One-electron Reduction Synthesis of Uranium Pentafluoride

By Larmed B. Asprey and Robert T. Paine*

(*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico* 87544)

Summary The reactions of uranium hexafluoride with hydrogen gas in the presence of u.v. radiation or with silicon powder in an anhydrous HF slurry provide useful, high yield syntheses of pure uranium pentafluoride.

Several synthetic routes to uranium pentafluoride have been reported,[1] but none of the methods is satisfactory for the preparation of high yields of pure UF_5. We report here two novel reduction routes to UF_5 from UF_6.

Uranium hexafluoride reacts with hydrogen gas at room temperature in a 30 ml Kel-F tube according to reaction (1).

$$UF_6 + 1/2\,H_2 \xrightarrow[\text{1 day}]{\text{u.v.}} UF_5 + HF \qquad (1)$$

The reaction rate is greatly enhanced by radiation from a low pressure mercury lamp. One gram of UF_6 is completely converted into pure β-UF_5 powder in 1 day, and the HF produced is easily removed by pumping. In a second procedure, UF_6 reacts at room temperature with silicon powder in a stirred anhydrous HF slurry contained in a Kel-F tube according to reaction (2). The UF_5 is virtually

$$UF_6 + 1/4\,Si \xrightarrow[\text{1–3 day}]{\text{HF}} UF_5 + 1/4\,SiF_4 \qquad (2)$$

insoluble in the anhydrous HF, and the SiF_4 and HF are removed by pumping. One gram of UF_6 is completely converted into pure β-UF_5 powder in 2—3 day. Working in a dry box, the free-flowing β-UF_5,[2] ranging in colour from white to yellow-green, is easily recovered from the reaction tubes. Identification is provided by the i.r. spectrum of a powder sample held at −196° (cm^{-1}): 623s,sh, 567s, 508s, 405s, 405s,sh; and the Raman spectrum of a powder sample held at 23° ($\Delta\nu$ cm^{-1}): 623s, 610s, 280m. All attempts to evaporate UF_5 from a resistively heated crucible into the ion source of a TOF mass spectrometer resulted in disproportionation of the UF_5 as shown by the resulting mass spectrum of UF_6. The β-UF_5 obtained from the above reactions is converted into α-UF_5 at *ca.* 120°, and the α-UF_5 was identified by *X*-ray powder diffraction. Attempts were made to carry the chemical reduction from UF_6 to UF_4 by adding further H_2 or Si, but no evidence for reduction below UF_5 was obtained.

At present, the mechanism of the silicon reduction of UF_6 is not clearly understood; however, we have shown that the production of hydrogen from the reaction of liquid, anhydrous HF and silicon metal is slow compared to the uranium hexafluoride reduction.

The convenient high-yield reduction reactions described here appear to be general. To date, we have obtained high yields of the pure pentafluorides and tetrafluorides of Mo, Re, Os, and Ir from the corresponding hexafluorides.[3] The reductions of WF_6, RuF_6, XeF_6, SeF_6, TeF_6, and several metal pentafluorides are under investigation.

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[1] D. Brown, 'Halides of the Transition Elements, Halides of the Lanthanides and Actinides,' Wiley, New York, 1968, p. 36 and refs. therein.

[2] Proof of the molecular formula was accomplished by chemical analyses and by comparison of powder *X*-ray diffraction patterns; tetragonal $a = 11{\cdot}5$, $c = 5{\cdot}2$, see W. H. Zachariasen, *Acta Cryst.*, 1949, **2**, 296.

[3] R. T. Paine and L. B. Asprey, *Inorg. Chem.*, submitted for publication.