A direct route to niobium(V) and tantalum(V) fluoride fluorosulfates

Dingliang Zhang and Friedhelm Aubke
Department of Chemistry, The University of British Columbia, Vancouver, B. C. V6T 1Z1 (Canada)

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Abstract

A simple one-step synthesis for niobium(V) and tantalum(V) fluoride fluorosulfates is reported. The procedure involves the oxidation of the respective metal by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, in the presence of the corresponding metal pentafluoride at room temperature and leads to colorless, viscous liquids. Of the resulting products, those of the general composition $MF_n(SO_3F)_{5-n}$ ($M = Nb$, Ta; $n \geq 3$) can be distilled *in vacuo* without decomposition. As an example, the synthesis of $TaF_3(SO_3F)_2$ is described in detail.

Introduction

In spite of their extremely low oxidizing ability, niobium(V) and tantalum(V) pentafluorides, NbF_5 and TaF_5, have found surprisingly little use in conjugate superacid systems because of their low Lewis acidity (NbF_5) and their limited solubilities in anhydrous HF and HSO_3F [1]. In this communication, we wish to report a generally applicable, one-step synthetic route to niobium(V) and tantalum(V) fluoride fluorosulfate derivatives of the general formula $MF_n(SO_3F)_{5-n}$ ($M = Nb$, Ta; $0 \leq n < 5$). These compounds are miscible with HSO_3F in all proportions.

Experimental

Niobium and tantalum metal powder (60 mesh, 99.9% purity, Alfa Inorganics) and NbF_5 and TaF_5 (99% purity, Ozark–Mahoning, now known as Ato Chem, North America) were obtained from commercial sources. They were used without further purification. Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, was prepared by the catalytic fluorination of SO_3 as reported previously [2, 3]. Our drybox as well as the instrumentation and techniques to obtain IR, Raman, ^{19}F NMR spectra and conductivity data have been described elsewhere [4]. To illustrate the general synthetic procedure used, the preparation of $TaF_3(SO_3F)_2$ is described in detail below.

In a typical preparation, 0.8277 g (4.575 mmol) tantalum powder and 1.8894 g (6.856 mmol) TaF_5 were added to a two-part glass reactor inside

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a drybox. 8.069 g (40.73 mmol) $S_2O_6F_2$ was added by vacuum-transfer. As the mixture warmed up to room temperature, the reaction proceeded vigorously and exothermically. The reactor needed to be cooled in an ice–water bath at this stage to avoid pressure build-up and the possible decomposition of the product. Following this initial phase, the reaction continued smoothly at room temperature. The mixture was stirred for *c.* 2 d until all the metal powder was consumed. The resulting turbid mixture was filtered *in vacuo* to remove a small amount of a white precipitate, using an apparatus as described by Shriver [5]. The filtrate was then pumped at room temperature *in vacuo* to remove excess $S_2O_6F_2$, monitored by the 800 cm^{-1} band (ν_{O-O}) in the Raman spectrum [6]. After the removal of $S_2O_6F_2$, a pale-yellow viscous liquid was obtained as a crude product. A colorless viscous liquid was isolated in about 90% yield by further distillation *in vacuo*. Elemental analysis data for $TaF_3(SO_3F)_2$ are listed in Table 1, together with the data for other products obtained in a similar manner.

Infrared bands (cm^{-1}) and estimated intensities for $TaF_3(SO_3F)_2$: 1440 w, sh; 1410 vs, b; 1325 w, sh; 1235 s; 1170 m; 1100 m; 1040 m; 980 s; 880 m, sh; 840 s; 730 m, sh; 680 s; 630 w; 565 s; 440 m.

Raman shifts (cm^{-1}), estimated intensities and polarization data for $TaF_3(SO_3F)_2$: 1448 w; 1415 m, (p); 1235 s, (p); 1190 vw; 1115 s, (p); 1090 sh; 980 w, b; 886 s, (p); 840 m s, (p); 740 vs, (p); 710 w, sh; 685 w, sh; 640 s, (p); 600 vw; 560 m, (dp); 430 wm; 280 m, sh, (p); 240 s, (dp); 180 w; 130 vw.

^{19}F NMR chemical shifts of neat $TaF_3(SO_3F)_2$ (ppm, relative to $CFCl_3$) δ: 39.68 (singlet, sharp); 148.7, 183.0, 191.8 (singlet, broad).

TABLE 1

Elemental analysis data for $MF_n(SO_3F)_{5-n}$ (M = Nb, Ta)

Compound		M (%)	S (%)	F (%)
$Nb_2F_9(SO_3F)$	found	40.55	7.03 7.54[a], 7.49[a]	41.68
	calculated	40.81	7.04	41.72
$NbF_4(SO_3F)$	found	34.40	12.11 11.93[a], 11.82[a]	35.27
	calculated	34.71	11.98	35.49
$NbF_3(SO_3F)_2$	found	27.00 26.90	18.15 18.33	27.58 27.48
	calculated	26.72	18.44	27.32
$TaF_4(SO_3F)$	found	50.55	9.15	26.69
	calculated	50.87	9.01	26.71
$TaF_3(SO_3F)_2$	found	41.35	14.46	22.06
	calculated	41.52	14.71	21.80

[a]Data from Mr P. Borda of the Chemistry Department, University of British Columbia. All others from Analytische Laboratorien, Gummersbach, Germany.

Conductivity ($\times 10^{-4}$ Ω^{-1} cm^{-1}) of neat liquid $TaF_3(SO_3F)_2$: 1.07 (20 °C); 1.28 (25 °C); 1.53 (30 °C); 1.78 (35 °C); 2.05 (40 °C).

Results and discussion

Previously reported routes to ternary fluoride fluorosulfates involve:

(i) The decomposition of binary fluorosulfates via SO_3 elimination, which was accidental rather than intentional, e.g. the isolation of $GeF_2(SO_3F)_2$ during the intended preparation of $Ge(SO_3F)_4$ [7].

(ii) The addition of $S_2O_6F_2$ (or FSO_3F) to binary fluorides with the metal in a lower oxidation state, e.g. the syntheses of $Sb_2F_9(SO_3F)$, $SbF_4(SO_3F)$, $SbF_3(SO_3F)_2$ [8] and $AsF_3(SO_3F)_2$ [9]. This approach is limited in scope and requires the existence of stable, well-defined and oxidizable precursors such as SbF_3 or AsF_3, which is not the case for niobium and tantalum [10].

(iii) The partial insertion of SO_3 into metal–fluorine bonds. This method has been used with NbF_5 and TaF_5 as reactants and has led to products with the compositions $NbF_5 \cdot 2.1SO_3$ and $TaF_5 \cdot 2.6SO_3$, respectively, which were claimed to be complex mixtures with inserted SO_3 and free SO_3 in equilibrium [11].

The method proposed here involves the oxidation of niobium or tantalum by $S_2O_6F_2$, either alone or in the presence of the corresponding metal pentafluoride according to the general equation:

$$nMF_5 + (5-n)M + \text{excess } S_2O_6F_2 \xrightarrow[1-4\ d]{\text{room temp.}} 5MF_n(SO_3F)_{5-n} \quad (1)$$

(M = Nb, Ta; $0 \leq n < 5$)

The reactions were carried out at room temperature. An excess of $S_2O_6F_2$ functioned both as a fluorosulfonating reagent and as a reaction medium since both NbF_5 and TaF_5 were found to be soluble in $S_2O_6F_2$. Complete removal of excess $S_2O_6F_2$ was found to be difficult for materials of the composition $MF_n(SO_3F)_{5-n}$ (M = Nb, Ta; $n < 3$), as this led to very viscous and thermally unstable systems. The pale-yellow color of the crude product is attributed to grease contamination since two-part reactors were used.

Interestingly, both niobium and tantalum metals are oxidized by $S_2O_6F_2$ alone at room temperature over a period of 3 d, to yield very viscous, slightly yellow oils as crude products. The oxidations proceeded in a similar manner as reported previously, where $S_2O_6F_2$ was dissolved in HSO_3F [4], and took a similar length of time, but the complete removal of excess $S_2O_6F_2$ from the reaction mixture proved to be as difficult as the removal of HSO_3F, and only partly decomposed materials resulted in both instances.

Five pure products with the compositions $Nb_2F_9(SO_3F)$, $NbF_4(SO_3F)$, $NbF_3(SO_3F)_2$, $TaF_4(SO_3F)$ and $TaF_3(SO_3F)_2$ were obtained by distillation *in vacuo* without decomposition. All of these are moisture-sensitive, colorless, viscous liquids. Upon long standing at room temperature, $Nb_2F_9(SO_3F)$

disproportionated to give solid crystalline NbF_5 and $NbF_4(SO_3F)$. $TaF_4(SO_3F)$ obtained in this manner was different, both in terms of physical properties and vibrational spectra, from a reported high-melting white solid product, which was obtained in *c.* 50% yield from a ligand redistribution reaction between TaF_5 and $Ta(SO_3F)_5$(solv.) in HSO_3F [12].

All materials are believed to be SO_3F-bridged polymers or oligomers with approximately octahedral coordination around the central atom. This is apparent from the vibrational spectra, which are very similar to those of $Sb_2F_9(SO_3F)$, $SbF_4(SO_3F)$, $SbF_3(SO_3F)_2$ [8] and $AsF_3(SO_3F)_2$ [9] reported previously. The absence of fine structure in the ^{19}F NMR spectrum suggests fast exchange between terminal and bridging SO_3F groups and, probably, between fluoride ligands as well. The neat products of general formula $MF_n(SO_3F)_{5-n}$ (M = Nb, Ta; $n = 3$, 4) exhibited electrical conductivities in the order of $10^{-5} \sim 10^{-4}$ Ω^{-1} cm^{-1}. The electrical conductivities of the neat liquid increased with increasing temperatures, which also suggests an ionic dissociation of SO_3F-bridged oligomers and possible ligand exchange via ionic intermediates.

The resulting products are not necessarily well-defined, stoichiometric compounds. Similar conclusions were reached some time ago regarding viscous liquids of compositions $BrF_n(SO_3F)_{3-n}$ ($n \approx 1$) [13] and recently for $IF_n(SO_3F)_{3-n}$ ($n \approx 1.5$) [14]. The compositions apparent from the analytical data listed in Table 1 are strictly the results of the M/MF_5 ratio at the outset of the reactions. The exact stoichiometries were chosen to allow a comparison of the products to the corresponding antimony(V) and arsenic(V) fluoride fluorosulfates reported previously [8, 9].

All Nb(V) and Ta(V) fluoride fluorosulfates are miscible with HSO_3F in all proportions, while the corresponding solid pentafluorides show only limited solubilities. Their use in superacid systems over a wide concentration range is possible. Details of the vibrational and ^{19}F NMR spectra, the electrical conductivities of the neat liquids or their mixtures with HSO_3F and their use in superacid systems will be reported shortly [15].

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References

1 G. A. Olah, G. K. S. Prakash and J. Sommer, *Superacids*, Wiley, New York, 1984.
2 J. M. Shreeve and G. H. Cady, *Inorg. Synth.*, *7* (1963) 124.
3 G. H. Cady, *Inorg. Synth.*, *11* (1967) 155.
4 W. V. Cicha and F. Aubke, *J. Am. Chem. Soc.*, *111* (1988) 4328.
5 D. F. Shriver, *The Manipulation of Air Sensitive Compound*, McGraw-Hill, New York, 1969.

6 A. M. Qureshi, L. V. Levchuk and F. Aubke, *Can. J. Chem.*, *49* (1971) 2544.
7 S. P. Mallela, K. C. Lee and F. Aubke, *Inorg. Chem.*, *23* (1984) 653.
8 W. W. Wilson and F. Aubke, *J. Fluorine Chem.*, *13* (1979) 431.
9 H. Imoto and F. Aubke, *J. Fluorine Chem.*, *15* (1980) 59.
10 F. Fairbrother, in V. Gutmann (ed.), *Halogen Chemistry*, Academic Press, New York, 1967, Vol. 3, p. 123.
11 H. C. Clark and H. J. Emelèus, *J. Chem. Soc.*, (1958) 190.
12 W. V. Cicha and F. Aubke, *J. Fluorine Chem.*, *47* (1990) 317.
13 W. P. Gilreath and G. H. Cady, *Inorg. Chem.*, *2* (1963) 496.
14 H. Willner, F. Mistry and F. Aubke, accepted for publication in *J. Fluorine Chem.*
15 D. Zhang and F. Aubke, to be published in *Can. J. Chem.*