the windows were made from silver bromide, AgBr. Even these were sometimes attacked although only after prolonged exposure. KRS5 windows were severely attacked and both sodium chloride and silver chloride windows were of too limited range to use. $IBr_2SO_3CF_3$ was unreactive towards Cesium iodide and these windows were used. All windows were supplied by Harshaw Chemicals. Gaseous samples were contained in a monel cell fitted with a Whitey IKS4 valve and AgCl windows.

2. Raman Spectrophotmeter

The Raman spectra of the compounds were measured with a Cary 81 spectrophotometer using a Spectrophysics Model 125 He-Ne laser

source with an exciting line at 6328 Å. The pyrex sample tubes were filled in the drybox. The tubes were 5 mm outer diameter pyrex glass with an optically flat end. The tube was about 120 mm long and after filling was sealed with a flame.

3. Visible and Ultraviolet Spectrophotometer

U.V. visible spectra were recorded on a Cary 14 spectrometer. The samples were contained in 1 mm path length quartz cells fitted with airtight teflon stoppers. The cells were obtained from ISC Instruments Ltd. All dilutions and filling of cells were performed in the dry box.

III Results and Discussion

A. Introduction

Compounds of positively polarized halogens with strong oxyacids as pointed out in the introduction have been known for many years. The number of compounds obtainable from any one acid is found to be proportional to the strength of the acid. By far the largest number of compounds which have been synthesized are derivatives of fluorosulfuric acid. There are three main reasons for this abundance:

a. Fluorosulfuric is one of the strongest oxyacids known.

b. The peroxide of HSO_3F, $S_2O_6F_2$, is a strong oxidizing agent and very suitable as a synthetic reagent.

c. Halogen fluorosulfates unlike perchlorate are very thermally stable.

A relatively new acid, trifluoromethanesulfonic acid should be comparable in acid strength (or protonating ability) to HSO_3F. There have been claims[36] that it is the strongest acid known.

It became interesting, therefore, to see what halogen trifluoromethanesulfonates might be synthesized. The most common type of cationic compound formed generally by the largest number of oxyacids are the iodineIII compounds. It seemed reasonable to attempt first the synthesis of iodine(III) tristrifluoromethanesulfonate, $I(SO_3CF_3)_3$.

B. Synthesis

1. Iodine(III) tristrifluoromethanesulfonate, $I(SO_3CF_3)_3$. Iodine trisfluorosulfate[33], the pattern compound for $I(SO_3CF_3)_3$ was originally

prepared with the peroxide, $S_2O_6F_2$, which can be regarded as a pseudo halogen[37] according to:

$$I_2 + 3(SO_3F)_2 \longrightarrow 2I(SO_3F)_3 \qquad (8)$$

in a simple and straightforward way. The $S_2O_6F_2$ in the reaction above has been written as $(SO_3F)_2$ to illustrate more clearly its pseudohalogen character. Unfortunately and somewhat surprisingly, the analogous peroxide $S_2O_6(CF_3)_2$ had been found previously to be thermally unstable[25]. Thus the analogous route to $I(SO_3CF_3)_3$ did not appear to be feasible.

The fact that HSO_3CF_3 is known to liberate HCl from metal chlorides such as NaCl[17], dimethyl tin dichloride[23] and titanium tetrachloride[25] suggested that the replacement of chlorine in ICl_3 might be feasible. As excess of HSO_3CF_3 was added to freshly prepared ICl_3 but when the excess acid was removed after 72 hours the dark red product was identified by its Raman spectrum as ICl. It appears that ICl_3 undergoes decomposition which is not unexpected for this compound and the method was unsuccessful.

A similar attempt involved the replacement of fluorosulfate with trifluoromethanesulfonate in $I(SO_3F)_3$. Initially the simple reaction of $I(SO_3F)_3$ with excess HSO_3CF_3 was attempted as:

$$I(SO_3F)_3 + 3HSO_3CF_3 \xrightarrow{HSO_3CF_3} I(SO_3CF_3)_3 + 3HSO_3F \qquad (9)$$

$I(SO_3F)_3$ is soluble in HSO_3F and it was hoped that it would also be soluble HSO_3CF_3. When the reaction was attempted the following observations were made. The $I(SO_3F)_3$, a clear viscous supercooled

liquid at room temperature, turned into a yellow solid material upon contact with HSO_3CF_3. However, upon removal of the excess acid in vacuo the weight of the solid indicated less than complete replacement of SO_3F by SO_3CF_3. The gummy sticky appearance of the solid also suggested an incomplete reaction producing a mixture of $I(SO_3F)_3$ and $I(SO_3CF_3)_3$.

Two useful conclusions may be drawn from this experiment. First, SO_3F groups may be replaced by SO_3CF_3 groups in the iodine III compound and second, the resulting products, in contrast to $I(SO_3F)_3$, may be insoluable in the parent acid. However, it appears that the formation of the solid upon contact with HSO_3CF_3 occluded some of the very viscous $I(SO_3F)_3$ preventing a complete replacement reaction.

In order to prevent this occlusion the synthesis of $I(SO_3F)_3$ in HSO_3CF_3 by method 2a (see experimental) was considered.

$$I_2 + 6HSO_3CF_3 + 3S_2O_6F_2 \xrightarrow{HSO_3CF_3} 2I(SO_3F)_{3(solv)} + 6HSO_3CF_3$$
$$\xrightarrow{HSO_3CF_3} 2I(SO_3CF_3)_{3(s)} + 6HSO_3F \qquad (10)$$

After about 20-30 minutes at room temperature the colour of the solution undergoes changes from dark murky brown to pale clear yellow. The changes noted are: dark brown to dark blue green to pale yellow. Some slowly decreasing amounts of solid iodine are present in both the dark brown and dark blue green phases. When the solution turns yellow all iodine has been consumed. The yellow solid product which is formed appears either during the green phase or after the solution turns yellow. When the solid formation occurs in the clearyellow solution small needlelike crystals

may be observed forming. If insufficient peroxide is used the final solid material is tinged with blue green. Whether the solid forms before or after the yellow phase appears seems to depend on whether the reaction mixture is warmed to room temperature quickly or slowly. The final stage indicated by the colour change from blue green to yellow, appears to be exothermic.

The colour changes observed deserve some comment. Molecular iodine is only slightly soluable in HSO_3CF_3 giving rise to faintly purple solutions. The presence of an oxidizing agent will, however, produce brown coloured solutions initially and large amounts of iodine will go into solution. The colour is due to polyiodine cations such as I_5^+ and I_3^+ which have been previously identified[38] in other strong protonic acids such as HSO_3F and H_2SO_4. Further oxidation should produce the blue I_2^+ cation. The green colour observed in this reaction may be due to mixtures of blue I_2^+ with either brown I_3^+ (or I_5^+) or the yellow I(III) species. Note the increase in the formal oxidation state of iodine from 0 through +1/5 and +1/3 to +1/2. The I_2^+ cation is only existent in very strong acids i.e. HSO_3F or $H_2S_2O_7$ or in some superacid media i.e. HSO_3F/SbF_5. The final yellow colour is due to the complete oxidation of iodine(0) to iodine(III) and this is substantiated by the faint yellow tinge of the solid product. While previously none of these polyiodine cations have been found in HSO_3CF_3 the colours observed here may serve as a first indication that they do exist. Further evidence obtained by recording the electronic spectra is required and will be presented in a later chapter.

As a precaution in the synthesis described above a large excess of $S_2O_6F_2$ should be avoided. A mixture of $S_2O_6F_2$ and HSO_3CF_3 showed complete miscibility and no apparent sign of reaction. However, after about 30 minutes exothermic evolution of a volatile compound, later identified by infrared spectroscopy as CF_3SO_3F [25] was noted. This indicates the attack of the S-C bond in HSO_3CF_3 by $S_2O_6F_2$.

The success of the synthesis of $I(SO_3CF_3)_3$ via the above route may be due to the fact that oxidation of iodine takes precedence over the attack of the S-C bond in the solvent. Any additional side reactions, perhaps with the excess of $S_2O_6F_2$ normally used would result in such rather volatile by products as HSO_3F, CF_3SO_3F and SO_3. None of these should interfere with the isolation of the product.

Another method for synthesizing $I(SO_3CF_3)_3$ was subsequently developed. The original method even though very successful is somewhat wasteful of HSO_3CF_3 ($150 a liter) since a large (10-20 fold) excess is required and separation from the HSO_3F formed during the reaction would be extremely difficult considering the similar physical properties of the acids. We therefore added a slight excess of HSO_3CF_3 to a solution of $I(SO_3F)_3$ in HSO_3F. $I(SO_3CF_3)_3$ was formed immediately and could be isolated as in the first method.

Iodine tristrifluoromethanesulfonate, $I(SO_3CF_3)_3$ is a pale yellow solid melting at +117-120°C and decomposing at approximately 170°C. This is a rather noticeable departure from other iodine(III) compounds of strong oxyacids. Iodine trisperchlorate decomposes when warmed from -45°C to room temperature[39] and iodine trisfluoro-

sulfate melts at +33.7°C[40] and is often found as a supercooled liquid at room temperature. A similar melting point is found for iodine tristrifluoroacetate. In particular the difference between $I(SO_3F)_3$ and $I(SO_3CF_3)_3$ is intriguing.

The solubility of $I(SO_3CF_3)_3$ in both HSO_3F and HSO_3CF_3 is slight and this also is quite different from $I(SO_3F)_3$ which is very soluble in the parent acid. Where $I(SO_3F)_3$ is said to disproportionate upon heating according to:

$$I(SO_3F)_3 \longrightarrow ISO_3F + IF_3(SO_3F)_2 + 3SO_3 \qquad (11)$$

thermal decomposition of $I(SO_3CF_3)$, occurs at 170°C in vacuo and accompanied by partial sublimation. Decomposition produces SO_3 and $CF_3SO_3CF_3$ as volatiles and a small amount of yellow residue containing iodine in the +3 oxidation state and sulfate. The observed properties of a high melting point, high thermal stability and insolubility in the parent acid indicate that $I(SO_3CF_3)_3$ may be a polymer as has been suggested for $I(SO_3F)_3$ [33]. All the differences mentioned above, however, indicate a basic structural difference between $I(SO_3F)_3$ and $I(SO_3CF_3)_3$. Hopefully the vibrational spectrum will allow further clarification of these differences. Elemental analysis of $I(SO_3CF_3)_3$ is found in table 4.

Subsequent to this synthesis of $I(SO_3CF_3)_3$ a report has appeared of the synthesis[41] by:

$$I(OCOCF_3)_3 + 3HSO_3CF_3 \xrightarrow[72\ hours]{60^\circ} I(SO_3CF_3)_3 + 3HOCOCF_3 \qquad (12)$$

TABLE 4

Elemental analysis and Melting (decomposition) Points

Compound	I%		S%		F%		M.P.
	Calc'd	Found	Calc'd	Found	Calc'd	Found	
$I(SO_3CF_3)_3$	22.10	22.21	16.76	16.79	29.78	29.64	119°C
$RbI(SO_3CF_3)_4$	15.69	15.92	15.86	16.07	28.19	28.07	208-212°C d.
$K\ I(SO_3CF_3)_4$							210-215°C d.
$Cs\ I(SO_3CF_3)_4$							190-200°C d.
$I\ SO_3CF_3$	45.98	46.16	11.62	11.57	20.65	20.45	122°C
$I\ Br_2SO_3CF_3$	29.12	29.46	*		13.08	13.39	72-75°C d.
$IO_2SO_3CF_3$	41.20	41.40	10.41	10.26	18.51	18.28	315-230°C d.
$IOSO_3CF_3$	43.46	43.20	10.98	11.15	19.52	19.26	235-240°C d.

*For $IBr_2\ SO_3CF_3$ Br% was calculated rather than S%.calc. 36.67 found 36.18

Elemental analysis of C and I indicate the formation of $I(SO_3CF_3)_3$ but the reported decomposition point (190°-192°C) is not in agreement with our findings. As no further evidence was given it is not possible to draw a conclusion at this time.

2. $I(SO_3CF_3)_2^+$ cation

Like many iodine(III) derivatives, e.g. ICl_3 and $I(SO_3F)_3$ the new compound, $I(SO_3CF_3)_3$ may act as an $SO_3CF_3^-$ ion donor towards strong Lewis acids and as an $SO_3CF_3^-$ ion acceptor towards compounds containing the SO_3CF_3 group. Whereas the latter group is well represented, with alkali metal salts the most obvious case, no well proven Lewis acid of the type $E(SO_3CF_3)_n$ was available to us.

Recently Yeats and Aubke[42] had found that SbF_5 and AsF_5 may abstract the SO_3F^- ion from fluorosulfates such as ClO_2SO_3F. It seemed reasonable to attempt the $SO_3CF_3^-$ abstraction with SbF_5. However, the addition of SbF_5 to $I(SO_3CF_3)_3$ caused an immediate colour change from yellow to deep blue, indicating the formation of the I_2^+ ion, an ion which is perfectly stable in SbF_5. This observation is best explained by assuming a disproportionation of $I(SO_3CF_3)_3$. As a result of this failure further studies in this system were not undertaken. As in the fluorosulfate system where $Sn(SO_3F)_4$ proved to be an SO_3F acceptor[43] more success may be expected from $Sn(SO_3CF_3)_4$, however, this compound was synthesized only after this study had been completed.

3. Alkali metal tetrakis (trifluoromethanesulfonato) iodate(III) $M[I(SO_3CF_3)_4]$

The synthesis of several compounds containing the $[I(SO_3CF_3)_4]^-$

anion was successful. This species should be stabilized best by the heavier alkali metal cations; K^+, Rb^+ and Cs^+. Accordingly $K[I(SO_3CF_3)_4]$, $Rb[I(SO_3CF_3)_4]$, and $Cs[I(SO_3CF_3)_4]$ were prepared, each by a different synthetic route.

The synthesis of $K[I(SO_3CF_3)_4]$ was carried out according to method 2b in the experimental section:

$$KI + 2S_2O_6F_2 + 4HSO_3CF_3 \xrightarrow{HSO_3CF_3} K[I(SO_3CF_3)_4] + 4HSO_3F \qquad (13)$$

in a manner similar to the original synthesis of $I(SO_3CF_3)_3$ equation 10. Not unexpectedly the salt $K[I(SO_3CF_3)_4]$ was quite soluable in HSO_3CF_3 and could only be isolated by removal of the solvent. No mixed salts were found as shown by the vibrational spectra. Whether the resulting product was a mixture of KSO_3CF_3 and $I(SO_3CF_3)_3$ will depend upon an analysis of the spectra. However, the high melting point 210-215°C may serve as a preliminary indication of the purity of the compound.

$Rb[I(SO_3CF_3)_4]$ was synthesized by the method 2b' given in the experimental section as:

$$Rb[I(SO_3F)_4] + 4HSO_3CF_3 \xrightarrow{HSO_3CF_3} Rb[I(SO_3CF_3)_4] + 4HSO_3F \qquad (14)$$

Again a complete conversion from the fluorosulfate to the trifluoromethanesulfonate was obtained.

Finally, the synthesis of $Cs[I(SO_3CF_3)_4]$ was carried out according to the method given in section 2b'' of the Experimental:

$$CsSO_3CF_3 + I(SO_3CF_3)_3 \xrightarrow{HSO_3CF_3} Cs[I(SO_3CF_3)_4] \qquad (15)$$

All these methods are very straightforward and yield high melting (190-215°C) pale yellow hygroscopic solids. The composition of $Rb[I(SO_3CF_3)_4]$ was confirmed by an elemental analysis (given in table 4) and the cesium and potassium salts were checked by comparing their infrared spectra with that of the rubidium salt. Melting points for all three compounds are listed in table 4.

4. Iodine monokistrifluoromethanesulfonate, ISO_3CF_3

The only previously known iodine(I) compounds of oxyacids are a poorly characterized yellow nitrate,[44] which is reported to be stable only below room temperature, an iodine(I) perchlorate[45] which was originally postulated as a reaction intermediate, but has never been isolated in substance, despite recent attempts[39] and an Iodine(I) fluorosulfate[34].

The latter compound has been produced from the interaction of a stoichiometric amount of I_2 and $S_2O_6F_2$ and has been extensively investigated. The brown solid product (m.p. 51.6°C) is found to be extensively dissociated in strong protonic acids such as HSO_3F according to:

$$5ISO_3F \longrightarrow 2I_2^+ + I(SO_3F)_3 + 2SO_3F^- \qquad (16)$$

to give blue green solutions[34]. The observation of similar colours in the formation of $I(SO_3CF_3)_3$ by oxidation of I_2 in HSO_3CF_3 indicate a similar dissociation in this acid. The dissociation will preclude the synthesis of ISO_3CF_3 in HSO_3CF_3.

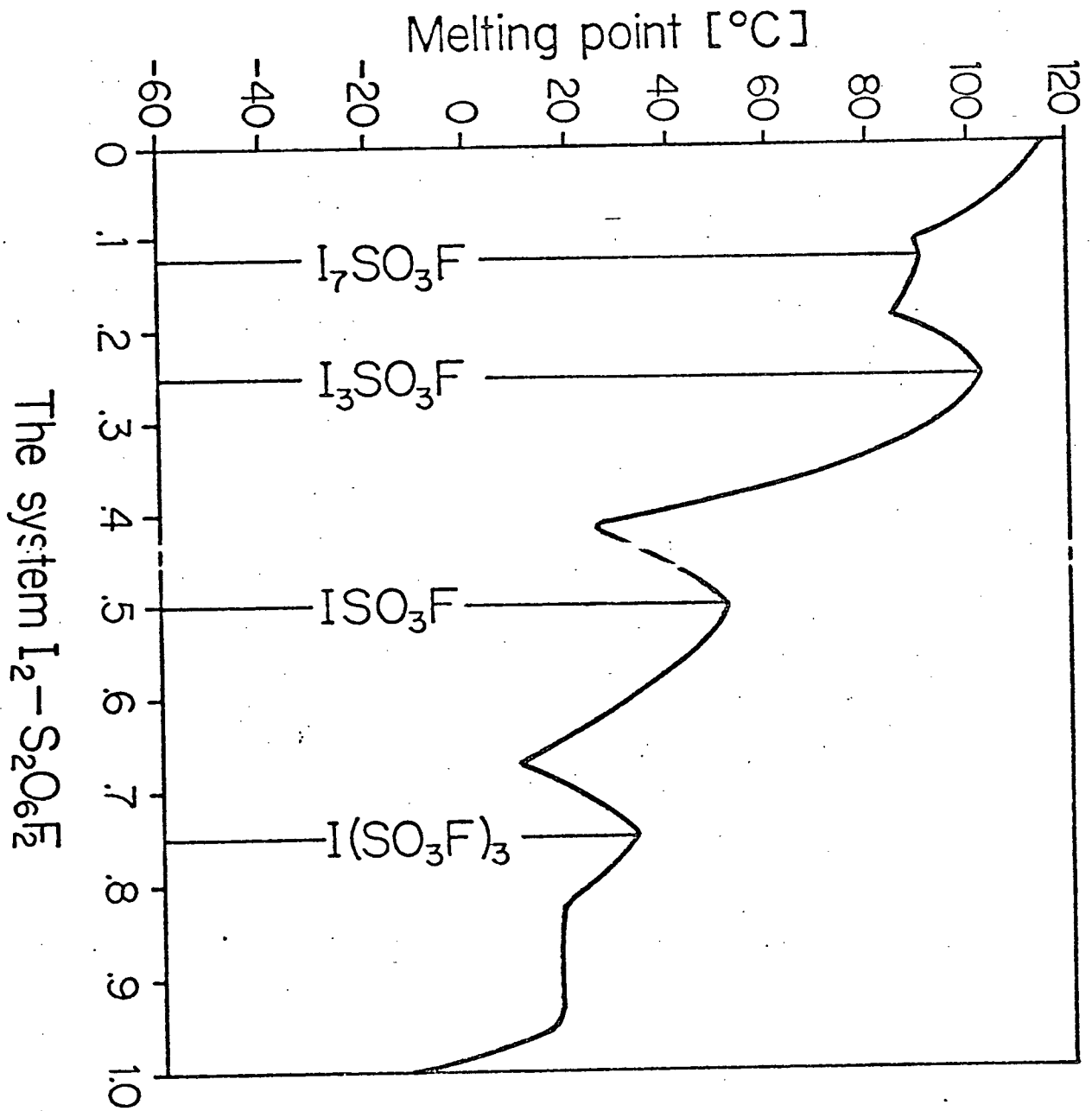
In their study of the iodine-fluorosulfate system, Chung and Cady[40] have produced the phase diagram for the iodine-peroxydisulf-

uryldifluoride system (figure 5). It was this phase study which led to the choice of a synthetic route to ISO_3CF_3. This phase diagram shows, first of all, that ISO_3F is a real compound. Secondly, no I_2^+ or species giving rise to paramagnetism or the characteristic blue colour was found in the melt. Thirdly, the transitions from $I(SO_3F)_3$ over ISO_3F and I_3SO_3F to I_7SO_3F occur without a gap, which implies that any compound can be converted into any other by addition of I_2 or $S_2O_6F_2$. Our method draws on the analogy to the fluorosulfate system. Although we do not have the corresponding peroxide, $S_2O_6(CF_3)_2$, as mentioned earlier, by combining I_2 and $I(SO_3CF_3)_2$ in the correct mole ratio in the melt all the compounds richer in iodine than $I(SO_3CF_3)_3$ such as ISO_3CF_3, $I_3SO_3CF_3$ and $I_7(SO_3CF_3)$ should, if they exist, be formed. The synthesis of ISO_3CF_3 was successfully carried out by the method given in the experimental section 1.a.iii according to:

$$I_{2(\ell)} + I(SO_3CF_3)_{3(\ell)} \xrightarrow{140°C} 3ISO_3CF_3 \qquad (17)$$

The high reaction temperature was necessary to obtain both reactants in the molten state. Higher temperatures (e.g. 170°C) resulted in thermal decomposition. Initially there was noticeable purple iodine vapour above the brown black melt. However, as the reaction proceeded this vapour was consumed. Because the iodine and the iodine(III) trifluoromethanesulfonate were combined in stoichiometric proportions elemental analysis is not conclusive proof of a new compound. The analysis is reported in table 4. The high

Figure 5


Melting point [°C]
-60
-40
-20
0
20
40
60
80
100
120
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
I_7SO_3F
I_3SO_3F
ISO_3F
$I(SO_3F)_3$
The system $I_2-S_2O_6F_2$

melting point 122°C and more conclusively the vibrational spectrum do indicate that the compound is ISO_3CF_3. Proof that the product is indeed ISO_3CF_3 rests on the analysis of the infrared spectrum.

ISO_3CF_3 is a dark brown hygroscopic solid. Its melting point is 121-122°C and it is thermally stable to 170°C under atmospheric pressure. At its decomposition point the formation of I_2, SO_3, and $(CF_3)_2SO_3$ is noted suggesting the decomposition reaction:

$$2ISO_3CF_3 \longrightarrow I_2 + SO_3 + (CF_3)_2SO_3 \qquad (18)$$

It should be noted as evidence that ISO_3CF_3 is a true compound and not a mixture, that no iodine vapour is observed at the melting point or below, even under vacuum.

The dark brown colour of ISO_3CF_3 is in good agreement with the colour of ISO_3F and also ICl and does not agree with the yellow colour found for iodine(I) nitrate. The melting point of ISO_3CF_3 (+122°C) is much higher than that of the fluorosulfate. This is very similar to the situation for $I(SO_3CF_3)_3$ and $I(SO_3F)_3$.

5. Polyhalogen and interhalogen trifluoromethanesulfonates $IX_2SO_3CF_3$ X=I,Br,Cl

The phase diagram of the iodine-peroxydisulfuryldifluoride system also indicates the existence of iodine rich fluorosulfates of the composition I_3SO_3F and probably I_7SO_3F. Even though some decomposition to I_2 and ISO_3F seems to occur I_3SO_3F [34] was isolated and characterized but I_7SO_3F which seemingly undergoes more extensive decomposition could not be isolated.

In an attempt to extend the fluorosulfate analogy to trifluoromethanesulfonates attempts were made to synthesize $I_3SO_3CF_3$ according to:

$$I_{2(\ell)} + ISO_3CF_{3(\ell)} \xrightarrow{\sim 140°C} I_3SO_3CF_3 \qquad (19)$$

However, despite repeated attempts only incomplete uptake of I_2 from the gas phase occured. Unlike the similar synthesis of ISO_3CF_3, the gas phase remained coloured during the reaction. All that was obtained upon removal of the volatiles under vacuum was a black, inhomogeneous, tar like substance containing small amounts of crystalline iodine. The temperature needed for reaction necessitated by the high melting point of ISO_3CF_3 is probably higher than the decomposition temperature of the I_3^+ group in a hypothetical $I_3SO_3CF_3$. One should keep in mind that the conversion of ISO_3F (m.p. 50.2°C) to I_3SO_3F may be performed at +65°C whereas in this reaction the 140°C necessary is already 70°C above the decomposition point of the I_3^+ cation in I_3SO_3F [34].

Two fluorosulfates, similar to I_3SO_3F, that is IBr_2SO_3F and ICl_2SO_3F [6] are both obtainable by straight addition as:

$$X_2 + ISO_3F \longrightarrow IX_2SO_3F \quad \text{where X = Cl or Br} \qquad (20)$$

An attempt was made to prepare the corresponding SO_3CF_3 compounds by combining solid ISO_3CF_3 with the halogens at room temperature or slightly below.

Chlorine gas was condensed onto ISO_3CF_3 at low temperatures, around 0°C, and was absorbed immediately. The resulting orange solid was warmed to room temperature where it became liquid and then solidified again to a yellow solid. The Raman spectrum of the yellow solid gave strong evidence for a mixture of $(ICl_3)_2$ [46] mixed with $I(SO_3CF_3)_3$, suggesting the following rearrangement:

$$3ICl_2SO_3CF_3 \longrightarrow (ICl_3)_2 + I(SO_3CF_3)_3 \qquad (21)$$

All attempts to prevent this rearrangement and to isolate the original orange compound at low temperatures were unsuccessful. Even in samples produced at low temperatures the Raman lines due to $(ICl_3)_2$ are found.

Bromine vapour and ISO_3CF_3 reacted to give a product which is stable at room temperature. Bromine vapour was allowed to react with solid ISO_3CF_3 at 0°C. It would seem that the synthesis of $IBr_2SO_3CF_3$ is possible because the reaction occurs at 0°C in the solid state. A melt, where rearrangements are achieved more readily is never formed. In addition IBr_3 is apparently nonexistent so that a mixture of IBr and Br_2 are the probable products of a rearrangement reaction. When liquid bromine was allowed to react with solid ISO_3CF_3 at room temperature the product was a black sticky solid which was lighter than expected for $IBr_2SO_3CF_3$. The loss in weight could be due to loss of bromine in the rearrangement according to:

$$3IBr_2SO_3CF_3 \longrightarrow 2IBr + 2Br_2 + I(SO_3CF_3)_3 \qquad (22)$$

$IBr_2SO_3CF_3$ is a dark red brown hygroscopic solid which melts at 72-75°C with partial decomposition. The solid has a slight tendency to decompose and become "sticky" if it is not pure; i.e. if formation of $IBr_2SO_3CF_3$ is incomplete. The results of elemental analysis are shown in table 4 and the vibrational spectra will be discussed later.

$IBr_2SO_3CF_3$ is one of a very limited group of IBr_2 derivatives. The only other examples known are IBr_2SO_3F [6] and $IBr_2Sb_2F_{11}$ [47]. IBr_2SO_3F was synthesized in the manner mentioned above and $IBr_2Sb_2F_{11}$ was obtained by reacting IBr_2SO_3F with SbF_5 according to:

$$IBr_2SO_3F + 3SbF_5 \longrightarrow IBr_2Sb_2F_{11} + SbF_4SO_3F \qquad (23)$$

It appears that a duplication of the halogen-ISO_3F addition reactions is successful only for $IBr_2SO_3CF_3$. However, it should be possible to form these compounds in solution, provided a suitable solvent can be found. HSO_3CF_3 was studied as a possible solvent and ultraviolet and visible spectra were taken on solutions of halogen X_2 and ISO_3CF_3 and compared with spectra of the corresponding IX_2SO_3F compounds in HSO_3F.

ISO_3CF_3 alone in HSO_3CF_3 gave a spectrum attributable to I_2^+. The spectrum is very similar to that of ISO_3F in HSO_3F [48] which has also been assigned to I_2^+ and the positions of the absorption maxima are similar to those found by Kemmit et al. [49] for solutions of I_2^+ in SbF_5. By comparing the extinction coefficients in each of these

cases, see table 5a, it can be seen that although they vary considerably in magnitude, they are always in the same relative proportions. The ability of HSO_3CF_3 to support I_2^+ in solution is thus demonstrated and the previous attribution of the blue-green colour formed during the synthesis of $I(SO_3CF_3)_3$ as being due to I_2^+ is further substantiated.

The existence of IX_2^+ (X = I, Br, or Cl) in HSO_3CF_3 was postulated, based on a study by Senior and Grover[50] demonstrating the existence of these species in 100% sulfuric acid and their existence in HSO_3F,[39] Solutions of I_2 and ISO_3CF_3; Cl_2 and ISO_3CF_3; as well as $IBr_2SO_3CF_3$ were investigated. The electronic spectra of these solutions are identical to spectra of solutions of IX_2SO_3F in HSO_3F which have been shown to have been due to the species IX_2^+ [6].

Having obtained the solvated cations as desired in solution the isolation of the compounds was attempted. The formation of $I_3SO_3CF_3$ was particularly hopeful. However, no stable compound was isolated. Upon removal of HSO_3CF_3 under vacuum all that remained were inhomogeneous tar like materials while the volatile products contained some molecular iodine.

6. Iodine-Oxygen Trifluoromethanesulfonates

Some of the earliest known compounds of positively polarized iodine are the iodine oxygen derivatives of oxyacids[13]. Two types of compound are encountered, the IO-derivatives, named in analogy to NO compounds iodosyl compounds and the IO_2 derivatives labelled iodyl compounds. The former ones were also regarded as "basic" salts of trivalent oxyacid derivatives suggesting, at least formally, the

Table 5a

Extinction Coefficients for I_2^+

λmax. (mμ) for ISO_3CF_3	638	465	400
sample		εmax. (per I_2)	
ISO_3CF_3 in HSO_3CF_3	2368	836	815
ISO_3F in HSO_3F	2186	580	630
I_2 in oleum	1850	460	490
I_2 in IF_5	884	326	301
I_2 in SbF_5	1410	462	504

existence of a base $I(OH)_3$, incomplete salt formation, and dehydration:

$$I(OH)_3 + HY \longrightarrow IOY + 2H_2O \qquad (24)$$

It became interesting to extend this study to SO_3CF_3 derivatives of these two types.

a. Iodyl trifluoromethanesulfaonate $IO_2SO_3CF_3$

Iodyl salts are known for some oxyacids including HSO_3F [51]. Again where the SO_3F compound had been obtained via:

$$I_2O_5 + S_2O_6F_2 \longrightarrow 2IO_2SO_3F \qquad (25)$$

Because of the unavailability of the peroxide an alternate route had to be devised. The synthesis of $IO_2SO_3CF_3$ was carried out as described in section [illegible] of the experimental as:

$$HI_3O_8 + 3HSO_3CF_3 \longrightarrow 3IO_2SO_3CF_3 + 2H_2O \qquad (26)$$

The starting material, HI_3O_8, was at first thought to be iodine pentoxide, I_2O_5, and in fact is sold as such. However, when the purity was checked by infrared spectroscopy it was found to be almost entirely HI_3O_8. This fact is extensively discussed by Selte and Kjekshus[29] who found most commercial samples of I_2O_5 and HIO_3 were contaminated with HI_3O_8, or in the case of I_2O_5 even with HIO_3. Because both the starting material and the product are white solids it was difficult to judge whether a reaction was complete or not. Therefore, stirring for more than 72 hours was found necessary to ensure complete reaction.

$IO_2SO_3CF_3$ is a white hygroscopic solid which decomposes between 310-320°C with purple iodine vapour released. The high melting point is not unexpected for an iodyl compound. Elemental analysis given in table 4 indicates that the compound is indeed $IO_2SO_3CF_3$. The infrared, and more conclusively, the Raman spectrum confirms this and will be discussed later.

The principle reason why conversion is so readily accomplished can be seen in the fact that HSO_3CF may act as a dehydrating agent. The water which is formed during the synthesis immediately reacts with the HSO_3CF_3, present in a large excess, to form the stable monohydrate[27]. In addition, unlike the S-F bond in most fluorosulfates the S-C bond in SO_3CF_3 compound appears to be resistant to hydrolytic attack.

b. Iodosyl trifluoromethanesulfonate, $IOSO_3CF_3$

A modification of the synthesis of iodyl compounds suggested by Masson and Argument[52] afforded a route to the iodosyl trifluoromethanesulfonate. The synthesis of $IOSO_3CF_3$ was carried out using HI_3O_8 and I_2 in HSO_3CF_3 according to the method described in section 2(i) of the experimental via:

$$HI_3O_8 + I_2 + 5HSO_3CF_3 \xrightarrow{HSO_3CF_3} 5IOSO_3CF_3 + 3H_2O \qquad (27)$$

$IOSO_3CF_3$ is a yellow hygroscopic solid which decomposes between 235 and 240°C. The product was identified by elemental analysis (table 4) as $IOSO_3CF_3$. Vibrational analysis discussed later confirmed this.

An unsuccessful attempt was made to synthesize $IOSO_3CF_3$ by controlled hydrolysis of $I(SO_3CF_3)_3$ in suspension in HSO_3CF_3 according to:

$$I(SO_3CF_3)_3 + H_2O \xrightarrow{HSO_3CF_3} IOSO_3CF_3 + 2HSO_3CF_3 \qquad (28)$$

However, the addition of trace amounts of water to $I(SO_3CF_3)_3$ results instantaneously in the occurence of the familiar blue-green colour of I_2^+. This indicates a disproportionation or redox reaction rather than a straightforward solvolysis.

For any previously synthesized iodine trifluoromethanesulfonate a fluorosulfate analogue was known. However, in the case of $IOSO_3CF_3$, no such analogue had been prepared. The formation of $IOSO_3F$ had been mentioned only briefly in the literature[34] as a product of the hydrolysis of $I(SO_3F)_3$ according to:

$$I(SO_3F)_3 + H_2O \longrightarrow IOSO_3F + 2HSO_3F \qquad (29)$$

The reaction is accompanied by a blue colour (I_2^+) suggesting a disproportionation reaction. The solid product, however, was found to contain substantial amounts of pentavalent iodine, suggesting the claim of $IOSO_3F$ may be erroneous. It is difficult to assess the claim as no analysis is reported.

Subsequent to this work $IOSO_3F$ was prepared[53] by a method analogous to that used for $IOSO_3CF_3$. Attempts to form $IOSO_3CH_3$, $IOCO_2CF_3$ and $(IO)_2PO_2F_2$ failed. During the synthesis of $IOSO_3CF_3$ the familiar colour change sequence from brown to blue green to

yellow was observed. A similar change was observed for the formation of the fluorosulfate. In the three unsuccessful cases the solutions were at all times faintly tinged with red, indicating iodine in the 0 oxidation state. This would seem to suggest that a possible prerequisite for the formation of iodosyl compounds by this method is the capability of the acid to stabilize I_3^+ (or I_5^+) and I_2^+ as intermediates in the oxidation of I(0) to I(III). The acids HPO_2F_2, HSO_3CH_3 and HCO_2CF_3 are weaker protonic acids than either H_2SO_4, H_2SeO_4, HSO_3CF_3 and HSO_3F, incapable of stabilizing even the least electrophilic of the polyiodine cations I_3^+. This point could be confirmed by experiment. Addition of I_3SO_3F to either HPO_2F_2 or HCO_2CF_3 resulted in the instantaneous formation of molecular iodine[55].

7. Bromine tristrifluoromethanesulfonate

After the field of iodine trifluoromethanesulfonates had been extensively investigated attempts were made to form other halogen trifluoromethanesulfonates. Observing table 3 in the introduction it can be seen that for the fluorosulfate group the following compounds exist. $Br(SO_3F)_3$, $BrSO_3F$ and $BrSO_3F_4^-$. We therefore attempted the synthesis of $Br(SO_3CF_3)_3$ as an entry into this area. Complexation hopefully would lead to $Br(SO_3CF_3)_4^-$ and reduction to $BrSO_3CF_3$.

The first attempt to form the $Br(SO_3CF_3)_3$ was to follow the synthesis of $I(SO_3CF_3)_3$ using Br_2 in place of I_2. Unfortunately the results were inconclusive and alarming. Upon warming, the mixture of $S_2O_6F_2$, Br_2, and HSO_3CF_3 detonated shattering the reaction vessel

and thus deterring any further attempts via this route.

The addition of HSO_3CF_3 to $Br(SO_3F)_3$ gave a red-brown solution which at first looked promising. However removal of the solvent did not yield the expected product. A brown volatile material, comparable in volatility to HSO_3CF_3 was obtained and it was impossible to effect a complete separation of the two.

An alternate route was sought by the reaction of BrF_3 and HSO_3CF_3 as follows:

$$BrF_3 + 3HSO_3CF_3 \longrightarrow Br(SO_3CF_3)_3 + 3HF \qquad (30)$$

The reaction was carried out on a monel metal vacuum line in a quartz reactor. Upon warming the clear liquid formed detonated with no visible sign of decomposition. At this point the investigation was abandoned. Attempts to solvolyse BrF_3 in HSO_3CF_3 in a monel reactor again only yielded volatile materials and no separation was attempted.

Cationic bromine oxygen compounds are also more unstable than the corresponding iodine compounds. Naumann et al.[69] have prepared the compound $KIO_2(OCOCF_3)_2$ by reacting KIO_3 with $(CF_3CO)_2O$ but attempts to prepare this bromine analogue resulted only in an explosion. H.A. Carter's[70] attempts to prepare Bromine-oxygen compounds of fluorosulfuric acid also met with failure. There still may be a possibility of forming some bromine trifluoromethanesulfonates; however, the field should not prove to be as extensive as that of iodine trifluoromethanesulfonates.

C. Vibrational Spectroscopy

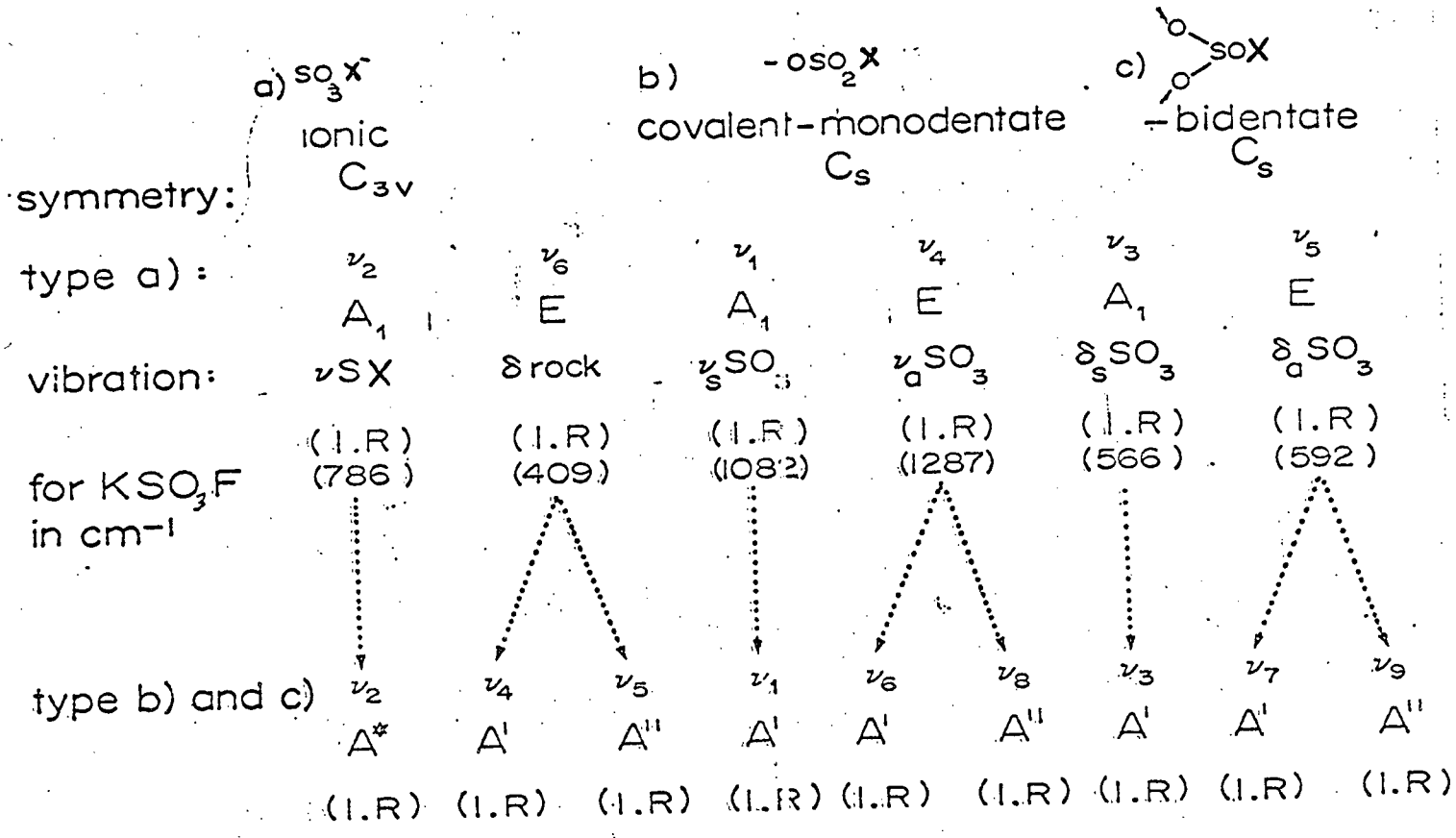
1. General Introduction

The main interest in the vibrational spectra of iodine trifluoromethanesulfonates is centered on the SO_3CF_3 group, and even more narrowly on the S-O vibrational modes, because bonding of the SO_3CF_3 group to iodine or any other central atom will most likely occur through the oxygen of the SO_3 group. In a general way the SO_3CF_3 group can be considered as SO_3X with $X = CF_3$. An SO_3X group can be either ionic, i.e. in compounds of the type M^ISO_3X where M^I = K or NO^+ or covalently bonded. In all of the cationic halogen compounds, the SO_3X will probably be covalent due to the relatively large electronegativity of iodine.

The highest symmetry for the SO_3X^- ion is C_{3v}. If the ion is bonded covalently through one oxygen, monodentate, or two oxygen, bidentate, then the symmetry will be reduced to C_s. What this will mean in terms of the vibrational frequencies is summarized in the correlation diagram of SO_3X in figure 6.

When the SO_3X group has C_{3v} symmetry there are 6 normal vibrational modes. These are three A_1 modes, one symmetric SO_3 stretch, one SX stretch and one SO_3 bend, and three degenerate E modes, one asymmetric SO_3 stretch, one asymmetric SO_3 bend and one rocking mode. If the SO_3X group acts as a monodentate or bidentate ligand then the reduction of symmetry to C_s results in the splitting of the degenerate E modes and all 9 fundamental vibrations are observed.

Figure 6. Correlation Diagram for the SO_3X group.



A = nondegenerate
E = doubly degenerate
I = infrared active
R = Raman active
a = antisymmetric
s = symmetric

In the SO_3 stretching region there is a change from two stretching modes to three. The E mode is split into an A' and A" mode. In the bending region a similar splitting is observed. The rocking mode is also split in the same manner. To complete the circle, if the SO_3X group is tridentate, i.e. each oxygen is bonded, then the symmetry is once more C_3v.

This is the general case for SO_3X. The particular case of SO_3CF_3 is somewhat more complicated. Assuming the CF_3 group, which in the anion maintains the C_3v symmetry, can be considered to have localized C_{3v} symmetry in the covalent situation where the SO_3 symmetry is reduced, then there are another 5 fundamentals to be expected. And, if the symmetry of the CF_3 group is reduced there would be another three bands in addition. This is shown in the correlation diagram for SO_3CF_3 shown in figure 7.

As has been mentioned earlier, vibrational studies of the SO_3CF_3 anion, including normal coordinate analyses and valence force field calculations have been reported by two groups[20,21]. These two studies do not agree on the assignment of the spectra. The major difficulty in assigning the bands is that the SO_3 and CF_3 stretching vibrations are of identical symmetries for the ion (E and A_1) and unfortunately occur in the same region of the spectrum. Considerable mixing of the frequencies occurs resulting in a very complex spectrum. For the purpose of this discussion the assignment of Burger et al.[21] is used. The reason for this is that the SO_3 and CF_3 bands are assigned by comparing the bands observed with bands assigned previously for other

FIGURE 7

Normal Vibrations of SO_3CF_3 groups with C_{3v} Symmetry

Description	A_1	A_2	E
ν CF_3	ν_1		ν_7
δ CF_2	ν_2		8
δ FCS			9
ν CS	ν_3		
ν SO_3	ν_4		10
δ SO_2	ν_5		11
δ C-S-O			12
torsion C-S		$^*\nu_6$	

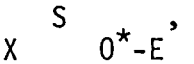
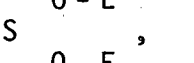
*This band is inactive in both infrared and Raman.

compounds containing only SO_3 and CF_3 groups. Also, the assignments are in accord with trends observed in other sulfonates[54].

The assignment of spectra for covalent, either mono, bi, or tridentate groups should not be quite as difficult as the ionic case because the local symmetry for the SO_3 part of the molecule is reduced, eliminating extensive mixing. Complications may arise when there is more than one type of SO_3CF_3 group present. This results in more bands, which often coincide. This leads to rather unresolved broad band contours. When attempting an assignment of the compounds synthesized in this thesis considerable help can be derived from the fact that examples of each coordination type for the SO_3CF_3 group may be found in the literature. Monodentate SO_3CF_3 groups are found in $(CF_3)_2SO_3$ whose infrared spectrum has been reported by Noftle and Cady[25] in $FXeSO_3CF_3$ [55] and in $(CH_3)_3GeSO_3CF_3$ [56]. Bidentate bridging SO_3CF_3 is found for organotin(IV) derivatives $(CH_3)_3SnSO_3CF_3$ [54] and $(CH_3)_2Sn(SO_3CF_3)_2$ [18] where structural proposals are based on ^{119}Sn Mossbauer spectra and the X-ray diffraction study of the analogous tin compound $(CH_3)_2Sn(SO_3F)_2$ [57]. A tridentate group has been proposed for the compound $TiCl_3SO_3CF_3$ [22].

It may also be noted that the spectrum of any of these SO_3CF_3 compounds is quite similar to the spectra of the analogous SO_3F compound. The SO_3 frequencies for the SO_3CF_3 compounds are slightly lower than for the corresponding fluorosulfates. This is in accord with the electronegativity arguments and also the underlying bonding concept, that of $d\pi$-$p\pi$ interaction based on the model discussed by

Cruickshank[58]. This trend is illustrated in table 5 where a comparison of $(C_2H_5)_2Sn(SO_3F)_2$ and $(C_2H_5)_2Sn(SO_3CF_3)_2$ is made.

As may be seen from the examples quoted above a differentiation between monodentate and bidentate bridging SO_3X groups is possible even through the symmetry of both is C_s. In the SO_3 stretching region there is a definite difference. In the monodentate case, i.e.  , where O^* is the bonding oxygen, there are three stretching modes. SO_2 as (A") SO_2sym(A') and SO^*(A'). The position of the last mentioned band is dependent on the nature of the group "E" to which the O^* is bonded. On the other hand in the bidentate case,  , where again O^* indicates the bonding oxygens there are 3 different S-O stretching bands. These are νSO(A'), νSO_2^* as (A") and νSO_2^*sym (A'). Here the position of νSO is independent of the moiety to which the SO_3X is bonded and the position of the other two modes is dependent on the nature of E. By comparing spectra, the shifts of one SO stretching mode only, indicates a monodentate SO_3X group while the shifting of two modes is a good indication of a bidentate SO_3X group. The particular case of the SO_3CF_3 group will be considered later in the assignment of $CF_3SO_3CF_3$.

In summary, these are the ways in which the vibrational spectra of SO_3CF_3-I compounds will be studied. Assignments of the spectra will be made with reference to the study of the anion by Burger et al.[21] and the published spectra of covalent SO_3CF_3 groups. The decision of whether or not the compound contains ionic SO_3CF_3 groups will be made on the basis of the number of SO_3 modes present.

TABLE 5

A comparison of SO_3X infrared vibrational frequencies in $(C_2H_5)_2\ Sn(SO_3F)_2$ and $(C_2H_5)_2\ Sn(SO_3CF_3)_2$ [23]

$(C_2H_5)_2Sn(SO_3F)_2$		$(C_2H_5)_2\ Sn(SO_3CF_3)_2$		Assignment
cm^{-1}	intensity*	cm^{-1}	intensity	
1360	vs, b	1340	vs, b	SO_3 stretch (A")
1170	vs, b	1138	s, b	SO_3 stretch (A')
1070	s	1036	vs	SO_3 stretch (A')
612	m, sh	632	s	SO_3 bend (A")
585	s, sh	581	m	SO_3 bend (A')
575	s	512	s	SO_3X bend (A')
416	ms	356	m	SO_3X rock
355	m	320	ms	SO_3S torsion

* Term meanings:

vs - very strong s - strong m - medium w - weak

vw - very weak b - broad sh - shoulder

Whether a compound contains monodentate, bidentate, or both mono- and bidentate SO_3CF_3 groups will be decided by comparing the spectra with spectra of compounds known to contain mono- or bidentate SO_3CF_3 groups. These and other features of the spectra will be discussed in conjunction with the analogous fluorosulfate compounds. Finally, because of the complex symmetry of the SO_3CF_3 group it should be noted, from a purely practical point of view that all vibrational modes should be both Raman and Infrared active.

2 $M[I(SO_3CF_3)_4]$

The vibrational frequencies observed for $Rb[I(SO_3CF_3)_4]$ are listed, along with estimated intensities in table 6 as well as the SO_3CF_3 vibrations found for $(CH_3)_3GeSO_3CF_3$ [56]. It is interesting that because of the unreactiveness of the SO_3CF_3 compound the infrared spectrum was obtained below the silver halide region in contrast to the situation for $I\text{-}SO_3F$ compounds. The assignment of the spectra is based mainly on the assignment by Burger et al.[21]. The small splitting of the absorption bands for the $[I(SO_3CF_3)_4]^-$ ion which are particularly obvious in the Raman spectrum in the S-O and C-F stretching range is attributed to solid state splitting caused probably by weak coupling of the individual SO_3CF_3 groups. Precedent for such splittings are found in a number of fluorosulfate anions, i.e. $[I(SO_3F)_4]^-$ [59]. Many features observed in the spectrum of $Rb[I(SO_3CF_3)_4]$, such as the very broad infrared absorption bands and the discrepancies in position between the infrared and Raman

Table 6

Vibrational Frequencies for $Rb[I(OSO_2CF_3)_4]$ and $(CH_3)_3 Ge\ OSO_2CF_3$ [56]

$Rb[I(OSO_2CF_3)_4]$		$(CH_3)_3GeOSO_2CF_3$	
Raman [cm^{-1}]	Infrared [cm^{-1}]	Infrared [cm^{-1}]	Approximate description
1376 mw 1368 w	1365 vs,b	1365 s	$\nu_{as}SO_2$
1251 m 1234 mw	1242 s sh	1241	$\nu_{as}CF_3$
1214 w	1210 vs,b	1205 vb	$\nu_{sym}SO_2$
1170 ms	1150 s,b	1164 s	$\nu_{as}CF_3$
1074 vw	~1080 vw,sh		impurity of $I(OSO_2CF_3)$
974 vw			
854	865 s,sh 830 vs, b	984 vs,b	νS-OX
777 vs	770 s	768 m	νCS
652 ms 642 w	632 s,b	634 s	δSO_2
620 ms	615 m,sh	620 m,sh	SO_2 rocking
598 vs	590 m	590 s	$\delta_{sym}CF_3$
576	578 w	572 ms	δSO_2X
536 s	528 s	515	$\delta_{as}CF_3$
515 sh	510		
	435 ms		$\nu_{as}IO$
408 w 394 s			νIO sym in phase
383 ms			νIO sym out of phase
346 ms	352 vs		ρSO_2
322 s	315 ms		δCS
264 ms			
253 w			ρCF_3

bands are also present for $FXeSO_3CF_3$, indicating a strong structural similarity. There are, nevertheless, some differences in the proposed assignments.

The three sulfur-oxygen vibrations expected for a monodentate SO_3CF_3 group are found at 1365, 1210 and 850 cm^{-1}. This is in relatively good agreement with corresponding bands for $(CH_3)_3GeSO_3CF_3$ except for the 850 cm^{-1} band which is assigned to S-OX and is definitely affected by the electronegativity of the group X. The comparable bands for $FXeSO_3CF_3$ are at 1390, 1200, and 840 cm^{-1} respectively[55].

The C-F stretching modes are found at 1251, 1234, and 1170 cm^{-1}, a region similar to that for the SO_3CF_3 ion. This indicates that the CF_3 group is little affected by the bonding through oxygen. The local symmetry for the CF_3 moiety remains C_{3v} and is not reduced. The number and position of the stretching modes is in every way consistent with a monodentate SO_3CF_3 group.

In the region of the bending modes good agreement between the findings for $Rb[I(SO_3CF_3)_4]$ and both $(CH_3)_3GeSO_3CF_3$ and $FXeSO_3CF_3$ is found. The infrared and Raman spectra are well resolved and consistent in this region. The only exception occurs around 400 cm^{-1}. Bands of fairly high intensity which occur at 394 and 383 cm^{-1} in the Raman spectrum are absent in the infrared spectrum while a band at 435 cm^{-1} only appears in the infrared spectrum. The two Raman bands are assigned as the symmetric in phase and out of phase I-O stretching modes. The 435 cm^{-1} band is assigned as the asymmetric I-O stretching

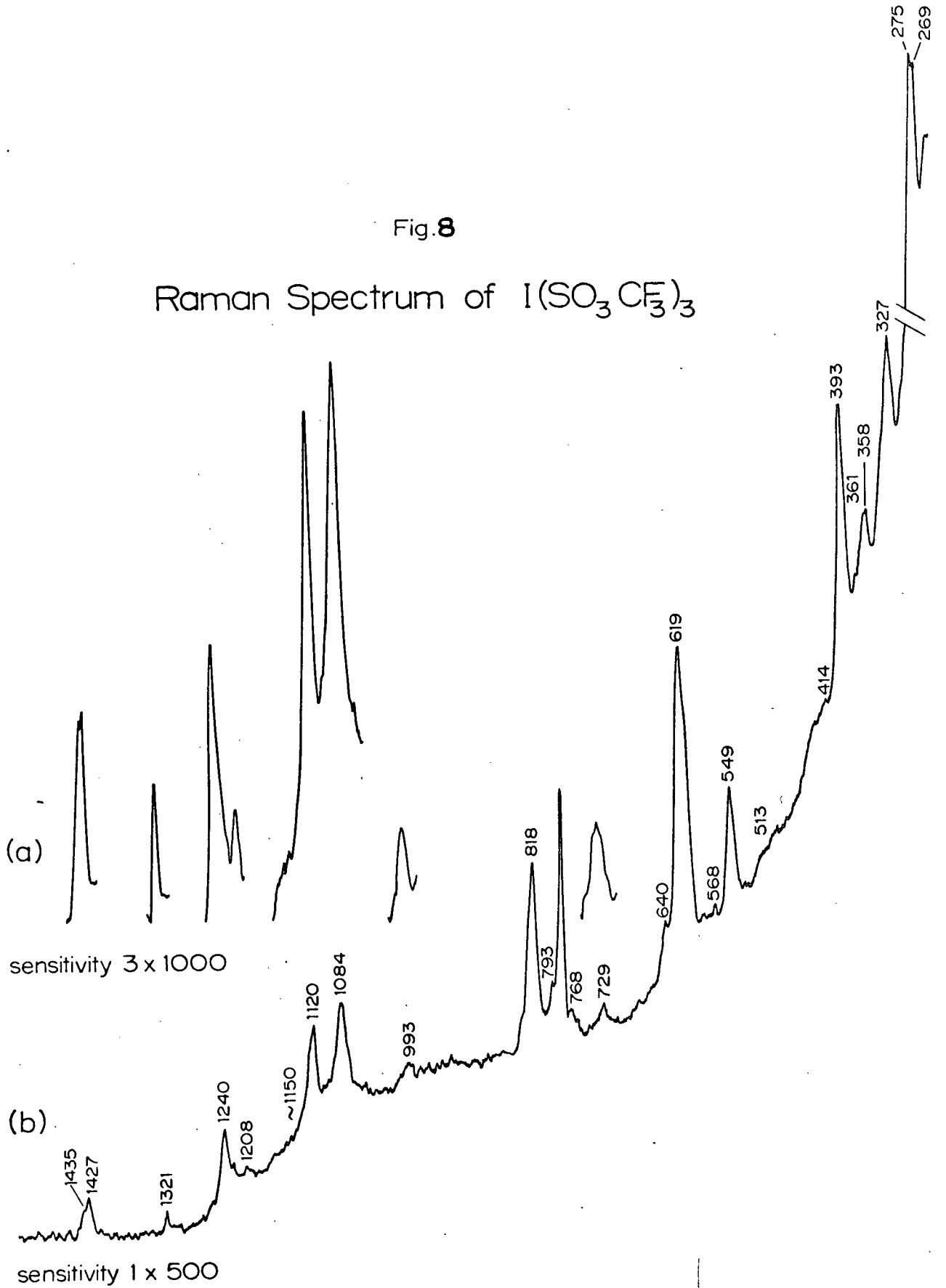
mode. This mutual exclusion is what is expected for a square planar configuration around iodine. Several precedents have been reported[60] where the asymmetric stretching band occurs at a higher wave number than the two symmetric bands. However, this is not found for ICl_4^- [61]. The positions observed for the $[I(SO_3CF_3)_4]^-$ ion are slightly lower than those observed for the $[I(SO_3F)_4]^-$ ion[59]. The extremely low I-O stretching modes found for $[I(ClO_4)_4]^-$ [39] are unusual but may perhaps be due to a very weak I-O bond. This is indicated by the low thermal stability (up to room temperature) of $Cs[I(ClO_4)_4]$ [39] compared with the thermal stability of the $[I(SO_3F)_4]^-$ and $[I(SO_3CF_3)_4]^-$ ions which can be as high as 200°C. This trend is also found for $I(ClO_4)_3$ [39], stable up to -45°C and $I(SO_3CF_3)_3$ which begins to decompose only above 170°C. The iodine oxygen deformation modes which should occur below 200 cm^{-1} were not observed. The spectra of $K[I(SO_3CF_3)_4]$ and $Cs[I(SO_3CF_3)_4]$ presented an almost identical picture. Only very minor discrepancies were observed.

3. $I(SO_3CF_3)_3$

The assignment of the spectrum of $I(SO_3CF_3)_3$ presents a more complex problem than was encountered for $I(SO_3CF_3)_4^-$. This is seen by the increased number of bands observed in the S-O and C-F stretching region from 1450-700 cm^{-1}. There are ten bands assignable as fundamentals in the spectrum of $I(SO_3CF_3)_4^-$ while there are 14 bands for $I(SO_3CF_3)_3$. The difficulty in assigning these bands is increased by the fact that many of them are extremely broad in the infrared spectrum. In addition, accidental coincidence of bands,

Fig.8

Raman Spectrum of $I(SO_3CF_3)_3$



particularly in the 1280-1150 cm^{-1} region may present additional complications. Because of this complexity only approximate assignments of the S-O and C-F stretching modes are possible and some ambiguity is unavoidable. The complexities observed are most likely due to SO_3CF_3 groups of different functionality. The infrared and Raman spectra are listed in table 7.

Bands occurring at 1420, 1210 and 830 cm^{-1} are assigned as S-O stretching modes for a monodentate SO_3CF_3 group. This assignment is based mainly on the similarity of these bands to the corresponding bands for $I(SO_3CF_3)_4^-$. The shift to slightly higher wavenumbers for νSO_2 is also observed in the corresponding fluorosulfate compounds and may reflect the electronic differences between a neutral species and an anion. The bands at ~1320, 1120, and 980 cm^{-1} on the other hand are remarkably similar to sulfur-oxygen stretching bands for a bidentate bridging SO_3CF_3 group as found in both $(CH_3)_3$ Sn SO_3CF_3 [54] and $(CH_3)_2$ $Sn(SO_3CF_3)_2$ [18]. The remaining three bands in this region at 1240, 1160, and 1084 cm^{-1} are assigned to CF stretching modes. It might be expected that these bands should occur at different wavenumbers for different SO_3CF_3 groups. However, it seems reasonable to assume that the CF_3 groups are not affected much by the environment of the SO_3 moiety. All of these bands occur as shoulders in the infrared spectrum (see table 7) and any splitting may be either too small to be observed or obscured by the adjacent broad SO_3 bands.

Table 7

Vibrational Spectrum of $I(OSO_2CF_3)_3$

Raman [cm^{-1}]	Int.	IR [cm^{-1}]	Int.	Approximate description	Raman [cm^{-1}]	Int.	IR [cm^{-1}]	Int.	Approximate description
1435	m,sh	1420	s,b	$\nu_{as}SO_2(t)$	619	vs	625	s,b	
1427	ms								
					568	vw	580	ms,sh	
1321	m	1324	ms	$\nu SO(br)$					
					549	s	542	w,sh	
1240	ms	1235	m,sh	νCF_3					
					513	w	515	s	
1208	mw	1210	vs, b	$\nu_{sym}SO_2(t)$					
							452	w	
1160	w,sh	1165	w,sh	νCF_3					
					414	w	415	w	
1120	s	1130	s,b	$\nu SO(br)$					
					393	s	390	s	
1084	s	1090	s,sh	νCF_3	361				
					358	s	362	s	
993	mw	980	ms	$\nu SO(br)$					
					327	s	318	s	
818	vs	830	vs,b	νSO					
					275	s			
					269	s			
793	w								
780	vs	780	s,b	νSC					
768	w								
729	vw	730	s,b						
640	w								

As was explained for $Rb[I(SO_3CF_3)_4]$ a square planar configuration of oxygen around iodine is to be expected. However, in the case of $I(SO_3CF_3)_3$ it is not possible to make a definite assignment of the I-O stretching bands based on a square planar arrangement. Almost all the bands observed in the region from 430-380 cm^{-1} are infrared and Raman active. This may be due to a distortion of the square planar arrangement of oxygen caused by the presence of two non-equivalent SO_3CF_3 groups.

4. ISO_3CF_3

For this very dark red brown compound no Raman spectrum was obtained, despite repeated attempts on several different samples. The infrared spectrum is very complex. The spectrum is listed in table 8. Although the spectrum is very complex and difficult to assign it is different from the spectra for $I(SO_3CF_3)_3$, $(I(SO_3CF_3)_4]^-$ or $SO_3CF_3^-$. ISO_3CF_3 is, therefore, a unique compound rather than merely a mixture of I_2 and $I(SO_3CF_3)_3$. Unusual ionic formulations such as $I_3^+[I(SO_3CF_3)_4]^-$ or $I^+(SO_3CF_3)^-$ are also highly unlikely. The most likely structure is a polymer with polydentate SO_3CF_3 groups. Any assignment of the infrared spectrum is difficult and a more detailed description of the structure would be only guesswork. The I in ISO_3CF should be positively polarized and extensive anion-cation interaction could result. The x-ray diffraction study on the two modifications of ICl[62] may serve as an illustration for complications which may be expected in such a case.

TABLE 8

Vibrational Spectrum of ISO_3CF_3

infrared , cm^{-1}	
1340	w, sh*
1210	vs
1135	j, b
1025	m
930	m
770	ms
684	m, sh
624	ms, b
585	m, sh
555	sh
518	ms
455	vw
371	m, sh
358	vs
338	m, sh
312	ms

*For explanation of terms see Table 5

5. $IBr_2SO_3CF_3$

The spectra of $IBr_2SO_3CF_3$, listed in table 9 will be considered as derived from IBr_2^+ and $SO_3CF_3^-$ with allowance for some cation-anion interaction. This treatment is based on studies of analogous fluorosulfate compounds[6]. In considering the $SO_3CF_3^-$ anion spectra the assignments of Burger et al[21] will be used, while the IBr_2^+ cation spectrum will be compared with the spectra of other compounds containing the IBr_2^+ cation. In contrast to the interhalogen fluorosulfates[6] which were found to react with most conventional I.R. window materials $IBr_2SO_3CF_3$ gave well resolved infrared spectra with both AgBr and KRS-5 windows and spectra were recorded down to 200 cm^{-1}.

More anion bands were observed for $IBr_2SO_3CF_3$ than were observed by Burger for $AgSO_3CF_3$. This most likely is due to the removal of the degeneracies of the E modes of the SO_3 and CF_3 vibrations. In particular anion-cation interaction would result in the splitting of the SO_3 modes, and this is the most likely source of additional bands. The IBr_2^+ cation, unlike the Ag^+ cation, is not spherical and some symmetry lowering due to this asymmetry may split the CF_3 modes as well.

The only major changes from the assignment made by Burger is for the CF_3 stretching frequencies. Burger assigns the band at 1237 cm^{-1} as an A mode and the band at 1167 as an E mode. Spectra for $IBr_2SO_3CF_3$ indicate that the band at 1237 is split and thus the A and E modes should be interchanged. Burger bases his assignments on comparisons made with other CF_3 containing compounds. In every other case the A

TABLE 9

Infrared Spectra of $IBr_2SO_3CF_3$ and $AgSO_3CF_3$ [21]

$IBr_2SO_3CF_3$	$SO_3CF_3^-$ in $AgSO_3CF$	Approximate description
1400, vw, sh*[a]		comb. band
1280 vs, b	1270 vs, b	S-O stretch
1220 s, sh	1237 s	CF stretch
1205 vs		CF stretch
1165 s, sh	1167 s	CF stretch
1025 s (1026m)[b]	1043 vs	S-O stretch
935 vw		comb.
770 ms (770w)[b]	760 m	C-F stretch
650 m, sh		O-SO bend
625 vs	647 s	C SO bend
580 ms	582 m	FCF bend
565 w, sh	579 sh	Comb. band
525 s	525	OSO bend
515 s	515	OSO bend
360 vw, sh		Comb. band
345 s (354)[b]	351 m	C-S-O bend
315 ms	320 m	F-C-F bend
258 s (260s)[b]		IBr_2 stretch
248 s (253vs)[b]		
215 m	217 s	F-C-S bend

a. For explanation of terms see table 5.

b. Raman Spectrum

mode occurs at a lower wavenumber than the E mode. $SO_3CF_3^-$ is the only case where the E mode is lower. It would seem reasonable, therefore, in view of the splitting observed for $IBr_2SO_3CF_3$ to interchange the two assignments.

The CF_3 stretching bands occur at 1220, 1205 and 1165. The SO_3 stretching modes which are expected to be split more than the CF_3 bands occur at 1280 and 1025. The band at 1280 which is assigned to the E mode for SO_3 is very broad and some splitting is indicated. That the SO_3 bands are broader than the CF_3 bands has been observed for other SO_3CF_3 compounds[22].

The bending modes occur much as would be expected for an $SO_3CF_3^-$ ion. The only difference is that the SO_3 E mode is split. The SO_3 bending vibrations occur at 650, 525 and 515 cm^{-1}, while the CF_3 bending vibrations occur at 580 and 315 cm^{-1}. All the other bands between 1400 and 300 cm^{-1} can be assigned to $SO_3CF_3^-$ vibrations except for three bands at 1400, 935 and 565 cm^{-1}. These bands are very weak and are assigned as combination bands of the $SO_3CF_3^-$ ion. The remaining two bands at 258 and 248 cm^{-1} are assigned as IBr_2 stretching vibrations. As can be seen from table 10 bands in this region agree quite well with the bands assigned for IBr_2SO_3F. Unlike the case for IBr_2SO_3F, however, the IBr_2 stretching modes appear to be split into a symmetrical and an asymmetrical band. Both are Raman active, as would be expected for a bent IBr_2^+ group. When discussing their finding for IBr_2SO_3F, where only one IBr stretch was observed in the Raman spectrum, Wilson et al. invoked accidental degeneracy for the

TABLE 10

Vibrational frequencies for IBr_2^+ in $IBr_2SO_3CF_3$ and IBr_2SO_3F[6]

Compound	ν IBr_2 asym.	ν IBr_2 sym	δIBr_2
$IBr_2SO_3CF_3$	258 cm^{-1}	248 cm^{-1}	
IBr_2SO_3F	256 cm^{-1}	256 cm^{-1}	127 cm^{-1}

two stretching modes (a situation which had been previously found for Br_3^+ [63]) rather than a linear cation where only one band would be Raman active. The results for $IBr_2SO_3CF_3$ clearly point to a bent tri atomic cation as would be expected using a simple valence electron pair repulsion treatment. The only remaining band at 215 cm^{-1} is assigned to an S-C-F bending mode.

6. $IO_2SO_3CF_3$

Iodyl trifluoromethanesulfonate is a very good Raman scatterer and a well resolved Raman spectrum was obtained. The infrared spectrum obtained on a finely powdered sample held between two silver bromide plates was also well resolved. In assigning the spectra two main features were considered. For the SO_3CF_3 group, attention was focussed on the S-O and C-F stretching region while for the IO_2 moiety a comparison with other iodyl salts was made. The band frequencies of $IO_2SO_3CF_3$ and the assignments are listed in table 11.

For the SO_3CF_3 group, the presence of three S-O stretching modes at 1326, 1221 and 941 indicate that the SO_3CF_3 group is interacting with the IO_2 and is not just a simple $SO_3CF_3^-$ ion. The position of the bands is compatible with either a monodentate or bidentate bridging group, but the fact that only 3 bands occur would suggest that only one type of SO_3CF_3 group is involved. The CF_3 stretching frequencies are at 1225 and 1125 cm^{-1}. The lack of splitting of the E mode suggests that they retain a local C_3V symmetry. Again the other bands have been assigned by comparison

TABLE 11

Vibrational frequencies for $IO_2SO_3CF_3$ and IO_2SO_3F

IO_2SO_3F Raman Cm^{-1}	$IO_2SO_3CF_3$ Raman Cm^{-1}	IR Cm^{-1} Int.	Approximate Description
		1424 vw	
1335	1326 ms[a]	1332 s	SO_3 str
	1233 m	1225 s, sh	CF_3 sym str.
1195	1221 mw	1210 s	SO_3 str.
1170			
	1125 s	1125 s	CF_3 as. str.
1070		1055 w, sh	
1030	975 w	965 m, sh	SO_3 str.
1010	941 s	938 s	
900			
878	849 ms	860 vs	IO_2 as. str.
865	823 vs	830 vs	IO_2 sym. str.
843			S-F str.
	774 ms	780 m	S-C str.
	678 s	680 w, sh	
660	645 m	642 s	
615	628 w	630 s, sh	
	589 ms	600 s, sh	
	578 m	585 s, sh	
	542 s	540 s	
	522 ms	520 m, sh	
459			
428		395 s	
415	367 w, sh	360 ms	
	345 s	340 m, sh	
	328 ms	320 w, sh	
310	311m		

continued...

TABLE 11, continued

IO_2SO_3F	$IO_2SO_3CF_3$
	290 m
	258 ms
	235 vs
	217 mw
	190 vs
	163 m
	115 w, sh

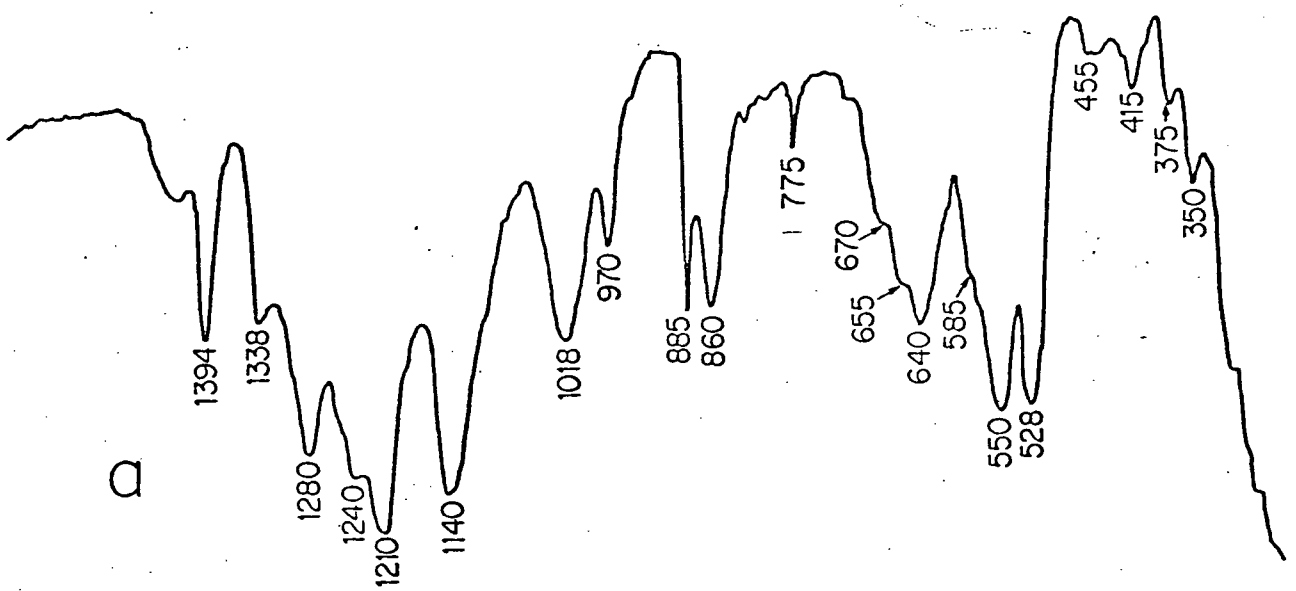
a. For explanation of terms see table 5.

to the assignment of Burger et al.[21] on the $SO_3CF_3^-$ ion. The band at 780 cm^{-1} which is characteristic of the SO_3CF_3 group is present and is not split. This is further evidence for only one type of SO_3CF_3 group.

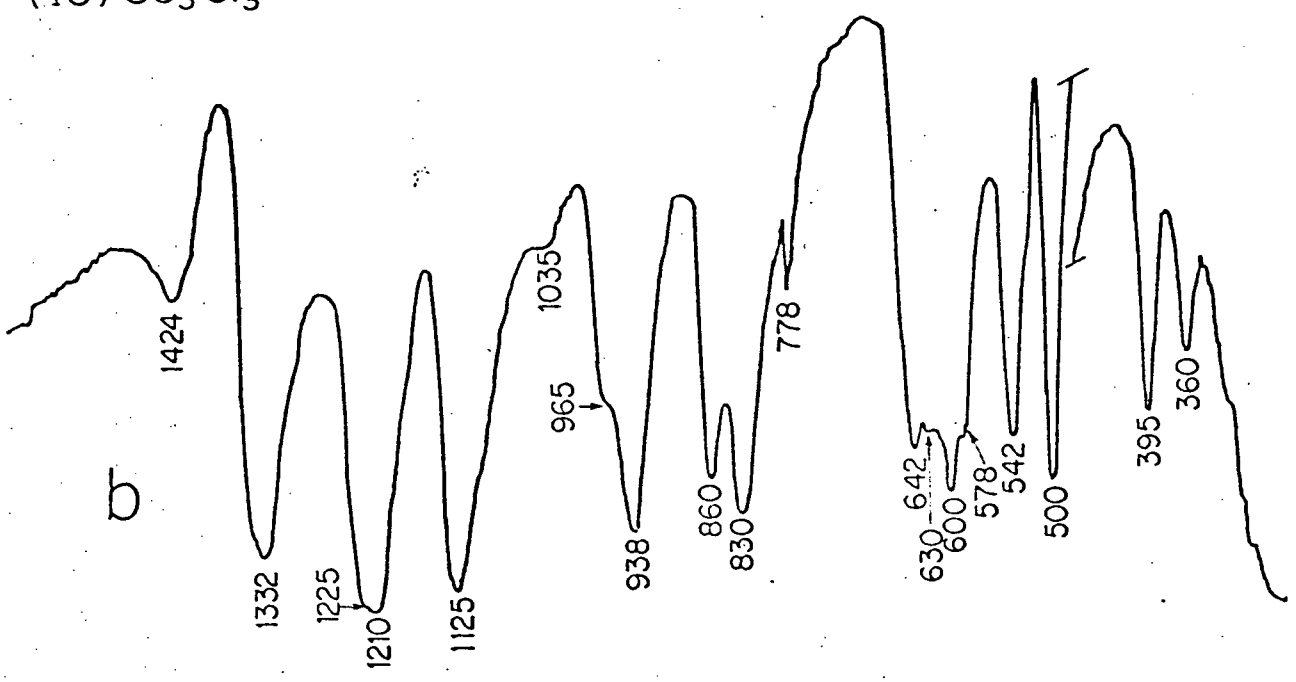
The iodine oxygen stretching vibrations occur in IO_2SO_3F at 878 and 865 cm^{-1} in the Raman Spectrum. In the corresponding $IO_2SO_3CF_3$ these same bands are at 823 and 849 cm^{-1}. All indications are that the IO_2 group in the SO_3F compound is similar to the same group in the SO_3CF_3 compound. Structural proposals for IO_2SO_3F and several other IO_2 compound are given by Carter and Aubke[64]. Based on vibrational spectra and solution studies they suggest that discreet IO_2^+ groups are associated by bridging anions. The stretching frequencies which occur between 800 and 950 cm^{-1} are indicative of an iodine oxygen multiple bond e.g. IO for IOF_5 is 927 cm^{-1} [65]. The results for $IO_2SO_3CF_3$ agree with these structural proposals.

In conclusion, association over I-O---I bridges is probably very slight judging from the position of IO_2. The obvious polymeric nature of the material must, therefore, be due to anion bridging between discreet IO_2 groups. The position of the third S-O stretching mode at 940 cm^{-1} is somewhat lower than for the same band in $(CH_3)_3SnSO_3CF_3$ where a bidentate bridging group is present. The relatively low position of this band in $IO_2SO_3CF_3$ seems to indicate preferential bonding to one IO_2 group (a) rather than ideal

Infrared Spectra of $(IO)SO_3CF_3$ and $(IO_2)SO_3CF_3$ from 1500-250 cm^{-1}

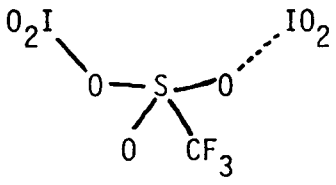


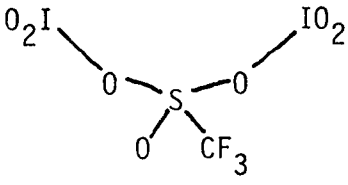
$(IO)SO_3CF_3$



$(IO_2)SO_3CF_3$

bridging (b).

(a) 

(b) 

The large number of bands in the spectra are presumably due to extensive coupling of vibrational modes and a more detailed assignment of the spectra is not possible.

7. $IOSO_3CF_3$

Well resolved infrared and Raman spectra were obtained for $IOSO_3CF_3$. The vibrational frequencies and the proposed assignments are given in table 12. The discussion of the assignments will again center on the SO_3CF_3 group and the IO stretching frequencies.

The SO_3CF_3 group is not merely an anion with C_3V symmetry. The splitting of the E mode S-O stretching frequency indicates a lowering of symmetry by association through the oxygen. The S-O stretching bands at 1390, 1210 and 970 cm^{-1} are assigned to an unsymmetrical bidentate bridging SO_3CF_3 group. (See the discussion for $IO_2SO_3CF_3$) The CF_3 stretching frequencies, found at 1242 and 1133 cm^{-1}, indicate the local symmetry of the CF_3 group remains C_3v. The lower frequency bending and deformation region below 1000 cm^{-1} has a large number of bands indicating an extensive degree of vibrational coupling between different vibrational modes. This allows only an approximate description of the bands. The attempted assign-

TABLE 12

Vibrational Frequencies for $IOSO_3CF_3$

Raman		Infared		Approximate Description
cm^{-1}	intensity	cm^{-1}	intensity	
		1420	vw	
1395	w[a]	1390	ms	SO_3 stretching
1284	ms	1280	ms	
1242	m, sh	1240	ms	sym.CF_3 stretching
1214	ms	1210	s	SO_3 stretching
1133	s	1140	vs	as.CF_3 stretching
1040	w, sh			
1025	s	1018	s,b	SO_3 stretching
969	ms	970	m	
883	vs	885	s	IO stretch
865	vw	860	s	
779	s	777	ms	S-C stretch
		670	m, sh	
662	s	655	m, sh	
634	s	640	s	
624	ms	625	m, sh	
587	s	585	m, sh	
560	w	550	s	
535	w, sh			
529	s	528	s	
453	vs	455	w,b	
		418	mw	
380	ms	375	m, sh	
360	m	350	m, sh	
355	m			
329	m	320	w, sh	
316	m			
290				
248	ms			
155	vw			

a. For explanation of terms see table 5

ment is given in table 12. Notice that once again the characteristic band at 777 cm^{-1} is present as a single band indicating the presence of only one type of SO_3CF_3 group.

Structural proposals for iodosyl compounds have been based mainly on a polymer of $(IO)_n^{n+}$ units surrounded by anions. The main thrust of this proposal comes from the rather low I-O stretching frequencies found for most iodosyl salts. As mentioned before in the case of $IO_2SO_3CF_3$ an iodine oxygen double bond would result in a stretching frequency between 800 and 900 cm^{-1} while as has been shown for several iodosyl compounds the I-O stretching frequencies occur somewhat lower, around 600 cm^{-1}. Dasent and Waddington[66] proposed the chain polymer for $(IO)_2SO_4$ and $(IO)_2SeO_4$ on this basis as well as for I_2O_4. Subsequent to the preparation of $IOSO_3CF_3$ the iodosyl fluorosulfate $IOSO_3F$ was also prepared[53]. It was found to conform to this general description. That is, the stretching frequencies were much lower than 800 cm^{-1} and a chain polymer of IO^+ units is proposed.

For $IOSO_3CF_3$, however, there are no suitable vibrations in the region from 550-600 cm^{-1} which could be assigned as I-O stretching bands. Two bands at 860 and 885 cm^{-1} are assigned as νIO. The splitting into two bands is due to solid state effects. The compound IOF_3 which has been shown by an x-ray diffraction study[67] to contain a short IO bond has I-O at 883 cm^{-1} [64]. In IOF_5 [65] the I-O stretching frequency is found at 927 cm^{-1}. Several different I-O stretching frequencies which have been found are shown in table 13. The

Table 13

I-O stretching frequencies in several compounds

Compound	νIO cm^{-1}	I-O proposed structure
$(IO)_2SO_4$[66]	562 577	chain polymer
$(IO)_2SeO_4$[66]	553 600	chain polymer
$IOSO_3F$[53]	650	chain polymer
$IOSO_3CF_3$	885 860	discrete IO groups
IOF_3[64]	907	discrete IO groups
IOF_5[64]	927	discrete IO groups

singularly high νIO for $IOSO_3CF_3$ would seem to indicate the presence of discreet IO units in $IOSO_3CF_3$ as opposed to polymeric IO structures for other iodosyl compounds.

In comparing this finding to the situation for $IOSO_3F$ it must be concluded that any extensive I-O---I association is absent for the $IOSO_3CF_3$. It should be kept in mind that all previous IO salts; $(IO)_2SO_4$, $(IO)_2SeO_4$ and $(IO)SO_3F$ have relatively small anions. The larger anion in $IOSO_3CF_3$ may prevent the formation of I-O---I bridges in the compound. A similar situation would be expected for $IOSO_3CH_3$ or $IOCO_2CF_3$. However, as mentioned previously all attempts to obtain these compounds have been unsuccessful to this point.

In conclusion for the vibrational spectra of all the $I\text{-}SO_3CF_3$ compounds studied in this work there is a complete analogy to the spectra of the corresponding fluorosulfates except for the rather unique case of the iodosyl compounds.

8. $CF_3SO_3CF_3$ Trifluoromethyl trifluoromethanesulfonate

This compound had already been reported by Noftle and Cady[25] who also list infrared frequencies in the NaCl region. In this work the thermal decomposition of $I(SO_3CF_3)_3$ was found to yield $CF_3SO_3CF_3$ as a volatile product. The vibrational spectrum of $CF_3SO_3CF_3$ is interesting in that it may be expected to provide an example of a monodentate covalent trifluoromethanesulfonate group. Only limited information on vibrational spectra of this monodentate group are available[25]. The spectrum should illustrate several arguments which have been invoked previously regarding the differences in functionality

Table 14

Vibrational Spectra of $CF_3SO_3CF_3$

This work		Reference no. 25	Assignment
Raman cm^{-1}	infrared cm^{-1}	infrared cm^{-1}	
1470 w*			not assigned
1460 w	1462 s	1461 s	SO_2 asym. stretch
	1370 w		not assigned
	1350 w		not assigned
1272 s	1270 s,sh		SO_2 sym. stretch
1253 w,sh	1262 vs	1258 s	CF_3-O asym. stretch
1228 vw	1232 vs	1230 s	CF_3-S asym. stretch
1154 s	1150 w,sh		CF_3-O sym. stretch
1130 m,sh	1135 vs	1134 s	CF_3-S sym. stretch
1074 m			SO_3 impurity
954 w	950 s	954 s	S-O* stretch
		868 vw	not assigned
805 m			S-C stretch
770 vs	785 m	786 m	CF_3-S bend
	760 w	766 m	not assigned
	745 w		not assigned
	715 w		not assigned
610 vw	620 m,sh		SO_3 asym. bend
585 m	595 m		CF_3 deformation
	580 m,sh		CF_3 deformation
547 m			SO_3 deformation
	528 w		
	490 w,sh		
397 w			
349 ms			
325 m			
305 m			
281 s			

of the SO_3CF_3 group. The infrared and raman spectra of $CF_3SO_3CF_3$ obtained by thermally decomposing $I(SO_3CF_3)_3$ are reported in table 14. along with the infrared bands reported by Noftle and Cady.

The main interest in the vibrational assignment of SO_3CF_3 groups of different functionalities is in the unambiguous identification of the S-O stretching frequencies. The observed positions should be comparable to those for the fluorosulfate group. The CF_3 positions are only of secondary interest as the group may be expected to retain local C_3V symmetry regardless of the symmetry of the functionality with only small splittings of the degenerate E modes.

In summarizing the monodentate, bidentate, and ionic SO_3CF_3 and SO_3F cases the ranges expected for S-O are shown in table 15. along with the assignment for $CF_3SO_3CF_3$. The presence of two different CF_3 groups in one molecule is detectable in the stretching region only. Overlap and superposition of bands obscure the deformation region. The SO_3 stretching frequencies are clear and the assignment is clear in the region from 830-1500 cm^{-1}.

For the ionic SO_3X group (X being CF_3 of F), the symmetry of the SO_3 moiety is C_3v and there are only two SO_3 stretching modes, a degenerate E mode and an A_1 mode. These occur at 1260 and 1050 cm^{-1} respectively. For a monodentate SO_3CF_3 group the symmetry is lowered to C_5 and the E mode is no longer degenerate. The two bands obtained from the splitting of the E mode can be considered as an SO_2 asymmetric stretch between 1470 and 1370 cm^{-1} and an SO_2 symmetric stretch between 1180 and 1270 cm^{-1}. The A' mode can now be thought of as an SO^* stretch where the O^* indicates the oxygen through which bonding

Table 15

S-O stretching frequencies in ionic, monodentate, and bidentate SO_3F and SO_3CF_3 groups.

GROUP	Ranges for νS-O cm^{-1}		
ionic	E mode	A_1 mode	
SO_3F	1280	1080	
SO_3CF_3	1260	1050	
monodentate	νSO_2 asymmetric	νSO_2 symmetric	νSO^*
SO_3F	1400-1500	1200-1250	980-850
SO_3CF_3	1370-1470	1180-1270	950-830
bidentate	νSO_2^* asymmetric	νSO_2^* symmetric	ν SO
SO_3F			
SO_3CF_3	1300-1380	1145-1220	1000-1060
$CF_3SO_3CF_3$	1461	1270	950

occurs. This band is considerably lowered and occurs between 830 cm^{-1} and 950 cm^{-1}. Finally, for the bidentate SO_3CF_3 group the symmetry is also C_s and the E mode is split. The two bands derived from the E mode can be considered as SO^*_2 stretches, here O^* referes to the two oxygens through which bonding occurs. The bands are considerably lowered compared to the unsplit E mode of the ion. The asymmetric band occurs between 1300 and 1380 cm^{-1} and the symmetric between 1145 and 1220 cm^{-1}. The A_1 mode, an S-O stretch, occurs between 1000 and 1060 cm^{-1} and is not changed too much from the ionic position. Note that a tridentate SO_3CF_3 group would again have C_3v symmetry and have two S-O stretching modes. These modes should occur considerably lower than they would for an ionic SO_3CF_3 group.

Comparing the SO vibrational band assignments for $CF_3SO_3CF_3$ with the scheme outlined above and summarized in table 15 we can see that it falls neatly within the monodentate group with all bands at the upper limits. This treatment is only feasible for stretching vibrations i.e. above 550 cm^{-1} as below 550 cm^{-1} the number of bands is too great to allow unambiguous assignment.

IV General Conclusions

It was shown earlier that the number of positive halogen compounds available obtainable from any oxyacid depends somewhat upon the strength of the acid. Trifluoromethanesulfonic acid has been found to be a very strong acid, comparable to fluorosulfuric acid. A reasonably large number of $I\text{-}SO_3CF_3$ compounds have been obtained. These display, with one exception, $IOSO_3CF_3$, structural similarities to the analogous fluorosulfates.

The structures proposed for these compounds, both SO_3CF_3 and SO_3F, have been based, for the most part on the analyses of their vibrational spectra. The complexity of the spectra for SO_3CF_3 compounds is due to the near coincidence of the S-O and C-F stretching region. However, much information which is unobtainable for the fluorosulfates because of their reactivity with infrared cell window material was obtained for the trifluoromethanesulfonates which are relatively unreactive.

Finally, here are a few suggestions for further study in this area.

1. The solvolysis of BrF_3 in HSO_3CF_3 might be studied further with a view to obtaining $Br(SO_3CF_3)_3$. However, the detonations recorded for other attempts to form $Br(SO_3CF_3)_3$ suggest extreme caution.

2. The solvolysis of ClF in HSO_3CF_3 may yield $ClSO_3CF_3$. $ClNO_3$ is known while $BrNO_3$ is not.

3. The solvolysis of $BrSO_3F$ in HSO_3CF_3 may yield $BrSO_3CF_3$. The solvolysis of I(I) compounds result in the formation of iodine cations I_3^+ and I_5^+ along with I_2^+. There might be more success with bromine(I) compounds.

4. The interaction of $CsSO_3CF_3$ with $BrSO_3F$ may lead to formation of $BrSO_3CF_3$.

5. The interaction of $I(SO_3CF_3)_3$ with $Sn(SO_3CF_3)_4$ might yield $[I(SO_3CF_3)_2]_2\ Sn(SO_3CF_3)_6$. Attempts to form the $I(SO_3CF_3)_2^+$ cation using SbF_5 were unsuccessful. This method using the just recently available compound $Sn(SO_3CF_3)_4$ as a Lewis acid and $SO_3CF_3^-$ ion acceptor looks promising.

6. Finally, some of the structures proposed for compounds synthesized in this work may hopefully be confirmed by x-ray diffraction studies.

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