Hydrolysis Reactions of Transition Metal Fluorides in Liquid Hydrogen Fluoride: Oxonium Salts with Nb, Ta and W

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ABSTRACT

The hydrolysis reactions of the hexafluorides of molybdenum and tungsten, the pentafluorides of niobium and tantalum and the tetrafluorides of zirconium and hafnium have been studied in liquid hydrogen fluoride. The following new compounds have been isolated and characterized: $H_3O^+WOF_5^-$, $H_3O^+NbF_6^-$ and $H_3O^+TaF_6^-$. Hydrolysis of MoF_6 leads to $MoOF_4$, but in HF solution there is evidence for the existence of $MoOF_5^-$ ion.

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INTRODUCTION

In a previous communication [1] hydrolysis reactions of the hexafluorides of Os, Ir, Pt, Ru and Rh in liquid hydrogen fluoride were described. It was found that the hydrolysis behavior of hexafluorides could be classified according to electron affinity. Thus, the relatively low electron affinity hexafluorides of rhenium and osmium undergo fluorine substitution to form the metal oxide tetrafluoride, while the high electron affinity hexafluorides of Ir, Pt and Ru oxidize water forming oxonium salts of the type $H_3O^+MF_6^-$ or $(H_3O^+)_2MF_6^=$. It is to be expected, therefore, that the hexafluorides of molybdenum and tungsten would undergo hydrolysis to form the metal oxide tetrafluorides and thus provide a useful pathway to these compounds, in addition to the thermal synthesis [2]. Indeed, in a variation of this method, $MoOF_4$ and WOF_4 were prepared by the reaction of the respective hexafluorides with quartz wool (SiO_2) in anhydrous HF[3].

We have found that $MoOF_4$ can be prepared by the direct hydrolysis of MoF_6 with H_2O in HF. However, WF_6 leads to the oxonium salt, $H_3O^+WOF_5^-$, instead. The pentafluorides of niobium and tantalum lead to the oxonium salts $H_3O^+NbF_6^-$ and $H_3O^+TaF_6^-$ as might be expected by analogy with previous syntheses of $H_3O^+SbF_6^-$, $H_3O^+AsF_6^-$[4] and $H_3O^+UF_6^-$[5]. No new products were formed in attempts to hydrolyze HfF_4 and ZrF_4, perhaps because of the very limited solubility of the tetrafluorides, but more likely because the fluoride ion affinities were insufficient to stabilize MF_5^- or $MF_6^=$ with H_3O^+ counterions.

Experimental

The apparatus and manipulation of the compounds have been described previously [1], as has the characterization of compounds by analysis and x-ray diffraction. The hexafluorides of tungsten and molybdenum were obtained from Varlacoid and Allied Chemical, respectively, and the tetrafluorides from Ozark-Mahoning. The pentafluorides were prepared in our laboratory. For the hydrolysis of MoF_6 and WF_6, a given amount of H_2O was pipetted into a 3/4" FEP tube and, after outgassing at $-196''$, about 1-2 cm^3 of HF were distilled on top of it. An appropriate amount of the hexafluoride was then distilled in, and the solution was allowed to

come to room temperature with vigorous agitation. Materials volatile at room temperature were removed and the solid residue characterized. To synthesize the NbF_6^- and TaF_6^- salts, the pentafluorides were placed in FEP tubes in a dry box and, after addition of HF, the appropriate amount of H_2O was distilled in from a side arm. The mixture was left standing overnight before processing. Raman spectra were obtained on a J-Y Raman HG2S spectrometer using 5145 Å excitation. Fourier transform ^{19}F nmr spectra were recorded at 84.66 MHz on a Bruker WH-90 spectrometer. Teflon FEP tubes containing the samples dissolved in tetramethylenesulfone were placed in 5 mm glass nmr tubes. Acetone-d_6 and hexafluorobenzene were placed in the annulus to serve as external lock and reference.

Hydrolysis of MoF_6 - The preparation of $MoOF_4$

In a typical hydrolysis of MoF_6, H_2O (4.17 millimoles) and MoF_6 (4.94 millimoles) yielded about 620 mg of white solid. The solid residue was identified as $MoOF_4$ on the basis of its Raman spectrum, identical to a sample prepared by the thermal method, and its mass spectrum [3]. Reaction of MoF_6 with excess water in HF or of $MoOF_4$ with water in HF led to an ill-defined product, which showed no observable $Mo-F$ stretching vibrations in the 700 cm^{-1} region of the Raman spectrum.

Hydrolysis of WF_6 - the preparation of $H_3O^+WOF_5^-$

In a typical hydrolysis of WF_6, H_2O (4.17 millimoles) admixed with WF_6 (4.34 millimoles) yielded a white solid which was identified as $H_3O^+WOF_5^-$. Chemical analysis: F: found, 29.2; calc. 30.3%; W, found, 59.0, calc. 58.6%. The Raman spectrum of the solid showed peaks at 1038 (vs), 701 (m), 323 (m) and ~ 300 (w,sh) cm^{-1}. Infrared spectra of the solid in a KBr disk showed broad bands at 3300 and 1600 cm^{-1} characteristic of H_3O^+ [4]. The ^{19}F nmr spectrum contained a doublet-quintet pattern characteristic of the WOF_5^- ion with the doublet at $\delta_{CCl_3F} = -19.1$ ppm and the quintet at $\delta_{CCl_3F} = 146.2$ ppm. The spin coupling constants were $J(W-F) = 48.8$ Hz, J(F-F) $= 70.2$ Hz. The ratio of doublet : quintet intensities

was $3.4\pm.1$. Additional singlets of low intensity were seen at $\delta_{CCl_3F} = -63.4$ ppm with $J(W-F) = 67.1$ Hz and at $\delta_{CCl_3F} = 184.6$ ppm with no splitting. These can be assigned to WOF_4 and HF, respectively.

Thermal decomposition of solid $H_3O^+WOF_5^-$ at $150''$ leads to a white product which is probably mostly WO_2F_2, but which could not be fully characterized. Chemical analysis: found; F, 15.7%; W, 72.7%. Calculated for WO_2F_2: F, 15.0%; W, 72.4 %. The Raman spectrum showed strong but very broad peaks at 1032, 993, 807 and 690 cm^{-1}. A mass spectrum showed both $WO_2F_2^+$ and WOF_3^+ ions; thus the product probably contained WOF_4. WO_2F_2 has recently been made by controlled hydrolysis of $WOF_4(6)$, but apparently not in HF solution.

Hydrolysis of NbF_5 - The preparation of $H_3O^+NbF_6^-$

In a typical hydrolysis of NbF_5, 522 mg (2.78 millimoles) of NbF_5 yielded 534 mg of a white solid. The Raman spectrum of the solid showed peaks at 701 cm^{-1} (m) and poorly resolved broad peaks at 288 and 268 cm^{-1}. These are characteristic of NbF_6^- [7]. The x-ray powder pattern showed the material to be isostructural with $NO^+NbF_6^-$ [8]. The cell was indexed as primitive cubic with a $= 5.04$ Å. However, a $CsCl$ structure with $a = 10.08$ Å cannot be ruled out. Chemical analyses were inconclusive, but the x-ray and Raman spectra indicate the compound to be $H_3O^+NbF_6^-$.

Hydrolysis of TaF_5 - the preparation of $H_3O^+TaF_6^-$

In a typical hydrolysis of TaF_5, 650 mg. (2.36 millimoles) TaF_5 yielded 626 mg. of a white solid. The Raman spectrum of the solid showed peaks at 700 (s), 586 (w), 283 (m) and 266 (m) cm^{-1} which are characteristic of TaF_6^- [7]. The x-ray powder pattern showed the material to be isostructural with $NO^+TaF_6^-$ and $H_3O^+NbF_6^-$ and was indexed as a primitive cubic cell with a = 5 .01 Å. However, the structure may also be of the $CsCl$ type, as above. Chemical analyses were inconclusive but x-ray and Raman spectra indicate the compound to be $H_3O^+TaF_6^-$.

DISCUSSION

This study has resulted in the isolation of several oxonium salts in addition to those previously known [1,4,5]. The hydrolysis of MoF_6 leads to the rapid formation of $MoOF_4$ in a synthesis which may be more convenient than the thermal synthesis. The method lends itself more easily to large scale preparations, because it neither involves high pressures of $O_2 + F_2$ [2] nor does it generate the side product SiF_4 [3]. For the preparation of WOF_4, however, the method of Paine and McDowell [3] is obviously superior. The formation of $H_3O^+WOF_5^-$ is perhaps not too surprising, when compared with the reaction of $NO + OsOF_5$ carried out in WF_6 solution. This reaction leads apparently to a solid solution of $NOWOF_5$ in $NOOsF_6$ [9]. Bartlett has hypothesized the reaction to be catalyzed by HF. The WOF_5^- ion seems to be exceptionally stable, the hypothetical WOF_5 molecule being a better electron acceptor than WF_6 because of its unsaturated oxygen valence [9].

Both Raman and ^{19}F nmr spectra indicate that the anion in $H_3O^+WOF_5^-$ may be distorted. The vibrational spectrum of $CsWOF_5$ has been reported [10]. The W-O stretching frequency occurs at 989 cm^{-1}, markedly lower than the 1038 cm^{-1} observed for the oxonium salt. The remaining bands are shifted considerably less. Similarly, the ^{19}F nmr spectral parameters differ somewhat from those reported elsewhere for WOF_5^- [11], although the chemical shifts, particularly of the axial fluorine atom, are very much solvent dependent. The coupling constants $J(WF)$ and $J(FF)$ would be sensitive to solvent for a pseudooctahedral structure. The doublet-quintet pattern in the proper ratio, however, argues in favor of a C_{4v} configuration and rules out the dimer anion, $W_2O_2F_9^-$. The oxonium cation could conceivably distort the anion or otherwise influence it by way of hydrogen bonding. The 1038 cm^{-1} band does not belong to solvent shifted WOF_4. A solution of WOF_4 in HF showed a strong band at 1050 cm^{-1} essentially unshifted from the solid. Raman spectra were obtained on HF solutions containing different ratios of WF_6 to H_2O. For $WF_6:H_2O = 2:1$ and 1:1, bands appeared *inter alia* at 1050 and 1035 cm^{-1}, showing that WOF_4 and $H_3O^+WOF_5^-$ coexist in solution. These solutions show also the presence of unreacted WF_6, since a $WF_6:H_2O$ ratio of 1:2 would be required for complete reaction.

There is also evidence that $MoOF_5^-$ ion exists in HF solution. A solution of $MoOF_4$ in HF shows a strong band at 1039 cm^{-1}, unshifted from the solid. Solutions of $MoF_6:H_2O = 1:3$ and 1:2 in HF show, however, a strong band at 1022 cm^{-1} with a weak shoulder at around 1037 cm^{-1}. From such solutions no fluorine containing solids were obtained, however, while from solutions containing $MoF_6:H_2O = 1:1$ only $MoOF_4$ was isolated.

Because the species existing in solution are other than those assumed in a previous study (12) of the hydrolysis of the hexafluorides in HF, the hydrolysis constants of the hexafluorides obtained from conductivity studies will have to be recalculated.

ADDENDUM

The oxonium salt, $(H_3O^+)_2PtF_6^-$, reported in the previous paper [1] is isostructural with the hydrolysis products of $O_2^+PtF_6^-$ and of $XeF^+PtF_6^-$ [13]. The hydrolysis product has been indexed as a tetragonal unit cell with cell constants a $= 8.025$ Å and c $= 6.019$ Å [13].

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