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Contribution from the Department of Inorganic and Analytical Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel

Spectroscopic Study of Telluric Acid and Selenic Acid in Hydrogen Fluoride and the Hydrolysis of Tellurium Hexafluoride

URI ELGAD and HENRY SELIG*

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The equilibrium $Te(OH)_6 + nHF \rightleftharpoons Te(OH)_nF_{6-n} + nH_2O$ has been studied, mainly by ^{19}F nmr spectroscopy. In the solvolysis of $Te(OH)_6$ in HF, products up to $n = 3$ have been identified, while in the hydrolysis of TeF_6 products with $n = 0–5$ have been observed. The stereochemical configuration of most of the species has been determined. Solvolysis of selenic acid in HF leads to pentafluoroorthoselenic acid and two other products, one of which is probably $HSeO_3F$.

Introduction

The chemistry of pentafluoroorthotelluric acid and of pentafluoroorthoselenic acid has received considerable attention after their initial syntheses.[1,2] Among its many chemical properties, pentafluoroorthotelluric acid dissolves in water to give a strongly acidic solution which hydrolyzes to mixtures of other fluorotelluric acids.[3] Some of these fluorotelluric acids have been isolated by chromatographic separation of a mixture obtained by dissolving telluric acid in 40% hydrofluoric acid.[4] In such mixtures the following equilibria obtain

$$Te(OH)_6 + nHF \rightleftharpoons Te(OH)_nF_{6-n} + nH_2O$$

but only acids with $n = 2–6$ were thus obtained on the developed chromatogram, and their R_f values were determined.[4] A number of salt derivatives of the di- and tetrafluorotelluric acids were isolated. Nothing is known about their structures, but it was assumed that in each case the symmetric trans complex is involved.[4,30]

It has been our experience that isolation or separation of products from such reaction mixtures does not necessarily throw light on the nature of the species in solution, and we have therefore investigated several systems by studying their fluorine nmr spectra or the Raman spectra of the solutions directly. We have found, for instance, that solutions of iodate,[5] perrhenate,[5] pertechnetate,[6] and periodate[7] in anhydrous hydrogen fluoride (AHF) lead to solutions of iodine pentafluoride, perrhenyl fluoride, pertechnetyl fluoride, and tetrafluoroorthoperiodic acid, respectively. The system $Te(OH)_nF_{6-n}$–HF has now been investigated by fluorine nmr and partially by Raman spectroscopies. In order to achieve maximum ligand exchange, large amounts of HF would be required. The resulting solutions are too dilute to lend themselves readily to spectroscopic investigation. We have therefore also approached the equilibrium from the opposite direction by controlled hydrolysis of tellurium hexafluoride. Parallel experiments with selenic acid and selenium hexafluoride were also carried out.

Experimental Section

Materials. Orthotelluric acid was prepared by the oxidation of tellurium dioxide (Fluka, practical grade) with potassium permanganate.[8] Raman spectra of aqueous solutions of the product were in agreement with those cited in the literature.[9,10] Selenic acid was obtained in the form of a concentrated solution from BDH. Tellurium hexafluoride and selenium hexafluoride were prepared from the elements and purified by fractional distillation until vibrational spectra attested to their purity. Anhydrous hydrogen fluoride (AHF) was obtained from a still previously described.[11]

Apparatus. High-resolution fluorine nmr spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 MHz. Spectra were calibrated by the method of side bands using a Hewlett-Packard Model 4204A oscillator. The side band frequency could be varied so as not to interfere with other signal lines. Chemical shifts are reported with respect to CCl_3F used as an external standard, and in the case of proton nmr spectra with respect to an external TMS standard. Some of the $Te(OH)_nF_{6-n}$ species observed, having sets of nonequivalent fluorine atoms, displayed rather complex spectra. The parameter determining the exact appearance of these spectra is $R = J_{AB}/\delta_{AB}$, where J_{AB} is the coupling constant between axial and equatorial fluorines and δ_{AB} the chemical shift difference between these fluorines expressed in hertz. The AB_4 spectra assigned to $HOTeF_5$ were analyzed by the method of Harris and Packer.[12] A useful, brief description of the procedure has also been given by Seppelt.[13] Spectra of the types AB_2 and A_2B_2 were analyzed according to procedures given by Bovey.[14] The latter also gives useful calculated line spectra enabling visual identification of complex spectra.

Raman spectra were obtained in Kel-F or Teflon FEP tubes on an apparatus previously described.[7] Raman lines of the plastic container were eliminated by positioning the tube so that the bright spots created by the laser beam entering and exiting the tube were masked by the slit height attenuator. Spectra were calibrated by reference to emission lines of neon and are accurate to ±2 cm^{-1} on the sharp bands.

Procedure. Samples were prepared in $^3/_{16}$-in. o.d. Kel-F tubes by

Table I. Species Observed in Solutions of $Te(OH)_6$–HF

Compd	Nmr system	Chem shift[a]	J_{AB}[b]	$J_{^{125}Te-F}$[b]	$J_{^{123}Te-F}$[b]	Remarks
$(HO)_5TeF$	A	24.7–27.6		2965–3105		Only species present in $Te(OH)_6$–48% HF
trans-$(HO)_4TeF_2$	A_2	34.2–36.3		3185–3230	2690	See text and Figure 5
cis,trans-$(HO)_3TeF_3$	AB_2	29.8–31.9 (F_A) 37.1–39.9 (F_B)	137			
cis,cis-$(HO)_3TeF_3$	A_3	43.0–44.5		3405	2905	Could be *trans*-$(HO)_2TeF_4$; see text

[a] In ppm relative to external CCl_3F. Estimated uncertainty ±0.2 ppm, but considerable variation due to solvent and concentration effects. [b] In Hz, estimated uncertainty ±20 Hz.

condensing AHF on top of weighed amounts of degassed telluric acid (*viz.*, selenic acid) and subsequently sealing the tube under vacuum. Conversely, tellurium hexafluoride (*viz.*, selenium hexafluoride) was condensed on top of a weighed amount of outgassed water and the tube was sealed off under vacuum.

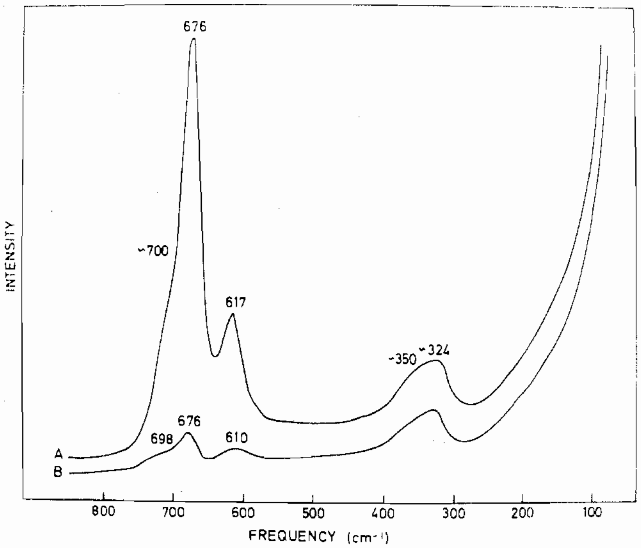

Figure 1. Raman spectrum of $(HO)_5TeF$ in 48% HF: A, ∥; B, ⊥. Spectral slit width 3 cm^{-1}, scan speed 25 cm^{-1}/min, time constant 1 sec, laser power 400 mW at 6471 Å.

Results and Discussion

Reactions of Telluric Acid with HF. Initial experiments were performed on solutions of telluric acid in 48% HF. Both fluorine nmr spectra and Raman spectra showed that only one species was obtained over the concentration range studied ($Te(OH)_6$:HF:H_2O = 1:98.7:107.5 to 1:14.1:15.2). The latter solutions were saturated. Nmr spectra gave only a singlet at δ_{CCl_3F} = 24.7 ppm, while Raman spectra remained invariant over the whole concentration range. This species must be monofluorotelluric acid. It is probably identical with one of the species obtained by the controlled hydrolysis of tellurium hexafluoride; namely, the one appearing at the lowest field of all species observed (δ_{CCl_3F} = 22.5 ppm). The skeletal vibrations of $(HO)_5TeF$ should by analogy with $HOTeF_5$ give a relatively simple vibrational spectrum as substitutions of a fluorine atom for an –OH group should be barely discernible. This is indeed the case, as can be seen in the Raman spectrum shown in Figure 1. This spectrum is also quite similar to that of $HOTeF_5$.[15] Since $(HO)_5TeF$ can be considered a monosubstituted derivative of octahedral $Te(OH)_6$, it should belong to point group C_{4v}. Excluding the hydrogens, the 11 normal modes span the representations 4 a_1 + 2 b_1 + b_2 + 4 e, all of which are Raman allowed. The Raman spectrum is not sufficiently well resolved to allow complete assignments, especially in the bending region which features a broad, poorly resolved band structure. The strongest, highly polarized band at 676 cm^{-1} can be assigned to the Te–OH in-phase stretching vibration, and the medium-intensity, polarized band at 617 cm^{-1} to the out-of-phase stretching vibration. A weak shoulder at about 700 cm^{-1} probably belongs to the Te–OH antisymmetric stretch of symmetry e, as a corresponding absorption of strong intensity is observed in the infrared spectrum. The Te–F vibration is apparently also hidden under this band structure.

It should be noted that some of our results are at variance with those of Kolditz and Fitz.[4] The latter reported as many as four fluorotelluric acids in the system $Te(OH)_6$–40% HF, whereas we see evidence only for monofluorotelluric acid at all concentrations. These workers, however, concentrated their mixture by evaporating it nearly to dryness and drying over P_2O_5, before subjecting it to chromatographic separation. This procedure apparently changed the equilibria in favor of more ligand exchange.

Treatment of telluric acid with AHF, on the other hand, yielded $Te(OH)_nF_{6-n}$ up to n = 3. Solutions with $Te(OH)_6$:HF of 1:22.7 to 1:155 were studied. The species observed in the fluorine nmr spectra are tabulated in Table I. In addition, to the lowest field species assigned to the monofluoro acid, three more species appear consisting of two singlets and a doublet triplet. Visual inspection and comparison with calculated spectra[14] show that the latter is an AB_2 spectrum with $R \approx$ 0.1–0.2. This species, which increases in relative intensity upon increased dilution with AHF, can be assigned to the cis,trans configuration of $Te(OH)_3F_3$. The assignment of the remaining singlets is more problematical. The one appearing at $\delta \sim 44$ ppm roughly follows the AB_2 spectrum in intensity, while the singlet at $\delta \sim 35$ ppm decreases relative to the AB_2 spectrum with increased AHF addition. This, combined with their relative positions on the chemical shift scale, leads us to assign the higher field singlet to *cis,cis*-$Te(OH)_3F_3$ and the lower field singlet to $Te(OH)_4F_2$. The latter is probably the trans isomer, as inferred from systematics discussed later. It is of interest that a similar regularity of chemical shift with number of fluorines attached to the central atom occurs in the series $W(OCH_3)_nF_{6-n}$,[16,17] although the direction of fluorine shielding is in the opposite sense to that observed in the series $Te(OH)_nF_{6-n}$. No fluorotelluric acids with $n < 3$ were detected up to $Te(OH)_6$:HF = 1:155. At higher dilutions, the sensitivity of detection diminishes markedly, especially since for $n < 3$, complex multiline spectra are expected.

Hydrolysis of Tellurium Hexafluoride. Tellurium hexafluoride dissolves slowly in water giving at first two liquid phases—the upper layer being the aqueous phase and the lower layer liquid TeF_6. Without agitation, reaction continues slowly at the interface over a period of several hours. Only with ratios of H_2O:TeF_6 > 4:1 is a single-phase system attained at equilibrium. Fluorine nmr spectra showed the presence of several new species, the concentration of which depended markedly on the ratio H_2O:TeF_6. At a concentration of 1.10:1 (Figure 2), nmr spectra showed the following signals.

(1) A strong singlet at δ 54.5 ppm. This signal belongs to TeF_6, as its location and ^{123}Te and ^{125}Te satellite peaks correspond closely to those reported in the literature.[18] The TeF_6 signal is seen only in the presence of two phases and is particularly intense when the lower liquid phase is centered in the nmr probe.

(2) A strong singlet at δ 57.5 ppm. This singlet is the highest field signal observed under any of our experimental

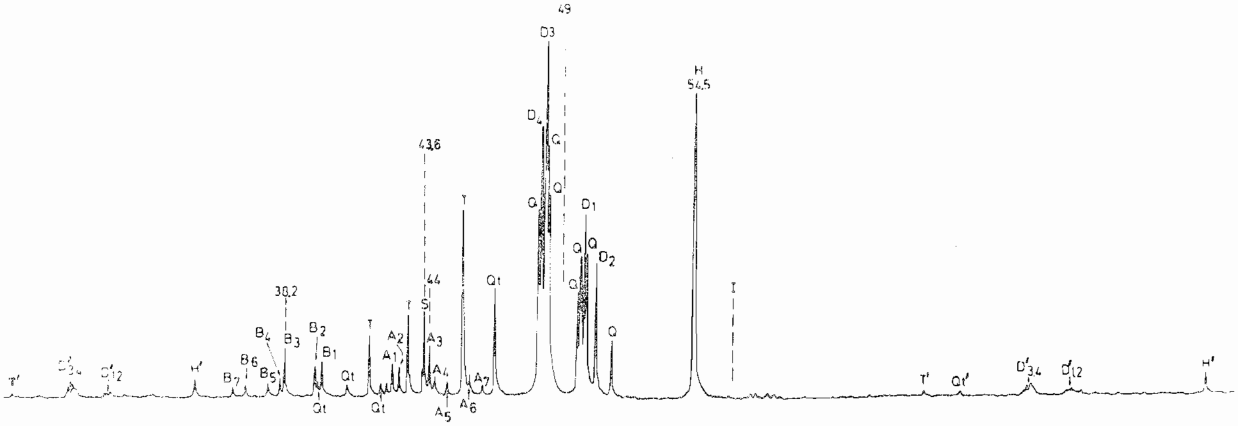

Figure 2. ^{19}F nuclear magnetic resonance spectrum of $TeF_6:H_2O$ = 1:1.10. For identification of species see Table II. Primed letters belong to ^{125}Te satellites of signals labeled by unprimed letters. Chemical shift values are indicated above the centers of the band systems. The signal belonging to species I is not shown as it disappears with time. Initial intensity is same as that of signal H (TeF_6).

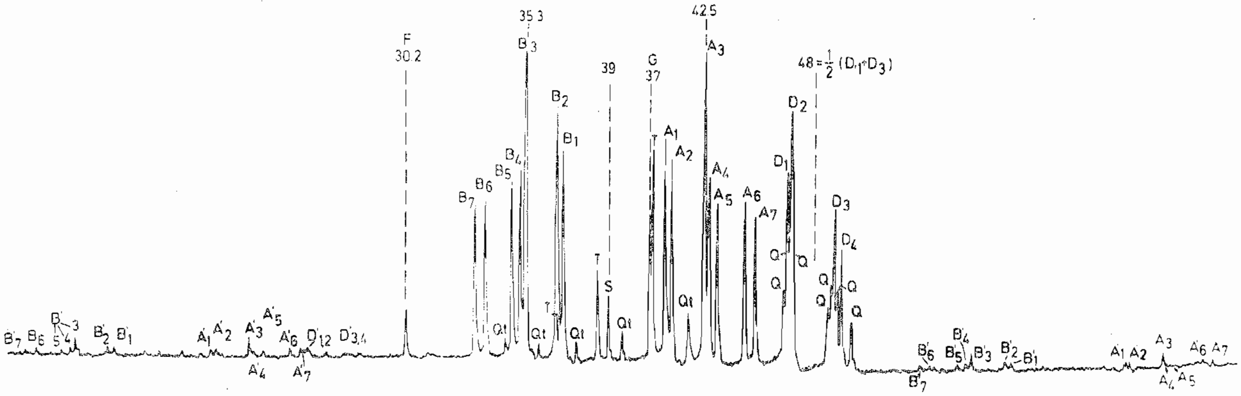

Figure 3. ^{19}F nuclear magnetic resonance spectrum of $TeF_6:H_2O$ = 1:4.05. Same legend as for Figure 2.

conditions. Since, as will be seen below, replacement of fluorine atoms by OH groups causes a trend of chemical shifts to lower fields, this signal may arise from coordination of TeF_6 with HF formed during hydrolysis to form an ion of the type TeF_7^- or TeF_8^{2-}. On the other hand, it has been shown that the salts $CsTeF_7$ and Rb_2TeF_8 are unstable in AHF.[19] We have found, however, that this signal, although initially strong, disappears after several days. A positive identification of this species cannot be made.

(3) An AB_4 spectrum with δ_A 43.6 ppm, δ_B 49 ppm, J_{AB} = 205 Hz. This spectrum has the highest intensity of any observed at this concentration and undoubtly belongs to $HOTeF_5$. Its appearance strongly resembles that given for solutions of $HOTeF_5$ in CCl_3F.[13] The values of shifts and coupling constants differ somewhat from those in other solvents and are attributable to solvent effects.

(4) An A_2B_2 system with δ_A 44 ppm, δ_B ~38.2 ppm, and J_{AB} = 165 Hz. This system can be assigned to *cis*-$(HO)_2TeF_4$. This signal is quite weak but easily discernible at this concentration. No singlet of comparable intensity was observed, so the existence of the trans isomer appears to be ruled out (see, however, discussion of systematics below). This result is in contrast to the assumption of Kolditz and Fitz[4] that the tetrafluoro acid must be the trans isomer but is in comformance with the cis structure found for $TeF_4(OMe)_2$.[20] The latter upon hydrolysis reportedly forms the intermediate *cis*-$TeF_4O_2^{2-}$ ion but no trans isomer.[20]

At a concentration ratio of $TeF_6:H_2O$ = 1:4.05 (Figure 3), the lower phase as well as the TeF_6 signal at 54.5 ppm disappears. The AB_4 signal belonging to $HOTeF_5$ is now relatively weak, while the strongest signal arises from the A_2B_2 system. In addition, two rather weak singlets are observed at δ ~37 and ~30 ppm. These can be assigned to *cis,cis*-$(HO)_3TeF_3$ and $(HO)_4TeF_2$, respectively. The AB_2 system corresponding to *cis,trans*-$(HO)_3TeF_3$ is not observed. Its total intensity would be distributed over eight lines and is thus buried in the background.

At a concentration of $TeF_6:H_2O$ = 1:13.5 (Figure 4), the A_2B_2 system is quite weak, the AB_4 system having disappeared, while a new AB_2 system of strong intensity shows up. The latter is assigned to *cis,trans*-$(HO)_3TeF_3$ with δ_B ~37 ppm, δ_A ~24 ppm, J_{AB} = 130 Hz. In addition, the aforementioned singlets at δ ~34 and 29 ppm grow markedly in intensity and a new singlet at δ 22.5 ppm makes its debut. The latter can probably be identified with a partially ionized form of monofluorotelluric acid, which has been encountered as the only fluorine-containing species in 48% HF solutions of telluric acid. The singlet at 29 ppm, from its position on the chemical shift scale and relative intensity changes, is assigned to *trans*-$(HO)_4TeF_2$, and the singlet at 34.4 ppm to the cis,cis isomer of $(HO)_3TeF_3$. The assignment of this singlet cannot be unequivocally determined from nmr data alone, and the possibility that the singlet at 34.4 ppm is due to another species should not be entirely discounted (see discussion of systematics below).

It should also be pointed out that Raman spectra and proton nmr spectra failed to contribute much useful information. Raman spectra showed the presence of more than one species and helped to confirm the presence of other fluorotelluric acids as revealed in the fluorine nmr spectra. Thus, spectra of $TeF_6:H_2O$ = 1:1.10 solutions showed the presence of the very strong and highly polarized TeF_6 frequency at 697 cm^{-1} and the strong, polarized bands at 685 and 652 cm^{-1} belonging to $HOTeF_5$. Changes in relative intensities paralleled those obtained in the nmr spectra. Proton nmr spectra showed in all cases a sharp singlet which shifted from δ_{TMS} −7.8 ppm

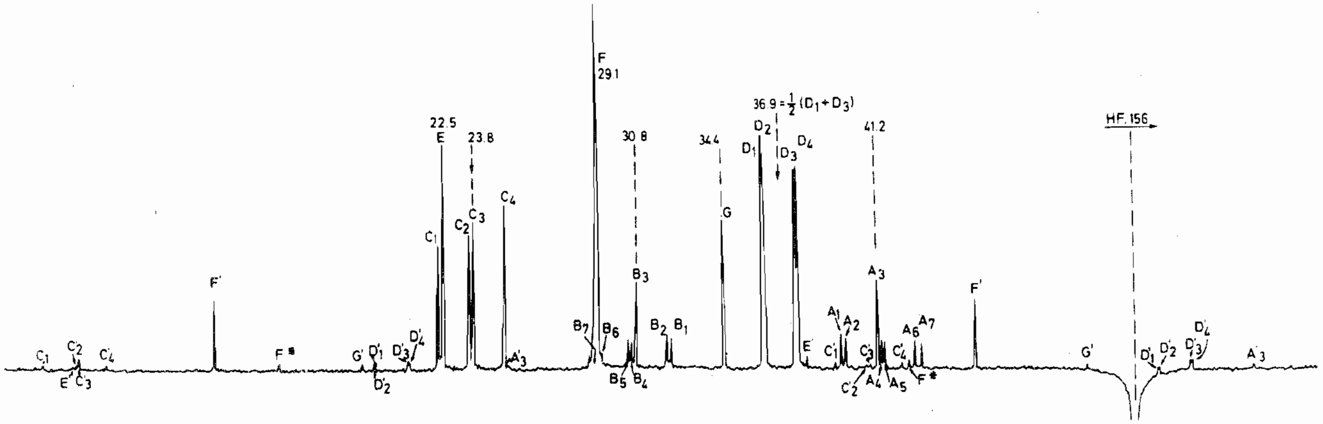

Figure 4. ^{19}F nuclear magnetic resonance spectrum of $TeF_6:H_2O = 1:13.5$. Same legend as those for Figures 2 and 3. Lines marked with an asterisk belong to ^{123}Te satellites of signals labeled by unprimed letters. A side band of HF is shown.

Table II. Species Observed in Hydrolysis of TeF_6

Compd	Nmr system	Chem shift[a]	J_{AB}[b]	$J_{^{125}Te-F}$[b]	$J_{^{123}Te-F}$[b]	$R = J_{AB}/\delta_{AB}$	Symbols in figures	Remarks
TeF_8^{2-} or TeF_7^-?	A_{6+n}^{n-}	57.0		3740	3085		I	Disappears with time
TeF_6	A_6	54.5		3715	3085		H	Only for $TeF_6:H_2O = 1:1.10$
$HOTeF_5$	AB_4	49–48 (F_B) 43.6–39 (F_A)	205	3775	2640	~0.40	D_{1-4}, Q_n S, T_{1-3}, Qt_n	Max intens at $TeF_6:H_2O = 1:1.10$
cis-$(HO)_2TeF_4$	A_2B_2	44–41.2 $(F_A)_{ax}$ 38.2–30.8 $(F_B)_{eq}$	165	3485		~0.30	A_{1-7} B_{1-7}	Max intens at $TeF_6:H_2O = 1:4.05$
trans-$(HO)_2TeF_4$ or *cis,cis*-$(HO)_3TeF_3$	A_4 or A_3	37–34.4					G	
cis,trans-$(HO)_3TeF_3$	AB_2	36.9 (F_B) 23.8 (F_A)	130	3115		0.105	D_{1-4} C_{1-3}	
trans-$(HO)_4TeF_2$	A_2	30.2–29.1		2995	2490		F	
$(HO)_5TeF$	A	22.5		2860			E	Only present at $TeF_6:H_2O = 1:13.5$

[a] In ppm relative to external CCl_3F. Estimated uncertainty ±0.2 ppm, but considerable variation due to solvent and concentration effects.
[b] In Hz, estimated variation ±20 Hz.

for $TeF_6:H_2O = 1:1.10$ to δ_{TMS} −6.6 ppm for the ratio 1:13.5. This is a result of the dilution of the concentrated HF initially formed. The shift of δ_{TMS} −7.8 ppm is close to that reported for AHF at room temperature.[21] The sharp signal and gradual shift point to rapid proton exchange between the fluorotelluric acids and solvent.

The hydrolysis of TeF_6 in the presence of initial concentrations of AHF was also studied. No new species other than $HOTeF_5$ were detected. In the presence of HF most of the water is protonated,[22] in effect repressing the hydrolysis reactions.

Attention should be drawn to the range of chemical shifts observed for each of the species as shown in Tables I and II. These displacements obviously arise from solvent effects. In the solvolysis reactions of telluric acid, the trend is always from low field to high field with increased HF addition, while in the hydrolysis reactions of TeF_6 the trend is in the opposite sense. It must be borne in mind that the former solutions are essentially concentrated HF solutions, while the latter become aqueous solutions. Thus, in the hydrolysis reactions the strong acids ($n < 3$) are ionized, while in the solvolysis reactions the weaker acids ($n > 3$) are present mainly as un-ionized species.

Nmr Systematics. It has been shown for a number of systems that the chemical shift information can be correlated in terms of a linear function of the type $\delta(Z) = pC + qT$ where C and T are adjustable parameters characteristic of a ligand while p and q are the number of fluorides cis and trans, respectively, to the group Z, the resonance of which is to fit this equation.[23] Such a scheme, in conjunction with proton–fluorine coupling constants, has been successful in making unequivocal assignments for the series $(CH_3O)_nWF_{6-n}$.[17] Other systems which have been analyzed by this procedure are $TeCl_nF_{6-n}$[24] and $SnL_nF_{6-n}^{2-}$.[23] In the present case, proton–fluorine coupling was not observed, because of rapid exchange of the protons with the solvent as shown by an examination of the proton nmr spectra. It is tempting, however, to try fitting our data to an equation of this type. The results are presented graphically in Figure 5. Since our chemical shift data were obtained on solutions containing more than one component, we have taken the shift values at highest field, which would approach most closely those of the un-ionized acids. Reference value was the chemical shift of $(HO)_5TeF$ for the highest ratio of HF to $Te(OH)_6$, δ 27.6 ppm. For the $Te(OH)_nF_{6-n}$ series, q is either 0 or 1, while p ranges from 0 to 4. Experimental points are hence expected to fall on two separate curves.

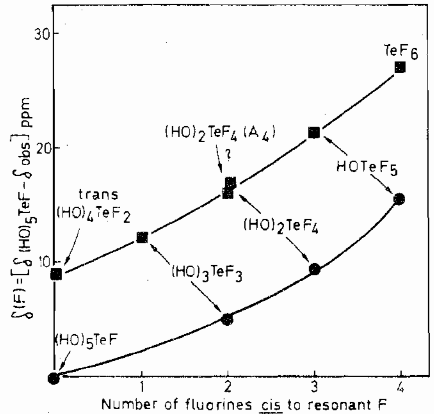

Figure 5. $Te(OH)_nF_{6-n}$ chemical shifts. Plot of $\delta(Z)$ vs. number of fluorines cis to resonant F: ■, for $q = 1$; ●, for $q = 0$.

The points given for n = 0, 1, 3, and 5 uniquely define the

Table III. Species Observed in Solvolysis of H_2SeO_4

Compd	Nmr system	Chem shift, ppm	J_{AB}, Hz	$J_{^{77}Se\text{-}F}$, Hz	R
$HOSeF_5$	AB_4	$-74.4\ (F_A)$ -60 to $-65\ (F_B)$	222	1300	~0.20
$HSeO_3F$ (?)	A_n	-38.3 to -43		1390	
?	A_n	-33.6 to -37.5			

curves on the basis of their known identity or the distinctive line patterns of their spectra. The points for $n = 2$ fit gratifyingly on the curves, if the A lines are assigned to the axial fluorines and the B lines to the equatorial fluorines. This conclusion is reinforced by the relatively slight shift changes of the axial group ($\Delta\delta = 2.8$ ppm) compared to those of the equatorial group ($\Delta\delta = 7.4$ ppm) upon increased dilution with water. Such a "trans" effect has been noted for the pentafluoroorthotelluric acid derivatives, for which the chemical shifts of the fluorine atoms opposite the OH group are much more influenced by the nature of the substitutions at this position.[13]

Assignment of the singlet at $\delta \sim 36$ ppm can be made to *trans*-$(HO)_4TeF_2$, as this point fits perfectly on the $q = 1$ curve. On the other hand, the singlet at $\delta \sim 44$ ppm presents difficulties. According to the systematics, it should belong to *trans*-$(HO)_2TeF_4$. However, this signal is quite intense in $Te(OH)_6$–AHF solutions while no trace of the A_2B_2 isomer is seen simultaneously. Conversely, in TeF_6–H_2O solutions (Figure 3) this signal is much weaker than the A_2B_2 system. In other words, this singlet follows the AB_2 system much more closely in relative intensity than the A_2B_2 system. This discrepancy is not readily resolved. One possibility may be that this singlet belongs to $(HO)_2TeF_4$ after all and that relative concentrations of its isomers are drastically influenced by the acidity of the solution. Thus, in strongly acidic solutions only the trans isomer may be stable, accounting for the absence of the A_2B_2 pattern, while in aqueous solutions the cis isomer would be more stable. Another possibility may be that the solutions on which measurements were made had not attained kinetic equilibrium. However, even after several weeks and mild heating of the solutions, no substantial changes were observed. The gratifying fit of all other points in the systematics does not warrant abandoning the other conclusions.

Reactions of Selenic Acid with AHF. Selenic acid dissolves rapidly in AHF to give clear, colorless solutions. The concentration range H_2SeO_4:HF = 1:3.8 to 1:35.4 was studied. Investigations of the fluorine nmr spectra showed the presence of three species (besides HF) of which only one could be identified with certainty. All three species were present at all concentrations, albeit with varying intensities. A typical spectrum is given in Figure 6, and pertinent data are summarized in Table III. The only species identified unequivocally is pentafluoroorthoselenic acid. Nmr spectra for this compound in a number of solvents have been given.[13] Our results agree most closely with that of $HOSeF_5$ in fluorosulfuric acid. This is understandable, because the latter is a strong acid of comparable strength with HF. In the original communication reporting the preparation of $HOSeF_5$,[2] a number of synthetic pathways were given. The common denominator for all of these is the presence of HF. Our results indicate that HF, in fact, is the only reagent required and the task of other reagents such as HSO_3F may be to scavenge the water formed as a by-product.

The other major species observed in HF is a broad, strong singlet at −39 ppm. Its intensity decreases with increased HF addition indicating that it contains less fluorine atoms than $HOSeF_5$. A possible assignment may be monofluoroselenic acid, $HSeO_3F$. This acid has been prepared by treatment of SeO_3 with AHF.[25] Its ^{77}Se and ^{19}F nmr spectra have been measured[26] and a coupling constant $J_{^{77}SeF} = 1454$ Hz has been reported. This is close to our measured value of 1390 Hz, but, on the other hand, hexavalent selenium compounds such as SeF_6 and SeO_2F_2 have similar coupling constants, so that identification is not conclusive. No ^{19}F chemical shift value for $HSeO_3F$ has been found by us in the literature.

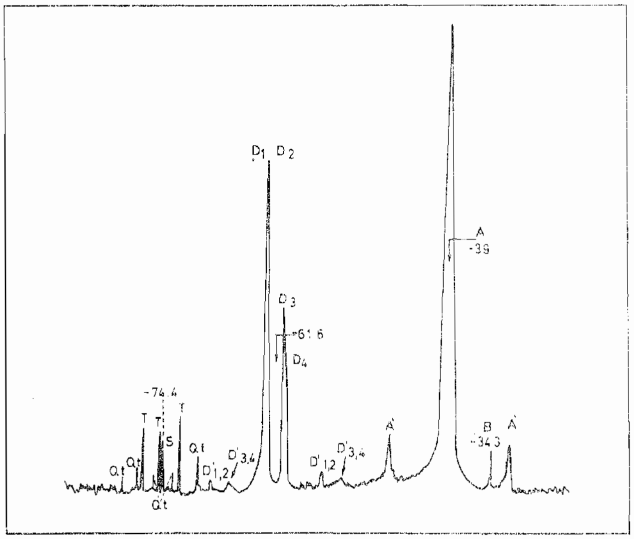

Figure 6. ^{19}F nuclear magnetic resonance spectrum of H_2SeO_4:HF = 1:17.3 at −40°. Primed letters belong to ^{77}Se satellites.

Raman spectra of these solutions were of little help in elucidating the nature of this species. Spectra of concentrated solutions resemble those of selenic acid. Among others, a strong, polarized band is seen at 890 cm^{-1} throughout the whole range of concentrations. Although selenic acid itself has a strong polarized band at 898 cm^{-1}, it is not plausible that appreciable concentrations of H_2SeO_4 persist at a ratio H_2SeO_4:HF = 1:20, so that the singlet species at $\delta \sim -39$ ppm almost certainly contains an Se=O double bond. Another prominent feature of the Raman spectra is a strong, polarized band at 692 cm^{-1}, especially at higher dilutions. This band is assigned to $HOSeF_5$ for which the strongest band has been reported at 685 cm^{-1},[27] the others being quite weak in intensity.

An additional low-intensity nmr signal at −34.3 ppm cannot be identified. The paucity of features in the nmr spectra and the lack of a clear trend in chemical shifts make assignments particularly problematical.

Attempts to detect additional species by hydrolysis of selenium hexafluoride failed. Mixtures of H_2O and SeF_6 appear not to interact at room temperature over long time intervals. Warming the tubes resulted in their rupture, because of the high vapor pressure of SeF_6. Those results confirm the reported inertness of SeF_6 with respect to hydrolysis.[28] It is interesting to note that SeF_6 is extremely toxic and is hydrolyzed in the respiratory tract.[29] Presumably this environment is somewhat basic or contains other reducing substances.

Registry No. $Te(OH)_6$, 7803-68-1; $(HO)_5TeF$, 53011-49-7; *trans*-$(HO)_4TeF_2$, 53078-11-8; *cis,trans*-$(HO)_3TeF_3$, 53011-50-0; *cis,cis*-$(HO)_3TeF_3$, 53108-93-3; TeF_6, 7783-80-4; $HOTeF_5$, 30880-30-9; *cis*-$(HO)_2TeF_4$, 53011-51-1; H_2SeO_4, 7783-08-6; $HOSeF_5$, 38989-47-8; $HSeO_3F$, 14986-53-9; TeF_8^{2-}, 53011-08-8; TeF_7^-, 53011-09-9; *trans*-$(HO)_2TeF_4$, 53108-94-4; ^{77}Se, 14681-72-2; ^{125}Te, 14390-73-9; ^{123}Te, 14304-80-4.

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Contribution from Rocketdyne,
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Halogen Perchlorates. Reactions with Fluorocarbon Halides

CARL J. SCHACK,* DON PILIPOVICH, and KARL O. CHRISTE

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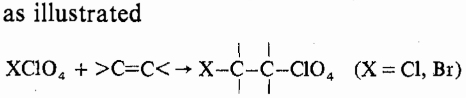
The reactions of chlorine perchlorate and bromine perchlorate with numerous fluoroalkyl halides were examined. In the case of fluorocarbon iodides, these reactions were generally found to produce high yields of the novel fluorocarbon perchlorates CF_3ClO_4, $CF_3CF_2ClO_4$, $n\text{-}C_7F_{15}ClO_4$, $O_4ClCF_2CF_2ClO_4$, and $ICF_2CF_2ClO_4$. Important insight into the mechanism of formation of these compounds was obtained through the isolation of complex intermediates such as $(CF_3)_2CFI(ClO_4)_2$ and $n\text{-}C_7F_{15}I(ClO_4)_2$. Based on their vibrational spectra, these intermediates have the ionic structure $[(R_f)_2I]^+[I(ClO_4)_4]^-$. Fluorocarbon bromides reacted less readily but sometimes did produce perchlorate derivatives such as $(O_4ClCF_2CFBr\text{-})_2$, $CF_3CFBrCF_2ClO_4$, and $BrCF_2CF_2ClO_4$. Neither mono nor di, primary nor secondary chlorine contained in saturated R_fCl materials interacted with these halogen perchlorates. These and other related reactions are discussed and characteristic data are given for this new and interesting class of compounds.

Introduction

Until recently the study of covalent perchlorates was restricted to a few derivatives,[1,2] mainly inorganic, because of the extreme shock sensitivity of the known hydrocarbon derivatives. Also the available intermediates for forming covalent perchlorates were quite limited and themselves difficult to manipulate. With the discovery of chlorine perchlorate ($ClOClO_3$ or Cl_2O_4)[3] and bromine perchlorate ($BrOClO_3$ or $BrClO_4$),[4] useful reagents became available for the synthesis of new perchlorate species. This has been realized and has led to the preparation of the new inorganic materials $I(ClO_4)_3$,[5] $CsI(ClO_4)_4$,[5] and $CsBr(ClO_4)_2$[6] and improved syntheses of $Ti(ClO_4)_4$ and $CrO_2(ClO_4)_2$.[7] Furthermore, the reactions of Cl_2O_4 and $BrClO_4$ with perhaloolefins were shown[8] to produce the previously unknown perhaloalkyl perchlorates, in high yield, as illustrated



$$XClO_4 + {>}C{=}C{<} \rightarrow X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}ClO_4 \quad (X = Cl, Br)$$

Of paramount interest though, was the finding that these fluorocarbon perchlorates were stable, tractable species quite unlike their hydrocarbon and some of their inorganic analogs. Thus it was decided to investigate further this new class of compounds and, in particular, to search for additional preparative routes which result exclusively in the introduction of a perchlorato group without simultaneous addition of bromine or chlorine atoms.

Experimental Section

Caution! The halogen perchlorates and the alkyl perchlorates are potential explosives. Safety precautions should be taken in handling and using these materials.

Apparatus and Materials. The equipment used in this work has been described.[5] Chlorine perchlorate[3] and bromine perchlorate[4] were prepared as reported. The fluoroalkyls were purchased (except where noted) and purified by fractional condensation. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å line of an Ar ion laser as the exciting line and a Claassen filter[9] for the elimination of plasma lines. Sealed quartz tubes (~2-mm i.d.) or glass melting point capillaries were used as sample containers in the transverse-viewing, transverse-excitation technique. While exposed to the laser beam, the sample tube was kept below −80° in a vacuum-jacketed flow tube by flowing a stream of dry N_2 through it. Mass spectra were recorded using a Quad 300 (Electronic Associates, Inc.) quadrupole mass spectrometer equipped with a passivated all stainless steel inlet system. The ^{19}F nmr spectra were recorded on a Varian Model DA60 spectrometer at 56.4 MHz using $CFCl_3$ as internal standard. Chemical shifts and coupling constants were determined by the side-band technique. Analytical data were obtained using Orion specific ion electrodes (F^-, Cl^-, or ClO_4^-) and solutions prepared after Na fusion or hydrolysis. These data together with some physical properties are summarized in Table I.

CF_3I–Cl_2O_4 Reactions. Trifluoromethyl iodide (2.02 mmol) and Cl_2O_4 (4.24 mmol) were combined at −196° in a 30-ml stainless steel cylinder which was subsequently slowly warmed to −45° during several days. Recooling to −196° showed the absence of noncondensable products. While rewarming to room temperature, the volatile products evolved were separated by fractional condensation. These consisted essentially of Cl_2 (2.07 mmol), trapped at −196°, and CF_3ClO_4 (2.01 mmol), trapped at −112°; the yield of CF_3ClO_4 was 99% based on CF_3I. The molecular weight observed by vapor density measurements was 167 *vs.* a value of 168.4 calculated for CF_3ClO_4. Measured quantities of CF_3ClO_4 and $CFCl_3$ reference were used to confirm by ^{19}F nmr peak area ratio measurements that the compound contains three fluorine atoms per molecule. The purity of the product was further indicated by its tensiometric homogeneity. The mass spectrum showed *m/e* peaks for $CF_3ClO_4^+$ (parent), $CF_3ClO_2^+$, CF_3ClO^+, ClO_3^+ (base peak), CF_3^+, ClO_2^+, COF_2^+, ClO^+, CF_2^+, COF^+, CO_2^+, O_2^+, CF^+, and CO^+ ions.

On standing at room temperature, the nonvolatile product of this reaction, "$IClO_4$," evolved O_2, Cl_2, and Cl_2O_7 in a manner similar to $I(ClO_4)_3$[5] eventually leading to the formation of I_2O_5. Occasionally the reaction of CF_3I with Cl_2O_4 deflagrated, particularly when warmed up too rapidly. The deflagration resulted in the generation of much O_2 (*e.g.*, 9.4 mmol from 6.0 mmol of Cl_2O_4), CO_2, COF_2,