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REDOX REACTIONS OF URANIUM HEXAFLUORIDE. COMPARISON WITH PHOSPHORUS PENTAFLUORIDE AND PREPARATION OF COPPER(I) HEXAFLUOROURANATE(V) [1]

DILIP K. SANYAL, DAVID W.A. SHARP, and JOHN M. WINFIELD.*

Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, U.K.

SUMMARY

Molecular iodine is oxidised by phosphorus pentafluoride in iodine pentafluoride at room temperature giving I_2^+, PF_6^-, and PF_3. I_2^+ is formed from uranium hexafluoride under similar conditions, but further oxidation occurs depending on the reaction stoicheiometry used. In all cases uranium pentafluoride is formed. Copper(II) fluoride reacts with UF_5 in acetonitrile at room temperature to give copper(II) hexafluorouranate(V), which is reduced by copper metal to give the copper(I) salt. The latter compound is formed from UF_6 and Cu metal, via the Cu^{II} salt, only if a fresh Cu surface is used for the reduction step.

INTRODUCTION

Uranium hexafluoride behaves as an oxidising agent both in iodine pentafluoride and in acetonitrile solutions. Redox reactions involving iodine, copper metal, or thallium metal, which give β-uranium pentafluoride [2] and copper(II) or thallium(III) hexafluorouranates(V) [3] in IF_5 and MeCN respectively, have been reported. This work has been extended by making a comparison between UF_6 and phosphorus pentafluoride, normally regarded as a weak oxidising agent, towards I_2 in IF_5, and by the preparation of copper(I) hexafluorouranate(V) in MeCN from UF_5 or UF_6.

RESULTS AND DISCUSSION

The behaviour of UF_6 towards I_2 in IF_5 solution at room temperature depends on the mole ratio $UF_6:I_2$ although in all cases the I_2^+ cation [4] is formed initially. Whenthe mole ratio $UF_6:I_2$ is 10:1 or greater, the concentration of I_2^+ in solution decreases rapidly, UF_5 is precipitated from solution, and the overall reaction is represented by equation(1).

$$10UF_6 + I_2 \rightarrow 10UF_5 + 2IF_5 \qquad (1)$$

This situation has been described previously [2]. When the mole ratio is 8~9:1, the reaction is similar, but occurs more slowly. I_2 is formed on the removal of the colourless liquid. When the mole ratio $UF_6:I_2$ is 2:1, the I_2^+ cation persists in solution even after 2h, and the UF_5 isolated is heavily contaminated with I_2. The near i.r. spectrum of the reaction mixture indicates that UF_6^- is present in solution.

The formation of I_2^+ from I_2 and UF_6 cannot be followed spectroscopically due to the production of insoluble UF_5. Oxidation of I_2 to I_2^+ by PF_5 in IF_5 has been reported briefly [4b], and is a convenient reaction for spectroscopic study by following the increase in I_2^+ optical density at 636nm and the concomitant decrease in I_2 optical density at 510nm with time. An isosbestic point is observed at 562nm, indicating that no intermediate is involved in the oxidation, and pseudo-first-order behaviour is observed over the first 3 hours of reaction. The other identified products are PF_6^- and PF_3. The reaction can be described by equation(2), and further oxidation or disproportionation of I_2^+ are apparently not important.

$$2I_2 + 3PF_5 \rightarrow 2I_2^+ + 2PF_6^- + PF_3 \qquad (2)$$

The stability of I_2^+ under these conditions is qualitatively similar to that of I_2^+ generated from I_2 and ReF_6 in IF_5 [2].

The initial step in the I_2, UF_6 reaction results in the formation of $I_2^+UF_6^-$. We have suggested previously [2] that the rapid disappearance of I_2^+ may be due to the formation of I_2F followed by its disproportionation. Although the pathway cannot be excluded completely, for example formation of I_2F would not be expected in the presence of the weak base PF_6^-, oxidation of I_2^+ appears to be a more attractive hypothesis. We suggest that the extent to which iodine is oxidised depends on the $UF_6:I_2$ mole ratio, and that I_2 isolated from solution when the ratio is < 10:1 arises from the disproportionation of IF_3 or a related species [5]. Therefore, from this and previous work [1], the following order of effective oxidising ability in IF_5 is indicated; $UF_6 > ReF_6, PF_5 > MoF_6, WF_6$. UF_6 is a good oxidising agent in both IF_5 and MeCN, whereas PF_5 is inferior to MoF_6 and WF_6 in the latter solvent [6].

UF_5 reacts with anhydrous copper(II) fluoride in MeCN at room temperature to give $Cu(NCMe)_6^{2+}$ and UF_6^-. The solid isolated from solution is identical spectroscopically to $Cu(UF_6)_2 \cdot 5MeCN$ prepared by the oxidation of Cu metal with UF_6 in MeCN [3]. The Cu^{II} salt prepared from CuF_2 and UF_5 is reduced by Cu in MeCN solution, the solid isolated being $Cu(UF_6) \cdot 2MeCN$. At first sight this observation is inconsistent with previous work in which formation of the Cu^I salt was not observed from the reaction of UF_6 with excess Cu metal in MeCN, even after several days [3]. However $Cu^{II} \rightarrow Cu^I$ reduction does occur when fresh Cu metal is added, and the solid isolated is $Cu(UF_6) \cdot 3MeCN$. The lack of reaction between $Cu(NCMe)_6^{2+}$ and Cu metal which has been in contact with UF_6, is ascribed to the strong adsorption of UF_6, or a related U^{VI}-F species, on the metal surface. The adsorbed species competes successfully with $Cu(NCMe)_6^{2+}$ for the electron transfer sites. The phenomenon is not observed in analogous reactions involving MoF_6 or WF_6; in these cases Cu^I salts are formed when excess metal is used [7].

The usual stoicheiometry of Cu^I fluoroanion salts is $Cu(MF_6) \cdot 4MeCN$, M=P, Ta, Mo, W, Re, [2,6,7] and the significance of the different numbers of MeCN molecules obtained in the present work is not clear. Spectra of the two samples are identical; both contain coordinated MeCN, but there is no evidence for coordination of UF_6^-. Unlike other Cu^I fluoroanion salts, the hexafluorouranates(V) are photosensitive, giving Cu^{II} as one decomposition product.

EXPERIMENTAL

All operations were carried out using vacuum and glove box techniques and instrumentation described previously [6]. UF_6 (British Nuclear Fuels, Ltd.) was pumped at 195K to remove HF, then sublimed from predried NaF at least twice before use. IF_5 (Fluorochem, Ltd.) was treated with predried NaF, then Hg metal, the process being repeated until all traces of I_2 were removed. PF_5 (Fluorochem, Ltd.) was purified by low temperature trap-to-trap distillation over NaF. I_2 (B.D.H., Ltd.) was sublimed several times at 263K in an all glass manifold with generous 'topping and tailing' at each stage. Solutions of purified I_2 in IF_5 did not form I_2^+ even on standing for several hours, indicating that trace H_2O was absent [8]. MeCN (Fisons, Ltd., HPLC grade)was purified by a standard procedure [9], degassed and stored over activated 4A sieves. Anhydrous CuF_2 (Fluorochem, Ltd. 99.5%) was used as received. Cu foil was abraided, washed with dilute HNO_3, and dried. Microanalyses were by Malissa and Reuter, F.R.G.

Oxidation of iodine by uranium hexafluoride

Twelve reactions were carried out with the mole ratio $UF_6:I_2$ varied from 30:1 to 1·6:1, using 2·4-0·2 mmol UF_6 in 5ml IF_5. Times required for complete reaction varied from 20 min for the highest mole ratio, to > 2h for the smallest. I_2^+ formed in solution was identified by its electronic spectrum [4,2], although spectral quality was poor due to suspended UF_5. The latter compound and I_2, when present, were identified by their electronic spectra in MeCN [2]. The near i.r. spectrum of the blue solution obtained from $UF_6:I_2=1{\cdot}6:1$ contained a weak feature assignable to the $\Gamma_{7'} \leftarrow \Gamma_7$ transition of UF_6^- with associated vibronic fine structure [10], and the visible and u.v. region showed the presence of I_2^+ even after 2h.

Oxidation of iodine by phosphorus pentafluoride

PF_5 (5·66mmol) was added to a solution of I_2 (0·04mmol) in IF_5 (3·5ml) contained in a 10mm Spectrosil cell. The electronic spectrum (800-200nm) of the solution was recorded at 10 or 20 min intervals over several hours, the cell being thermostatted at 295·1K. Over this period the solution's colour changed from brown to blue. Linear pseudo-first-order plots of the increase in I_2^+, and decrease in I_2 optical densities with time were obtained by Guggenheim's method [11], the derived rate constant being $3{\cdot}2\pm0{\cdot}3\times10^{-2}$ min^{-1}.

Spectra of solutions in which $PF_5:I_2$ was 8:1 or 9:1 were similar and showed similar time dependences.

Preparation of copper(I) hexafluorouranate(V)

A mixture of UF_5 (0·17mmol), CuF_2(~ 10mmol) and MeCN (4ml) shaken at room temperature in a 10mm Spectrosil cell showed the presence of $Cu(NCMe)_6^{2+}$ and UF_6^- ions [3] in its electronic spectrum after 1h. The UF_6^- spectrum was partially obscured by the Cu^{II} d-d band, however the $\Gamma_{7'} \leftarrow \Gamma_7$ feature was observed. MeCN was removed by distillation, Cu foil followed by MeCN (5ml) added, and the spectrum recorded at intervals over a 5 hour period. The Cu^{II} d-d band intensity at 740nm had decreased significantly after 15 min, and after 3·25h only peaks due to UF_6^- were observed.

A mixture of UF_5 (0·35mmol), CuF_2(~ 15mmol) and Cu foil in MeCN (5 ml) shaken for 6h at room temperature,gave a pale green solution, although the solution's colour during the initial stages of reaction was blue. The pale green solid isolated from solution, was identified as copper(I) hexafluorouranate(V) bis(acetonitrile). Found C, 9·5; H, 1·2; Cu, 12·7; F, 22·7; N, 5·7; U, 47·6. $C_4H_6CuF_6N_2U$ requires C, 9·65; H, 1·2; Cu, 12·8; F, 22·9; N, 5·6; U, 47·8%. Its i.r. spectrum contained peaks, ν_{max} 2295 and 520cm^{-1}, assigned to $\nu(C{\equiv}N)$ and to ν_3 of UF_6^- respectively.

A mixture of UF_6 (0·65mmol), excess Cu foil, and MeCN (4 ml), contained in a 10mm Spectrosil cell, reacted rapidly at room temperature, the 740nm d-d Cu^{II} band being observed in the spectrum after 5 min. The reaction was left for 0·5h, volatile material removed, and the involatile product pumped overnight. Fresh MeCN (4ml) was added and the d-d band intensity monitored over 1 day, however no decrease was observed. Solvent and foil were both removed and further quantities of each were added. The Cu^{II} d-d band intensity decreased rapidly and was unobservable after 0·75h.

The procedure was repeated, and a pale green solid was isolated, identified as copper(I) hexafluorouranate(V) tris(acetonitrile). Found C, 13·1; H, 1·5; Cu, 12·0; F, 20·95; N, 7·6; U, 44·4. $C_6H_9CuF_6N_3U$ requires C, 13·4; H, 1·7; Cu, 11·8; F, 21·2; N, 7·8; U, 44.2%. Its spectra were identical to those reported above.

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