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ELECTROCHEMICAL STUDIES OF HEXAFLUOROTUNGSTATE(V) AND TUNGSTEN OXIDE TETRAFLUORIDE IN ACETONITRILE

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SUMMARY

High oxidation state fluorides can be studied electrochemically in the conventional solvent acetonitrile. Alkali metal hexafluorotungstates(V) are substantially soluble in acetonitrile and have been studied by cyclic voltammetry using vacuum line techniques for solution manipulation. $[WF_6]^-$ is oxidised to WF_6 at +0.81 V vs SCE and is not reduced over a wide potential range. WOF_4 in acetonitrile is reduced at -1.1 V vs SCE. Electrogenerated WF_6 is slowly hydrolysed to WOF_4 in acetonitrile.

INTRODUCTION

It has previously been shown [1] that solutions of tungsten hexafluoride in acetonitrile react with various transition metals to give hexafluorotungstate(V) salts of solvated metal

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cations; in no case was there further reduction of the tungsten (V) species. Detailed electrochemical studies of these species are hampered by the redox activity of the cations.

Alkali metal hexafluorotungstates(V) have been previously prepared by reduction of tungsten hexafluoride in liquid sulphur dioxide with alkali iodides [2] or in anhydrous hydrogen fluoride with metallic cadmium [3]. The first method does not reliably give pure products whilst the second method involves the use of anhydrous HF which presents experimental difficulties It is now found that the reduction of WF_6 by sodium or potassium iodides can be carried out in acetonitrile to give clean products which are soluble to 1M in that solvent. The solutions show a characteristic Raman band between 695 and 700 cm^{-1} [1].

The observation that such highly reactive fluorine-containing compounds could be successfully handled in acetonitrile suggested the possibility of using this solvent and these solutions in electrochemical studies.

The electrochemistry of fluorotungstates(V) has been studied in anhydrous hydrogen fluoride [3,4]. However, this solvent has a fairly limited potential range and requires specialised apparatus and techniques [4] for its manipulation. Further, as the solvent is a fluorinating agent its use cannot be extended to related non-fluorine-containing species.

We now report that the hexafluorotungstates(V) can be studied electrochemically in acetonitrile. In contrast to hydrogen fluoride, acetonitrile may be handled by conventional vacuum line techniques and is an excellent electrochemical solvent with a very wide potential range (+2.4 to -2.7 V vs Ag/AgCl) at a platinum electrode [5]. This conventional electrochemical solvent allows direct comparison between fluoro-species and halometallates [6] and other species.

Because of the highly reactive nature of high oxidation state fluorometallates, particularly towards hydrolysis, existing methods of solvent purification [7] have proved inadequate and have needed improvement. Tetraethylammonium tetrafluoroborate, Et_4NBF_4, was used as the supporting electrolyte as perchlorate ion was found to react with tungsten hexafluoride in acetonitril

The electrochemical studies were carried out by cyclic voltammetry in an evacuable all-glass cell for which all manipulations involving addition of reactants or solvents could be carried out on a vacuum line. To assist in the exclusion of moisture, design complexity was minimised by sealing three platinum wires into the vessel walls to serve as working, auxiliary, and quasi-reference [8] electrodes respectively.

The findings detailed below suggest that a simple satisfactory method for electrochemical studies of highly reactive species, particularly fluorides in high oxidation states, has been developed.

RESULTS AND DISCUSSION

Cyclic voltammetry establishes that the hexafluorotungstate(V) ion does not undergo reduction in acetonitrile at a platinum electrode over the wide cathodic range. Hexafluorotungstate(V) does, however, undergo a one electron oxidation at +0.8 V vs SCE (Table). For approximately 10^{-2}M hexafluorotungstate(V) at moderate scan rates (ν >200 mV s^{-1}) the anodic to cathodic peak current ratio is close to 10 although the peak to peak separation is greater than the 60 mV expected for a fully reversible one electron oxidation. At lower concentrations of hexafluorotungstate(V) there is an irreversible reaction of the tungsten hexafluoride formed at the electrode and this is ascribed to hydrolysis of solvated tungsten oxide tetrafluoride by residual traces of water. The return (cathodic) wave becomes much smaller than the forward (anodic) wave particuarly at slower scan rates. Deliberate microaddition of water removes the cathodic peak, further establishing that hydrolysis of the electrogenerated tungsten hexafluoride is the cause of the irreversibility. The decrease in the return peak height coincides with the appearance of a quasi-reversible reduction at -1.10 V vs SCE indicating the hydrolysis product also to be electroactive giving rise to a characteristic ECE voltammagram [9].

TABLE

Cyclic voltammetric data

Compound	$E_{\frac{1}{2}}$/V vs SCE*	ΔE_p/mV	I_{Pa}/I_{Pc}	Couple
KWF_6	+0.82	100	1.1	VI/V
$NaWF_6$	+0.81	95	1.1	VI/V
WOF_4	-1.10	100	1.0	VI/V
$NaWCl_6$ (ref.6)	+1.65	85	0.9	VI/V
$NaWCl_6$	+0.35	70	1.0	V/IV
$NaWCl_6$	-1.2	100	0.9	IV/III

*$E_{\frac{1}{2}}$ values measured vs added ferrocene and corrected by +0.35 volt.

Independently prepared tungsten oxide tetrafluoride undergoes a quasi-reversible reduction in acetonitrile at this same potential and with the same peak to peak separation confirming solvated WOF_4 as the immediate hydrolysis product of electrogenerated WF_6. The electrochemical reduction of tungsten oxide tetrafluoride in acetonitrile appears to be simpler than in anhydrous hydrogen fluoride. The extra waves observed [3] in the latter solvent may represent a genuine difference in stability of the reduced WOF_4 species in the two solvents or may be due to impurities. The quasi-reversible nature of the WOF_4 reduction in acetonitrile suggests that substantial structural rearrangement is unlikely and that tungsten(V) oxide fluoride species have a definite stability in acetonitrile.

Thus, the electrode processes may be summarised as follows. In the absence of water WF_6^- undergoes a simple almost fully reversible charge transfer.

$$[WF_6]^-_{solv.} \xrightleftharpoons[+0.82V]{e} WF_6$$

In the presence of trace water the process becomes

$$[WF_6]^-_{solv.} \xrightleftharpoons[+0.82V]{-e} WF_6 \xrightarrow{H_2O} [WOF_4]_{solv.} \xrightleftharpoons[-1.10V]{+e} [WOF_4]$$

Comparison of the present electrochemical data for hexafluorotungstate(V) in acetonitrile with previous studies of hexachlorotungstate(V) in that solvent (Table) quantifies the marked stabilising effect of fluoride over chloride in higher oxidation states. In acetonitrile the Vl/V couples differ by 0.8 V and, strikingly, no further reduction is observed for the fluoride over a 3 volt cathodic range. The previous studies in anhydrous hydrogen fluoride, being restricted to 0.7 volt negative of the $WF_6/[WF_6]^-$ couple, could not reveal this feature. It is, however, consistent with the failure of metals to reduce $[WF_6]^-$ [1] and with the failure of caesium fluoride to react with tungsten tetrafluoride formed in acetonitrile [10]. It appears that hexafluorotungstate(IV) anions have little stability in acetonitrile.

The unexpected reaction between tungsten hexafluoride and perchlorate in acetonitrile was first detected electrochemically but it was subsequently observed that a mixture of solutions of WF_6 and Et_4NClO_4 in acetonitrile rapidly turns yellow and then dark brown. The ^{19}F n.m.r. spectrum of the coloured solution shows a tungsten oxide fluoride peak at -70 p.p.m. (reference $CFCl_3$). Although positive identification of products was not possible owing to the deep colour of the solution which prevented Raman spectroscopy, it appears likely that there is oxygen-abstraction or, more probably, oxygen-fluoride exchange between chlorine and tungsten and that the reactive chlorine species formed, possibly a chlorine oxide fluoride, attacks the solvent.

EXPERIMENTAL

Acetonitrile (BDH) was first purified by the method of Walter and Ramaley [7]. This material was then distilled three times from P_2O_5 and, whilst still warm was passed through an alumina (Woelm - neutral heated for 24 hours at 350 - 400°) column. The treated acetonitrile was distilled five times over 3A molecular sieves which had been previously heated at 250 - 300° for 24 hours. The method described removes most of the water and also acrylonitrile. One litre acetonitrile yields 500 ml purified solvent. This procedure is very similar to that of Burfield et al [11].

Tungsten hexafluoride (Ozark-Mahoning) was stored over NaF before use. NaI, KF, KI (Hopkins and Williams) and NaF (BDH) were dried in vacuo for 24 hours after an initial heating in vacuo. Hexamethyldisiloxane (Koch-Light) was distilled over 4A molecular sieves before use.

All manipulations involving purified acetonitrile and tungsten hexafluoride were carried out on a flamed out vacuum line fitted with RotaFlo stopcocks.

Sodium and potassium hexafluorotungstates(V) were prepared by reacting 0.4 g alkali metal iodide with excess tungsten hexafluoride in acetonitrile. The reactants were allowed to stand at room temperature for 4 - 6 hours and volatiles (solvent iodine, and other by products) were removed under dynamic vacuum. Trace iodine was removed by successive readdition of acetonitrile followed by pumping for 2 - 3 hours. The hexafluorotungstate(V) formed is completely soluble in about 2.5 ml acetonitrile (0.1M).

Tungsten oxide tetrafluoride was prepared [12] by reaction between 0.35 g hexamethyldisiloxane dissolved in 3.74 g acetonitrile and excess of tungsten hexafluoride.

Tetraethylammonium fluoroborate, Et_4NBF_4, was prepared by neutralising (pH meter) tetraethylammonium hydroxide with fluoroboric acid. The crude product was recrystallised from methanol and the sample dried in vacuo at 80 - 100° for 24 hours. Tetraethylammonium perchloriate was prepared similarly.

Electrochemical measurements were carried out using the cell described in the Discussion employing 0.1M supporting electrolyte and 10^{-2} to 10^{-3} of the electroactive species. Positive feedback circuitry (PAR 170 system) was used throughout to provide full compensation for ohmic losses. Added ferrocene was used to provide an internal reference potential [13]. Hexafluorotungstate(V) does not react with ferrocene although there is oxidation of ferrocene by WF_6. All electrochemical measurements were preceded by Raman confirmation of the species and monitoring of impurities present; where feasible, Raman identification also followed the electrochemical measurements.

Raman spectroscopy was carried out using a Spex-Ramalog spectrophotometer. N.m.r. spectra were recorded on a Jeol C60HL high resolution n.m.r. spectrometer.

Solutions of tetraethylammonium tetrafluoroborate and sodium hexafluorotungstate(V) slowly give a white precipitate of sodium tetrafluoroborate on standing. $NaBF_4$ is soluble in acetonitrile to less than 0.05M but the precipitation does not appear to affect the electrochemical results.

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