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# Raman Spectra and Structure of Bromine Tris(fluorosulfate) and Iodine Tris(fluorosulfate) and the Anions Bromine Tetrakis(fluorosulfate) and Iodine Tetrakis(fluorosulfate)

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*Received May 18, 1970*

Alternative routes for the preparation of $K[I(OSO_2F)_4]$ and $K[Br(OSO_2F)_4]$ are described. The Raman spectra of these compounds, of $Na[I(OSO_2F)_4]$, and of the halogen tris(fluorosulfates) $I(OSO_2F)_3$ and $Br(OSO_2F)_3$ are reported. A square-planar configuration is proposed for the anions, whereas the presence of two types of fluorosulfate groups in the tris(fluorosulfates) suggests a polymeric structure.

Peroxydisulfuryl difluoride,[1] $S_2O_6F_2$, has been found particularly useful in the preparation of halogen fluorosulfate derivatives, where its behavior can best be rationalized as that of a pseudohalogen. The reaction of bromine and iodine with excess $S_2O_6F_2$ has been found to yield the tris-fluorosulfate compounds $Br(OSO_2F)_3$ and $I(OSO_2F)_3$, respectively.[2] Under similar conditions potassium bromide and iodide have been found[3] to give complex salts of the composition $K[Br(OSO_2F)_4]$ and $K[I(OSO_2F)_4]$, respectively. Subsequent studies[4-6] with the tris(fluorosulfates) have yielded some information on their chemical and physical properties as well as their solution behavior in fluorosulfuric acid. However, no structural information on any of the compounds is available at present. The assumption that the tetrakis(fluorosulfate) anion is a reaction product of the tris(fluorosulfate) and the fluorosulfate anion, according to

$$\mathrm{Hal(OSO_2F)_3 + SO_3F^- = Hal(OSO_2F)_4^-} \quad (\mathrm{Hal = Br, I})$$

is logical in view of the related systems $BrF_3$ *vs.* $BrF_4^-$ and $ICl_3$ *vs.* $ICl_4^-$. This, however, has not previously been substantiated by synthesis or vibrational spectra.

The present study was undertaken in order to search for new synthetic routes for the fluorosulfate complexes which might be used as evidence for the above assumption and to obtain, if possible, vibrational spectra of this group of compounds. Their rather high reactivity has prevented any infrared studies so far. Since none of the compounds is deeply colored—the tris(fluorosulfates) are pale yellow to yellow and the anion complexes white to slightly cream colored—it should be possible to obtain laser Raman spectra.

The most feasible structural models for the tris(fluorosulfates) are provided by analogs from among the interhalogen compounds of the $AB_3$ type: (a) the T-shaped monomeric molecule as found for $BrF_3$[7] and $ClF_3$[8,9] and (b) the fluorosulfate-bridged dimer or possibly polymer similar to the $I_2Cl_6$[10] structure. The fact that the $^{19}F$ nmr spectrum of the melt or the solution in $S_2O_6F_6$[6] shows only a single line for both tris(fluorosulfates) might imply that neither model is satisfied, but rapid inter- or intramolecular exchange is a definite possibility. Vibrational spectra, however, have previously[11] been found to be very helpful in distinguishing between bridging and terminal fluorosulfate groups in compounds such as $Sn(SO_3F)_4$ and $Cl_2Sn(SO_3F)_2$.

## Experimental Section

**Materials.**—Analytical grade $KBrO_3$, KI, and NaI from Fisher Scientific Co. were used. Sublimed analytical grade $I_2$ was supplied by BDH. Bromine (BDH) was purified before use according to literature methods.[12] $KICl_4$ was prepared over the $KIBr_2$ intermediate.[13] Peroxydisulfuryl difluoride was prepared in a catalytic reaction as described in principle by Cady and Shreeve.[14] The purity was checked by infrared and $^{19}F$ nmr spectra. Potassium fluorosulfate was prepared from KCl (BDH) and double distilled $HSO_3F$ (Baker and Adamson). The crude product was recrystallized from water. All reactions involving $S_2O_6F_2$ were carried out in 50–100-ml flat-bottom reaction flasks, fitted with Fisher and Porter greaseless Teflon stem stopcocks. The reaction mixture was stirred magnetically in case of the complex salt preparations. All reactions were followed by weight. A five to tenfold excess of $S_2O_6F_2$ was used. The details are given below.

$K[I(OSO_2F)_4]$ was prepared by combining equimolar amounts (3.48 mmol each) of $KSO_3F$ and $I(OSO_2F)_3$ in a drybox. To complete the mixing of the products, a large excess of $S_2O_6F_2$ or $S_2O_5F_2$ was added. White crystals were formed and separated by distillation of solvent; 3.43 mmol was obtained. The decomposition point of ∼+165° compares well with the previously reported one of 167–168°.[3]

In the ligand replacement reaction, 1.722 mmol of $KICl_4$ was treated with a large excess of $S_2O_6F_2$. Chlorine was evolved immediately. In order to complete the reaction, the mixture was heated at 70° for 24 hr. The products were separated by distillation of the volatile components at room temperature; 1.709 mmol of $K[I(OSO_2F)_4]$ with a decomposition point of +168° was obtained.

The composition of both products was checked by iodine analysis. Identical X-ray powder patterns were obtained for $K[I(OSO_2F)_4]$ prepared by the different routes.

**Preparation of $K[Br(OSO_2F)_4]$.**—An excess of $S_2O_6F_2$ was dis-

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tilled *in vacuo* onto 6.503 mmol of $KBrO_3$. Upon warming to 0°, the reaction proceeded moderately fast with the formation of a bright orange intermediate. The reaction mixture was kept at 0° until oxygen evolution had ceased. After removal of the oxygen and the excess $S_2O_6F_2$ by pumping, 6.50 mmol of $KBr(OSO_2F)_4$ was obtained. A decomposition point of 170° was found. The sample was analyzed for bromine after hydrolysis.

**Raman Spectra.**—A Cary 81 spectrophotometer equipped with a Spectra Physics Model 125 laser was used. The samples were contained in flat-bottom Pyrex tubes (5-mm o.d.).

## Results

The Raman spectra of $K[Br(OSO_2F)_4]$, $K[I(OSO_2F)_4]$, and $Na[I(OSO_2F)_4]$ are listed in Table I, together with the estimated intensities and a tentative assignment. A correlation diagram for the $SO_3F$ group is given in Table II. The spectra for $Br(OSO_2F)_3$ and $I(OSO_2F)_3$ are listed in Table III. Approximate polarization ratios for the most intense peaks of iodine tris(fluorosulfate) were also obtained since the spectrum was obtained for the supercooled melt. All compounds, particularly the first four, were found to give well-resolved spectra at rather low sensitivities. The accuracy is judged to be ~±2.0 $cm^{-1}$.

TABLE I

VIBRATIONAL FREQUENCIES FOR THE $Hal(OSO_2F)_4^-$ ANION

| $KBr(OSO_2F)_4$ | $NaI(OSO_2F)_4$ | $KI(OSO_2F)_4$ | Assignment | | |
|---|---|---|---|---|---|
| 1424 mw | 1407 m | 1409 m | $\nu_7$ | $\nu_{as,SO_3}$ | A′′ |
| 1407 mw | 1395 w | | | | |
| 1237 s | 1236 s | 1250 s | $\nu_1$ | $\nu_{s,SO_3}$ | A′ |
| 1220 w, sh | 1222 w, sh | 1222 w, sh | | | |
| 970 ms | 1001 m | 1002 m | $\nu_4$ | $\nu_{as,SO_3}$ | A′ |
| | 859 w | | | | |
| 834 m | 834 m | 837 | $\nu_2$ | $\nu_{SF}$ | A′ |
| 615 vs | 612 vs | 620 vs | $\nu_3$ | $\delta_{dd}$ | A′ |
| 578 ms | 580 ms | 582 m | $\nu_5$ | | A′ |
| 553 w | 551 ms | 554 m | $\nu_8$ | | A′′ |
| 447 s | 440 s | 442 s | $\nu_1$ | Hal–O | $A_{1g}$ |
| 406 w | 405 w | 407 w | $\nu_9$ | | A′′ |
| 399 w | 394 w | 397 w | $\nu_4$ | Hal–O | $B_{2g}$ |
| 270 s | 252 s | 260 s | $\nu_2$ | Hal–O | $B_{1g}$ |
| 239 vs | 231 vs | 239 vs | $\nu_6$ | | A′ |

TABLE II

CORRELATION DIAGRAM OF THE $SO_3F$ GROUP

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SO_3F^-$ ion ($C_{3v}$ symmetry), vibrational modes | $\nu_1$ ($A_1$) | $\nu_2$ ($A_1$) | $\nu_3$ ($A_1$) | $\nu_4$ (E) | | $\nu_5$ (E) | | $\nu_6$ (E) | |
| | $\nu_{s,SO_3}$ | $\nu_{SF}$ | $\nu_{s,SO_3}$ | $\nu_{as,SO_3}$ | | $\delta_{as,SO_3}$ | | $\delta_{rock}$ | |
| Example $KSO_3F$ | 1082 | 786 | 566 | 1287 | | 592 | | 409 | |
| | ↓ | ↓ | ↓ | ↙ | ↘ | ↙ | ↘ | ↙ | ↘ |
| $-OSO_2F$ group, vibrational modes | $\nu_1$ (A′) | $\nu_2$ (A′) | $\nu_3$ (A′) | $\nu_4$ (A′) | $\nu_7$ (A′′) | $\nu_5$ (A′) | $\nu_8$ (A′′) | $\nu_6$ (A′) | $\nu_9$ (A′′) |
| Example $Br(OSO_2F)_4^-$ | 1237, 1220 | 834 | 615 | 970 | 1424, 1407 | 578 | 553 | 239 | 406 |

The Raman spectra of $K[I(OSO_2F)_4]$, $K[Br(OSO_2F)_4]$, and $Br(OSO_2F)_3$ are shown in Figure 1. All attempts to obtain well-resolved infrared spectra by avoiding window attack did not lead to satisfactory results.

## Discussion

The two new synthetic routes employed for the preparation of $K[I(OSO_2F)_4]$ are quite logical in view of the postulated nature of the complexes: (a) the interaction of equimolar amounts of $KSO_3F$ and $I(OSO_2F)_3$ with $S_2O_6F_2$ as the liquid phase and (b) the ligand replacement reaction where $KICl_4$ is allowed to react with an excess of $S_2O_6F_2$ at room temperature according to $KICl_4 + 2S_2O_6F_2 = K[I(OSO_2F)_4] + 2Cl_2$. The obtained products are found to have the required composition and appear to be identical with the previously reported one[3] as shown by the decomposition points and X-ray powder diagrams. The outcome of the preparative reactions seems to agree well with expectations but is, however, insufficient as structural proof.

None of the two routes discussed above presents an improvement over the previous preparation with KI as the simplest starting material. When potassium iodide is substituted by sodium iodide, $Na[I(OSO_2F)_4]$ is formed as expected.

The alternative route for the preparation of $K[Br(OSO_2F)_4]$ is far easier than the interaction of KBr with $S_2O_6F_2$. When $KBrO_3$ is allowed to react with $S_2O_6F_2$ at temperatures below 0°, a rather vigorous reaction with oxygen evolution takes place and $K[Br(OSO_2F)_4]$ is formed instantaneously. The net reaction is best described as $KBrO_3 + 2S_2O_6F_2 = K[Br(OSO_2F)_4] + 1.5O_2$. When the reaction flask is kept below −40°, only moderate oxygen evolution occurs and bright orange platelike crystals are formed which decompose vigorously upon further warming under $O_2$ release. Since the analogous reactions of $S_2O_6F_2$ with $KClO_3$[15] and $KIO_3$[16] result in the formation of $ClO_2SO_3F$ and $IO_2SO_3F$, respectively, it seems feasible that the observed intermediate is possibly thermally unstable $BrO_2SO_3F$. The only known $BrO_2$ derivatives $FBrO_2$[17] and $BrO_2ONO_2$[18] are of very limited thermal stability, being comparable to the bromine oxides. Because the complex $K[Br(OSO_2F)_4]$ is formed instantaneously, this route offers some advantages over the previous preparation where heating to 50° and a reaction time of several days are required. A difference in decomposition points—we find 170° while that reported[3] is 100°—is not too meaningful since decomposition points can be influenced by small impurities and do not present a good criterion for identification.

The Raman spectra of $K[Br(OSO_2F)_4]$, $K[I(OSO_2F)_4]$, and $Na[I(OSO_2F)_4]$ are listed in Table I. All

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TABLE III

VIBRATIONAL FREQUENCIES FOR $Br(OSO_2F)_3$ AND $I(OSO_2F)_3$

| | | Assignment | |
|---|---|---|---|
| $Br(OSO_2F)_3$ | $I(OSO_2F)_3$ | Terminal | Bridging |
| 1490 mw | 1469 m | $\nu_7$ | |
| 1467 w | | | |
| 1372 m | 1381 mw | | $\nu_1'$ |
| 1356 mw, sh | | | |
| 1241 s | 1233 s, p (0.34) | $\nu_1$ | |
| 1230 m, sh | | | |
| 1168 mw | 1182 w, sh | | $\nu_7'$ |
| 1122 m | 1076 w, sh | | |
| | 1050 m, p (0.62) | | $\nu_4'$ |
| 1010 m | 963 m, p (0.29) | $\nu_4$ | |
| 1015 m | | | |
| 859 m | 869 p (0.40) | | $\nu_2'$ |
| 827 vw | 826 w | | |
| 801 m | 800 m | $\nu_2$ | |
| 721 ms | 700 w | | $\nu_5'$ |
| 645 vs, br | 642 vs, p (0.49) | | $\nu_3'$ |
| 612 vs | 619 p (0.48) | | |
| 583 ms | 580 m, sh | $\nu_5$ | |
| 563 m | 556 | | $\nu_8'$ |
| 551 vw | | | |
| 540 w | 540 m, sh | $\nu_8$ | |
| 455 s | 457 s, p (0.39) | $\nu_1$ Hal–O | |
| 430 m | 430 w, sh | | $\nu_9'$ |
| 408 mw | 412 m | $\nu_9$ | |
| 384 mw, sh | 386 mw, sh | $\nu_4$ Hal–O | |
| 303 vs | 290 vs, p (0.46) | | $\nu_6'$ |
| 276 vs | 270 s, sh | $\nu_2$ Hal–O | |
| 225 ms | | $\nu_6$ | |
| 206 | | | |
| | 181 m | | |
| | 148 m | | |

three show considerable similarity, indicating structurally related compounds. The three vibrations found in the sulfur–oxygen stretching region of 1500–900 cm$^{-1}$ suggest that all four fluorosulfate groups are identical. Some small splittings or the presence of shoulders could be due to solid-state splitting. Also a single band attributed to the S–F stretching vibration is found at ~835 cm$^{-1}$. The observed frequencies differ markedly[19–21] in total number and position of the absorption bands from that of an $SO_3F^-$ ion.

Covalent interaction will increase the number of vibrational modes from 6 for the $SO_3F^-$ ion with $C_{3v}$ symmetry to 9 for the covalent monodentate or bidentate $SO_3F$ group, both with $C_s$ symmetry, by the removal of degeneracy for the three E modes. All vibrations for $C_{3v}$ and $C_s$ symmetry will be ir and Raman active.

The change in band positions is illustrated nicely for the monodentate covalent compounds by $S_2O_5F_2$ and related compounds, where bands at ~1500 and 1250 cm$^{-1}$ are found,[22] indicating a larger degree of multiple bonding for the remaining terminal sulfur–oxygen bonds.

A correlation diagram, where a tentative assignment for the $Hal(OSO_2F)_4^-$ ion is made, is shown in Table II. The degree of splitting of the E modes, best recognized for the S–O stretching modes, will indicate the degree of covalency in the halogen–oxygen bond. This is well illustrated when the $Br(OSO_2F)_4^-$ ion is compared to $I(OSO_2F)_4^-$ ion where a slightly smaller splitting for the latter indicates a slightly more polar bond.

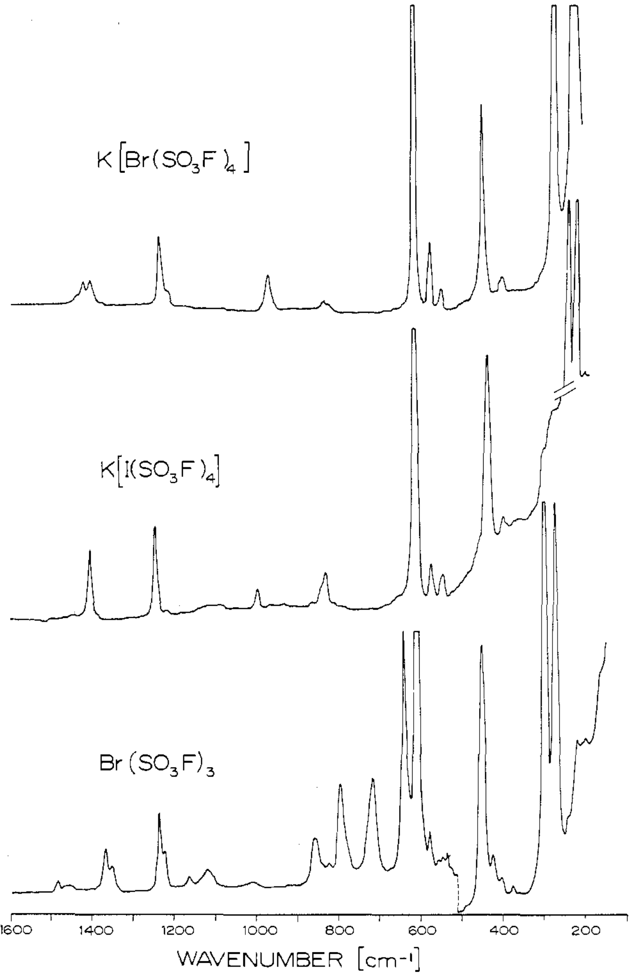

Figure 1.

For the anions, the vibrational frequencies can best be interpreted as being due to a covalently bonded monodentate $SO_3F$ group. The remaining bands at ~445, ~395, and ~260 cm$^{-1}$ are most probably due to halogen–oxygen vibrations and for the bromine species occur at slightly higher frequencies than the iodine species, as expected from the difference in masses.

The number of vibrational modes agrees well with a square-planar configuration, already suggested by the structure of the $BrF_4^-$ ion[23,24] which is found to have $D_{4h}$ symmetry. To obtain some indication of the approximate position of the vibrational bands in the fluorosulfate compounds, we have recorded the Raman spectrum of $KBrF_4$ which shows a pattern of three absorption lines at 532 (s), 457 (ms), and 246 cm$^{-1}$ (m). Due to the above-mentioned thermal instability of bromine–oxygen bonds, no other comparable assignments could be found in the literature.

The same lack of comparable systems is found for the $[I(OSO_2F)_4]^-$ ion. All vibrational studies on tervalent iodine–oxygen compounds are concerned with in-

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frared spectra of iodosyl derivatives[25] where the iodine–oxygen bond appears to have appreciable multiple-bond character.

The Raman spectra of both tris(fluorosulfates) indicate structural similarity but are far more complex than those of the anionic species. The vibrational frequencies are listed in Table III, together with a tentative assignment. For both compounds, a total number of six vibrational modes is found in the sulfur–oxygen stretching region and two strong bands become assignable to sulfur–fluorine stretching. A similar duplication of vibrations is found in the lower range of the bending and rocking modes. Bands previously assigned to halogen–oxygen are found again with comparable intensity in the same place as the anionic species.

The obvious explanation for the multitude of bands is that two types of fluorosulfate groups are present in both compounds. One set of bands is in approximately the same place as found for the tetrafluorosulfatohalate(III) anions, even though the asymmetric S–O stretching frequency appears at a higher wave number. Again the shift is larger for the bromine compound, indicating a higher degree of covalency, as found before.

The second set of nine vibrational modes could possibly be due to a second covalently bonded monodentate $SO_3F$ group as expected for a T-shaped molecule or for a bidentate bridging group. We clearly prefer the latter alternative for the following reasons. The halogen–oxygen frequencies would be found in a different place and a total of six Raman-active bands would be expected for the $C_{2v}$ model with three in the stretching range. Only minor positional changes for a second terminal $SO_3F$ group would be expected. In addition, fair agreement with the bridging fluorosulfate group in the hexacoordinated compounds $Sn(SO_3F)_4$ and $Cl_2Sn(SO_3F)_2$[11] is found.

All this points to the fact that the two halogen tris(fluorosulfates) are not monomeric in the solid state. The most likely models are a chain-type polymer or a bridged dimer, both with a square-planar configuration for the halogen. Even though the observed solubility in solvents such as $S_2O_5F_2$ and $S_2O_6F_2$ points to low molecular weight species, no clear distinction is possible at this point.

The occurrence of many doublets in the spectrum of bromine tris(fluorosulfate) is best explained by assuming different conformations of both the terminal and the bridging group. Only singlets are observed for most corresponding bands of $I(OSO_3F)_3$ present as a melt. All assignments for the two fluorosulfate groups are tentative particularly in the lower frequency range. The higher frequency S–F vibration is assigned to the bridging $SO_3F$ group, based on the $Cl_2Sn(SO_3F)_2$[11] example. Vibrational modes at 200 cm$^{-1}$ and lower could possibly be due to lattice modes.

**Acknowledgment.**—We acknowledge financial support from the National Research Council of Canada.

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# Solution Properties of 12-Heteropoly Acids of Molybdenum

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*Received April 13, 1970*

Conductivity and pH measurements were made on the heteropoly acids $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ at 25° in mixed oxygen-containing solvents to establish the stability and electrolyte strength of the compounds. Measurements of pH were also obtained on $H_3[PMo_{12}O_{40}]$ and $H_4[SiMo_{12}O_{40}]$. The conductivity data show that the vanadium compounds exhibit typical behavior of unsymmetrical strong electrolytes in the oxygen-containing solvents. The pH data show that the heteropoly acids studied are strong, stable acids in these media. The acid $H_3[PMo_{12}O_{40}]$ is hydrolytically unstable in water, but it is stabilized by mixed oxygen-containing solvents. Diffusion coefficients were calculated for $PMo_{11}VO_{40}^{4-}$ and $PMo_{10}V_2O_{40}^{5-}$ using conductivity data.

## Introduction

A previous paper[1] reported the stability and acid strength of the heteropoly acids $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ as determined by conductivity and pH measurements in aqueous solution. These data showed that $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ are strong 1:4 and 1:5 electrolytes, respectively, having conductivities that obey the Onsager–Fuoss equation.[2,3]

The present work constitutes an extension of the conductivity studies on these compounds into dioxane–water and *tert*-butyl alcohol–water solvent mixtures; the compounds are expected to find usefulness in solvents other than water alone. In addition, pH measurements of the acids $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, $H_4[PMo_{11}VO_{40}]$, and $H_5[PMo_{10}V_2O_{40}]$ were obtained in

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