reflux for 12 hr. The reaction mixture was then concentrated by removing toluene under *ca.* 20 mm pressure at room temperature, when the product crystallized out as white needle crystals. These were purified as in part xxiib and were shown to be identical with XXIVa.

(xxiv) Diethyltrimethyldialuminum Sodiosulfide, $[Et_2AlSNa][AlMe_3]$ (XXV). The procedure was as in part xxiib using XXVI (1.40 g, 0.01 mol) with $AlMe_3$ (0.96 ml, 0.01 mol) in 5 ml of toluene. Colorless needle crystals were obtained. *Anal.* Calcd for $C_7H_{19}SNaAl_2$: Al, 25.5; (Et + Me):Al ratio, 2.5; Me:Et ratio, 1.50. Found: Al, 25.0; (Et + Me):Al ratio, 2.4; Me:Et ratio, 1.48.

(xxv) Dissociation of XXIV. (a) The complex XXIV (*ca.* 5 g) was washed five times with 10-ml portions of *n*-hexane at 0°, and 15 ml of toluene was then added. This dissolved nearly all of the solid, and the undissolved residue (*ca.* 0.1 g) was identified as XXVI.

(b) XXIV (*ca.* 2 g) was dissolved in toluene (10 ml), and the solution was allowed to stand for 1 week in a sealed tube at room temperature. During this time a white solid was deposited (*ca.* 0.2 g) which was identified as XXVI.

(c) On heating pure XXIV above 50°, it gradually decomposed.

Infrared spectra were obtained with a Nihon Bunko far-infrared GC-402G instrument, using a compensation technique with a variable-spacing cell. Nmr spectra were measured on a Varian A-60 instrument at room temperature.

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Registry No. $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; $Al(i\text{-}Bu)_3$, 100-99-2; LiOH, 1310-65-2; NaOH, 1310-73-2; KOH, 1310-58-3; CsOH, 21351-79-1; PhNHLi, 20732-26-7; $PhCH_2NHLi$, 38225-27-3; *n*-BuNHLi, 41487-32-5; NaSH, 16721-80-5; Me_2AlOLi, 31390-21-3; Et_2AlOLi, 20888-82-8; Et_2AlONa, 31390-22-4; $Et_2AlNPhLi$, 41509-70-0; Et_2AlSNa, 29794-98-7; $[Me_2AlOLi][OC_2H_4]$, 41509-62-0; $[Me_2AlOLi][OEt_2]$, 41509-64-2; $[Me_2AlOLi][O(CH_3)(C_6H_5)]$, 40902-31-6; $[Et_2AlOLi][AlEt_3]$, 15407-37-1; $[Et_2AlONa][AlEt_3]$, 18347-70-1; $[Et_2AlOK][AlEt_3]$, 29467-77-4; $[Et_2AlOCs][AlEt_3]$, 38118-15-9; $[Me_2AlOLi][AlMe_3]$, 18347-68-7; $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$, 38194-35-3; $[(i\text{-}Bu)_2AlONa][Al(i\text{-}Bu)_3]$, 38118-18-2; $[Et_2AlOLi][AlMe_3]$, 15492-22-5; $[Et_2AlOLi][Al(i\text{-}Bu)_3]$, 41509-73-3; $[Me_2AlOLi][AlEt_3]$, 41562-78-1; $[Et_2AlONa][AlMe_3]$, 38118-21-7; $[Et_2AlNPhLi][AlEt_3]$, 25136-39-4; $[Me_2AlNPhLi][AlMe_3]$, 15137-70-9; $[(i\text{-}Bu)_2AlNPhLi][Al(i\text{-}Bu)_3]$, 38194-36-4; $[Et_2AlN(CH_2Ph)Li][AlEt_3]$, 15680-63-4; $[Et_2AlN(n\text{-}Bu)Li][AlEt_3]$, 15695-70-2; $[Et_2AlNPhLi][AlMe_3]$, 15694-28-7; $[Et_2AlNPhLi][Al(i\text{-}Bu)_3]$, 41562-79-2; $[Et_2AlSNa][AlEt_3]$, 38118-17-1; $[Et_2AlSNa][AlMe_3]$, 41509-78-8.

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Trifluoromethanesulfonates of Iodine

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Iodine tris(trifluoromethanesulfonate), $I(OSO_2CF_3)_3$, is obtained in the oxidation of iodine by stoichiometric amounts of $S_2O_6F_2$ in trifluoromethanesulfonic acid, as a sparingly soluble precipitate. The compound is thermally stable up to +170° and its vibrational spectrum indicates the presence of both monodentate and bidentate bridging SO_3CF_3 groups. Reaction with the stoichiometric amount of iodine at +140° results in the formation of iodine(I) trifluoromethanesulfonate. Several routes to salts of the type $M^I[I(OSO_2CF_3)_4]$, with M^I = K, Rb, or Cs, are also described. Vibrational spectra for these and for $IOSO_2CF_3$ are reported.

(A) Introduction

Reports on the synthesis of trivalent iodine derivatives of strong organic and inorganic protonic acids extend well into the last century.[1] More recent examples of this class of compounds include iodine trisfluorosulfate,[2] $I(OSO_2F)_3$, formed by the interaction of peroxydisulfuryl difluoride,[3] $S_2O_6F_2$, with iodine and iodine trisperchlorate,[4] $I(OClO_3)_3$, synthesized from I_2 and chlorine perchlorate, $ClOClO_3$.[5] Also, iodine tristrifluoroacetate, $I(O_2CCF_3)_3$, has been reported. The compound is obtained *via* a number of synthetic routes.[6-8] This suggests that iodine tris(trifluoromethanesulfonate), $I(OSO_2CF_3)_3$, may also be obtainable.

Structural studies on these compounds are restricted to detailed Raman and some infrared work on $I(OSO_2F)_3$[9] and $I(OClO_3)_3$,[4] suggesting polymeric configurations with both bridging and terminal oxy acid groups, rather than older formulations[1] involving a tripositive iodine cation.

The structural relationship of these compounds to the salts $M^I(IOSO_2F)_4$[10] and $M^I(IOClO_3)_4$[4] was first recognized in the above-mentioned vibrational studies.[4,9] Carter, *et al.*,[9] also report a number of suitable synthetic routes to $[I(OSO_2F)_4]^-$ salts, thus complementing the original method by Lustig and Cady,[10] the interaction of KI with $S_2O_6F_2$. The fairly high thermal stability of these salts again suggests the existence of the $[I(OSO_2CF_3)_4]^-$ analog.

In contrast to the above-described situation for tripositive iodine derivatives, reports on univalent iodine oxy acid compounds are rather limited. The only documented examples are iodine(I) nitrate, $IONO_2$,[11] which is thermally stable only below room temperature, and iodine(I) fluorosulfate,[12,13] $IOSO_2F$. An iodine(I) perchlorate, whose existence as a reaction intermediate has been widely suggested,[14] was found to be rather elusive.[4]

Synthetic efforts to obtain trifluoromethanesulfonic acid derivatives of the three above types are affected by the facts

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that no other halogen trifluoromethanesulfonates are known and that the corresponding peroxide, $(CF_3)_2S_2O_6$,[15] is thermally unstable. This implies that analogous synthetic routes to those leading to the above-mentioned fluorosulfates,[2,9,10,12,13] perchlorates,[4] and the nitrate[11] cannot be employed and suitable alternatives must be found.

(B) Experimental Section

(I) Chemicals. The alkali metal halides and resublimed iodine were obtained from commercial sources in the highest grade purity available. Trifluoromethanesulfonic acid (Minnesota Mining and Manufacturing Co.) and technical grade fluorosulfuric acid (Allied Chemical Corp.) were purified by reduced pressure and double distillation, respectively. Peroxydisulfuryl difluoride was prepared according to Cady and Shreeve[16] in a catalytic flow reaction from SO_3 and F_2 (both obtained from Allied Chemical Corp.). $Rb[I(OSO_2F)_4]$ was synthesized in analogy to the reported synthesis of the potassium salt by Lustig and Cady.[10] Cesium trifluoromethanesulfonate was obtained from CsCl and HSO_3CF_3.

(II) Instrumental. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Silver chloride, silver bromide, and barium fluoride windows (all from Harshaw Chemicals) were used without any mulling agent. Gaseous samples were contained in a monel infrared cell, fitted with a Whitey Iks4 valve and AgCl windows.

Raman spectra on the solid samples were obtained with a Cary 81 spectrometer, equipped with a Model 125 He-Ne gas laser (Spectra Physics Corp.). The 6328-Å wavelength line was used as exciting light. The samples were contained in 5-mm o.d. Pyrex tubes with flat bottoms.

All manipulations of solid materials were carried out in a Vacuum Atmosphere Corp. "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 drybox, a Mettler P 160 toploading balence was used.

(III) Synthetic Reactions. (a) General. The syntheses of $I(OSO_2CF_3)_3$ and the salts of the formula $M^I[I(OSO_2CF_3)_4]$ were accomplished in about 100-ml two-part reaction flasks, fitted with Teflon-coated magnetic stirring bars, a Teflon stem stopcock (Kontes Glassware), and a pair of B19 ground glass joints. The synthesis of $IOSO_2CF_3$ was performed in a sealed-off thick-wall Pyrex tube of 20-mm o.d. All reactors were charged in the drybox. The excess trifluoromethanesulfonic acid was removed by vacuum distillation along with any volatile reaction products.

(b) $I(OSO_2CF_3)_3$. I_2 (0.958 g, 3.78 mmol) was suspended in 29 g of HSO_3CF_3 and 2.453 g (12.38 mmol) of $S_2O_6F_2$ was added by vacuum distillation from a calibrated container. The mixture was allowed to warm to room temperature and shaken up manually from time to time. The color changed instantaneously to brown and later to blue and blue green. After 20–30 min the color had turned to light yellow and a precipitate began to form immediately afterward. The volatile products were removed *in vacuo* and 4.307 g of $I(OSO_2CF_3)_3$ was obtained.

(c) $K[I(OSO_2CF_3)_4]$. KI (0.239 g) was dissolved in 19 g of HSO_3CF_3 and oxidized by 0.607 g of $S_2O_6F_2$. The mixture was treated as described above. White to slightly yellowish crystals began to form only after the volume of the liquid had been sufficiently concentrated. $K[I(OSO_2CF_3)_4]$ (1.170 g) was obtained.

(d) $Rb[I(OSO_2CF_3)_4]$. $Rb[I(OSO_2F)_4]$ (0.892 g) was dissolved in 10 g of HSO_3CF_3. After removal of all volatiles *in vacuo*, 1.071 g of $Rb[I(OSO_2CF_3)_4]$ was obtained.

(e) $Cs[I(OSO_2CF_3)_4]$. $CsSO_3CF_3$ (0.245 g) was dissolved in 10.7 g of HSO_3CF_3 and 0.472 g of $I(OSO_2CF_3)_3$ was added. A clear yellow solution formed from which $Cs[I(OSO_2CF_3)_4]$ crystallized out after evacuation of the solvent.

(f) $IOSO_2CF_3$. In a typical preparation 0.982 g (1.72 mmol) of $I(OSO_2CF_3)_3$ and 0.460 g (1.81 mmol) of I_2, both finely ground, were combined into the reaction tube. After sealing off this reactor at atmospheric pressure, the tube was immersed into an oil bath of 135°. Both reactants melted to a viscous dark brown liquid. No appreciable quantities of I_2 could be detected in the gas phase. The temperature was raised to about +145° and the reactor was left in the oil bath for 1 hr. After annealing the product solidified instantaneously to a black-brown mass.

The reactor was opened in the inert atmosphere box and the contents were transferred to a two-part reactor after powdering the large lumps. To ensure complete reaction, the powder was liquefied again at +130–145° and then allowed to anneal slowly. All volatiles were removed by vacuum distillation. The final product was stored and handled in the drybox.

Table I

Compound	I, %		S, %		F, %	
	Calcd	Found	Calcd	Found	Calcd	Found
$I(OSO_2CF_3)_3$	22.10	22.21	16.76	16.79	29.78	29.64
$IOSO_2CF_3$	45.98	46.16	11.62	11.57	20.65	20.45
$Rb[I(OSO_2CF_3)_4]$	15.69	15.92	15.86	16.07	28.19	28.07

Only relatively broad infrared bands could be obtained since no suitable mulling agent could be found. The following bands are observed in cm^{-1}: 1340 (w, sh), 1210 (vs), 1135 (m, b), 1025 (m), 930 (m), 770 (ms), 684 (m, sh), 624 (ms, b), 585 (m, sh), 555 (sh), 518 (ms), 455 (vw), 412 (vw), 371 (m, sh), 358 (vs), 338 (m, sh), 312 (ms).

(IV) Analytical Results. Chemical analysis was performed by Alfred Bernhardt Microanalytical Laboratories, Elbach, West Germany, for iodine, sulfur, and fluorine. The data for $I(OSO_2CF_3)_3$, $IOSO_2CF_3$, and $Rb[I(OSO_2CF_3)_4]$ are tabulated (see Table I) together with the calculated values in per cent. Both $K[I(OSO_2CF_3)_4]$ and $Cs[I(OSO_2CF_3)_4]$ were identified by following the reactions by weight and characterized by infrared and Raman spectra.

(C) Results and Discussion

(I) Synthesis. Initial attempts were directed at the synthesis of $I(OSO_2CF_3)_3$. A preliminary experiment had shown that when trifluoromethanesulfonic acid is added to supercooled liquid $I(OSO_2F)_3$ at room temperature a yellow solid is formed instantaneously. Removal of the excess acid by vacuum distillation leads to a solid mass of increased weight. However, the weight ratio indicated an incomplete replacement of $-OSO_2F$ by $-OSO_2CF_3$. This was confirmed by vibrational spectroscopy.

A suitable route was developed subsequently. A known amount of iodine is suspended in trifluoromethanesulfonic acid and peroxydisulfuryl difluoride ($S_2O_6F_2$) is added in a very slight excess over the amount required to oxidize iodine into the 3+ oxidation state. The solution which was originally faintly purple turns instantaneously brown, then blue, later blue-green, and after about 25 min from green-brown to light yellow. The process is mildly exothermic. All iodine, which is very sparingly soluble in HSO_3CF_3, is dissolved during the reaction. Immediately after completion a white solid separates out in the form of small needles. Removal of the excess HSO_3CF_3 results in the isolation of pure $I(OSO_2CF_3)_3$ in quantitative yield indicating the net process

$$I_2 + 3S_2O_6F_2 + 6HSO_3CF_3 \rightarrow 2I(OSO_2CF_3)_3 + 6HSO_3F$$

The intermediates giving rise to the observed colors are in all likelihood the polyiodine cations I_3^+ and I_2^+.[17] Since trifluoromethanesulfonic acid is a very strong protonic acid, comparable to HSO_3F,[18] there can be little doubt that polyiodine cations can also exist in HSO_3CF_3. An identical color change is observed when I_2 is oxidized by $S_2O_6F_2$ in fluorosulfuric acid.

Iodine tris(trifluoromethanesulfonate) is obtained as a white to yellow white hygroscopic solid melting at +119°. The compound is thermally stable up to +170° *in vacuo*, where partial sublimation and partial decomposition are noted. The thermal decomposition results in the formation of the volatiles SO_3 and $(CF_3)_2SO_3$ first observed by Noftle and Cady[15] when $(CF_3)_2S_2O_6$ decomposes. A yellow residue is obtained in small yield containing iodine in the 3+ oxidation state and sulfate. The thermal behavior of $I(OSO_2CF_3)_3$

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is thus quite different from the reported behavior for $I(OSO_2F)_3$[12] where disproportionation into $IOSO_2F$ and a mixture of $IF_3(SO_3F)_2 + SO_3$ is observed.

The described synthesis, the oxidation of iodine in acid by a chemically different oxidizing agent, is, as summarized by Fichter and Kappeler,[1] a very general route to trivalent iodine compounds; *e.g.*, the oxidation of iodine in acetic acid or acetic anhydride to form iodine tris(acetate) can be accomplished by Cl_2O,[19] O_3,[20] or N_2O_4.[21] N_2O_4 has also been used in the synthesis of $I(O_2CCF_3)_3$. It is surprising, however, since $I(OSO_2F)_3$ is known,[2] that the use of $S_2O_6F_2$ as an oxidizing agent does not lead to mixed products of the type $I(OSO_2F)_x(OSO_2CF_3)_{3-x}$. The reason can be seen in another important difference between $I(OSO_2F)_3$ and $I(OSO_2CF_3)_3$. Whereas the former is extremely soluble in HSO_3F[12,22] the latter is only sparingly soluble in HSO_3CF_3. It is not too surprising, then, that $I(OSO_2CF_3)_3$ can also be formed when trifluoromethanesulfonic acid is added in a slight excess to a solution of $I(OSO_2F)_3$ in HSO_3F. The reason for this solubility difference is that there is a different degree of polymerization for $I(OSO_2F)_3$ and $I(OSO_2CF_3)_3$. In keeping with this view, there is also a difference in melting points. $I(SO_3F)_3$ melts at +33.7°[13] and is often found as a supercooled liquid, whereas $I(OSO_2CF_3)_3$ melts at +119°.

Salts of the type $M^I[I(OSO_2CF_3)_4]$ can be synthesized *via* three different routes: (a) the oxidation of MI (M being potassium) by $S_2O_6F_2$ in HSO_3CF_3; (b) the ligand substitution of $-OSO_2F$ by $-OSO_2CF_3$ by treating $M[I(OSO_2F)_4]$ (M being rubidium) with an excess of HSO_3CF_3; and (c) the interaction of MSO_3CF_3 (M being cesium) with $I(OSO_2CF_3)_3$ in HSO_3CF_3. Our claim that the products obtained are the expected salts rather than mixtures of MSO_3CF_3 and $I(OSO_2CF_3)_3$ is based on the high melting points (listed in the Experimental Section) and the vibrational spectra (discussed below). Again no evidence for mixed $-OSO_2F-OSO_2CF_3$ compounds in routes a and b is obtained. The vibrational spectra are identical for all three salts, regardless of the cation.

Finally, $IOSO_2CF_3$ is obtained by the reduction of $I(OSO_2CF_3)_3$ with the exact stoichiometric amount of I_2 at *ca.* +140° in a sealed, nitrogen-filled tube. Precedents for this reaction are found in the interaction of I_2 and $I(ONO_2)_3$[1] and indirectly in the excellent study by Chung and Cady[13] of the phase diagram of I_2 and $S_2O_6F_2$.

Iodine(I) trifluoromethanesulfonate is a brown, very hygroscopic solid, melting at 122° under atmospheric pressure. The compound is thermally stable up to about +170° where the formation of I_2, SO_3, and $(CF_3)_2SO_3$ is observed. The products of this decomposition suggest the reaction

$$2IOSO_2CF_3 \rightarrow I_2 + SO_3 + (CF_3)_2SO_3$$

The identification of $IOSO_2CF_3$ as a true compound is based on its infrared spectrum and the fact that no I_2 is released at the melting point or below, even under vacuum.

Alternative formulations such as $I_3[I(OSO_2CF_3)_4]$ must be ruled out as well. As already noted in the $I_2-S_2O_6F_2$ system,[13] the nonexistence of the I^+ cation in protonic acid solution,[17] where I_2^+ is found instead, does not preclude the existence of compounds of the form $IOSO_2X$ (X being F and CF_3) in the solid state.

A final comment remains to be made. Solutions of $S_2O_6F_2$ in HSO_3CF_3 are surprisingly metastable. A clear solution is initially obtained; however, after about 30 min the evolution of heat is noted and shortly thereafter gas evolution and a pressure buildup is noted. We have not as yet fully investigated this system. The presence of I_2 and the absence of any appreciable excess of $S_2O_6F_2$ during any of the reactions described involving HSO_3CF_3 and $S_2O_6F_2$ allow safe handling of the mixtures.

(II) Vibrational Spectra. Adequately resolved infrared spectra in the silver halide region were obtained for the ion $[I(OSO_2CF_3)_4]^-$, for $I(OSO_2CF_3)_3$, and for $IOSO_2CF_3$. We were unsuccessful in obtaining a Raman spectrum of the latter compound. The remaining two gave well-resolved Raman spectra. Quite in contrast to this, the corresponding fluorosulfates proved to be too reactive, so that only Raman spectra were obtained, which should help in the assignment. Previous vibrational studies include normal coordinate analysis of the $SO_3CF_3^-$ ion by Tobias, *et al.*,[23a] and by Burger, *et al.*[23b] The noticeably poor agreement between the assignments proposed by both groups, in particular in the CF- and SO- stretching range, is very indicative of the complex situation, caused by coincidence as well as internal coupling of the two types of stretching modes. In addition, the infrared spectrum of $NH_4SO_3CF_3$ has been reported.[24] Precedents for a covalently bonded monodentate $-OSO_2CF_3$ group can be found in $(CF_3)_2SO_3$, whose ir spectrum is reported by Noftle and Cady,[15] in a recently reported xenon compound, $FXeOSO_2CF_3$,[25] and in $(CH_3)_3GeOSO_2CF_3$.[26] Assignments of a bidentate bridging SO_3CF_3 group are found in the organotin(IV) derivatives $(CH_3)_3SnSO_3CF_3$[27] and $(CH_3)_2Sn(SO_3CF_3)$,[28] where the structural proposals are based on ^{119}Sn Mossbauer spectra and the reported X-ray diffraction study for the analogous compound $(CH_3)_2Sn(SO_3F)_2$.[29] By analogy to the ions $[I(OSO_2F)_4]^-$ [9] and $[I(OClO_3)_4]^-$ [4] it appears reasonable to expect for $[I(OSO_2CF_3)_4]^-$ the presence of monodentate trifluoromethanesulfonate groups and a rather less complex situation. Therefore, the interpretation will best start here. Emphasis is placed on the identification of the functionality of SO_3CF_3 group, recognizable from the number and the position of the sulfur-oxygen stretching vibrations, and the detection of the iodine stretching modes. Previous assignments, based primarily on Raman spectra, differ widely for $[I(OSO_2F)_4]^-$,[9] $[I(OClO_3)_4]^-$,[9] and $[I(OClO_3)_4]^-$.[4] For the former the symmetric in-phase I-O vibration is found at 442 cm^{-1}, whereas for $[I(OClO_3)_4]^-$ [4] this mode is found at 261 cm^{-1}.

The observed frequencies for $Rb[I(OSO_2CF_3)_4]$ are listed in Table II, together with SO_3CF_3- vibrations found for $(CH_3)_3GeOSO_2CF_3$ and the estimated intensities. The proposed assignment is largely based on the assignment for $SO_3CF_3^-$ proposed by Burger, *et al.*[23b] The observed small splitting of absorption bands for the $[I(OSO_2CF_3)_4]^-$ ion, most obvious in the Raman spectrum and detectable in the SO- and CF- stretching range, may be explained by solid-

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Table II. Vibrational Frequencies for Rb[I(OSO_2CF_3)$_4$] and $(CH_3)_3GeOSO_2CF_3$[a]

Rb[I(OSO_2CF_3)$_4$]		$(CH_3)_3$-$GeOSO_2CF_3$	
Raman, cm^{-1}	Ir, cm^{-1}	Ir, cm^{-1}	Approximate description
1376 mw, 1368 w	1365 vs, b	1365 s	ν_{asym} SO_2
1251 m, 1234 mw	1242 s, sh	1241	ν_{asym} CF_3
1214 w	1210 vs, b	1205 vb	ν_{sym} SO_2
1170 ms	1150 s, b	1164 s	ν_{asym} 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	ν S-OX
777 vs	770 s	768 m	ν CS
652 ms, 642 w	632 s, b	634 s	δ SO_2
620 ms	615 m, sh	620 m, sh	SO_2 rocking
598 vs	590 m	590 s	δ_{sym} CF_3
576	578 w	572 ms	δ SO_2X
536 s	528 s	515	δ_{asym} CF_3
515 sh	510		
	435 ms		ν_{asym} IO
408 w			ν IO (sym in phase)
394 s			
383 ms			ν IO (sym out of phase)
346 ms	352 vs		ρ SO_2
322 s	315 ms		δ CS
264 ms, 253 w			ρ CF_3

[a] Only bands assigned to the -OSO_2CF_3 group are listed. vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder, ν = stretching mode, δ = bending mode, ρ = rocking mode.

Table III. Vibrational Spectrum of I(OSO_2CF_3)$_3$

Raman, cm^{-1}	Ir, cm^{-1}	Approximate description	Raman, cm^{-1}	Ir, cm^{-1}
1435 m, sh; 1427 ms	1420 s, b	ν_{asym} SO_2 (t)	619 vs	625 s, b
			568 vw	580 ms, sh
1321 m	1324 ms	ν SO (br)		
			549 s	542 w, sh
1240 ms	1235 m, sh	ν CF_3		
			513 w	515 s
1208 mw	1210 vs, b	ν_{sym} SO_2 (t)		
				452 w
~1160 w, sh	1165 w, sh	ν CF_3		
			414 w	415 w
1120 s	1130 s, b	ν SO (br)		
			393 s	390 s
1084 s	1090 s, sh	ν CF_3	361	
			358 s	362 s
993 mw	980 ms	ν SO (br)		
			327 s	318 s
818 vs	830 vs, b	ν SO		
			275 s	
			269 s	
793 w				
780 vs	780 s, b	ν SC		
768 w				
729 vw	730 s, b			
640 w				

state splitting. Precedents for such splittings are found in a number of fluorosulfato anions such as $[I(OSO_2F)_4]^-$ [9] and $[Sn(OSO_2F)_6]^{2-}$.[30] Many features observed in the spectrum of Rb[I(OSO_2CF_3)$_4$], such as the very broad infrared absorption bands and discrepancies in the band positions between ir and Raman bands, are also found for $FXeOSO_2CF_3$[25] indicating strong structural similarity. There are, however, some differences in the proposed assignments.

The three expected sulfur-oxygen vibrations are found at ~1365, 1210, and 850 cm^{-1}, in relatively good agreement with the corresponding bands for $(CH_3)_3GeOSO_2CF_3$ except for the last band, assigned to ν S-OX which is definitely affected by the electronegativity of group X. Comparable bands for $FXeOSO_2CF_3$[25] are found at ~1390, ~1200, and ~840 cm^{-1}, respectively.

The C-F stretching modes are found in a similar region as those of the $SO_3CF_3^-$ ion. There appears little doubt that the stretching modes are consistent with a monodentate OSO_2CF_3 group.

In the region of the bending modes good agreement between our findings and observations for $(CH_3)_3GeOSO_2CF_3$ and $FXeOSO_2CF_3$ is found. Generally good agreement of the band positions between infrared and Raman bands is found in this spectral region. An exception, however, is found at around 400 cm^{-1}. Bands at 394 and 383 cm^{-1} of fairly high intensity are found only in the Raman spectrum, whereas a band at 435 cm^{-1} is only found in the ir spectrum. The Raman bands are assigned as the two symmetric in-phase and out-of-phase IO stretching modes, expected for a square-planar configuration around iodine to be only Raman active. The infrared absorption band is assigned to ν_{asym} I-O. Several precedents are reported, where this band occurs at higher wave numbers than the two symmetric vibrations, for square-planar ions;[31] however, this does not seem to be the case for ICl_4^-.[32] The observed positions are slightly lower than for $[I(OSO_2F)_4]^-$ [9] which may reflect the difference in mass for the two groups. The extremely low IO stretching modes in $[I(OClO_3)_4]^-$ [4] may be indicative of very weak iodine-oxygen bonds. The reported thermal stability of both the $[I(OSO_2F)_4]^-$ and $[I(OSO_2CF_3)_4]^-$ ions can be as high as +200°, whereas for Cs[I($OClO_3$)$_4$] thermal stability up to ambient temperature is found.[4] The same drastic difference is noted for I($OClO_3$)$_3$, stable up to −45°, and I(OSO_2CF_3)$_3$, which begins to decompose above +170°. We were unable to observe any of the iodine-oxygen deformation modes which should occur below 200 cm^{-1}. As mentioned before, only very minor discrepancies were found in the spectra of K[I(OSO_2CF_3)$_4$] and Cs[I(OSO_2CF_3)$_4$]. As can be seen from the vibrational frequencies listed in Table III and from Figure 1, the spectra for I(OSO_2CF_3)$_3$ indicate a far greater complexity, in particular in the region of 1450-700 cm^{-1}. This finding agrees with observations for both I(OSO_2F)$_3$[9] and I($OClO_3$)$_3$.[4] Approximate assignments of absorption bands appear to be possible only in the S-O and CF stretching region and even here ambiguities are unavoidable. The observed complexity is presumed to be caused by SO_3CF_3 groups of different functionality. Bands at ~1420, ~1210, and ~830 cm^{-1} are interpreted as sulfur-oxygen stretching modes of a monodentate trifluoromethanesulfonate group, primarily on the basis of their similarity to the corresponding bands for this group in $[I(OSO_2CF_3)_4]^-$. The shift to higher wave numbers for ν (SO_2) ahd also been found for this band in the corresponding fluorosulfato compounds.

On the other hand, bands at 1320, 1120, and 980 cm^{-1} are remarkably similar in position to sulfur-oxygen stretching modes for a bidentate bridging SO_3CF_3 group in both $(CH_3)_3Sn(SO_3CF_3)$[27] and $(CH_3)_2Sn(CO_3CF_3)_2$. The remaining bands in this region at 1240, 1160, and 1084 cm^{-1} may be

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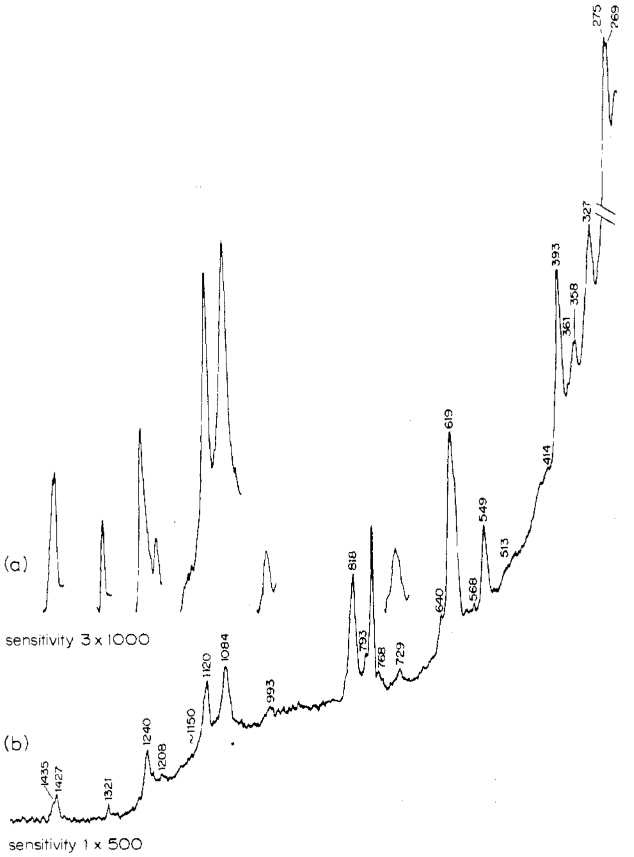

Figure 1. Raman spectrum of $I(OSO_2CF_3)_3$.

due to CF_3 stretching modes. No definite assignment of IO stretching modes is possible since almost all observed bands in the region of 430-380 cm^{-1} are found to be ir and Raman active, which in turn may be due to distortions of a possible square-planar IO_4 group by nonequivalent SO_3CF_3 groups.

The infrared spectrum of $IOSO_2CF_3$, the observed frequencies are listed in the Experimental Section, is distinctly different from the ones obtained for $I(OSO_2CF_3)_3$ and $[I(OSO_2CF_3)_4]^-$ and also for the $SO_3CF_3^-$ ion. This implies that $IOSO_2CF_3$ cannot be considered merely as a stoichiometric mixture of I_2 and $I(OSO_2CF_3)_3$ and that the structural formulations such as $I_3[I(OSO_2CF_3)_4]$ or the very unlikely ionic $I^+SO_3CF_3^-$ must be ruled out as well. A polymeric structure with a polydentate SO_3CF_3 group appears to be most likely, but a more detailed discussion of the infrared spectrum appears to be rather hazardous.

(D) Summary and Conclusion

Even though in both $I(OSO_2F)_3$[9] and in $I(OSO_2CF_3)_3$ monodentate and bridging bidentate sulfonate groups are evident from the respective vibrational spectra, the observed differences in thermal stability, reactivity, and solubility in the parent acids are best explained by assuming a different degree of polymerization. In addition to dimers, perhaps reminiscent of I_2Cl_6,[33] higher chain type polymers are feasible. It is this structural difference which allowed the isolation of pure $I(OSO_2CF_3)_3$ in the first place.

Iodine(I) trifluoromethanesulfonate, produced by the reduction of $I(OSO_2CF_3)_3$ with stoichiometric amounts of I_2, can be useful as a precursor for polyiodine cations in HSO_3CF_3. The oxidation by halogens to form interhalogen trifluoromethanesulfonates of the type $IX_2OSO_2CF_3$, with X = Cl, Br, and I, is currently being studied.

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Registry No. I_2, 7553-56-2; $S_2O_6F_2$, 13709-32-5; $I(OSO_2CF_3)_3$, 41524-03-2; KI, 7681-11-0; $K[I(OSO_2CF_3)_4]$, 41523-89-1; $Rb[I(OSO_2CF_3)_4]$, 41523-90-4; $CsSO_3CF_3$, 41524-04-3; $Cs[I(OSO_2CF_3)_4]$, 41523-91-5; $IOSO_2CF_3$, 41524-06-5; HSO_3CF_3, 1493-13-6; $(CH_3)_3GeOSO_2CF_3$, 41524-05-4.

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Condensed Methyl Phosphates. Separation by Molecular Distillation[1]

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Pentamethyl triphosphate and hexamethyl tetraphosphate were isolated with small amounts of analogous polymers as byproducts. It was found that the triphosphate reorganized to form the tetraphosphate and diphosphate esters with an apparent second-order reaction rate having an approximate half-life of 1.00×10^7 sec.

Introduction

The preparation of hexaethyl tetraphosphate has been described before[2] but was subsequently shown to consist of a mixture of condensed polyphosphates with differing chain lengths.[3] Similar mixtures have been shown to form when differing amounts of phosphorus pentoxide and trimethyl phosphate are brought to equilibrium.[4] Separation of the diphosphate from these mixtures has been described.[3,5] The technique of gas-liquid chromatography failed to separate[6] all the constituents of these mixtures at 150°.

It has been reported[7] that although ester interchange in the

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