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## Electrochemical Studies of Molybdenum Hexafluoride and Related Compounds in Anhydrous Hydrogen Fluoride

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Electrochemical investigations in anhydrous hydrogen fluoride on molybdenum hexafluoride and related compounds, at platinum and glassy carbon electrodes, have shown that a series of chemically reversible, one-electron redox processes occur:  $\text{MoF}_6 + e^- \rightleftharpoons \text{MoF}_6^- + e^- \rightleftharpoons \text{MoF}_6^{2-}$  and  $\text{MoOF}_4 + e^- \rightleftharpoons \text{MoOF}_4^-$ . From the electrochemical data derived from this work, molybdenum hexafluoride is shown to be a stronger oxidant than tungsten hexafluoride by approximately 1 V. While the order of oxidant strengths is consistent with the previously reported chemistry of both hexafluorides, the magnitude of the difference is unexpectedly large.

### Introduction

As in the case of its tungsten analogue, the preparation of molybdenum hexafluoride was first reported by Ruff and Eisner in 1907.<sup>1</sup> However, because of the very limited experimental procedures then available, a detailed account of its chemical reactivity could not be provided. All that was established was the extreme ease with which it is hydrolyzed and some very simple observations were made on its apparent reaction with a few unrelated compounds. Subsequent investigations on MoF<sub>6</sub>, rather than being chemical, were restricted almost entirely to determination of some of its physical properties.<sup>2-5</sup>

Studies of the chemical reactions of MoF<sub>6</sub> were not attempted in any systematic fashion until the mid-sixties. Geichman et al. investigated its reduction with nitric oxide<sup>6</sup> while O'Donnell and Stewart looked at reactions with a series of nonmetal fluorides, carbon disulfide, and other compounds.<sup>7</sup> In addition, the latter workers qualitatively compared its strength as an oxidant with that of WF<sub>6</sub> and CrF<sub>5</sub>,<sup>8</sup> and reached the conclusion that MoF<sub>6</sub> was a mild oxidant, stronger than WF<sub>6</sub> but not as strong as CrF<sub>5</sub>.

This observation was at variance with the commonly held view to that time that MoF<sub>6</sub> and WF<sub>6</sub> were both vigorous fluorinating agents and virtually identical in their chemical behavior.<sup>9,10</sup> More recently, Prescott and co-workers have reported that in acetonitrile MoF<sub>6</sub> will oxidize silver metal to silver(II) while WF<sub>6</sub> gives only silver(I) compounds.<sup>11</sup> In their paper they claimed that "definitive evidence" had been lacking for the difference in reactivity between MoF<sub>6</sub> and WF<sub>6</sub>. Certainly, up until now, no quantitative measurement of the difference has been available.

As part of a program of voltammetry in AHF, the electrochemical behavior of WF<sub>6</sub> and related compounds was investigated and a value was obtained for  $E^\circ$  for the WF<sub>6</sub>/WF<sub>6</sub><sup>-</sup> couple.<sup>12</sup> An analogous study of the corresponding molybdenum system and determination of a value for the  $E^\circ$  for the MoF<sub>6</sub>/MoF<sub>6</sub><sup>-</sup> couple allows quantitative comparison of the oxidant strength of the two hexafluorides based on measured  $E^\circ$  values.

It was shown to be necessary in the investigation of the tungsten system to include a study of the oxide tetrafluoride in the interests of reliability. Therefore the same procedure was adopted here. As before, the reversibility of the Mo(VI)/Mo(V) system in AHF was checked by studying sodium hexafluoromolybdate(V) as well. Again, water was deliberately added to the solutions of both MoF<sub>6</sub> and NaMoF<sub>6</sub> to correlate the observations.

### Experimental Section

**Reagents.** The purity and source of the reagents used (sodium fluoride, potassium hydroxide, sodium tetrafluoroborate, etc.) have already been reported.<sup>12</sup>

Table I. Peak and Half-Wave Potentials for the Reduction of MoF<sub>6</sub> in Neutral Media at Platinum and Glassy Carbon Electrodes under Conditions of Cyclic Voltammetry (Scan Rate 200 mV/s)

Electrode	$E_{p_c}$ , V	$E_{p_a}$ , V	$\Delta E_p$ , mV	$E_{1/2}$ , V
Platinum	0.90	0.96	60	0.91
	0.29 <sup>a</sup>	0.35 <sup>a</sup>	60 <sup>a</sup>	0.31 <sup>a</sup>
Glassy carbon	0.93	1.02	90	
	0.28	0.38	100	

<sup>a</sup> This wave becomes progressively more irreversible with aging of the electrode surface.

**Molybdenum Hexafluoride.** Direct fluorination of molybdenum metal, which had been heated with hydrogen before use to reduce surface oxide contamination, gave MoF<sub>6</sub> as outlined in the literature.<sup>7</sup>

**Molybdenum Oxide Tetrafluoride.** Molybdenum oxide tetrafluoride was prepared by the method of Burns, O'Donnell, and Waugh<sup>13</sup> and was characterized by analysis and by its known infrared spectrum.<sup>14</sup>

**Sodium Hexafluoromolybdate(V).** This was prepared by the method involving reduction with cadmium, described for sodium hexafluorotungstate(V).<sup>12</sup> It was characterized by its infrared spectrum, by its x-ray powder pattern, and by analysis. Anal. Calcd for NaMoF<sub>6</sub>: Mo, 41.2; F, 49.0. Found: Mo, 40.2; F, 49.0.

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

**Apparatus, Instrumentation, and Procedure.** The electrochemical instrumentation was identical with that detailed in an earlier publication.<sup>12</sup> The electrochemical cell was similar to that previously described but did not include the mercury electrode, since mercury reacts with both MoF<sub>6</sub> and MoOF<sub>4</sub>.<sup>15</sup> The supporting electrolyte was KBF<sub>4</sub> or NaF and the reference electrode was Cu/CuF<sub>2</sub> (1.0 M NaF/HF). Ambient temperatures of approximately 20 °C were used to record all voltammograms.

### Results and Discussion

**Molybdenum Hexafluoride in 0.5 M Potassium Tetrafluoroborate (neutral) Solution.** It had been found experimentally that MoF<sub>6</sub> was reduced by mercury,<sup>15</sup> therefore its electrochemistry was studied at platinum and glassy carbon electrodes. The electrochemical behavior of MoF<sub>6</sub> was simple in neutral media (KBF<sub>4</sub> solution). It was characterized by two well-defined reduction waves. Table I summarizes the data obtained and Figure 1 shows a cyclic voltammogram run with a Pt electrode.

**Molybdenum Hexafluoride in Sodium Fluoride (Basic) Solution.** The addition of the basic fluoride ion had no effect on either the position or shape of the waves which remained equally well defined in both neutral and basic media.

Analysis of the waves obtained on Pt showed that they were the result of two successive chemically reversible, one-electron reductions having half-wave potentials ( $E_{1/2}$ ) of 0.91 and 0.31 V, respectively (Table I). The fact that the reduction waves were reversible suggests that the electrode processes were

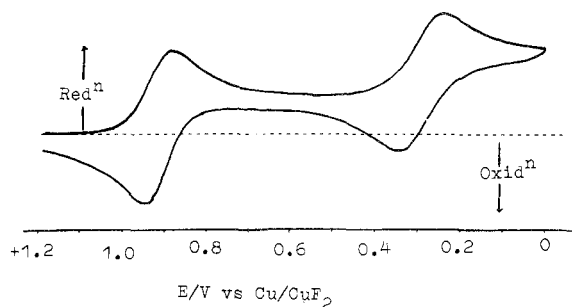


Figure 1. Cyclic voltammogram for the reduction of  $\text{MoF}_6$  in 0.5 M  $\text{KBF}_4$  at a platinum electrode; scan rate 200 mV/s.

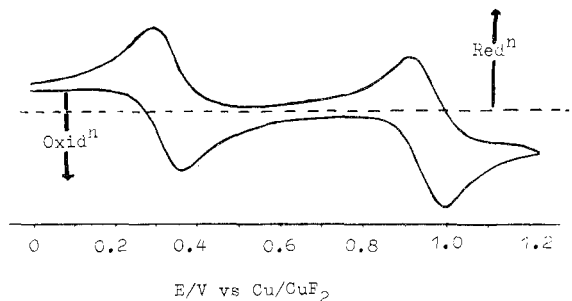


Figure 2. Cyclic voltammogram for the oxidation and reduction of  $\text{NaMoF}_6$  in 0.5 M  $\text{KBF}_4$  at a platinum electrode; scan rate 200 mV/s.

Table II. Peak and Half-Wave Potentials for the Oxidation and Reduction of  $\text{NaMoF}_6$  in 0.5 M  $\text{KBF}_4$  at a Platinum Electrode under Conditions of Cyclic Voltammetry (Scan Rate 200 mV/s)

$E_{p_c}$ , V	$E_{p_a}$ , V	$\Delta E_p$ , mV	$E_{1/2}$ , V
0.29	0.35	60	0.31
0.91	0.97	60	0.93

occurring with retention of stereochemistry. On glassy carbon the waves were quasi-reversible.

The observation that neither the position nor shape of either wave was dependent on fluoride ion concentration indicates that fluoro anions such as  $\text{MoF}_7^-$  and  $\text{MoF}_8^{2-}$  do not play a significant part in the first electrode process. This is consistent with the findings of Frlec and Hyman,<sup>16</sup> who showed by Raman spectroscopy and conductance measurements that  $\text{MoF}_6$  exists as a noncharged monomer in AHF solution. The electrochemical reactions involved can be described by



Under ac conditions two well-defined symmetrical waves were obtained implying fast electron transfer for both steps.

**Sodium Hexafluoromolybdate(V) in 0.5 M Potassium Tetrafluoroborate Solution.** In neutral medium two chemically reversible one-electron waves were observed on Pt (Figure 2 and Table II). The more negative of these involved a reduction process; the more positive involved oxidation. Each of these was at the same potentials as the two reduction waves obtained for  $\text{MoF}_6$  (Table I), providing conclusive proof that the product of the initial reduction of  $\text{MoF}_6$  is  $\text{MoF}_6^-$  and that the second step involves reduction of  $\text{MoF}_6^-$ . This is also proof that the electrode process is chemically reversible.

**Sodium Hexafluoromolybdate(V) in Sodium Fluoride Solutions.** The addition of fluoride ion to a solution of  $\text{MoF}_6^-$  in basic AHF gave waves with the same shape and position as those obtained for  $\text{MoF}_6^-$  in neutral media, suggesting that anions such as  $\text{MoF}_7^{2-}$  and  $\text{MoF}_8^{3-}$  are probably not taking major parts in the electrode processes. Thus the reduction and

Table III. Peak and Half-Wave Potentials for the Reduction of  $\text{MoOF}_4$  in Neutral Media at a Platinum Electrode under Conditions of Cyclic Voltammetry (Scan Rate 200 mV/s)

$E_{p_c}$ , V	$E_{p_a}$ , V	$\Delta E_p$ , mV	$E_{1/2}$ , V
0.43	0.49	60	0.47

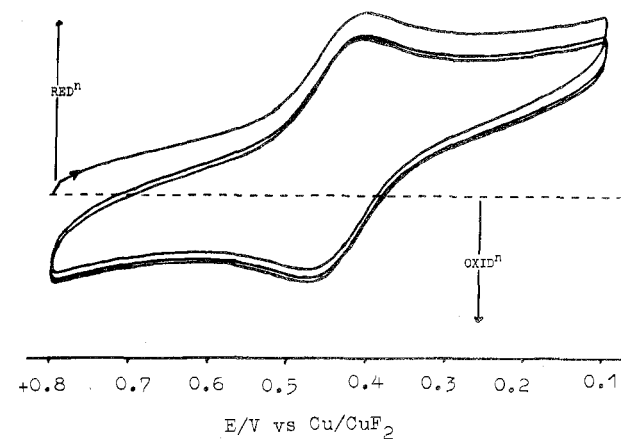


Figure 3. Cyclic voltammogram for the reduction of  $\text{MoOF}_4$  in 0.5 M  $\text{KBF}_4$  at a platinum electrode; scan rate 200 mV/s.

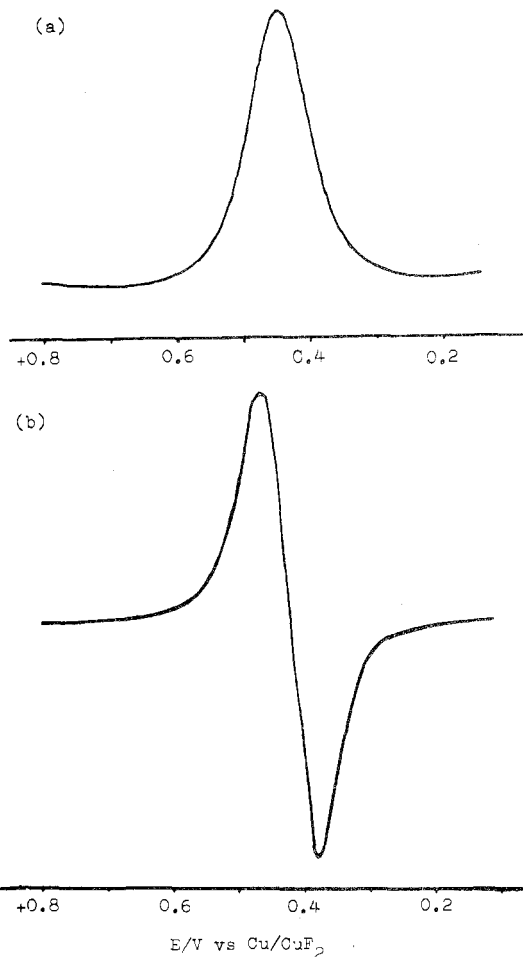


Figure 4. Reduction of  $\text{MoOF}_4$  in 0.5 M  $\text{KBF}_4$  at a platinum electrode: (a) ac voltammogram; (b) second harmonic voltammogram; amplitude 10 mV peak to peak at 200 Hz; scan rate 50 mV/s.

oxidation steps can best be described by eq 1 and 2 in both neutral and basic media.

**Molybdenum Oxide Tetrafluoride in 0.5 M Potassium Tetrafluoroborate Solution.** Although expected to be a weaker oxidant than  $\text{MoF}_6$ , molybdenum oxide tetrafluoride was also

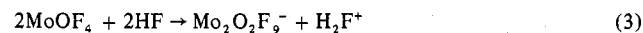
Table IV. Specific Conductances of Solutes 0.50 M in Anhydrous Hydrogen Fluoride ( $\Omega^{-1} \text{ cm}^{-1}$ )

AHF	$1.8 \times 10^{-4}$	KBF <sub>4</sub>	$1.8 \times 10^{-2}$
MoOF <sub>4</sub>	$3.5 \times 10^{-4}$	NaF	$3.7 \times 10^{-2}$
WOF <sub>4</sub>	$2.2 \times 10^{-2}$		

found to react with mercury;<sup>15</sup> therefore its electrochemistry was studied at a platinum electrode. One well-defined reduction wave was observed in neutral medium (Table III, Figure 3). Alternating current and second harmonic techniques were used as an additional check (Figure 4). One well-defined wave was obtained in each case, implying that the reduction involves fast electron transfer between two relatively simple species.

The structure of solid MoOF<sub>4</sub> is known to consist of endless chains of octahedra linked by fluorine bridges.<sup>17</sup> The compound has a high entropy of vaporization which suggests that it is polymeric in the liquid phase.<sup>18</sup> However, there is mass spectral evidence to indicate that in the gas phase, at least, it is monomeric.<sup>19</sup> Very little is known about its structure in HF solution.

As part of a detailed study of vapor pressures of various solutes in AHF, O'Donnell and Peel used a null-point bellows manometer to establish reliable experimental procedures for measuring vapor pressures in AHF and related lowering of vapor pressures to concentration, or degree of association or dissociation, of a solute in AHF.<sup>20</sup> Using their apparatus, Hutchison<sup>21</sup> was able to establish a  $\nu$  value of 1 for a solution of MoOF<sub>4</sub> in AHF. He proposed that MoOF<sub>4</sub> either exists in solution as a five-coordinate monomer or dimerizes according to the equation



Conductance measurements in AHF allow a choice between these possibilities; Table IV shows that a solution of MoOF<sub>4</sub> in AHF is nonconducting and hence the process represented by eq 3 does not occur to any significant degree.

In our previous paper we stated that the oxofluoro species formed by the dissolution of WOF<sub>4</sub> in AHF must be relatively simple because of its electrochemical behavior.<sup>12</sup> Vapor pressure measurements on solutions of WOF<sub>4</sub> in AHF gave a value for  $\nu$  of 2,<sup>22</sup> which suggests that WOF<sub>4</sub> is acting as a Lewis acid in AHF according to the equation



Further support for this proposition comes from conductance measurements (Table IV) which show that a solution of WOF<sub>4</sub> in AHF conducts and has a specific conductance typical of a 1:1 electrolyte. From Table IV it can be seen that the specific conductance of 0.5 M WOF<sub>4</sub> in AHF is slightly less than that of 0.5 M NaF which is probably a reflection of the abnormally high mobility of the fluoride ion.<sup>23</sup>

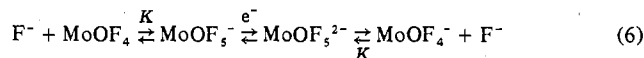
These conductances and colligative properties show that in neutral solution MoOF<sub>4</sub> exists predominantly as the monomer. Its electrochemistry in a neutral medium assuming no supporting electrolyte interaction is therefore described by a simple one-electron reduction



which has a value for  $E_{1/2}$  of 0.47 V. This can be contrasted with the behavior of WOF<sub>4</sub> where a chemically irreversible reduction process showing fluoride concentration dependence was found. The very different electrochemistry of the two oxide fluorides will be discussed after considering subsequent data.

**Molybdenum Oxide Tetrafluoride in Sodium Fluoride Solution.** The addition of fluoride to a solution of MoOF<sub>4</sub> and KBF<sub>4</sub> in HF had no effect on either the position or the shape

of the reduction wave. This behavior is somewhat surprising. Two possible explanations might be that either the oxide tetrafluoride exists as MoOF<sub>4</sub> even in strongly basic solutions or that both the anions MoOF<sub>5</sub><sup>-</sup> and MoOF<sub>5</sub><sup>2-</sup> are rapidly formed in supporting electrolyte solution with similar stability constants  $K$  and  $K'$ , respectively. The latter possibility is more likely chemically, suggesting that in basic media the electrode process should be represented by the equation



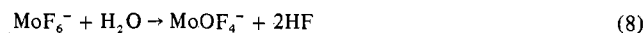
**Addition of Water to Molybdenum Hexafluoride in Anhydrous Hydrogen Fluoride.** When water was deliberately added to a solution of MoF<sub>6</sub> in either neutral or basic solution, the two reduction waves observed previously decreased in height and a new reduction wave appeared as a shoulder on the second wave. At a stoichiometric ratio of 1:1 for H<sub>2</sub>O to MoF<sub>6</sub>, only the new reduction wave could be observed, the potential of which corresponded to that found previously for MoOF<sub>4</sub> in the same medium.

This is consistent with the hydrolysis reaction



Additional water, up to a 2:1 mole ratio for H<sub>2</sub>O to MoF<sub>6</sub>, produced no further changes in the recorded voltammograms. This behavior was also observed when water was added to a solution in AHF of MoOF<sub>4</sub> itself.

**Addition of Water to Sodium Hexafluoromolybdate(V) in Anhydrous Hydrogen Fluoride.** The deliberate addition of water to solutions of NaMoF<sub>6</sub> in either neutral or basic medium caused the two previously observed waves to be replaced by a new oxidation wave at a stoichiometry of 1:1 for H<sub>2</sub>O to NaMoF<sub>6</sub>. The oxide fluoride species produced showed the same electrochemical behavior as that formed on reduction of MoOF<sub>4</sub>. Reaction 8 must therefore have occurred. Within



the time scale of the experiment no oxofluoro species of Mo(VI) were observed which suggests that the Mo(V) oxide fluoride formed by hydrolysis is more stable than its tungsten analogue which underwent rearrangement under similar conditions.<sup>12</sup>

In the light of this work and of the earlier experiments,<sup>12</sup> the marked difference in the electrochemistry of the WOF<sub>4</sub> and MoOF<sub>4</sub> systems appears to be bound up with the properties of the compounds in oxidation state V, rather than those in oxidation state VI. WOF<sub>4</sub><sup>-</sup> and WOF<sub>5</sub><sup>2-</sup> appear to have no inherent stability in anhydrous hydrogen fluoride in direct contrast to MoOF<sub>4</sub><sup>-</sup> and MoOF<sub>5</sub><sup>2-</sup>. Similar generalizations can be made from a consideration of the known chemistry of the binary pentafluorides of the two metals.

**Comparison of the Oxidant Strengths of Molybdenum and Tungsten Hexafluorides.** Since both systems gave reversible electrochemical behavior, the observed values for  $E_{1/2}$  are direct measures of the reduction potentials  $E^\circ$  for the WF<sub>6</sub>/WF<sub>6</sub><sup>-</sup> and MoF<sub>6</sub>/MoF<sub>6</sub><sup>-</sup> couples. Examination of the values of  $E^\circ$  for the two couples shows that WF<sub>6</sub> is a very mild oxidant since it is reduced at a negative potential (-0.11 V) with respect to the Cu/CuF<sub>2</sub> reference electrode.  $E^\circ$  for the MoF<sub>6</sub>/MoF<sub>6</sub><sup>-</sup> couple occurs at a much more positive potential and hence MoF<sub>6</sub> is shown to be the stronger oxidant of the two, which is in agreement with the findings of the earlier chemical studies<sup>6-8</sup> and with recent estimates of the electron affinities for the two hexafluorides.<sup>24</sup>

The observed difference of  $E^\circ$  of 1 V for the reduction of MoF<sub>6</sub> and WF<sub>6</sub> is much greater than had been anticipated, particularly when aqueous systems are considered. It provides quantitative evidence that MoF<sub>6</sub> is a much stronger oxidant than WF<sub>6</sub> in fluoride media.

The more negative of the two reversible one-electron waves observed for both  $\text{MoF}_6$  and  $\text{MoF}_6^-$  was assigned to the reduction of  $\text{MoF}_6^-$  to  $\text{MoF}_6^{2-}$ . A corresponding couple could not be satisfactorily characterized in the tungsten system. Assuming that the wave near the solvent limit was due to the reduction of  $\text{WF}_6^-$ ,<sup>12</sup> a comparison of the relative magnitudes of the values of  $E_p$  for both systems again shows a difference of about 1 V. This is the first reported information about chemical reactivity differences of transition metal fluorides in oxidation states lower than VI.

The reduction of  $\text{WF}_6$  to  $\text{WF}_6^-$  occurs at potentials more negative than the oxidation potential for mercury. Hence, mercury would therefore not be expected to reduce  $\text{WF}_6$  in AHF and we have found this experimentally.<sup>15</sup> It is therefore somewhat unexpected that  $\text{WF}_6$  has been reported as having reacted with mercury in the different solvent system, acetonitrile.<sup>25</sup>

The position of the observed values of  $E_{1/2}$  for both  $\text{MoF}_6/\text{MoF}_6^-$  and  $\text{WF}_6/\text{WF}_6^-$  couples showed no dependence on fluoride concentration. This, together with the findings of Frlc and Hyman,<sup>16</sup> means that fluoro anions of the type  $\text{MF}_7^-$  or  $\text{MF}_8^{2-}$  ( $M = \text{W}$  or  $\text{Mo}$ ) cannot be playing any significant part in the solution or the electrode processes. Evidence that the anion  $\text{WF}_7^-$  is unlikely to occur in AHF solution comes from the work of Geichman et al., who showed that AHF displaced  $\text{WF}_6$  from the salt  $\text{NOWF}_7$ .<sup>26</sup> The anion  $\text{WF}_7^-$  has however been postulated as existing in acetonitrile<sup>25</sup> but there has been no report of its existence in AHF. The apparently large difference in solution chemistry between AHF and acetonitrile is not easy to rationalize at this stage.

**Comparison of the Solution Chemistry of Molybdenum and Tungsten Oxide Tetrafluorides.** From both vapor pressure and conductance measurements on solutions of  $\text{WOF}_4$  and  $\text{MoOF}_4$  in AHF, it was established that their respective interactions with the solvent were totally different, in marked contrast to the identical solution processes for the two hexafluorides.

Molybdenum oxide tetrafluoride was found to exist as a five-coordinate monomer in solution while  $\text{WOF}_4$  exists essentially as the  $\text{WOF}_5^-$  anion. That  $\text{MoOF}_4$  shows no appreciable Lewis acidity in AHF is surprising since the synthesis of both the anions  $\text{MoOF}_5^-$ <sup>27</sup> and  $\text{Mo}_2\text{O}_2\text{F}_9^-$ <sup>28</sup> in the solid state has been reported. The analogous tungsten anions are also known in solid compounds<sup>28,29</sup> and therefore at first sight it is somewhat surprising that  $\text{WOF}_4$  acts as a strong Lewis acid in AHF while  $\text{MoOF}_4$  does not. However, it has been reported recently that in AHF,  $\text{WOF}_4$  is a stronger Lewis acid than  $\text{MoOF}_4$  although it was postulated from <sup>19</sup>F NMR observations that the charged tungsten entity was the dimeric anion.<sup>30</sup>

The cyclic voltammetric study of  $\text{MoOF}_4$  was fairly straightforward, in marked contrast to that for  $\text{WOF}_4$  which was complicated by irreversibility, fluoro-complexing, and a rearrangement reaction.<sup>12</sup> As expected, the reduction wave

for  $\text{MoOF}_4$  appeared at more negative potentials than that for the initial reduction of  $\text{MoF}_6$ , since the oxide fluoride results from the thermodynamically favorable hydrolysis of  $\text{MoF}_6$ .

The potential of the  $\text{MoOF}_4/\text{MoOF}_4^-$  couple is such that  $\text{MoOF}_4$  is a stronger oxidant than both  $\text{MoF}_6^-$  and  $\text{WF}_6$ . Because of its complex electrochemistry in AHF, it was not possible to assign a value for  $E^\circ$  for the  $\text{WOF}_4/\text{WOF}_4^-$  couple, but it occurs at more negative potentials than that obtained for the  $\text{WF}_6/\text{WF}_6^-$  couple. This means that  $\text{MoOF}_4$  and  $\text{WOF}_4$ , like the respective hexafluorides, differ in oxidant strength by a substantial amount.

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**Registry No.**  $\text{MoF}_6$ , 7783-77-9;  $\text{NaMoF}_6$ , 41729-23-1;  $\text{MoOF}_4$ , 14459-59-7;  $\text{WOF}_4$ , 13520-79-1; AHF, 7664-39-3;  $\text{KBF}_4$ , 14075-53-7; NaF, 7681-49-4.

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