Journal of Fluorine Chemistry, 57 (1992) 147–154

Oxidation of tellurium by molybdenum and uranium hexafluoride in acetonitrile and reactions between uranium hexafluoride and dichlorine or hydrogen chloride in acetonitrile*

Laurence McGhee and John M. Winfield
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ (UK)

Abstract

Reactions between elemental tellurium and UF_6 or MoF_6 at room temperature lead to the isolation of solid products formulated as $[Te^{IV}F_3(NCMe)_2][M^{V}F_6][M^{V}F_5(NCMe)]_3$ (M = Mo or U) on the basis of their spectroscopic properties. In contrast, oxidation of Te by SbF_5, AsF_5 or the $[NO]^+$ cation in MeCN appears to be limited to the formation of the $[Te_4]^{2+}$ cation. Uranium hexafluoride is reduced to $[UF_5(NCMe)]$ in the presence of Cl_2 or HCl in MeCN, the reduction being followed by Cl-for-F exchange to give $[UF_{5-x}Cl_x(NCMe)]$ mixtures. A rationalization of these reactions is presented.

Introduction

The oxidation of diiodine by molybdenum and uranium hexafluorides and dibromine by uranium hexafluoride, in all cases using acetonitrile as solvent, has been reported from these laboratories [2, 3]. Oxidation of I_2 leads to the solvated cation salts $[I(NCMe)_2][M^{V}F_6]$ (M = Mo or U) [2], while the product from Br_2 oxidation is $[Br(C_6H_9N_3)][U^{V}F_6]$ in which a bromine atom is bound to a MeCN trimer containing C=N bonds [3]. The examination of the reaction between these hexafluorides and elemental tellurium or chlorine is a natural extension of this work and the results of our study are now reported.

The oxidation of Te under acidic conditions to give polyatomic cations is well documented [4–8]. Crystal structures of salts containing $[Te_4]^{2+}$ [9, 10], $[Te_6]^{4+}$ [11] and $[Te_8]^{2+}$ [8] have been described and the vibrational spectra of $[Te_4]^{2+}$ [12, 13], the ^{125}Te NMR spectra of $[Te_4]^{2+}$ and $[Te_6]^{4+}$ [14], and the Mössbauer spectra of these cations [15] have all been studied. The only simple chlorine cation that has been described adequately appears to be the thermally unstable $[Cl_3]^+$ formed at 203 K from the reaction between AsF_5 and a $Cl_2 + ClF$ mixture [16].

---

*Some of this work was reported at the 9th European Symposium on Fluorine Chemistry, Leicester, Sept. 1989; see ref. 1.

0022-1139/92/$5.00

Experimental

The work was carried out in Pyrex vessels using vacuum, glove-box, reagent purification and spectroscopic techniques that, except where detailed below, have been described elsewhere [2, 3, 17].

Oxidation of tellurium

With MoF_6 and UF_6

A tellurium ingot (Specpure, 99.999%) was broken in the glove box and a small piece (0.25 g 1.96 mmol) added to one limb of a double-limb Pyrex vessel. Purified, dried MeCN (5 ml) followed by MoF_6 (10 mmol) were added by vacuum distillation. When the mixture reached room temperature a pink colouration developed at the tellurium surface and after *ca.* 1 h the solution was blood-red. Thereafter the colour faded and finally, after a further 4 h, a pale yellow solution was obtained. Removal of the material volatile at room temperature left an off-white solid (Found: C, 10.2; H, 1.2: F, 38.7; N, 5.9; Mo, 33.0, Te 10.8%. Calcd. for $C_{10}H_{15}F_{24}N_5Mo_4Te$: C, 10.2; H, 1.3; F, 38.9; N, 6.0; Mo, 32.7; Te, 10.8%). The solid was formulated as $[TeF_3(NCMe)_2][MoF_6][MoF_5(NCMe)]_3$ on the basis of its vibrational, electronic and ^{125}Te NMR spectra (Bruker WP 200 SY instrument at 63.194 MHz; Me_2Te as external reference). The solvent EtCN was used for spectra obtained below 243 K.

Termination of the reaction after 1 h, while the solution was still red, resulted in an off-white solid being isolated whose spectroscopic properties were identical to those of the solid described above. Apparently the reaction continued during the process of isolation and coloured solids were never isolated.

The reaction between Te and UF_6 was performed in an identical manner. A light green colouration was observed at room temperature, darkening to give a blue–green solution within 0.5 h. The reaction appeared to be faster than its MoF_6 counterpart and the red intermediate colouration was never observed. The pale green, crystalline solid was isolated (Found: C, 6.9; H, 0.8; F, 26.0; N, 4.1; Te, 7.1; U, 54.5%. Calcd. for $C_{10}H_{12}F_{24}N_5TeU_4$: C, 6.9; H, 0.9; F, 26.2; N, 4.0; Te, 7.3; U, 54.7%) was formulated as $[TeF_3(NCMe)_2][UF_6][UF_5(NCMe)]_3$.

With $[NO][PF_6]$, $AsF_5(NCMe)$ or $SbF_5(NCMe)$

Tellurium (0.1 g, 0.8 mmol) and $[NO][PF_6]$ (0.5 g, 2.8 mmol) were mixed in a double-limb vessel or evacuable Spectrosil cell in the glove box, and MeCN (5 ml) was added by vacuum distillation. A gas, presumed to be NO, was evolved at room temperature and a pink solution, $\lambda_{max} = 522$ nm, formed. Removal of volatile material always resulted in a brown, sticky solid being formed.

Reaction between Te (0.1 g, 0.8 mmol) and $MF_5(NCMe)$ (M = As or Sb; 4.8 mmol) in MeCN (5 ml) also resulted in pale pink solutions, $\lambda_{max} =$

523 nm, after shaking overnight. Little change occurred after 1 week. The pale pink solids isolated showed bands in their vibrational spectra characteristic of $MF_5(NCMe)$ and $[MF_6]^-$ anions [18].

Reactions involving dichlorine or hydrogen chloride

$Cl_2 + UF_6$ *in MeCN*

A solution of Cl_2 (2.0 mmol; Matheson Ltd., previously treated with $KMnO_4$ then P_2O_5) in MeCN (5 ml) was prepared *in vacuo* and UF_6 (*ca.* 0.5 mmol) was added to the frozen solution by vacuum distillation. On warming the mixture slowly to room temperature, a lime-green solution was formed from which a pale green solid could be isolated after low-temperature distillation. The spectroscopic properties of solids isolated from several reactions depended on the time of the reaction. Isolation of products at room temperature resulted in brown materials containing U, F and Cl being formed, presumably due to polymerization of MeCN. Changes in the electronic spectrum of the solution during reaction (up to 72 h) were followed by preparing an identical mixture in a Spectrosil cell and recording spectra at regular intervals.

$HCl + UF_6$ *in MeCN*

Anhydrous HCl (0.6 mmol; prepared as described in ref. 19) was distilled onto a frozen mixture of UF_6 (0.1 mmol) in MeCN (5 ml) at 77 K and the mixture was warmed slowly to room temperature. The electronic spectrum of the green solution that was formed resembled that reported for $[UFCl_4(NCMe)_x]$ [20]. A frangible ampoule containing triphenylphosphine oxide (0.5 g) was broken into a solution prepared from UF_6 (0.09 mmol), HCl (*ca.* 0.5 mmol) and MeCN (5 ml) after the solution had stood for 1 hour at room temperature. Removal of volatile material left a green crystalline solid whose IR and electronic spectra were consistent with it being predominantly $[UF_5(OPPh_3)]$ [20]. If the solution was allowed to stand for several hours before Ph_3PO was added, a yellow, sticky solid was isolated whose spectra indicated the presence of $[UF_{5-n}Cl_n(OPPh_3)]$ ($n \geqslant 3$) [20].

Results

Oxidation of tellurium in the presence of acetonitrile

Both UF_6 and MoF_6 react readily with elemental Te in the presence of acetonitrile at room temperature. The progress of the reaction may be followed conveniently by electronic spectroscopy. In the UF_6 case, the spectrum of the reaction mixture was dominated by groups of bands in the near IR, visible and near UV regions characteristic of the $[UF_6]^-$ anion [21] and $[UF_5(NCMe)_x]$ [22]. The spectrum of the green–blue solid isolated from the reaction and redissolved in MeCN was identical. The electronic spectrum of the MoF_6 reaction mixture consisted of a band, $\lambda_{max} = 445$ nm, whose intensity increased during the initial part of the reaction and a high absorbance near

300 nm. The former was tentatively assigned to the $[Te_4]^{2+}$ cation by comparison with the spectra of polyatomic tellurium cations recorded in strongly acidic solvents [11]. As the reaction proceeded, the band intensity at 445 nm decreased and the high energy region was resolved into three bands, $\lambda_{max} = 320$, 242 and 205 nm ($\epsilon = 44$, 33 and 19 $mol^{-1}dm^3cm^{-1}$). These bands were present also in the spectrum of the off-white solid isolated and redissolved in MeCN. They do not correspond to any of the polyatomic tellurium cations so far reported.

Both reaction products exhibited broad singlets in their ^{125}Te NMR spectra, recorded in EtCN/MeCN, $\delta(^{125}Te) = 1313$ (UF_6 product) and 1369 ppm. (MoF_6 product), with respect to Me_2Te, and were temperature invariant over the range 293 to 213 K. In SO_2 solution at 200 K, $\delta(^{125}Te) = 1325$ ppm. These data suggested strongly that Te^{IV} was present, by analogy with the spectra of TeF_4 and $[TeF_3]^+$ in SO_2 [23]. No signals were observed that could be attributed to polyatomic Te cations [14]. Attempts to resolve ^{19}F–^{125}Te coupling by adding $AsF_5(NCMe)$ to suppress exchange, a technique which was used for $[TeF_3][AsF_6]$ in SO_2 [23], were unsuccessful although a slight narrowing was observed in SO_2 at 200 K.

The vibrational spectra of both reaction products provided good evidence for the presence of $[MF_6]^-$ anions and the adducts $[MF_5(NCMe)]$ (M = U or Mo) (Fig. 1). The band identifications in Table 1 were made by comparison with spectra of salts containing $[UF_6]^-$ [21] or $[MoF_6]^-$ anions [2, 24], $[MoF_5(NCMe)]$ [25] and $[UF_5(NCMe)]$ [20, 22, 26]. Although there is disagreement regarding the nature of UF_5 in MeCN solution and the assignments appropriate in the vibrational spectrum of the solid adduct, the spectral data reported are in substantial agreement and the disagreement does not detract from the identification. Unfortunately, the spectra provide no definitive evidence for the existence of Te^{IV}–F species. By analogy with the vibrational spectrum of $TeF_4(py)$, ν(Te–F) bands would be expected in the region 600

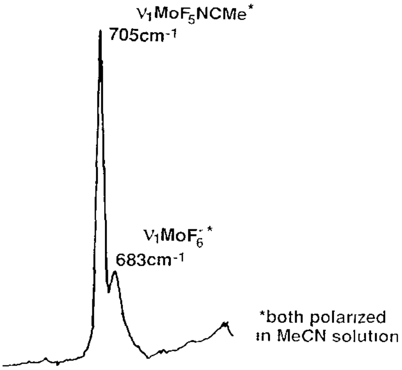

Fig. 1. Raman spectrum of solid $[TeF_3(NCMe)_2][MoF_6]3MoF_5(NCMe)$. *Polarized in MeCN solution.

TABLE 1

Vibrational spectra[a] of the products from the reactions of Te with UF_6 or MoF_6 in the presence of MeCN

IR solid $\nu_{(max)}$ (cm^{-1})	Raman $\Delta\nu$ (cm^{-1})		Assignments to MF species
	Solid	In MeCN	
(*a*) *UF_6* reaction product			
680m			
	612w	612m, pol	$[UF_6]^- \nu_1 + UF_5(NCMe)$
		604m, pol	$UF_5(NCMe)$
	592m		$UF_5(NCMe)$
570s			$UF_5(NCMe)$
520vs			$[UF_6]^- \nu_3 + UF_5(NCMe)$
315w	308m		
265w			
	243w		
(*b*) *MoF_6* reaction product			
703s	705s	705s, pol	$MoF_5(NCMe)$
	683m	683m, pol	$[MoF_6]^- \nu_1$
650s			$MoF_5(NCMe)$
635vs			$[MoF_6]^- \nu_3$ $[+MoF_5(NCMe)]$
295s			$MoF_5(NCMe)$
240s			$MoF_5(NCMe)$
225s	220m		$[MoF_6]^- \nu_5 + ?$
	215w		

s, strong; m, medium; w, weak; pol, polarized.

[a] Bands due to coordinated MeCN are not included.

to 500 cm^{-1} [27]. In the spectra of the reaction products, they were presumably obscured by metal–fluorine stretching bands.

In contrast to the above reactions, those between Te and $[NO][PF_6]$ or $[MF_5(NCMe)]$ (M = As or Sb), in the presence of MeCN at room temperature, were very slow. Even after 5 days, reaction was incomplete and appeared from electronic spectroscopy to be limited to the formation of $[Te_4]^{2+}$. There was no observable reaction between Te and WF_6 under identical conditions.

Reactions occurring in the dichlorine/uranium hexafluoride/acetonitrile system

Addition of UF_6 to a frozen solution of Cl_2 in MeCN (mole ratio, $Cl_2:UF_6 > 3:1$) led to the rapid formation of $[UF_5(NCMe)_x]$ followed by the progressive replacement of F by Cl with time. Species identified at various points in the reaction by electronic spectroscopy are given in Fig. 2, spectral assignments being made by comparison with previous studies of the stepwise chlorination of UF_5 in MeCN [20, 28]. The spectroscopic properties of the green solids isolated from this mixture depended on the reaction time and the isolation temperature, but in all cases there was evidence for $[UF_5(NCMe)]$,

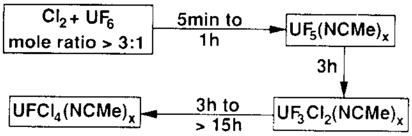

Fig. 2. Predominant species in MeCN solution identified by electronic spectroscopy up to 72 h at room temperature.

the anion $[UF_6]^-$ and the organic moieties $-C{\equiv}N$, $\gt C{=}N$, $\gt NH$, $-CH_2-$ and $-CH_3$. Substantial attack on the solvent occurred when long reaction times were used and this led to the isolation of brown solids. NMR spectra of the colourless material extracted after hydrolysis indicated that the organic groups listed above were present, and mass spectrometry results were consistent with the presence of CCl_3CN and related compounds.

Formation of uranium(V) occurred from the reaction between UF_6 and anhydrous HCl in MeCN, as indicated by the precipitation of $[UF_5(OPPh_3)]$ [20] on addition of Ph_3PO to the solution after the reaction had proceeded for several hours. However Cl-for-F exchange involving HCl appeared to be more rapid than in the Cl_2 case, since the electronic spectrum of a freshly prepared solution also contained bands attributable to $[UFCl_4(NCMe)_x]$ (cf. Fig. 2).

Discussion

Oxidation of tellurium by the strong one-electron oxidants molybdenum and uranium hexafluorides, in the presence of acetonitrile, leads to products which are distinctly different from those that result from iodine or bromine oxidation under comparable conditions [2, 3]. The micro-crystalline solids produced are formulated on the basis of analysis and the spectroscopic properties described above as $[Te^{IV}F_3(NCMe)_2][M^VF_6][M^VF_5(NCMe)]_3$ (M = Mo or U). Although no definitive evidence has been obtained for the cation $[TeF_3(NCMe)_2]^+$ (attempts to grow suitable single crystals for X-ray diffraction have so far proved unsuccessful), the formulation is reasonable in view of the formulation of 1:1 TeF_4 adducts with organic bases as $[TeF_3(L)_2][TeF_5]$ (L = py, Me_3N or dioxan) on the basis of their vibrational spectra [27].

The unsolvated $[TeF_3]^+$ cation in $[TeF_3][Sb_2F_{11}]$ has C_{3v} symmetry [29] and the ^{125}Te NMR spectrum of the $[AsF_6]^-$ salt in SO_2 at 200 K exhibits ^{19}F–^{125}Te coupling [23], the latter observation being confirmed in the present work. The lack of observable coupling in the compounds prepared here is attributed either to the presence of paramagnetic M^V species or to an increase in the lability of Te^{IV}–F bonds due to ligated MeCN. By analogy with $[I(NCMe)_2]^+$, the formation of $[Te(NCMe)_5]^{4+}$ might have been expected, but evidently the ligating power of MeCN is insufficient to stabilize such a high oxidation state. The anions $[MF_6]^-$ (M = Mo or U) are known to be good F^- ion donors in MeCN [30], therefore the overall composition of the products is not unexpected. Whether there are any interactions among the $[TeF_3(NCMe)_2]^+$, $[MF_6]^-$ and $[MF_5(NCMe)]$ moieties remains a matter for speculation.

Although there is some evidence in the reaction of Te with MoF_6 for the $[Te_4]^{2+}$ cation as an intermediate species, in the basic solvent MeCN, formation of mononuclear Te^{IV} is favoured over polynuclear lower oxidation state cations. This is the reverse of the situation in super acids or liquid SO_2 [11]. The pentafluorides SbF_5 and AsF_5 (which are strong oxidizing agents in SO_2) are less effective in MeCN, since in this solvent they exist as $[MF_5(NCMe)]$ (M = As or Sb) [31]. Oxidation of Te by these reagents, as by the $[NO]^+$ cation, which is a weaker oxidant than MoF_6 [32], appears to be limited to the formation of $[Te_4]^{2+}$.

The reaction between dichlorine and UF_6 in MeCN is not as straightforward as those involving I_2 or Br_2 [2, 3]. Although uranium(V) fluoride species are formed in solution very rapidly, there is no evidence for chlorine-containing cations even as reaction intermediates. The formation of halogen-exchanged uranium(V) products (Fig. 2) appears to be the result of reactions that involved HCl rather than Cl_2. Reduction of UF_6 by MeCN at room temperature is very slow [21b]. Chlorination of MeCN by Cl_2, which is very slow at room temperature, can be catalysed by redox-active halides, for example $FeCl_3$ [33]. An explanation for the observations made in terms of a redox chlorination of MeCN is therefore plausible.

Chlorination of MeCN by Cl_2 probably occurs by a free-radical mechanism, the products being CH_2ClCN, CCl_3CN and HCl. The presence of additional HCl in the system increases the reaction rate [34]. Our observations can be explained by postulating that HCl produced in the reaction between Cl_2 and MeCN is responsible for the reduction of uranium(VI) to uranium(V) and for the subsequent halogen-exchange reactions. We conclude, therefore, that while UF_6 is capable of oxidizing HCl or Cl^- to Cl_2 in MeCN it does not oxidize Cl_2.

References

1 L. McGhee and J. M. Winfield, *J. Fluorine Chem*, *45* (1989) 55.
2 G. M. Anderson and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, (1986) 337.
3 L. McGhee, D. S. Rycroft and J. M. Winfield, *J. Fluorine Chem.*, *36* (1987) 351.
4 N. J. Bjerrum and G. P. Smith, *J. Am. Chem. Soc.*, *90* (1968) 4472.
5 N. J. Bjerrum, *Inorg. Chem.*, *9* (1970) 1965.
6 J. Barr, R. J. Gillespie, G. P. Pez, P. K. Ummat and O. C. Vaidya, *Inorg. Chem.*, *10* (1971) 362.
7 P. A. W. Dean, R. J. Gillespie and P. K. Ummat, *Inorg. Synth.*, *15* (1974) 213.
8 J. Beck, *Angew Chem. Internat. Edn. Engl.*, *29* (1990) 293.
9 T. W. Couch, D. A. Lokken and J. D. Corbett, *Inorg. Chem.*, *11* (1972) 357.
10 G. Cardinal, R. J. Gillespie, J. F. Sawyer and J. E. Vekris, *J. Chem. Soc., Dalton Trans.*, (1982) 765.
11 R. C. Burns, R. J. Gillespie, W.-C. Luk and D. R. Slim, *Inorg. Chem.*, *18* (1979) 3086.
12 R. C. Burns and R. J. Gillespie, *Inorg. Chem.*, *21* (1982) 3877.

13 R. J. H. Clark, T. J. Dines and L. T. H. Ferris, *J. Chem Soc., Dalton Trans*, (1982) 2237.

14 G. J. Schrobilgen, R. C. Burns and P Granger, *J. Chem Soc , Chem. Commun*, (1978) 957.

15 C. H. W. Jones, *Can J. Chem., 55* (1977) 3076.

16 R. J. Gillespie and M. J. Morton, *Inorg. Chem , 9* (1970) 811.

17 L. McGhee, R. M. Siddique and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, (1988) 1309.

18 G. M. Begun and A. C. Rutenberg, *Inorg. Chem , 6* (1967) 2212.

19 R. N. Maxson, *Inorg. Synth., 1* (1939) 147.

20 J. H. Holloway, G. M. Staunton, J A. Berry and D. Brown, *J. Less-Common Metals, 120* (1986) 71.

21 (a) M. J. Reisfeld and G. A. Crosby, *Inorg. Chem , 4* (1965) 65; (b) J. A. Berry, R. T. Poole, A. Prescott, D. W. A. Sharp and J. M. Winfield, *J. Chem Soc., Dalton Trans*, (1976) 272.

22 J. A. Berry, A. Prescott, D. W. A. Sharp and J. M. Winfield, *J. Fluorine Chem , 10* (1977) 247.

23 M. J. Collins and G. J. Schrobilgen, *Inorg. Chem , 24* (1985) 2608.

24 J. Shamir and J. G. Malm, *J. Inorg Nucl. Chem., Suppl*, (1976) 107.

25 J. C. Fuggle, D. W. A. Sharp and J. M. Winfield, *J. Fluorine Chem., 1* (1971/72) 427, N. Bao and J. M. Winfield, *J. Fluorine Chem , 50* (1990) 339.

26 G. W. Halstead, P. G. Eller and M. P. Eastman, *Inorg Chem , 18* (1979) 2867.

27 N. N. Greenwood, A. C. Sharma and B. P. Straughan, *J Chem. Soc. (A)*, (1968) 1561.

28 J. A. Berry, J. H. Holloway and D. Brown, *Inorg Nucl. Chem. Lett., 17* (1981) 5.

29 A. J. Edwards and P. Taylor, *J Chem. Soc (A)*, (1973) 2150.

30 D. K. Sanyal and J. M. Winfield, *J. Fluorine Chem., 24* (1983) 75.

31 A. C. Baxter, J. H. Cameron, A. McAuley, F. M. McLaren and J M. Winfield, *J. Fluorine Chem., 10* (1977) 289.

32 G. M. Anderson, J. Iqbal, D. W. A. Sharp, J. M. Winfield, J. H. Cameron and A. G McLeod, *J. Fluorine Chem., 24* (1984) 303.

33 T Draper, J. M. Winfield, A. Prescott and N. Winterton, *J. Chem. Res. (S)*, (1982) 146.

34 E. M Movsum-Zade, *Russ. Chem. Rev., 48* (1979) 282.