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REDOX REACTIONS INVOLVING RHENIUM AND URANIUM HEXAFLUORIDES. A CONVENIENT SYNTHESIS OF β-URANIUM PENTAFLUORIDE

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SUMMARY

Rhenium and uranium hexafluorides oxidise elemental iodine in iodine pentafluoride at ambient temperature to give the I_2^+ cation. With UF_6 an additional reaction occurs to give β-uranium pentafluoride as one product. β-UF_5 is soluble in acetonitrile without disproportionation and is also formed from the reduction of UF_6 by MeCN. Copper, cadmium, and thallium metals are oxidised by ReF_6 in MeCN giving Cu^I, Cd^{II}, and Tl^I hexafluororhenates(V) but the reactions are complicated by reaction between ReF_6 and the solvent.

INTRODUCTION

We have shown previously that a number of transition and post-transition metals can be oxidised by molybdenum, tungsten [1], or uranium hexafluoride [2] in acetonitrile. Rhenium hexafluoride is considered to be a stronger oxidising agent than WF_6 [3], therefore it was of interest to examine its behaviour in this solvent. The redox behaviour of these hexafluorides towards iodine in iodine pentafluoride has also been examined. This extends a previous study [4], which involved the oxidation of I_2 to I_2^+ by the pentafluorides, MF_5, M = P, As, Sb, Nb, and Ta, and in the present work has resulted in a convenient synthesis of β-uranium pentafluoride.

RESULTS AND DISCUSSION

Reactions between hexafluorides and iodine in iodine pentafluoride

ReF_6 and I_2 react instantaneously in IF_5 above its melting point to form a deep blue solution containing the I_2^+ cation. This was identified by its electronic and resonance Raman spectra [5]. Raman spectra also show the presence of I_2, even in the presence of a large excess of ReF_6, suggesting the equilibrium (1).

$$I_2 + ReF_6 \rightleftharpoons I_2^+ + ReF_6^- \qquad (1)$$

However ReF_6^- was not identified as its ν_1 (a_{1g}) mode would be obscured by IF_5 bands. The solutions appear to be stable indefinately at room temperature in the absence of moisture, but on freezing I_2 and ReF_6 separate out. No solid products could be isolated at room temperature unlike the I_2-MF_5 (M = Sb or Ta) systems [4].

There is no reaction between ReF_6 and I_2 in WF_6 and neither MoF_6 nor WF_6 oxidise I_2 in IF_5. Reaction between UF_6 and I_2 in IF_5 does occur at ambient temperature to give I_2^+ initially. However, the blue colour fades within a few minutes and a pale green solid precipitates from solution. The solid is characterised as β-uranium pentafluoride from its analysis, x-ray powder data [6] and its Raman and i.r. spectra [7]. The stoicheiometry is consistent with equation (2).

$$10UF_6 + I_2 \rightarrow 10UF_5 + 2IF_5 \qquad (2)$$

and the reaction is similar to previously reported preparations of osmium, technetium, and neptunium pentafluorides [8], although the intermediate formation of I_2^+ was not reported in these cases. No reaction occurs between I_2 and UF_6 in WF_6 solution. A number of routes to uranium pentafluoride are known [9], most recently by reduction of UF_6 using silicon in anhydrous HF or H_2 in the presence of u.v. radiation [7b, 10]. The preparation described here requires no special equipment and is very convenient for small scale work.

The behaviour of MoF_6, WF_6, and UF_6 towards I_2 is consistent with previous work at elevated temperature without a solvent. Under these conditions MoF_6 and WF_6 do not react and UF_6 gives IF_5 and U_2F_9 [11], which presumably arises from the disproportionation of UF_5 [12]. A possible reason for the different behaviour of ReF_6 and UF_6 is that UF_6^- is more basic than ReF_6^- in IF_5. Formation of the species I_2F followed by its disproportionation would account for the observed products.

Properties of β-uranium pentafluoride and uranium hexafluoride in acetonitrile

UF_5 is very soluble in MeCN giving a pale green solution which is stable with respect to disproportionation. Removal of the solvent leaves a 1:1 adduct UF_5NCMe. Raman spectra of the solid complex and the solution are identical and consist of bands at 602 and 611 cm^{-1} (both polarised in the solution spectrum). The solid's i.r. spectrum contains bands characteristic of co-ordinated MeCN [13] and strong broad bands at 530 and 350 cm^{-1}. The electronic spectrum of UF_5 in MeCN consists of four groups of bands and is similar to that of UF_6^- [14, 2], but there are sufficient differences in band positions and in the associated vibronic structure to enable the two species to be distinguished. When thallium(I) fluoride is added to UF_5 in MeCN a spectrum characteristic of UF_6^- is obtained. Solid β-UF_5 is polymeric and contains eight co-ordinate uranium [15]. The symmetry of UF_5 as an isolated molecule [16] is not known but is believed to be C_{4v} [17]. Although the presence of polymeric species in MeCN cannot be ruled out, the electronic spectrum favours monomeric $UF_5 \cdot NCMe$ in which distortion from O_h symmetry at U^V is small. A similar situation exists in the complex $UCl_5 \cdot OPPh_3$ [18]. Band assignments for $UF_5 \cdot NCMe$ on this basis are 5120 sh, 5380 m br, $\Gamma_7 \rightarrow \Gamma_8$; 6910 s, 7210 s, 7310 sh, 7510 sh, 7900 m br, 8170 sh, $\Gamma_7 \rightarrow \Gamma_7'$; 10,150 m br, 11,150 m br, $\Gamma_7 \rightarrow \Gamma_8'$; 13,620 m vbr, 15,350 sh, 16,100 sh, cm^{-1} $\Gamma_7 \rightarrow \Gamma_6$.

The slow reaction between UF_6 and MeCN at ambient temperature has been noted previously [2] and a study of the reaction by monitoring electronic spectral changes with time indicates that UF_5 is formed. Initially the spectrum is dominated by an intense charge transfer band in the u.v. region which tails into the visible, but after 0•5 h weak absorptions in the near i.r. region are observed. After 2 h the spectrum is clearly that of UF_5. Subsequently the solution darkens and polymeric material is formed.

The observation of UF_5 as a product from the reduction of UF_6 in MeCN enables the formation of UF_6^- salts from reactions between thallium(I) or mercury(II) fluorides and UF_6 in MeCN [2] to be rationalised. The initial step is the formation of UF_5, and presumably fluorinated nitrile species although the latter were not observed. This is followed by reaction between UF_5 and F^- ion.

Reactions between rhenium hexafluoride and metals in acetonitrile

ReF_6 reacts with MeCN more rapidly than does UF_6 forming brown polymeric material. However, the oxidations of cadmium, copper, and thallium metals by ReF_6 are sufficiently fast to be examined in this solvent. Substantially pure metal hexafluororhenates(V) are obtained only when a large excess of metal is used and under these conditions the products are white $Cd(ReF_6)_6$,5MeCN, yellow $Cu^I(ReF_6)$, 4MeCN, and pale yellow $Tl^I(ReF_6)$,2MeCN. The compounds are soluble in MeCN without reaction and their vibrational spectra indicate that MeCN is co-ordinated [13]. Bands at 693 (Raman) and 615 cm^{-1} (i.r.) are assigned to ν_1 and ν_3 vibrations of ReF_6^- [19].

The reactions of ReF_6 with copper and thallium contrast with those of UF_6, where Cu^{II} and Tl^{III} salts are formed in the presence of excess metal [2], and we conclude that in MeCN, UF_6 is the more effective oxidising agent. Oxidation of copper to Cu^{II} by ReF_6 is observed using IF_5, to which has been added sufficient MeCN to solvate the cation formed, as solvent. The blue solid isolated corresponds to $Cu^{II}(ReF_6)_2$, 4MeCN,0•5IF_5. ReF_6 and copper do not react in IF_5 alone, demonstrating the importance of cation solvation by MeCN in these reactions.

EXPERIMENTAL

All reactions were carried out in a Pyrex vacuum line using techniques and instrumentation that has been described previously [1, 2]. Molybdenum and tungsten hexafluorides (Fluorochem Ltd.) were purified by trap to trap distillation over NaF, and were stored over NaF predried by pumping for 12 h at 420 K. Iodine pentafluoride (Fluorochem Ltd) was similarly distilled then shaken with Hg to remove I_2. Rhenium and uranium hexafluorides (Fluorochem Ltd and U.K.A.E.A. respectively) were freshly purified for each reaction by double vacuum sublimation from predried NaF. Acetonitrile (Koch-Light Ltd.) was dried by repeated reflux over P_2O_5 followed by treatment in vacuo with activated 4A molecular sieves. Iodine (B.D.H. Analar) was sublimed three times in vacuo and metals were abraided and well degassed before use Analyses were by A. Bernhardt, Elbach, W. Germany.

Oxidation of iodine in iodine pentafluoride

A mixture of IF_5, I_2, and ReF_6 was distilled into the side arm of a well dried u.v. cell and allowed to warm to room temperature. An intense blue colour developed as the IF_5 melted: λ_{max} 418, 512, and 637 nm. Similarly prepared was a Raman sample in a Pyrex capillary and the spectrum using 647•1 nm excitation consisted of bands due to IF_5, ν_1 of ReF_6, and a strong band at 238 cm^{-1} for which five overtones were observed.

Similar behaviour was observed for UF_6 and I_2 in IF_5 except that spectra were not well resolved due to the formation of a solid suspension. In a typical preparation I_2 (0•036 mmol) and UF_6 (0•6 mmol) in IF_5 (13 mmol) were shaken at room temperature for 1 h. Removal of the colourless volatile material gave a pale green solid identified as uranium pentafluoride (0•35 mmol). Found F, 28•5; U, 71•3. F_5U requires F, 28•5; U, 71•5%. Raman ν_{max} 615 m, 604 m, 492 w cm^{-1};

i.r. ν_{max} 575 vs, 520 s, 400 m cm^{-1}. UF_5 was soluble in MeCN and on removal of solvent a bulky solid, similar in colour to UF_5, remained whose weight corresponded to $UF_5 \cdot NCMe$. The X-ray powder patterns of UF_5 and $UF_5 \cdot NCMe$ were different from each other.

Oxidation of metals by rhenium hexafluoride

ReF_6 and MeCN reacted quickly at room temperature to give a dark brown sticky solid, which from its i.r. spectrum appeared to contain Re–F and N–H groups. Solvent attack was minimised in reactions between cadmium, copper, or thallium and ReF_6 in MeCN by using a large excess of metal, and by keeping the reaction mixture below room temperature. The white or yellow solids isolated, analysed as $Cd(ReF_6)_2$,5MeCN (Found C, 12·2; H, 1·8; Cd, 12·5; F, 25·3; N, 6·4; $C_{10}H_{15}CdF_{12}N_5Re_2$ requires C, 13·0; H, 1·6; Cd, 12·3; F, 24·9; N, 7·7%.), $Cu(ReF_6)$, 4MeCN (Found C, 18·9; H, 2·2; Cu, 12·2; F, 22·0; N, 8·05. $C_8H_{12}CuF_6N_4Re$ requires C, 18·2; H, 2·3; Cu, 12·0; F, 21·6; N, 10·6%), and $Tl(ReF_6)$,2MeCN (Found C, 8·0; H, 1·0; F, 20·5; N, 3·8. $C_4H_6F_6N_2ReTl$ requires C, 8·2; H, 1·0; F, 19·4; N, 4·8%).

Excess ReF_6 was added to a mixture of IF_5 (36 mmol), MeCN (2·5 mmol), and copper metal (0·3 mmol), the temperature of the reaction vessel being held just above the m.p. of IF_5. Under these conditions little attack of MeCN occurred, as ReF_6 reacted preferentially with Cu° giving a blue solution. Removal of the volatile material left a blue solid which analysed as $Cu(ReF_6)_2$, 4MeCN, 0·5IF_5. Found C, 10·7; H, 1·3; Cu, 7·1; F, 26·5; I, 7·2; N, 6·1. Required C, 10·2; H, 1·3; Cu, 6·8; F, 29·3; I, 6·8; N, 6·0%.

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