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OXIDATION OF MOLYBDENUM AND TUNGSTEN METALS BY MOLYBDENUM AND TUNGSTEN HEXAFLUORIDES IN ACETONITRILE. PREPARATION OF THE 1:1 PENTAFLUORIDE ACETONITRILE COMPLEXES

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SUMMARY

Molybdenum and tungsten metal powders are oxidized by their respective hexafluorides in the presence of acetonitrile at room temperature to give the 1:1 pentafluoride, acetonitrile complexes, $MF_5.NCMe$, M = Mo or W. Their i.r. spectra are consistent with C_{4v} symmetry for the MF_5N moiety. The tungsten pentafluoride complex appears to be stable with respect to disproportionation at room temperature.

INTRODUCTION

The ability of molybdenum and tungsten hexafluorides to function as one electron oxidizing agents in acetonitrile is well established and we have used these reagents to generate a number of solvated, metal and non-metal cations [1]. One way of preparing molybdenum pentafluoride is by the reduction of MoF_6 with Mo metal at 333 K [2]. We find that the reaction proceeds smoothly at room temperature in the presence of MeCN to give the 1:1 complex $MoF_5.NCMe$. Rather surprisingly an analogous reaction occurs between WF_6 and W metal in the presence of MeCN. The product is $WF_5.NCMe$ which, unlike the parent pentafluoride [3], is stable with respect to disproportionation under ambient conditions.

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EXPERIMENTAL

Standard Pyrex vacuum line techniques were used throughout and, except where described below, procedures and instrumentation used has been described elsewhere [1,4]. Molybdenum and tungsten metal powders, purity >4N, were heated *in vacuo* at 423 K for several hours before use and were stored in a N_2 atmosphere glovebox, $H_2O<5$p.p.m. Surface oxide on a Mo sample was undetectable using temperature programmed reduction measurements.

A mixture of purified MoF_6 (5 mmol) and purified MeCN (10 cm^3) was added by vacuum distillation to Mo powder (1.0 mmol), the latter being contained in one limb of a flamed out, double limb, Pyrex reaction vessel fitted with a P.T.F.E. Pyrex stop-cock (J. Young). On warming the mixture to room temperature a very pale yellow solution was obtained. The colour deepened rapidly on shaking the mixture at room temperature and after 2 min the deep yellow solution was decanted into the empty limb. Removal of material volatile at room temperature left a pale yellow solid, readily hydrolysed in moist air, which was identified as molybdenum pentafluoride, acetonitrile (1:1). Found C, 10.1; H, 1.15; F, 40.8; Mo, 41.0; N, 6.0. Required for $C_2H_3F_5MoN$, C, 10.4; H, 1.3; F, 40.9; Mo, 41.35; N, 6.0%.

The reaction between WF_6(5 mmol) and W powder (1.0 mmol) in the presence of MeCN (10 cm^3) was similar but it was necessary to shake the mixture mechanically overnight to obtain a reasonable yield of the pale yellow solid. The latter was identified as tungsten pentafluoride, acetonitrile (1:1). Found, C, 7.6; H, 0.7; F, 29.4; N, 4.35. Required for $C_2H_3F_5NW$, C, 7.5; H, 0.95; F, 29.7; N, 4.4%. The reaction between MoF_6 and W powder in the presence of MeCN under identical conditions gave a pale yellow solid. Found, C, 12.3; H, 1.2; Mo, 31.2; N, 7.1.

Required for $C_{16}H_{24}F_{30}Mo_5N_8,W$. C, 12.3; H, 1.55; Mo, 30.7; N, 7.2%. The reaction between WF_6 and Mo powder gave a very small quantity of a pale green solid for which satisfactory analytical data could not be obtained.

RESULTS AND DISCUSSION

Reduction of molybdenum hexafluoride by molybdenum metal occurs rapidly at room temperature in the presence of acetonitrile. The product is the 1:1 complex $MoF_5.NCMe$ which is spectroscopically identical to the complex as prepared from its constituents [5]. The present method is more convenient, since it avoids the necessity of preparing $(MoF_5)_4$ by, e.g. reduction of MoF_6 using Mo above room temperature [2] or by silicon or dihydrogen in anhydrous HF [6]. Reduction of tungsten hexafluoride by tungsten metal occurs under similar conditions although the reaction appears to be much slower than the molybdenum analogue. The pale yellow powder isolated is formulated as $WF_5.NCMe$ on the basis of its partial analysis and spectroscopic similarity to $MoF_5.NCMe$ (see below). Attempts to grow single crystals were unsuccessful, although the compound is stable with respect to disproportionation at room temperature under anhydrous conditions, both in MeCN and in the solid state. Its existence in MeCN has been postulated previously [1] as a product from the F^- ion transfer reaction between WF_6^- and WF_6 but it has apparently not been isolated prior to the present work.

The i.r. spectra of $MoF_5.NCMe$ and $WF_5.NCMe$, Table 1, are very similar and are consistent with the formulation of these compounds as monomeric species, a conclusion drawn also from the previous vibrational spectroscopic study of $MoF_5.NCMe$ [5]. The spectra are similar to those of $SbF_5.NCMe$ and $AsF_5.NCMe$ which have been analysed on the basis of local C_{3v} symmetry for coordinated MeCN and local C_{4v} symmetry for the $EF_5.N$, E=As or Sb, moiety [7]. A similar approach was used to make the partial assignments given in Table 1.

Reduction of MoF_6 occurs also with W metal in the presence of MeCN at room temperature. The reaction is slower than that using Mo metal and the pale yellow solid product is formulated as $5MoF_5.NCMe,WF_5.NCMe,2MeCN$ on the basis of a partial analysis and its i.r. spectrum. The latter is almost identical to the spectrum of $MoF_5.NCMe$ but contains additional bands assignable to coordinated MeCN.

TABLE 1

I.r. spectra of solid $MF_5.NCMe$, M = Mo or W

ν_{max}/cm^{-1}			Assignment [7]
$MoF_5.NCMe$	$MoF_5.NCCD_3$	$WF_5.NCMe$	
3010 w	2260 vw	3010 w	CH_3 str.
2944 m	2118 m	2944 mw	$A_1 + E$
2322 s	2310 s	2319 ms	C N str.
2297 ms		2297 ms	comb.
2255 vw			
1410 w	1018 m	1410 w	CH_3 def.
1364 w		1365 w	$E + A_1$
1028 mw		1026 m	CH_3 rock
953 w	867 w	942 w	CC str.
703 w	703 m	703 ms	M-F str.
650 vs	650 s	640 vs	$E + 2A_1$
635 sh	635 sh	610 sh	
418 w		418 w	CCN def.
285 ms	285 sh	270 s	M-F def. +
250 s	250 s	240 s	M-N str.

s = strong; m = medium; w = weak; v = very;
sh = shoulder.

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