Inorganica Chimica Acta, *118* (1986) L25–L26

The Chemistry of Uranium.
Part 33. The Reactions of Uranium Metal and Iodine in Non-aqueous Media and the Preparation of UI_4 Adducts

J. G. H. DU PREEZ and B. ZEELIE

Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, South Africa

(Received February 28, 1986)

A brief report on the isolation of new suitable starting materials for the preparation of UI_4 complexes has recently appeared in a communication [1]. These materials greatly simplified the preparation of iodo complexes of uranium(IV). We now provide more details of the reaction of uranium metal with iodine in a number of related non-aqueous systems. The main purpose was to obtain a simple rapid method for the preparation of either UI_4 adducts or a pure UI_4 solution which can conveniently be used for the preparation and study of iodo complexes of uranium(IV), in view of the existing laborious method of preparation of UI_4 [2].

Experimental

Materials

Iodine (B.D.H.), diphenyl ketone dpk) (Hopkin + Williams Ltd) and *N,N,N'N'*-tetramethyl urea (tmu) (Merck) were used as supplied. All solvents were dried over activated molecular sieves (3 Å) and distilled under nitrogen before use.

Uranium turnings (Atomic Energy Corporation of S.A.) were washed with concentrated nitric acid, twice with distilled H_2O followed by dry analar acetone and finally dried in a stream of dry nitrogen gas.

General Method

A clean Schlenck vessel was dried by heating the tube to 80 °C on a high vacuum (0.1 torr) for 5 min. Dry, oxygen-free nitrogen was then allowed to fill the vessel and the process was repeated twice. During the introduction of materials into the Schlenck tube, a constant stream of N_2 (g) was allowed to pass through the tube to maintain the dry, inert atmosphere in the tube.

Three grams (12.6 mmol) of clean uranium metal and 6398 g of I_2 (25.21 mmol) were suspended in 150 cm^3 of solvent, and, where applicable, 4.59 g (25.21 mmol) of dpk or 2.93 g (25.21 mmol) tmu was added. The tube was sealed and the mixture allowed to stir until no more solid uranium metal could be detected in the reaction mixture.

Analytical

Uranium was precipitated as the hydrous oxide, and weighed as U_3O_8 after ignition at 750 °C. Iodide was determined potentiometrically after precipitation of the uranium by ammonia.

Results and Discussion

The different solvent/ligand systems studied for the reaction of uranium metal with iodine were:

(i) Dry methyl cyanide as solvent: The reaction proceeded exothermically for the first 30 min. It took *ca.* 48 h for completion. The red precipitate formed was contaminated with black impurities, apparently uranium carbide. Some red powder could be separated with difficulty and was proved by analysis to be $UI_4 \cdot 4$mecn. *Anal.* Calc. for $UI_4 \cdot 4$mecn: U, 26.16; I, 55.79; C, 10.56; H, 1.33; N, 6.16. Found: U, 26.0; I, 55.3; C, 10.4; H, 1.38; N, 6.0%. IR spectroscopy confirmed the presence of coordinated methyl cyanide. Peaks at 2250 and 2290 cm^{-1} in the free ligand have been shifted to 2273 and 2300 cm^{-1} in the complex. Attempts to purify this product by recrystallisation from methyl cyanide solution were unsuccessful owing to its low solubility in the solvent. The reaction was very sensitive to the presence of small amounts of water in the solvent, in which case the reaction did not proceed to near completion and a dark product was obtained on the metal surface having U:I ratios of 1:~3.7. The extreme hygroscopic nature of the $UI_4 \cdot 4$mecn and its sensitivity towards oxygen complicated additional handling.

(ii) Dry methyl cyanide as solvent containing 2 equivalents of tmu per equivalent uranium: The reaction was completed after only 2.5 h. A yellowish green powder contaminated with the same black material as above was obtained. Recrystallisation of the green powder from hot methyl cyanide solution was only slightly more successful than in the previous case. The product proved to be $UI_4 \cdot 2$tmu by analysis. *Anal.* Calc. for $UI_4 \cdot 2$tmu: U, 24.34; I, 51.91; C, 12.28; H, 2.47; N, 5.73. Found: U, 24.2; I, 51.7; C, 12.1; H, 2.35; N, 5.5%.

(iii) Dry methyl cyanide as solvent containing 2 equivalents of dpk per equivalent uranium: the use of a weaker oxygen donor ligand was thought to produce a more soluble UI_4 complex species. Red $UI_4 \cdot 4$mecn was, however, again precipitated although the reaction took only 3 h for completion.

(iv) Dry methylene dichloride containing two equivalents of dpk per uranium as solvent: the reaction took 6 h for completion. A very dark solution containing some black solid and black carbide is formed (mixture A). When this mixture was pressure-

0020-1693/86/$3.50

filtered under nitrogen, the filtrate vacuum-concentrated to 50 ml and finally cooled to −18 °C, black, very hygroscopic, air-sensitive solid $UI_4 \cdot 2dpk$ was obtained. *Anal.* Calc. for $UI_4 \cdot 2dpk$: U, 21.44; I, 45.73; C, 28.13; H, 1.82. Found: U, 21.4; I, 45.3; C, 27.8; H, 1.79%. If mixture **A** (above) was vacuum-concentrated to dryness, 50 cm^3 of dry, oxygen-free methyl cyanide added under nitrogen, stirred, pressure-filtered and the final solution cooled to −18 °C, pure $UI_4 \cdot 4mecn$ crystallised out in a high yield.

(v) Dry methyl cyanide containing 6.5% ethyl acetate as solvent: the reaction between uranium and iodine was completed in *ca.* 12 h and a very dark red solution obtained. This was filtered under nitrogen giving a pure UI_4 solution which could be used for the preparation of many UI_4 complexes, e.g. $UI_4 \cdot 2tmu$, $(\psi_3Pet)_2UI_6$, etc. No solid $UI_4 \cdot 4mecn$ could, however, be prepared from this solution. Vacuum-evaporation of the above solution only produced a thick dark oil.

$UI_4 \cdot 2dpk$ contains weakly-bound dpk since no shift of the C=O stretch frequency upon complexation could be detected by IR spectroscopy either in the case of nujol mulls or in methylene dichloride solutions. This is very surprising since significant shifts have normally been obtained in complexes of this type, e.g. 40 cm^{-1} for $ZrCl_4 \cdot 2dpk$ [3]. The thermal instability of $UI_4 \cdot 2dpk$ is, however, in agreement with this fact as indicated by its gradual evolution of iodine after approximately three days in a pure nitrogen atmosphere. Its solid reflectance electronic spectrum resembles that of six-coordinated uranium(IV) in view of its strong absorption in the 2000 nm region. It is very soluble in acetone, tetrahydrofuran and methyl cyanide. It is a very good intermediate compound in the preparation of pure $UI_4 \cdot 4mecn$ (See system (iv) above). The latter is a much more suitable solid starting material for the preparation of any iodo complex of uranium(IV). It can be vacuum-dried for hours at room temperature (25 °C) without decomposition. It is indefinitely stable in a dry oxygen-free nitrogen atmosphere. Neither $UI_4 \cdot 2dpk$ nor $UI_4 \cdot 4mecn$ could be desolvated without loss of iodine. Thermogravimetric analysis of $UI_4 \cdot 4mecn$, which was performed in a pure dry nitrogen atmosphere, indicated that loss of CH_3CN starts at ~50 °C. This behaviour is very similar to that of $UX_4 \cdot 4mecn$ [4], X = Cl or Br, and $ThI_4 \cdot 4mecn$ [2]. There is somewhat of a plateau at *ca.* 90 °C corresponding with the loss of 4 mol of methyl cyanide, although some iodine vapour is visibly evolved at ~85 °C. Pure UI_4 could therefore not be prepared in this way. The conductivity of a 0.003 M solution of $UI_4 \cdot 4mecn$ in methyl cyanide is 100 cm^2 S mol^{-1}. This value is in the region expected for a 1:1 electrolyte.

In conclusion, this work indicated that both solid $UI_4 \cdot 4mecn$ and the UI_4 solution obtained in the methyl cyanide/ethyl acetate mixture (system (v)) can very conveniently be used to prepare and study iodo complexes of uranium(IV). $UI_4 \cdot 2dpk$ can be regarded as a very useful intermediate compound to facilitate the preparation of $UI_4 \cdot 4mecn$ in high yield. In view of the astonishingly weak bonding of the dpk, it could be regarded as very similar to UI_4 itself.

Acknowledgement

We thank the Council of Scientific and Industrial Research and the University of Port Elizabeth for financial assistance.

References

1 J. G. H. du Preez and B. Zeelie, *Chem. Commun.*, in press.
2 K. W. Bagnall, D. Brown, P. J. Jones and J. G. H. du Preez, *J. Chem. Soc.*, 3594 (1965); 350 (1965).
3 R. C. Paul and S. L. Chadha, *J. Inorg. Nucl. Chem.*, *31*, 1679 (1969).
4 K. W. Bagnall, D. Brown and P. J. Jones, *J. Chem. Soc. A*, 1763 (1966).