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INVENTION IDENTIFICATION

Title of invention SYNTHESIS OF PENTAFLUOROTELLURIUM HYPOFLUORITE	
Inventor(s) Carl J. Schack et al	Agency Sponsor AF
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Agency Case No. AF Invention No. 15,158	Patent No. (if any)

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SYNTHESIS OF PENTAFLUOROTELLURIUM HYPOFLUORITE

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

BACKGROUND OF THE INVENTION

This invention relates to hypofluorite compounds and to a novel method for their preparation. In a more particular aspect, this invention concerns itself with a novel route for effecting the synthesis of pentafluorotellurium hypofluorite (TeF_5OF) using fluorine fluorosulfate as a reaction component.

Hypofluorite compounds are well known and find utility for a wide variety of industrial applications. They are particularly useful as fluorinating agents for introducing fluorine atoms into another compound, and as intermediates in synthetic reactions. At the present time, however, there is no simple and convenient process for producing these compounds. Until recently, the number of elements known to form hypofluorites was limited to the nonmetal main group elements

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of hydrogen, carbon, nitrogen, oxygen, sulfur, selenium, fluorine and chlorine.

Generally, the method used heretofore for the synthesis of these hypofluorites involved the fluorination of the corresponding hydroxyl compounds or their metal salts with elemental fluorine. An attempt was made by Seppelt et al, Inorg. Chem. <u>1973</u>, 12, 2727, to apply this method to the synthesis of the hitherto unknown TeF_5OF. The attempt was unsuccessful. An analogous method, however, proved fruitful in synthesizing TeF_5OCl which led to the conclusion that TeF_5OF is unstable or actually nonexistant. Additionally, further research efforts, as reported by Christe et al, Inorg. Chem., <u>1981</u>, 20, 2104, proved to be successful in synthesizing a stable iodine hypofluorite with the observation that hypofluorites are generally more stable than the other hypohalites and the suggestion that TeF_5OF should exist and should also be stable.

In line with the observations noted above, additional experimental efforts proved successful and a novel method for synthesizing TeF_5OF was discovered. It was found that the hitherto unknown TeF_5OF compound could be produced in stable form and in relatively high yield by a process which provided for the use of fluorine fluorosulfate as the fluorinating agent.

SUMMARY OF THE INVENTION

The present invention concerns itself with a novel method for synthesizing hypofluorites by utilizing fluorine fluorosulfate as a fluorinating agent. The method of this invention proved successful in synthesizing in high yield the novel compound, pentafluorotellurium hypofluorite. Synthesis is achieved by effecting a reaction between $CsTeF_5O$ and $FOSO_2F$ at relatively low temperatures.

Accordingly, the primary object of this invention is to provide a novel method for synthesizing hypofluorite compounds.

Another object of this invention is to provide a method for synthesizing hypofluorite compounds that utilizes fluorine fluorosulfate as a fluorinating agent.

Still another object of this invention is to provide a method for synthesizing the novel compound, pentafluorotellurium hypofluorite.

The above and still other objects and advantages of the present invention will become more readily apparent upon consideration of the following detailed description thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Pursuant to the above-defined objects, the present invention is brought into effect by accomplishing a reaction between $CsTeF_5O$ and $FOSO_2F$ within a closed environment at temperatures ranging from about -10° to $-45^{\circ}C$. The known methods for preparing hypofluorites are quite limited and attempts at using these previously known methods for producing the hitherto unknown TeF_5OF have not been successful. For example, the fluorination of either $CsTeF_5O$ or $KTeF_5O$ with F_2 at -45 to -10°C resulted only in the formation of TeF_6. However, with the present invention, it was found that a fairly high yield synthesis of TeF_5OF could be accomplished by reacting $CsTeF_5O$ with $FOSO_2F$ at temperatures ranging from about -10° to -45°C. This reaction is illustrated by the following general equation:

$$CsTeF_5O + FOSO_2F \longrightarrow CsSO_3F + TeF_5OF \tag{1}$$

This novel reaction represents a new synthetic route to the preparation of hypofluorite compounds. Based on the general usefulness of the analogous $ClOSO_2F$ reagent for the syntheses of hypochlorites, it would appear that $FOSO_2F$ will become a similarly useful, versatile and general reagent for the synthesis of hypofluorite compounds.

When the synthesis of TeF_5OF from $CsTeF_5O$ and $FOSO_2F$ was carried out above -45°C, the amount of TeF_6 by-product sharply increased. For example, at -10°C and with a reaction time of 7 days, the TeF_6 to TeF_5OF ratio in the product increased to 1:1. The use of an excess of $CsTeF_5O$ in this reaction was found advantageous for the product purification since it eliminated the need for separating TeF_5OF from $FOSO_2F$.

The reaction scheme for synthesizing the novel TeF_5OF compound of this invention is further illustrated with greater specificity by Example I which follows.

EXAMPLE I

A 30 ml stainless steel Hoke cylinder was loaded with $CsTeF_5O$ (3.42 mmol) in the glove box. After evacuation and cooling of the cylinder to -196°C, $FOSO_2F$ (2.79 mmol) was added from the vacuum line. The closed cylinder was slowly warmed to -78°C in a liquid nitrogen-CO_2 slush bath and finally kept at -45°C for 9d. Upon recooling to -196°C. about 4-5 cm^3 of noncondensable gas was observed to be present. This was pumped away and the condensable products were separated by fractional condensation in a series of U-traps cooled at -78, -126, and -196°C. The -78°C fraction was TeF_5OH (0.19 mmol) while the -196°C fraction was TeF_6 (0.49 mmol).

A white solid was retained at -126°C which changed to a colorless glass and melted, over a range of a few degrees, near -80°C to a clear, colorless liquid. This material was identified as TeF_5OF (1.91 mmol, 68% yield) based on its vapor density molecular weight; found, 256.2; calc., 257.6 g/mol. Further identification was based on its spectroscopic properties and on the preparation of derivatives. The observed weight loss of the solid (0.375 g) agreed well with that calculated (0.389 g) for the conversion of 2.79 mmol $CsTeF_5O$ to $CsSO_3F$. Vapor pressure-temperature data of TeF_5OF were measured: T°C, Pmm; -79.3, 16; -64.2, 45, -57.6, 63; -46.9, 108; -32.5, 210; -23.0, 312.

The TeF_5OF compound of Example I is colorless as a gas and liquid. Its vapor pressure-temperature relationship for the range -79 to $-23^{\circ}C$ is given by the equation

$$\log P_{mm} = 6.9022 - 1101.2/T^{\circ}K$$

The extrapolated boiling point is $0.6^{\circ}C$. The derived heat of vaporization is $H_{vap} = 5039$ cal mol^{-1} and the Trouton constant is 18.4 indicating little or no association in the liquid phase. Vapor density measurements showed that in the gas phase the compound is also not associated. A sharp melting point for TeF_5OF was not observed because the samples showed a tendency to form a glass near $-80^{\circ}C$. The compound appears to be completely stable at ambient temperature and has been stored in stainless steel cylinders for more than four months without any sign of decomposition.

The mass spectrum of TeF_5OF is listed in Table I together with the spectra of TeF_5OCl and TeF_5OH which were measured for comparison. All of the listed fragments showed the characteristic tellurium isotope pattern and therefore the individual m/e listings were omitted for simplicity. The spectra of all three compounds show weak parent ions and TeF_3^+ as the base peak.

TABLE I

MASS SPECTRUM OF TeF_5OF COMPARED TO THOSE OF TeF_5OCl AND TeF_5OH

TeF_5OF		TeF_5OCl		TeF_5OH	
assignt	intens	assignt	intens	assignt	intens
TeF_5OF^+	vw	TeF_5OCl^+	vvw	TeF_5OH^+	w
TeF_4OF^+	vvw	TeF_4OCl^+	vw	TeF_4OH^+	vw
TeF_5O^+					
$TeF_5{}^+$	s	$TeF_5{}^+$	s	$TeF_5{}^+$	vs
$TeF_4{}^+$	w	$TeF_4{}^+$	vw	$TeF_4{}^+$	w
TeF_3O^+	m	TeF_3O^+	ms	TeF_3O^+	s
$TeF_3{}^+$	vs	$TeF_3{}^+$	vs	$TeF_3{}^+$	vs
$TeF_2{}^+$	m	$TeF_2{}^+$	m	$TeF_2{}^+$	m
$TeFO^+$	vw	$TeFO^+$	w	$TeFO^+$	w
TeF^+	w	TeF^+	w	TeF^+	w
Te^+	w	Te^+	w	Te^+	w

The infrared spectra of gaseous and of neon matrix isolated TeF_5OF and the Raman spectra of liquid and solid TeF_5OF were recorded and the observed frequencies are summarized in Table II.

TABLE II, VIBRATIONAL SPECTRA OF TeF_5OF

obsd freq, cm^{-1}, and rel intens[a]				assignment[b]
IR		Raman		
gas	Ne matrix	liquid -55°C	solid -110°C	
1800 vw				$2\nu_{12}$
1449 vw				$2\nu_1$
1403 w				$\nu_2 + \nu_8$
908 vw		905(0.4)p	904(0.8)	ν_{12}
738	738[c] vs	738 sh dp	735 sh	ν_8
	727 vs	721(1.1)p	721(1.3)	ν_1
	718 vw			impurity?
	709 vw			
	668 vw	669(10)p	670(10)	ν_2
		660(0.3)dp	662 sh	ν_5
616 m	618 m	613(3.8)p	613(4)	ν_3
324 vs	327 vs	325 sh, dp	325 sh	ν_9
	318 vs		319 sh	ν_{10}
	308 vw	309(1.0)dp	309(1.6)	ν_7
300 sh	302 m	301(0.5)p	301 sh	ν_4
280 mw	278 m	279(0.2)dp	279(0.2)	ν_{11}
241 mw	239 mw	240(0.2)p	240(0.2)	ν_{13}
		166(0.1)dp	167(0.1)	ν_{14}

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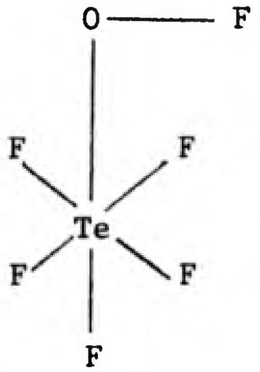
a) Uncorrected Raman intensities (peak heights)

b) For mode description see Table IV.

c) Band shows tellurium isotope fine structure with splittings of about 1.30 cm^{-1}

The vibrational spectra of TeF_5OF can be readily assigned as shown in Table III assuming a model with C_{4v} symmetry for the TeF_5O part and C_s symmetry for the TeOF part of the molecule.



Except for the symmetric out of phase, out of plane TeF_4 deformation mode in species B_1 which is usually observed for pseudo-octahedral molecules and is inactive under O_h symmetry, all fundamentals expected for the above C_{-4v}-C_s model were observed. Using the well established assignments of TeF_5Cl, the assignments (see Table III) are straight forward and show for the two molecules almost identical frequencies for the TeF_5 part of the molecules. The weak band observed at about 906 cm^{-1} in both the infrared and Raman spectra is characteristic for the OF stretching vibrations in hypofluorites.

Table III. Vibrational Spectra of TeF_5OF and their Assignment Compared to Those of TeF_5Cl

assignment		approx description of mode	obsd freq, cm^{-1}, and rel intens[a]			
			TeF_5Cl		TeF_5OF	
			IR(gas)	RA(liquid)	IR(gas, matrix)	RA(liquid)
C_{4v}						
A_1	ν_1	νTeF	711 sh,m	708(3.1)p	727 vs	721(1.1)p
	ν_2	$\nu_s TeF_4$	662 vw	659(10)p		669(10)p
	ν_3	νTeX	411 ms	413(7.7)p	616 m	613(3.8)p
	ν_4	$\delta_s TeF_4$	317 s	312(0.8)p	301 m	301(0.5)p
B_1	ν_5	$\nu_s TeF_4$		651(0.8)dp		660(0.3)dp
	ν_6	δTeF_4				
B_2	ν_7	$\delta_{sciss} TeF_4$		302(0.5)dp	308 vw	309(1.0)dp
E	ν_8	$\nu_{as} TeF_4$		726(0.6)dp	738 vs	738 sh, dp
	ν_9	$\nu FTeF_4$		327(0.9)dp	327 vs	325 sh, dp
	ν_{10}	$\delta XTeF_4$		167(1.8)dp	318 vs	(309-325)
	ν_{11}	$\delta_{as} TeF_4$		259(1.7)dp	280 mw	279(0.2)dp
C_s						
A'	ν_{12}	νXY			908 vw	905(0.4)p
	ν_{13}	$\delta TeXY$			240 mw	240(0.2)p
A"	ν_{14}	$\tau TeXY$				166(0.1)dp

a) Uncorrected Raman intensities (peak heights).

In preparing and testing the novel hypofluorite compound of this invention, the volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Telluric acid was prepared by the literature method of Mathers et al, Inorg. Syn., 1950, 3, 145, and also purchased from Cerac, Inc., and from Pfaltz and Bauer. Fluorosulfuric acid obtained from Allied was used both as received (light brown color) and after distillation to obtain the clear colorless material. The fluorine fluorosulfate was synthesized as described by Dudley et al, J. Am. Chem. Soc. 1956, 78, 290. The reaction of TeF_5OH with either $ClOSO_2F$ or ClF was used to prepare TeF_5OCl. Cesium and potassium chloride were oven dried, then cooled and powdered in the dry N_2 atmosphere of a glove box.

Infrared spectra were recorded in the range 4000-200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points, and the reported frequencies are believed to be accurate to ± 2 cm^{-1}. The spectra of gases were obtained using either a Teflon cell of 5-cm path length equipped with AgCl windows or a 10-cm stainless steel cell equipped with polyethylene windows which were seasoned with ClF_3. The spectra of matrix isolated TeF_5OF and TeF_5OCl were obtained at 6K with an Air Products Model DE202S helium refrigerator equipped with Csl windows. Research grade Ne(Matheson) was used as a matrix material in a mole ratio of 400:1.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488 nm exciting line of an Ar-ion laser and a Claassen filter for the elimination of plasma lines. Quartz tubes (3 mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A device described in Miller et al, Appl. Spectrosc. 1970, 24, 271 was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al in J. Appl. Spectrosc. 1969, 23, 8.

From an examination of the above, it can be seen that the $FOSO_2F$ is a useful reagent for the synthesis of hypofluorites. Furthermore, it is shown that TeF_5OF, as expected from comparison with TeF_5OCl, TeF_5OBr and $FOIF_4O$, indeed exists and is a stable molecule.

What is claimed is:

Claims not included

ABSTRACT

The present invention concerns itself with a method for synthesizing hypofluorite compounds by utilizing fluorine fluorosulfate as a fluorinating agent and to a novel pentafluorotellurium hypofluorite compound prepared thereby.