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Electrochemical Studies of Tungsten Hexafluoride and Related Compounds in Anhydrous Hydrogen Fluoride

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Electrochemical investigations in anhydrous hydrogen fluoride at mercury, platinum, and glassy carbon electrodes have provided considerable kinetic and thermodynamic information on tungsten hexafluoride and related compounds. The electrochemistry of WF_6 is relatively straightforward being characterized by a reversible one electron reduction step $WF_6 + e \rightleftharpoons WF_6^-$ in neutral and basic media, while that for WOF_4 is more complex. All thermodynamic data obtained are in accord with the known chemistry of WF_6 and show that it is a very mild oxidant.

Introduction

The fluoride¹ and oxide fluoride² of tungsten(VI) were first prepared by Ruff and coworkers early in this century, but with the limited experimental procedures then available, they were unable to provide any reliable information on the chemical reactivity of these compounds. Early work was restricted almost entirely to the determination of physical properties.³

Following investigations of the chemical reactions of WF_6 with nitric oxide,⁴ nonmetal fluorides, carbon disulfide, and other compounds,⁵ its reactivity as an oxidant was compared qualitatively⁶ and semiquantitatively⁷ with that of hexafluorides of other transition metals. More recently Galkin and Tumanov⁸ have proposed that force constants, bond energies, and bond lengths can be used as criteria in determining relative reactivities of hexafluorides.

Very little is known about the chemistry of WOF_4 except that it appeared to be less reactive than WF_6 since it did not attack glass below its melting point,⁹ although this type of complex hydrolytic reaction has been shown to be a poor basis on which to judge oxidant strength.⁶ The other oxide fluoride of tungsten, the dioxide difluoride, has never been isolated although it has been reported as having been prepared by controlled hydrolysis of WF_6 ¹⁰ and WOF_4 .¹¹

In chemical studies it had been observed that the presence of HF could markedly affect the kinetics of redox reactions involving higher fluorides of transition metals. However, in most reactions the nature of the final products was independent of the presence or absence of HF. Consequently electrometric studies in anhydrous hydrogen fluoride (AHF) were undertaken in order to provide a quantitative basis for the earlier chemical studies and to make the outcome of future chemical studies easier to predict. Oxidation and reduction by electrochemical techniques are more specific and can provide much more information on kinetic and thermodynamic factors than redox studies using selected chemical reagents. A comprehensive electrochemical program in AHF has been undertaken using the technique of cyclic voltammetry at mercury, platinum, and glassy carbon electrodes. The compounds included in this initial system were WF_6 , $NaWF_6$, and WOF_4 for reasons given immediately below.

The avidity of HF for water is now so well established that the possible hydrolysis product of WF_6 , the oxide tetrafluoride, was included in the study in the interest of reliability. In addition water was deliberately added to the system to correlate the observations. As a check on the reversibility of the W(VI)-W(V) couple in AHF, sodium hexafluorotungstate(V) was also studied.

Electrochemistry in AHF is a rapidly expanding field, as evidenced by the number of recent publications.¹²⁻¹⁸ It has previously been shown that Hg, Pt, and glassy carbon give reproducible electrode behavior in AHF.¹²⁻¹⁷ As well as electrode characteristics, solvent limits and the effects of the

addition of various electrolytes on them have been discussed.^{14,16,17}

This is the first report of electrochemical studies of solutions of transition metal fluorides in high oxidation states in AHF. Prior to this work the only other related studies have been in fluoride melts.¹⁹⁻²¹

In addition to the electrochemical investigation we report a new general preparative route for lower fluorides and hexafluorometallates of the transition metals. In particular we used the method to prepare $NaWF_6$ as the method previously reported did not always lead to a pure product.²² Endeavors to prepare tungsten pentafluoride failed to give sufficiently large quantities to allow its electrochemical characterization and this compound had to be omitted from the overall investigation.

Experimental Section

Reagents. Sodium fluoride, potassium hydroxide and sodium tetrafluoroborate were analytical reagent grade, and the potassium tetrafluoroborate was laboratory reagent grade. Tungsten and cadmium metals were in the form of high purity rods, and the HF (Matheson, N.J.) was distilled in a Teflon-packed fractionation column which was a modification of one previously reported.²³ The distilled HF regularly had a specific conductance of 7×10^{-5} to 1×10^{-4} ohm⁻¹ cm⁻¹ at 20°.

Tungsten Hexafluoride. The direct fluorination of the metal gave WF_6 as described previously for molybdenum hexafluoride.²⁴

Tungsten Oxide Tetrafluoride. Tungsten oxide tetrafluoride was prepared according to the method of Burns, O'Donnell, and Waugh²⁵ and was characterized by its infrared spectrum and by analysis.

Sodium Hexafluorotungstate(V). This is the product obtained when WF_6 in AHF is reduced by cadmium in the presence of a stoichiometric amount of NaF. Finely divided Cd metal was prepared by filing the required quantity from a high purity Cd rod, the initial filings being discarded because of possible oxide contamination. The metal and NaF were placed in a Kel-F tube on a vacuum line. Anhydrous hydrogen fluoride was distilled into the tube at -50° and a stoichiometric amount of WF_6 (1:1 WF_6 to NaF) was condensed onto the mixture at -196°. The reaction tube was allowed to warm to room temperature. It was then removed from the line and shaken for 8 to 12 hr. The precipitate was allowed to settle and the colorless supernatant liquid was decanted using all Kel-F components. The precipitate was washed several times with AHF by condensing the AHF back into the reaction tube several times. The washing procedure was similar to that reported for the purification of $Mo(CO)_2F_4$.²⁶ The AHF was finally removed by distillation, to leave a white powder.

Analytical Data. Found: W, 56.4; F, 35.5; $NaWF_6$ requires: W, 57.3; F, 35.5. The yield of $NaWF_6$ was quantitative since no free NaF was observed in the X-ray powder pattern. Similarly there was no trace of either Cd or CdF_2 in the X-ray powder pattern which showed that simple decantation was sufficient to separate the required product from the precipitate.

If a different cation than Na^+ were required the corresponding fluoride salt could be used.

Analysis. Tungsten was determined gravimetrically by precipitation with 8-hydroxyquinoline and analysis of fluoride was based on the Orion ion selective electrode.

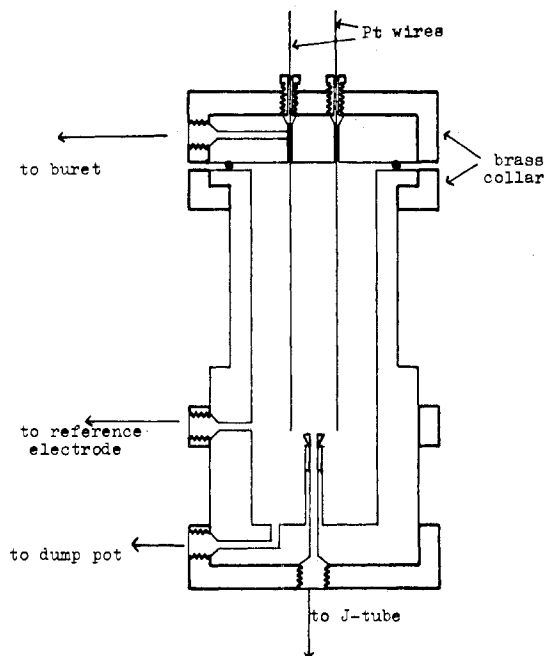


Figure 1. Electrochemistry cell.

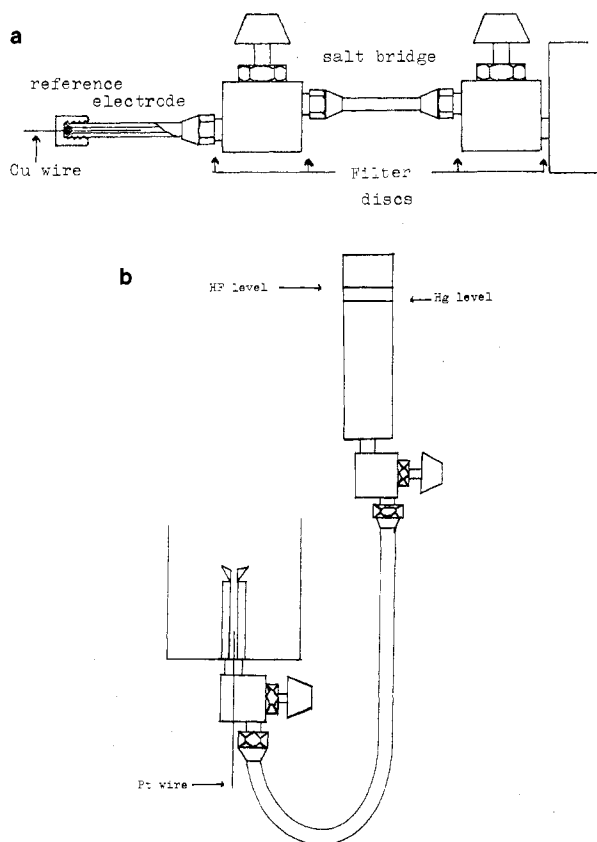
Apparatus, Instrumentation, and Procedure. Because of the highly corrosive and toxic nature of AHF and the extreme ease of hydrolysis of the high oxidation state fluorides of tungsten all manipulations were carried out in closed systems. An all Kel-F vacuum line was constructed which kept water contamination to a minimum. The method of construction of the units and the valves used have been reported previously.^{13,27,28} Figure 1 shows a detailed diagram of the electrochemical cell used.

Solutions containing supporting electrolyte and the electroactive species were prepared by condensing AHF into previously calibrated Kel-F tubes containing weighed amounts of the required compound.

Supporting electrolytes were KBF_4 or NaF , selected for reasons given later in the text. For convenience deliberate addition of water was achieved by reacting AHF with KOH which had been weighed into a Kel-F tube beforehand. Calibrated Kel-F tubing was used as a buret for the controlled addition of solutions of electrolytes, water, or fluoride when quantitative variation of concentrations was necessary.

Voltammograms were obtained with a P.A.R. Electrochemistry System, Model 170 (Princeton Applied Research Corp., Princeton, N.J.), using a three electrode system with a Pt wire as auxiliary electrode and either Pt, Hg, or glassy carbon as the working electrode.

An external Cu/CuF_2 (1.0 M NaF/HF) reference electrode was used, separated from the cell by a Kel-F bridge containing 1.0 M NaBF_4 in AHF (Figure 2a). Small disks cut from Teflon filters (Millipore Filter Corp.) were placed at each valve connection to prevent cross contamination of the salt bridge, reference, and working compartments. The Pt wires were shielded with heat shrinkable Teflon to within 1 mm of the end dipping into the solution. The stationary mercury electrode was constructed from Kel-F tubing and machined from Kel-F rod to give a J-tube (Figure 2b). Electrical connection with mercury was made by a Pt wire through a Kel-F valve which served as a regulator for the Hg, when a fresh working surface was required. The Hg reservoir was a Kel-F tube which also contained some AHF to counterbalance the vapor pressure of AHF in the cell. To improve the electrode characteristics the working surface of the glassy carbon electrode was polished with diamond dust. The three electrodes (reference, working, and auxiliary) were in the same plane and this arrangement coupled with positive feedback circuitry helped minimize ohmic losses. Scan rates of 200 mV/sec were used throughout. The peak potentials were reproducible to ± 10 mV. Degassing of the solutions was unnecessary since the use of vacuum line techniques had eliminated the possible presence of oxygen in solutions. All voltammograms were recorded at ambient temperatures. Spent solutions and Hg were periodically run off into a dump pot (Figure 1). This enabled the cell to be used indefinitely without being opened to the atmosphere which helped prevent moisture contamination. The AHF could be recycled to the source traps by distillation

Figure 2. (a) A 1.0 M NaBF_4/HF salt bridge and Cu/CuF_2 1.0 M NaF/HF reference electrode. (b) Mercury J-tube electrode.

and the cell was cleared of electroactive species by successive washings with pure AHF.

Results and Discussion

Hydrogen fluoride undergoes self-ionization which can be represented by eq 1. Thus species which increase the con-



centration of H_2F^+ are acids, while those which increase the concentration of HF_2^- are bases. Hence alkali metal fluorides will act as bases while tetrafluoroborate, since it produces neither H^+ nor F^- ions, will leave the solution neutral. These considerations affect the choice of supporting electrolyte.

Tungsten Hexafluoride in 0.5 M Potassium Tetrafluoroborate. The electrochemistry of WF_6 at Pt, Hg, and glassy carbon in neutral media is characterized by one well-defined wave. Table I summarizes the data and Figure 3 shows a cyclic voltammogram obtained at Pt.

Tungsten Hexafluoride in Sodium Fluoride. The deliberate addition of fluoride ion had no effect on the shape or position of the wave which was equally well defined in both neutral and basic media.

Analysis of data shows the reduction involves the transfer of one electron and is reversible on Pt and Hg but quasi-reversible on glassy carbon. Since the reduction is chemically reversible the electrode process is assumed to occur with retention of geometry. The absence of fluoride dependence of the electrode reactions suggests that anions such as WF_7^- and WF_8^{2-} do not play a significant part in the electrode process. The reaction involved can be best described by eq 2. The observed $E_{1/2}$ is consistent with the chemical redox



reactions previously reported which showed WF_6 to be a very

Table I. Peak and Half-Wave Potentials for the Reduction of WF_6 in Neutral Media at Pt, Hg, and Glassy Carbon Electrodes

WF_6				
Electrode Material	Cathodic Peak Potential (E_{p_c}) V	Anodic Peak Potential (E_{p_a}) V	Peak to Peak Separation mV	Half Wave Potential ($E_{1/2}$) V
Pt	-0.12	-0.06	60	-0.10
Hg	-0.11	-0.05	60	-0.09
Glassy Carbon	-0.14	-0.07	70	-0.11

Wave heights were linear functions of WF_6 concentration.

Table II. Peak Potentials for the Reduction of WOF_4 in Neutral and Basic Media at a Mercury Electrode

WOF_4			
Medium	First Forward Scan (E_p) V	First Reverse Scan (E_p) V	Second Forward Scan (E_p) V
0.1M NaF	-0.53, -0.8 ^(a)	-0.06	-0.12, -0.53, -0.8 ^(a)
0.5M KBF ₄	-0.25, -0.50 -0.8 ^(a)	-0.08	-0.12 ^(b) , -0.23, -0.50, -0.8 ^(a)

(a) merges with reduction wave of solvent.

(b) occurs as shoulder on wave with peak potential at -0.2V

mild oxidant.^{4,5} The lack of voltammetric evidence for charged fluoride complexes is in accord with the observations of Frlec and Hyman²⁹ who showed by conductance and Raman spectroscopy that WF_6 in AHF neither dissociated, associated, nor complexed in solution.

Sodium Hexafluorotungstate(V) in 0.5 M Potassium Tetrafluoroborate. A reversible one electron oxidation wave was observed at Hg and Pt with the same potentials as the reduction wave for WF_6 confirming that the product of reduction of WF_6 is WF_6^- (eq 2). Figure 4 is the voltammogram for the oxidation of WF_6^- on Pt.

Sodium Hexafluorotungstate(V) in Sodium Fluoride. The deliberate addition of fluoride ion made no difference to either the position or shape of the observed waves. This absence of any fluoride dependency of the electrode process confirms that it can best be described by eq 2 in both neutral and basic media.

As well as the waves reported for WF_6 in Table I the voltammogram at Hg also showed two other waves at more negative potentials. These were always present although to a varying degree in each electrochemical run. It was in order to identify the origin of these waves that the oxide fluoride was studied and it will be subsequently shown that these waves were due to partial hydrolysis of the hexafluoride.

Tungsten Oxide Tetrafluoride in 0.5 M Potassium Tetrafluoroborate. All voltammograms in this part of the study were recorded using a Hg electrode as the wave potentials were too negative to be observed with Pt. The overall behavior is summarized in Table II. From Figure 5a it can be seen that, in the first scan, there were three reduction waves. The first, with a peak potential of -0.25 V, was more symmetrical than the one usually associated with normal electron transfer reactions which suggests that adsorption phenomena are occurring. The second wave was at about -0.5 V and a third, near the solvent limit at about -0.8 V, could not be char-

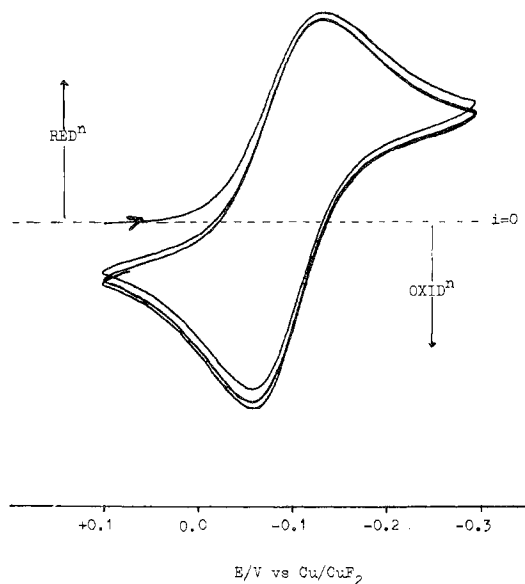


Figure 3. Cyclic voltammogram for the reduction of WF_6 in 0.5 M KBF_4 at a platinum electrode.

acterized and presumably involves reduction of W(V) to W(IV). On the reverse scan a wave with an E_p value of -0.08 V was observed.

In the second and subsequent scans a new reduction wave which was not observed on the first scan occurred as a shoulder on the symmetrical wave at -0.25 V.

Tungsten Oxide Tetrafluoride in Sodium Fluoride. The deliberate addition of fluoride to the KBF_4 solution of tungsten oxide tetrafluoride had quite a dramatic effect on the observed

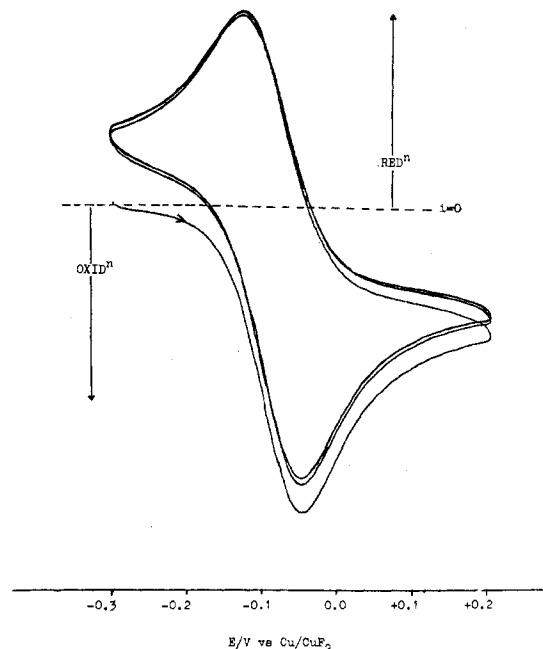


Figure 4. Cyclic voltammogram for the oxidation of NaWF_6 in 0.5 M KBF_4 at a platinum electrode.

voltammograms (Figure 5b). The adsorption controlled wave decreased in height while the second reduction wave increased. The fourth reduction wave which had previously been only a shoulder now became well defined. A slight shift in peak potentials was also observed. Further addition of fluoride ion caused the initial trends to be accentuated although the wave at -0.25 V did not disappear completely. If instead of KBF_4 as supporting electrolyte NaF is used, the voltammogram is further simplified (Figure 5c) and no wave is observed at -0.25 V . As before an extra reduction wave appears on the second cycle (Table II) and this time it is part of an almost reversible one electron couple.

If the scan is reversed at -0.65 V instead of -0.85 V the extra reduction wave still occurs, which means that it is a direct result of the initial reduction of the species formed by the dissolution of WOF_4 in AHF and is not due to the process occurring at more negative potentials. Two well-defined waves were observed under ac conditions implying fast electron transfer for both waves.

In the solid state WOF_4 exists as a fluorine bridged tetramer;³⁰ in the liquid state it has a high Trouton constant which suggests association;³¹ and in the vapor phase it is monomeric.³⁰ Thus in solution not only could monomeric anions or neutral species exist but also neutral and charged polymers. The ac voltammograms indicated that the oxide fluoride species were, however, relatively simple. The following reduction mechanism is therefore postulated. In AHF , tungsten oxide tetrafluoride is reduced to an oxofluorotungsten(V) species probably with structural similarities to the initial entity. This oxidation state V entity is unstable and rearranges. The most probable rearrangement would, in the presence of F^- , give WF_6^- and at least one other oxide fluoride of W(V). The formation of WF_6^- is postulated because of the observation of a reversible couple at the same potential as that established for the $\text{WF}_6 + e \rightleftharpoons \text{WF}_6^-$ couple. In the absence of F^- , WF_5 would most probably be formed. The pentafluoride has little Lewis acidity in HF and therefore the wave is not chemically reversible.

The impurity waves which were reported earlier in the voltammograms of WF_6 correspond exactly to waves for the reduction of WOF_4 which suggests that the impurity was indeed an oxide fluoride.

It can be stated as a generality that no electrochemical

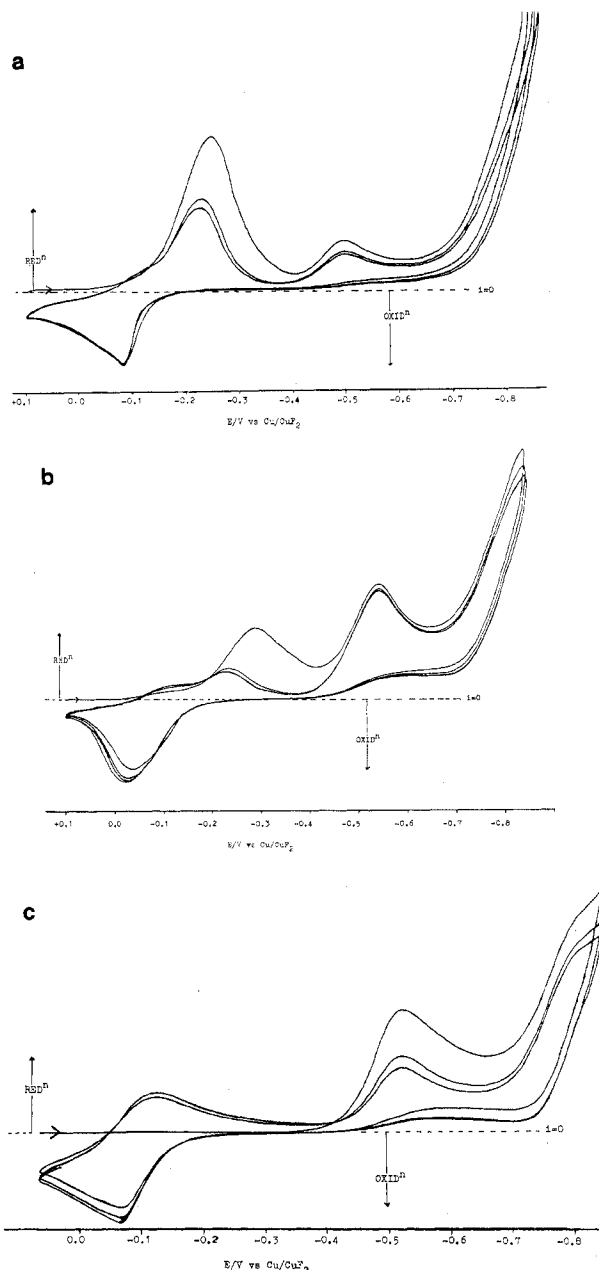


Figure 5. (a) Cyclic voltammogram for the reduction of WOF_4 in 0.5 M KBF_4 at a mercury electrode. (b) Cyclic voltammogram showing the effect of the addition of F^- on the reduction of WOF_4 at a mercury electrode. (c) Cyclic voltammogram for the reduction of WOF_4 in 0.1 M NaF at a mercury electrode.

investigation of high oxidation state fluorides in AHF should be considered to be complete without including a study of the corresponding oxide fluorides because of the ease of hydrolysis of the parent compounds by traces of water in AHF .

Addition of Water to Tungsten Hexafluoride. When the reaction was followed on the Pt electrode in neutral solution the reversible one electron reduction wave decreased in height proportionally to the addition of water. The reaction at Pt appeared to be stoichiometric with a 1:1 end point. On Hg, however, it was possible to observe the simultaneous decrease in size of the $\text{WF}_6/\text{WF}_6^-$ reduction wave and the appearance of the WOF_4 reduction waves at more negative potentials. Further addition of water up to a twofold excess had no effect on the remaining waves. The resultant voltammogram was identical with that obtained for a solution of the oxide tetrafluoride. The above behavior is consistent with a hydrolysis

reaction producing an oxide fluoride complex of tungsten in solution.

Addition of fluoride ion produced the changes observed previously for WOF₄.

Addition of Water to Sodium Hexafluorotungstate(V). The deliberate addition of water to a solution of NaWF₆ in basic AHF produced a voltammogram which was the same as that resulting from WOF₄ or the addition of H₂O to WF₆ in the same medium. This therefore suggests that an oxide fluoride of tungsten(V) must be produced which then disproportionates to give WOF₄ and an unidentified tungsten(IV) species. This is consistent with disproportionation of tungsten(V) species noted previously by Brownstein.³² In an NMR spectroscopic study of the reaction of KWF₆ with boron trifluoride in liquid sulfur dioxide, he found that some form of hydrolysis occurred to give WOF₄. Brownstein suggested that WOF₄ resulted from the reaction of water with WF₅ or its disproportionation product WF₄. Tungsten pentafluoride is known to be unstable disproportionating at room temperature to WF₆ and WF₄³³ and it is likely that this instability is enhanced by traces of moisture. This appears to explain our difficulty in preparing a large enough sample of WF₅ for voltammetric analysis. There was evidence that WF₅ was formed in HF solution, but that, on removal of solvent HF and consequent concentration of adventitious water, disproportionation and decomposition occurred, one of the products being WF₄.

Conclusions

In neutral and basic solutions of AHF, WF₆ was reduced and WF₆⁻ oxidized according to eq 2. This was a simple one electron reversible reaction with an average $E_{1/2}$ of -0.10 V whether the electrode was Pt, Hg, or glassy carbon. The addition of water to solutions of WF₆ or NaWF₆ produces oxofluoro species which have the same electrochemical behavior as solutions of WOF₄ in AHF. As the present knowledge of the nature and stability of tungsten oxide fluoride species in solution is extremely limited an electrochemical interpretation is necessarily incomplete. The half-wave potential obtained for the WF₆/WF₆⁻ couple shows that WF₆ is a very mild oxidant and indeed can be thought of as being relatively "inert", as has been demonstrated in a recent synthesis of a very reactive fluoro compound in which it was used as a solvent in a purification step.²⁶ In related work tungsten hexafluoride was found not to react with tungsten hexacarbonyl whereas the corresponding molybdenum compounds reacted readily.³⁴

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Registry No. WF₆, 7783-82-6; NaWF₆, 55822-76-9; WOF₄, 13520-79-1; Cd, 7440-43-9.

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