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A SIMPLE MULTIGRAM SYNTHESIS OF β-UF_5 - REDUCTION OF UF_6 BY PF_3 †

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SUMMARY

Controlled low-temperature reduction of UF_6 with commercially-available PF_3 in a standard metal vacuum system provides a convenient multigram synthesis of β-UF_5. A comparison is made with reduction reactions of UF_6 reported earlier and with the corresponding NpF_6 and PuF_6 reactions.

INTRODUCTION

Earliest preparations of UF_5 involved halogen-exchange between HF and UCl_5 or UCl_6 [1] or equilibration between stoichiometric amounts of UF_6 and UF_4 at elevated temperature [2]. Controlled oxidation by F_2 of UF_4 suspended in anhydrous hydrogen fluoride (AHF) required the preliminary preparation of UF_4 with a large surface area [3].

More recent methods have been based on reduction of UF_6 dissolved in AHF by H_2 [4], HBr [5], Si [6] and CO [7], UV irradiation being used in the latter cases. Other methods require prior preparation of complex starting materials, *e.g.* in the acid-base displacement by BF_3 of UF_5 from $NOUF_6$ dissolved in AHF [8]. These syntheses have been carried out in small Kel-F reaction tubes in order to obviate contamination through corrosion of metal reaction vessels by AHF. Therefore the preparative scale has necessarily

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been limited, usually, to about]g or less. The CO reduction method was scaled up by using UV irradiation of the gas phase reaction in a 1ℓ quartz bulb; but 'fogging' of the walls of the bulb by the involatile product UF_5 limited the optimum scale to about 5g [9]. Becker and Jacob have reported multigram preparation of β-UF_5 (*ca* 50g) by direct photodissociation of UF_6; but the necessary equipment is complex and expensive.

The procedure reported here uses simple, standard equipment and allows preparation of high-purity β-UF_5 in quantities well in excess of 20g and there appears to be no reason why it should not be scaled up significantly. It is based on controlled reduction at -78°C of UF_6 by PF_3 which is available commercially. Because F_2, HF and other highly corrosive fluorides are not involved, standard metal vacuum lines constructed from commercial stainless steel or Monel valves, connecting unions and gauges can be used. PF_5, produced in the reaction, and any unreacted PF_3 and UF_6 are all much more volatile than UF_5 and so UF_5 can be isolated easily in a high state of purity.

The experimental conditions now established for preparation of UF_5 by PF_3 reduction allow a rationalisation and interpretation of many previously-reported reactions involving reduction of UF_6 in terms of a relatively easy thermal disproportionation of UF_5. Np(V) has been shown to be less susceptible to disproportionation than U(V) and Pu(V) and so it is significant that, following this work, NpF_5 was prepared by reduction of NpF_6 with PF_3 under conditions where a pure sample of UF_5 might not have been expected and that under the same conditions reduction of PF_6 with PF_3 gave PuF_4 [11].

EXPERIMENTAL

The volatile reactants were manipulated in a Monel vacuum system based on the Argonne National Laboratory design [12]. A simpler, less expensive stainless steel line built from Whitey valves and Swagelok unions would be equally suitable [13]. In a typical run 44.5g (126 mmol) of UF_6 (Oak Ridge National Laboratory) and 107 mmol (measured by p-v-T relationships) of PF_3 (Ozark-Mahoning) were condensed at -196°C into a heavy walled stainless steel reaction vessel which was held at -78°C for 2 days and then allowed to warm slowly to room temperature. Reaction was not complete under these conditions and unreacted PF_3 and UF_6 as well as a reaction product PF_5 were distilled into traps at -78°C and -196° C and the system was then pumped for

2 hours. 17.5g (49.7 mmol) of unreacted UF_6 was condensed at -78°C. 24.8g of involatile product, identified as β-UF_5 by comparison of its X-ray powder pattern with that of pure β-UF_5 previously prepared, was recovered from the reaction vessel in a high-efficiency glove box. Its colour was pale yellow-green or pale blue-green in different runs. Variable colour has been reported previously for β-UF_5 [5,6,10] and this may result from very slight surface hydrolysis.

When in a separate experiment the reaction vessel was allowed to warm rapidly from -196°C and -78°C to room temperature, the solid product was not UF_5 but UF_4 or an intermediate fluoride such as U_4F_{17}, depending on reaction conditions.

In an alternative small-scale procedure, 0.22g (0.62 mmol) UF_6 was dissolved in about 3 ml of AHF at room temperature in a Kel-F tube provided with a Teflon-coated magnetic stirrer bar. The tube was cooled to -196°C and excess PF_3 (5.7 mmol) condensed on to the solid AHF. The mixture was allowed to warm to room temperature and stirring maintained for about 2 hours. A light blue-green solid precipitated which was identified as β-UF_5 by X-ray powder diffraction techniques, after removal of all volatile species by distillation and pumping and transfer of the solid residue to capillaries in a dry-box.

DISCUSSION

In earlier studies of the UF_6-PF_3 reaction at about the 1 gram scale in Kel-F reaction tubes, it had been reported that the solid reaction product was UF_4 when PF_3 was in excess and mixtures of UF_4, U_4F_{17} and UF_5 when UF_6 was in excess [14]. In that work PF_3 was condensed on to UF_6 at -196°C and the reaction mixture allowed to come to room temperature at a natural warming rate and then left to stand for equilibration. Under the experimental conditions reported in this paper of prolonged reaction at -78°C in a stainless steel reaction vessel and slow warming to room temperature, the product is UF_5 even with excess PF_3.

The earlier work can be rationalized by recognizing the very poor thermal transfer properties of Kel-F. Energy from the exothermic reduction reaction would be dissipated very slowly and, under these conditions, UF_5 formed initially would disproportionate to UF_4 and UF_6 which would then react with PF_3. With excess PF_3, all of the initial UF_5 would be converted to UF_4. The system would, of course, be much more complex when UF_6 was in excess because progressive disproportionation and reduction to UF_4 would not proceed to completion even on stoichiometry grounds. Furthermore, an excess of UF_6 would inhibit UF_5 disproportionation even at the somewhat elevated temperatures within the Kel-F tube.

In this work, UF_5 is formed slowly and incompletely at -78°C with ideal conditions for dissipation of the heat of reaction. The mass, thermal capacity and thermal conductance of the metal reaction vessel are such that disproportionation is prevented. Support for this postulate has been provided by allowing the metal reaction vessel to warm relatively quickly and the products of reaction were then found to include UF_4 and fluorides intermediate between UF_4 and UF_5. In earlier work [15], it has been shown that compounds thermally unstable at or below room temperature can be isolated if cold AHF or another solvent is used as a "heat sink". In the work reported here, 0.22g UF_6, dissolved in AHF, was not reduced beyond UF_5 even though the reaction was carried out in a Kel-F tube and with excess PF_3.

Thermal disproportionation of UF_5 at or above room temperature has been used here to account for differences in observed reaction products from the reduction of UF_6 by PF_3 depending on the experimental conditions. Many other older observations can be rationalized similarly, *e.g.* the high-temperature reactions of UF_6 with H_2, HCl, HBr and HI to give UF_4 [16], whereas controlled low-temperature reactions with H_2 and with HBr have been shown more recently to yield UF_5 [4,5]. It is significant that reduction of NpF_6 with excess PF_3 in a Kel-F tube gives NpF_5, under conditions where disproportionation of UF_5 might have been expected, and the corresponding reaction with PuF_6 gave PuF_4 [11]. These observations can be reconciled with the known facts that Np(V) is much less susceptible to disproportionation than U(V) and Pu(V).

The results reported here are not inconsistent with two recent reports on uranium pentahalide reactions although, as discussed earlier, they are different from results of O'Donnell *et al.* reported in 1966 [14]. In the 1966 work, UF_6 was reacted with PF_3 and with halogen exchange reactants in Kel-F tubes, which have poor heat-transfer properties, and without any appreciation of the ease of thermal disproportionation of UF_5 under these conditions and, therefore, without any control of the rate at which the reaction mixture warmed from -196°C to room temperature. Partial or complete formation of UF_4 is reasonable under these conditions. Very recent work by Brown, Berry and Holloway [17] has shown very clean interconversion of uranium pentahalides. These reactions were studied in glass, which has good heat-transfer properties, and under controlled conditions, using a solvent which acts as a thermal dissipant in bromine-exchange reactions. Also very recently, Sanyal, Sharp and Winfield [18] have reduced UF_6 to UF_5 with I_2 in the solvent IF_5, where again the solvent provides thermal control of reduction and prevents disproportionation.

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