Volume 15
Number 6
June 1976

Inorganic Chemistry

Contribution from the Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1W5

Iodine–Oxygen Compounds. 2.[1] Iodosyl and Iodyl Fluorosulfates and Trifluoromethanesulfonates

JOHN R. DALZIEL, HENRY A. CARTER, and FRIEDHELM AUBKE*

Received July 11, 1975

AIC504842

The synthesis of the new iodosyl compounds $IOSO_3F$ and $IOSO_3CF_3$ and the iodyl compound $IO_2SO_3CF_3$ is reported. Raman and infrared spectra for these and the related compounds I_2O_4 and $(IO)_2SO_4$ are recorded. The polymeric nature of the sulfate derivatives is partly caused by bidentate bridging SO_3F- and SO_3CF_3- groups and partly by polymeric $(IO)_n$ chains for $IOSO_3F$ as evidenced by the occurrence of iodine–oxygen stretching modes as low as 600–650 cm^{-1}. For the trifluoromethanesulfonates $IOSO_3CF_3$ and $IO_2SO_3CF_3$ the iodine–oxygen stretching modes are found at 850 cm^{-1}, more consistent with the presence of discrete IO– and IO_2– groups in these compounds.

(A) Introduction

Only a rather limited number of iodosyl (IO–) or iodyl (IO_2–) derivatives of inorganic acids have been synthesized and characterized. Interest has revolved primarily around the IO and IO_2 derivatives of sulfuric or polysulfuric acids,[2] where the earliest reports date well back into the last century.[3] However of the derivatives of monobasic, substituted sulfuric acids only iodyl fluorosulfate, IO_2SO_3F,[4] is known. A compound of the formula $IOSO_3F$ has been postulated[5] as a reaction product in the controlled hydrolysis of $I(SO_3F)_3$ dissolved in HSO_3F; however, this compound was apparently never isolated, analyzed, or characterized.

Since the recently reported trifluoromethanesulfonates of iodine[6] exhibited some formal and structural similarities to the corresponding fluorosulfates, we became interested in extending this comparison to the iodine–oxygen derivatives, provided suitable synthetic routes could be found and structural information could be gained.

Reliable structural information on IO and IO_2 derivatives was found to be rather scarce, even when the discussion was extended to the oxides I_2O_4 and I_2O_5, which may be regarded as iodosyl and iodyl iodate, respectively, and the aromatic iodoso and iodoxo compounds of the general type ArIO and $ArIO_2$. Up to date crystal structures have been reported for $(IO)_2SO_4$,[7] I_2O_5,[8] and $p\text{-}ClC_6H_6IO_2$.[9] Detailed vibrational studies are reported for IO_2SO_3F[10] and I_2O_5.[11] For I_2O_4,[12] $(IO)_2SO_4$,[12] and $(IO)_2SeO_4$[12] only poorly resolved infrared spectra are reported. Some iodine–oxygen force constant calculations for a number of aromatic derivatives are also reported,[13] where the IO and IO_2 groups are treated as nonassociated groups. For I_2O_4 an iodine-129 Mössbauer study was reported recently[14] with interesting structural implications. Because iodine–oxygen compounds are generally excellent Raman scatterers, it was hoped that well-resolved spectra would allow reasonable structural insights into this group of compounds.

(B) Experimental Section

(I) Chemicals. Resublimed iodine (Fisher Chemical Co.) and "iodine pentoxide" (BDH) (which in agreement with published observations[8] was found to be very pure anhydroiodic acid, HI_3O_8) were used in this study. Trifluoromethanesulfonic acid (3M Co.) was purified by a reduced-pressure distillation from 100% H_2SO_4 (Baker and Adamson). Technical grade HSO_3F (Baker and Adamson) was purified by double distillation at atmospheric pressure.

Literature methods were used for the preparation of I_2O_4,[2a] I_2O_5,[8] $(IO)_2SO_4$,[12] C_6H_5IO,[15a] $C_6H_5IO_2$,[15a] and $S_2O_6F_2$.[15b]

(II) Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Silver chloride, silver bromide, and KRS-5 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 Atmospheres Corp. "Dri-Lab", Model No. HE-43-2, filled with purified dry nitrogen and equipped with "Dri-Train", Model No. HE-93B.

(III) Synthetic Reactions. (a) General Work. The prepartions of $IOSO_3CF_3$, $IO_2SO_3CF_3$, and $IOSO_3F$ were performed in 50-ml round-bottom flasks fitted with Teflon-coated magnetic stirring bars and guard tubes filled with P_4O_{10}. The solid reaction products were filtered with precautions taken to exclude moisture. A suitable apparatus was described by Shriver.[16]

All reactions involving $S_2O_6F_2$ were carried out in the same manner as in the preparation of IO_2SO_3F[4] using identical reactors and transfer techniques.

(b) Individual Preparations. $IOSO_3CF_3$. In a typical reaction 0.683 mmol of HI_3O_8 and 1.20 mmol of I_2 were allowed to react in approximately 20 g of HSO_3CF_3 for 50 h at room temperature. A finely powdered yellow precipitate had formed but the solution showed an intense brown-green color. Iodosyl trifluoromethanesulfonate was obtained by filtration and repeated washing, first with HSO_3CF_3 and later with SO_2Cl_2. The moderately hygroscopic yellow material melted with decomposition at 235–240 °C. Instead of HI_3O_8 either HIO_3 or I_2O_5 may be used as starting material.

The preparation of $IOSO_3F$ was accomplished in a completely analogous fashion. The hygroscopic yellow material has a decomposition point of 178 °C.

$IO_2SO_3CF_3$. In a typical preparation 874 mg (0.993 mmol) of HI_3O_8 and about 20 g of HSO_3CF_3 are stirred for ~7 days at room temperature. After filtration and washing with HSO_3CF_3, iodyl

Table I

Compd	% sulfur		% iodine		% fluorine	
	Calcd	Found	Calcd	Found	Calcd	Found
$IOSO_3F$	13.25	13.32	52.45	52.13	7.85	7.67
$IOSO_3CF_3$	10.98	11.15	43.46	43.20	19.52	19.26
$IO_2SO_3CF_3$	10.41	10.26	41.20	41.40	18.51	18.28

trifluoromethanesulfonate was obtained as a white, hygroscopic solid, decomposing at ~300–305 °C. Again HI_3O_8 may be substituted by either HIO_3 or I_2O_5.

In all reactions of $IOSO_3F$, $IOSO_3CF_3$, or I_2O_4 with $S_2O_6F_2$, the last compound was used in a 5–10-fold excess. The final products were isolated by removing all volatile material by distillation from the reaction mixture.

(IV) Analysis. Chemical analysis was performed by Alfred Bernhardt Microanalytical Laboratories, Elbach, West Germany, for the elements sulfur, iodine, and fluorine. The data for $IOSO_3F$, $IOSO_3CF_3$ and $IO_2SO_3CF_3$ are listed in Table I together with the calculated values.

(C) Results and Discussion

(I) Synthesis. A very simple and convenient synthetic route to the iodosyl derivatives $IOSO_3F$ and $IOSO_3CF_3$ was found in the interaction of I_2 with HI_3O_8 in the corresponding acid[17] according to

$$HI_3O_8 + I_2 + 8HSO_3X \xrightarrow[24\ h]{25\ ^\circ C} 5IOSO_3X + 3H_3O^+ + 3SO_3X^- \quad (1)$$

with X = F or CF_3. This method had previously been used in the synthesis of $(IO)_2SO_4$[2a,12,17] and $(IO)_2SeO_4$.[2a,12]

The iodosyl sulfates are obtained as yellow, moderately hygroscopic precipitates. In order to avoid any formation of iodyl derivatives as by-products (see below), a very slight excess of iodine was used. Consequently, depending on the mole ratio of I_2 to HI_3O_8, solvated polycations of iodine[18] such as I_5^+, I_3^+, and I_2^+ are formed and impart intense brown or blue-green colors to the solution.

The occurrence of these deeply colored ions during the formation of both $IOSO_3F$ and $IOSO_3CF_3$ indicates that the iodine polycations may be reaction intermediates. It was therefore not surprising that we were unable to extend this synthetic route to other monobasic protonic acids such as HSO_3CH_3, HCO_2CF_3, or HPO_2F_2. All three are weaker acids than HSO_3F or HSO_3CF_3 and not even the least electrophilic cations I_5^+ and I_3^+ could be generated. Dissolution of solid I_3SO_3F in any of the acids results in the immediate formation of molecular iodine.

The controlled hydrolysis of $I(SO_3F)_3$[5] or $I(SO_3CF_3)_3$ in their respective acid solution or suspension was also attempted. The formation of I_2^+(solv) was noted together with yellow precipitates, which were heavily contaminated by IO_2SO_3F and $IO_2SO_3CF_3$, respectively.

The synthesis of the latter compound is readily accomplished by the action of HSO_3CF_3 on either iodic or anhydroiodic acid according to

$$HIO_3 + 2HSO_3CF \rightarrow IO_2SO_3CF_3 + H_3O^+ + SO_3CF_3^- \quad (2)$$

or

$$HI_3O_8 + 5HSO_3CF_3 \rightarrow 3IO_2SO_3CF_3 + 2H_3O^+ + 2SO_3CF_3^- \quad (3)$$

It appears that trifluoromethanesulfonic acid, which is known to form a well-defined, stable monohydrate,[19] acts as a rather efficient dehydrating agent, provided the acid is used in a large excess.

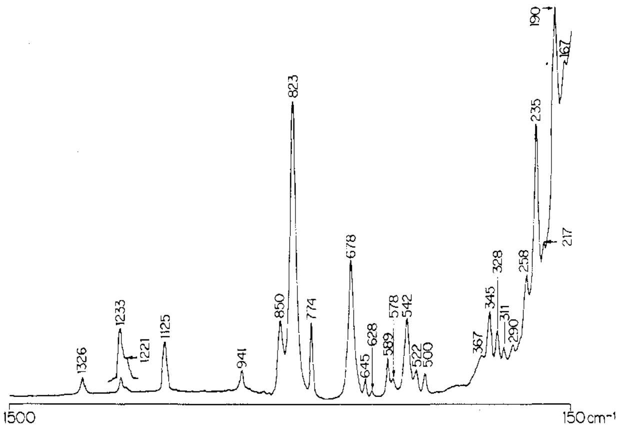


Figure 1. Raman spectrum of $IO_2SO_3CF_3$ from 1500 to 150 cm^{-1}.

Iodyl fluorosulfate, IO_2SO_3F, originally obtained from I_2O_5 and $S_2O_6F_2$[4]

$$I_2O_5 + S_2O_6F_2 \xrightarrow{25\ ^\circ C} 2IO_2SO_3F + {}^1/_2O_2 \quad (4)$$

may also be obtained by two additional routes, i.e.

$$IOSO_3F + S_2O_6F_2 \xrightarrow{25\ ^\circ C} IO_2SO_3F + S_2O_5F_2 \quad (5)$$

$$I_2O_4 + 2S_2O_6F_2 \xrightarrow{25\ ^\circ C} 2IO_2SO_3F + S_2O_5F_2 + {}^1/_2O_2 \quad (6)$$

It is interesting to note that reactions 4 and 6 have formal analogues in the interaction of peroxydisulfuryl difluoride with the nitrogen oxides N_2O_4 and N_2O_5.[20]

The oxidation of $IOSO_3CF_3$ with $S_2O_6F_2$ does not yield the expected $IO_2SO_3CF_3$ but a rather impure IO_2SO_3F in addition to volatile CF_3SO_3F. The ability of $S_2O_6F_2$ to cleave the S–C bond has been observed recently.[21]

(II) Vibrational Spectra. Like most iodine–oxygen compounds, the iodosyl and iodyl compounds gave very well-resolved Raman spectra and, in most cases, reasonable infrared spectra as well. (The Raman spectrum of $IO_2SO_3CF_3$ is shown in Figure 1.) The assignment of these spectra is however rather difficult for the following reasons.

(a) Similar to IO_2SO_3F, the new iodine–oxygen sulfates appear to be polymers. This is consistent with their high melting or decomposition points and their insolubility in their parent acids. The polymeric character of the compounds may be due either to bridging by the oxyacid group or to the formation of –I–O–I– chains as first postulated by Dasent and Waddington.[12] The recently reported structure of $(IO)_2SO_4$[7] provides an example of the occurrence of both types of association in the same molecule. The effect of such association is illustrated well in the Raman spectrum of IO_2SO_3F[10] where even nondegenerate modes of both the IO_2 and the SO_3F group are split into two or even three components. In addition bands down to about 50 cm^{-1} are sometimes observed, allowing often no clear distinction between internal and external (lattice) modes.

(b) As best exemplified by the structure of I_2O_5,[8] a relatively simple structure, two IO_2 groups (r_{I-O} = 1.77–1.83 Å) linked by an oxygen atom (r_{I-O-I} = 1.92–1.95 Å), is found. In addition to these bonding interactions a number of both inter- and intramolecular contacts between iodine and oxygen are observed ($r_{I\cdots O}$ = 2.23–3.25 Å). These contacts, all shorter than the sum of the van der Waals radii (3.65 Å), contribute appreciably to the polymeric nature of the compound and will further complicate the vibrational spectrum. Any detailed structural prediction beyond the molecular contours produced by bonding interactions will be quite impossible. This point is best illustrated by the attempts of Turner and Sherwood[11] on the vibrational assignment of I_2O_5.

(c) One of the peculiar features of iodine–oxygen compounds is the occurrence of iodine–oxygen stretching frequencies over a rather wide range. The upper limit is found at ~925 cm^{-1} for the oxyfluorides IOF_5[22] and IO_2F_3,[23] with the lower limit

Table II. Vibrational Spectra (cm^{-1}) of $IOSO_3F$ and IO_2SO_3F[a]

IO_2SO_3F[b]	$IOSO_3F$		Approx
Raman	Raman	Ir	description
1335	1366 mw	1350 s, b	$\nu(S{=}O)$
	1349 m		
1195	1160 m, sh	1160 vs, b	$\nu(SO_2^*)_{asym}$
1170	1148 ms	1120 s, sh	
	1112 w		
1070	1029 m	1002 vs, b	$\nu(SO_2^*)_{sym}$
1030	999 ms		
1010			
	897 vw	900 mw, sh	
843	851 m	815 s, b	$\nu(SF)$
	821 ms		
900	645 s	650 s, sh	$\nu(IO)_{asym}$
878	637 ms	632 vs, b	
865	598 ms	605 m	$\nu(IO)_{sym}$ + SO_2^* bend
	590 s	590 s	
615	Not observable	Not observable	SO_3 def modes
603			
592			
582			
685	447 w	440 ms	$\nu(IO^*)_{asym}$
660			
520	428 vs	440 s	$\nu(IO^*)_{sym}$
562	569 ms	560	SF wag
420	415 m, sh	410 s	FSO_3 twist
	404 vs		
310	360 w		SO_2^* torsion
288			
	228 m		IO and IO* def and lattice modes
	166 vs		

[a] Key for this and other tables: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; b, broad; wag, wagging; asym, asymmetric; sym, symmetric; bend, bending; str, stretching; def, deformation. The asterisk denotes oxygen in I–O–S linkages. [b] Reference 10.

Table III. Vibrational Spectra (cm^{-1}) of $IOSO_3CF_3$ and $IO_2SO_3CF_3$

$IOSO_3CF_3$		$IO_2SO_3CF_3$		Approx
Raman	Ir	Raman	Ir	description
	1420 w		1424 w	
1395 m	1394 ms	1326 ms	1332 s	S=O str
1284 ms	1338 w			
	1280 ms			
1242 m, sh	1240 m, sh	1233 ms	1225 m, sh	CF_3 sym str
1224 ms	1210 s	1221 m, sh	1210 s	CF_3 asym str
1133 s	1140 s	1125 s	1125 s	SO_2^* asym str
1040 w, sh	1018 s	975 w	1035 w	SO_2^* sym str
1025 s	970 m	941 s	1965 m, sh	
969 ms			938 s	
		849 ms	860 vs	IO_2 asym str
883 vs	885 s			IO str
865 w	860 s			
		823 vw	830 vs	IO_2 sym str
779 s	775 ms	774 ms	778 m	S–C str
662 s	670 m, sh	678 s	680 w, sh	IO_2^* sym str
	655 m, sh			
634 s	640 s	645 m	640 s	IO_2^* asym stretch
624 ms	625 w, sh	628 w	630 m, sh	SO_3 def
587 s	585 m, sh	589 ms	600 s	CF_3 asym bend
560 w	550 s	578 m	578 m, sh	
535 w, sh		540 s	542 s	SO_3 bend
529 s	528 s	522 ms	520 m	CF_3 sym bend
453 rs	455 w			
	415 m		395 s	
380 ms	375 m	367 w, sh	360 ms	Various unassigned def and lattice modes
360 m	350 m	345 s	340 m	
355 m	320 w, sh	328 ms	320 w, sh	
329 m	311 m	290 m		
316 m		258 ms		
290 vs		235 vs		
248 ms		217 mw		
155 vw		190 vs		
		163 m		
		115 ws		

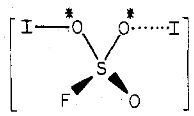
given by $(IO)_2SO_4$ and the corresponding selenate[12] where ν(IO–) bands are found as low as 553 cm^{-1}. Generally, iodine–oxygen stretching modes extend over the whole range in between. No clear subdivision into iodine–oxygen double or single bonds seems possible. E.g., the vibrational assignment for $HOIO_2$[24] (see Table V) may serve as a good illustration. The symmetric and asymmetric IO_2 bands are found at 713 and 780 cm^{-1}, respectively, with ν(I–OH) at 631 cm^{-1}.

Many of the general problems discussed here arise from the polymeric nature of the compounds. They could be avoided by either Raman studies on solutions or vibrational investigations of matrix-isolated molecules, but the lack of a suitable solvent and the involatility of the sulfates present serious drawbacks in the application of these techniques.

The vibrational frequencies of the solid sulfates are listed in Tables II and III together with a tentative assignment primarily in the stretching frequency range. To simplify the proposed assignment, we have labeled oxygen atoms involved in bridging between I and S with an asterisk. The following points of interest emerge.

The number of observed bands in particular in the lower frequency range is indicative of polymeric compounds. Any discrepancies between observed Raman and infrared band positions is not very significant and may be caused by the relatively broad ir bands. As mentioned in the Experimental Section, no suitable mulling agent could be found for these compounds.

$IOSO_3F$ has, in the SO_3 stretching region, bands at ~1350, ~1150, and 1000 cm^{-1}, some split into two or three components. Whereas the first two bands occur in a region characteristic for a bridging bidentate group, as, e.g., in IO_2SO_3F,[10] and in various tin and organotin fluorosulfates,[25] the third band is found at a slightly lower frequency, usually observed for monodentate SO_3F groups as, e.g., in $[Sn(SO_3F)_6]^{2-}$.[26] The most likely explanation is the presence of an unsymmetrical or "anisobidentate"[27] bridge as shown in I. Such a feature is certainly not unexpected in the structural



I

chemistry of iodine–oxygen compounds.

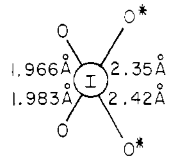
Table IV. Raman and Infrared Spectra (cm^{-1}) of $(IO)_2SO_4$

Raman	Approx description	Infrared	Raman	Approx description
1300 vw	2 × 653	1050 s, vb	360 (2)	Def and lattice modes
1180 (2)		632 s, b	287 (4)	
1142 (4)	$\nu_3(SO_4)$	582	232 (2)	
1080 (10)		550 s	211 (14)	
1042 (16)	$\nu_1(SO_4)$	420 m	180 (10)	
925 (0.3)	430 + 496		115 (3)	
852 (0.2)	2 × 430			
830 (0.8)	2 × 410 or 410 + 430			
653 (28)				
630 (8)	$\nu(IO)_{sym}$			
586 (4)	$\nu(IO)_{asym}$			
545 (2)	$\nu_4(SO_4)$			
496 (32)				
430 (90)	$\nu(IO)_{asym}$			
410 (100)	$\nu(IO^*)_{sym}$			

The highest band assignable to an iodine–oxygen stretch is found at ~650 cm^{-1}, indicative of strong I–O–I–O··· association as found for $(IO)_2SO_4$.[7] The rather intense bands in the iodine–oxygen stretching region (650–550 cm^{-1}) do not permit an assignment of the SO_3F deformation modes expected in this region.

Quite in contrast to this observation, **$IOSO_3CF_3$** has a strong band at 870 cm^{-1}, which can only be assigned as an I–O stretching mode. One can only speculate that the rather bulky SO_3CF_3 groups prevent any effective association of IO groups. The SO_3CF_3 bands here and for $IO_2SO_3CF_3$ are best attributed to a bidentate bridging group in analogy to some tin[25] and titanium compounds.[28] They are found in comparable positions for both compounds. The I–O stretching modes for $IO_2SO_3CF_3$ indicate, as is the case for IO_2SO_3F, discrete IO_2 groups without extensive association.

The vibrational spectra for **$(IO)_2SO_4$** are listed in Table IV. Here the reported molecular structure[7] helps in the interpretation and allows a more detailed assignment. Infinite IO chains are linked to tetradentate SO_4 groups, which retain T_d symmetry. The environment around iodine, as shown in II, is almost planar with two sets of I–O distances, labeled I–O and I–O*. The resulting four I–O stretching vibrations are assigned to the most intense bands in the spectrum.



II

Three of the four SO_4 fundamentals are detected, the remaining one, ν_2, is presumed to be obscured by the iodine–oxygen stretching modes. The band positions differ only slightly from those for sulfate ions.[29] The most noticeable difference is a shift of the ν_1 and ν_3 components to higher frequencies by about 30–40 cm^{-1}. The frequencies listed in the infrared spectrum extend to 420 cm^{-1} and agree well with the reports by Dasent and Waddington.[12] The rather broad unresolved bands illustrate the enormous advantage Raman spectroscopy offers.

A similar structure with polymeric $(IO)_n$ chains had been proposed for I_2O_4[12] on the basis of rather poor infrared spectra. The Raman spectrum, listed in Table V, is not consistent with such a postulation because strong bands, assignable to iodine–oxygen stretching modes, extend to about 550 cm^{-1} only but are very prominent in the 700–800-cm^{-1} region. In addition, remarkable similarity to the Raman spectrum for $HOIO_2$[24] is found and assignment of the compound as $OIOIO_2$ is indeed plausible. It should be however clearly understood that association via inter- and intramolecular iodine–oxygen contacts, as found for I_2O_5,[8] is a definite possibility. Such association can explain the complexity observed for the Raman spectrum and the occurrence of bands down to ~100 cm^{-1}. The proposed structure, similar to the one found for I_2O_5, has been previously postulated by Grushko et al.[14] on the basis of ^{129}I Mössbauer spectra and an orbital population analysis based on the Mössbauer data.

Table V. Vibrational Spectra (cm^{-1}) of I_2O_4 and Related Compounds

Na-IO_3[a] Raman	HI-O_3[a,b] Raman	Approx description[c]	I_2O_4 Raman	I_2O_4 Ir
817	834	$\nu(IO_2)$ + lattice mode	836 (2.5) 816 (1.0)	825 m, sh
774	780	$\nu(IO_2)$	778 (100)	782 s, b
754	741		. . . (15)	
		$\nu(IO)$	745 sh (15)	750 vs, b
	713	$\nu(IO_2)_{asym}$	723 s (25)	
	631	$\nu(IO^*I)_{asym}$[d]	642 (28) 623 sh	659 s 620 s
		$\nu(IO^*I)_{sym}$	548 (4)	578 s, b
373 355	378	O^*IO_2 rock	403 (8) 363 (8.5) 353 (8.5)	408 s, b 370 s, b
332	328	IO_2 def	326 (5)	315 s, b
	296	O^*IO bend	306 (2)	
			280	
220 199 158 132 108 76 12	220 192 158 124 111 91 72 58	Def and lattice modes unassigned	267 236 194 183 162 143 133	

[a] Reference 24. [b] Vibrations due to the OH group are omitted here. [c] As proposed in ref 24. [d] Asterisk denotes the bridging oxygen.

Finally the aromatic derivatives C_6H_5IO and $C_6H_5IO_2$ were investigated. The Raman spectra, not reported here in detail, show $\nu(IO)$ at 720–748 cm^{-1} for the former and $\nu(IO_2)$ at ~720 and ~760 cm^{-1} for the latter. All bands were split into two or three components indicating some association.

(D) Summary

As can be seen from Tables II–V, iodine–oxygen stretching frequencies for the compounds discussed here extend over a rather wide range from 900 to about 550 cm^{-1}. When comparison is made to $\nu(IO)$ for gaseous IOF_5,[22] this fact and the complicated spectra encountered may be taken as indications for varying degrees of *inter-* or even *intra*molecular iodine–oxygen–iodine association in the solid state.

The extent of this association seems to be greatest for the iodosyl derivatives $IOSO_3F$, $(IO)_2SO_4$, and also $(IO)_2SeO_4$[12]—not discussed here in detail. Here well-defined $(IO)_n$ chains are formed, with oxygen approximately equidistant between two iodine atoms, as has been shown by x-ray diffraction for $(IO)_2SO_4$.[7] Further association to the oxyacid group is relatively weak judging from the rather low position of $\nu(I–O–S^*)$ at ~450 cm^{-1}.

In contrast, for $IOSO_3CF_3$ and the IO_2 derivatives discrete IO– or IO_2– groups are found as indicated by the high iodine–oxygen stretching frequencies. Any ···I–O···I–O··· association seems rather weak, but strong bonding to the oxyacid group results in high $\nu(I–O^*–S)$ frequencies. As vibrational spectra indicate, bidentate, presumably bridging groups are found for the SO_3F and SO_3CF_3 groups with SO_4 in $(IO)_2SO_4$ acting as a tetradentate bridging group.[7]

Even though Raman spectroscopy was found to afford well-resolved spectra, the complexity observed and the reported molecular structures[7-9] indicate a complicated bonding situation. Not only simple ionic models such as $IO_2^+IO_3^-$ for I_2O_5 or $(IO^+)_n(IO_3^-)_n$[12] for I_2O_4 but also conventional views on molecular geometry, coordination number, covalent bonding, and van der Waals interaction are insufficient to describe the complex solid structures encountered in this group of compounds. It is hoped that more definitive x-ray data will become available on the iodine–oxygen derivatives of oxyacids.

Acknowledgment. The financial support of the National Research Council of Canada is gratefully acknowledged. Mrs. B. I. Kriszan and Miss M. Rosenberg are thanked for the technical drawings.

Registry No. $IOSO_3F$, 58735-49-2; IO_2SO_3F, 13537-35-4; $IOSO_3CF_3$, 58735-51-6; $IO_2SO_3CF_3$, 58735-54-9; $(IO)_2SO_4$, 25041-70-7; I_2O_4, 12399-08-5; HI_3O_8, 12134-99-5; HSO_3CF_3, 1493-13-6.

References and Notes

(1) For part 1 see ref 10.
(2) (a) G. Daehle and A. Kjekshuis, *Acta Chem. Scand.*, **18**, 144 (1964), and references quoted therein; (b) K. Selte and A. Kjekshuis, *ibid.*, **25**, 751 (1971).
(3) M. E. Millon, *Ann. Chim. Phys.*, **12**, 345, 353 (1844); *J. Prakt. Chem.*, **34**, 321, 337 (1845).
(4) F. Aubke, G. H. Cady, and C. H. L. Kennard, *Inorg. Chem.*, **3**, 1799 (1964).
(5) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1236 (1966).
(6) J. R. Dalziel and F. Aubke, *Inorg. Chem.*, **12**, 2707 (1973).
(7) S. Furuseth, K. Selte, H. Hope, A. Kjekshuis, and B. Klewe, *Acta Chem. Scand., Ser. A*, **28**, 71 (1974).
(8) K. Selte and A. Kjekshuis, *Acta Chem. Scand.*, **24**, 1912 (1970).
(9) E. M. Archer, *Acta Crystallogr.*, **1**, 64 (1948).
(10) H. A. Carter and F. Aubke, *Inorg. Chem.*, **10**, 2296 (1971).
(11) P. M. A. Sherwood and J. J. Turner, *Spectrochim. Acta, Part A*, **26**, 1975 (1970), and ref 1–4 therein.
(12) W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 3350 (1960); *J. Inorg. Nucl. Chem.*, **25**, 132 (1963).
(13) C. Furlani and G. Sartori, *Ann. Chim. (Rome)*, **47**, 124 (1957).
(14) Yu. S. Grushko, B. G. Lur'e, A. V. Motornyi, and A. N. Murin, *Fiz. Tverd. Tela (Leningrad)*, **10**, 3704 (1968) [*Sov. Phys.—Solid State (Engl. Transl.)*, **10**, 2944 (1969)]; Yu, S. Grushko, B. G. Lure, and A. N. Murin, *Fiz. Tverd. Tela (Leningrad)*, **11**, 2144 (1969) [*Sov. Phys.—Solid State (Engl. Transl.)*, **11**, 1733 (1970)].
(15) (a) "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 482; (b) G. H. Cady and J. M. Shreeve, *Inorg. Synth.*, **7**, 116 (1963).
(16) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(17) I. Masson and C. Argument, *J. Chem. Soc.*, 1702 (1938).
(18) R. G. Gillespie and M. J. Morton, *Q. Rev., Chem. Soc.*, **25**, 553 (1971).
(19) (a) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957); (b) T. Gramstad and R. N. Hazeldine, *J. Chem. Soc.*, 4069 (1947).
(20) A. M. Qureshi and F. Aubke, *Can. J. Chem.*, **49**, 35 (1971).
(21) R. L. Kirchmeier and J. M. Shreeve, *Inorg. Chem.*, **12**, 2886 (1973).
(22) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1965).
(23) A. Engelbrecht, O. Mayr, G. Ziller, and E. Schandara, *Monatsh. Chem.*, **105**, 796 (1974); H. A. Carter, J. N. Ruddick, J. R Sams, and F. Aubke, *Inorg. Nucl. Chem. Lett.*, **11**, 29 (1975).
(24) J. R. Durig, O. D. Bonner, and W. H. Breazeale, *J. Phys. Chem.*, **69**, 3886 (1965).
(25) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 2634 (1972).
(26) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **12**, 328 (1973).
(27) J. L. K. F. DeVries and R. H. Herber, *Inorg. Chem.*, **11**, 2461 (1972).
(28) J. R. Dalziel, R. D. Klett, P. A. Yeats, and F. Aubke, *Can. J. Chem.*, **52**, 231 (1974).
(29) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2d ed, Wiley-Interscience, New York, N.Y., 1970, p 112.

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

A Fluorine-19 Nuclear Magnetic Resonance and Raman Spectroscopic Investigation of the Structure of Iodine Dioxide Trifluoride

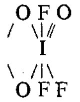
R. J. GILLESPIE* and J. P. KRASZNAI

Received May 21, 1975 AIC50355L

IO_2F_3 has been studied by ^{19}F NMR and Raman spectroscopy in the liquid state and at low temperature in perfluoro(methyl)cyclohexane and bromine pentafluoride solutions. It is concluded that IO_2F_3 exists as a cyclic trimer with cis-oxygen bridges, in the boat conformation, the I=O bonds being perpendicular to the plane containing the bridging bonds.

Introduction

The synthesis of iodine dioxide trifluoride was first reported by Engelbrecht and Peterfy,[1,2] who concluded from the ^{19}F NMR spectrum of the melt that it consisted of a mixture of C_{2v} and C_s isomers of a trigonal-bipyramidal IO_2F_3 molecule. Beattie and Van Schalkwyk,[3] however, obtained a simpler AX_2 NMR spectrum for the melt and they also found that vapor density measurements indicated polymerization in the vapor phase. On the basis of this evidence Beattie and Van Schalkwyk proposed that IO_2F_3 is a cis-oxygen-bridged polymer based on the two possible structural units A and B



A

B

and that there is an equilibrium between monomers and polymers in the gas, liquid, and solution phases. They observed a splitting of the X_2 doublet of the ^{19}F NMR spectrum of IO_2F_3 in perfluoro(methyl)cyclohexane solution at low temperature which they considered to be supporting evidence for a monomer–polymer equilibrium. More recently Engelbrecht and co-workers[4] have reported that their original sample of IO_2F_3 was contaminated with $HOIOF_4$ and that a pure sample gave a spectrum similar to that reported by Beattie and Van Schalkwyk.[3] Engelbrecht and his co-workers[4] also reported the mass spectrum of IO_2F_3 which shows the presence of dimeric and trimeric species in the gas phase and suggested that IO_2F_3 is polymeric with a low degree of polymerization ($n \leq 4$).

We have also studied the structure and properties of IO_2F_3 and in this paper we report the Raman spectrum of solid IO_2F_3 and the Raman and ^{19}F NMR spectra of molten IO_2F_3 and its solution in BrF_5 and perfluoro(methyl)cyclohexane. Where our work overlaps with that of Beattie and Van Schalkwyk,[3] it agrees reasonably well with theirs but the results of our more extensive investigation lead us to somewhat different conclusions.

Results and Discussion

^{19}F NMR Spectra. A freshly prepared solution of IO_2F_3 in perfluoro(methyl)cyclohexane at −36 °C gave a simple AX_2 ^{19}F NMR spectrum (Table I). The peaks of the X_2 doublet