Notes

CONTRIBUTION FROM UNION CARBIDE CORPORATION,
OAK RIDGE GASEOUS DIFFUSION PLANT,
OAK RIDGE, TENNESSEE

α-Uranium Pentafluoride. II. A New Preparation[1]

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Received November 2, 1964

Small amounts of white solid material were discovered when mixtures of condensed uranium hexafluoride and commercial liquid bromine were allowed to stand overnight at room temperature. Identification of the isolated product as β-uranium pentafluoride initiated a search for its origin, which turned out to be the hydrogen bromide impurity in the bromine. A mild reduction of the uranium hexafluoride takes place as shown in eq. 1. Based upon this discovery, a semi-

$$2UF_6 + 2HBr \longrightarrow 2UF_5 + 2HF + Br_2 \qquad (1)$$

continuous process was developed which involves the gas phase reaction of hydrogen bromide with a liberal excess of uranium hexafluoride in an open column operating at 65° and a total pressure of 1 atm. to produce uranium pentafluoride at a rate of 250 g./hr. The uranium pentafluoride was formed as a solid, crystalline material and fell into a receiver at the bottom of the column. Since the other normal products and the excess uranium hexafluoride were gases, they were evacuated through a sintered metal filter and a series of condensing traps. The duration of continuous operation was about 2 hr., a limitation imposed by the capacity of the product receiver. Although operated with an excess of uranium hexafluoride, when the receiver was full, it was necessary to expose the product overnight to a uranium hexafluoride pressure of 2.5 atm. at 200° to ensure reconversion of any other intermediate uranium fluoride which may have been formed to uranium pentafluoride. Under these conditions, the product was a chalky, light blue, powder which was identified as pure, polycrystalline α-uranium pentafluoride and gave an X-ray diffraction pattern identical with that of the sublimed product obtained during the vapor pressure measurements reported earlier.[3]

Experimental

A schematic diagram of the open reactor column is shown in Figure 1. The column proper was made of 3-in. nickel pipe, 33 in. in length, with welded flanges on both ends. A nickel product receiver 3 in. in diameter and 5 in. deep was attached at the bottom by means of a Teflon[4]-gasketed flange closure. Three inches above the lower flange an exhaust stack, made of 2-in. nickel pipe, was welded to the column at an angle of 45° to the column wall and extended vertically to within 5 in. of the top flange of the column. A Bourdon tube, compound gauge was installed on the side of the stack to measure the total column pressure. The top of the stack was fitted with a Teflon-gasketed flange closure into which was sealed a sintered nickel filter tube connected with the evacuation system through a Hoke 413 throttle valve. For a distance of 5 in. below the upper column flange, the column was wrapped with coils of 0.25-in. copper tubing through which cold water could be passed. This provision for heat exchange was necessary to control the temperature of the primary reaction zone. Seven iron–constantan thermocouples were placed in thermowells spaced along the column as shown and extending to its axial center. Another thermocouple was placed in a well extending into the product receiver. Other thermocouples were strategically placed at other critical points of the gas flow systems and all temperatures were followed on a Speedomax[5] 20-point recorder. The entire column, product receiver, and exhaust stack were wrapped with turns of insulated, electrical resistance wire and covered with magnesia pipe insulation to assist in the maintenance of the necessary temperature control during operation. The upper flange was used to attach the reactant gas jet assembly.

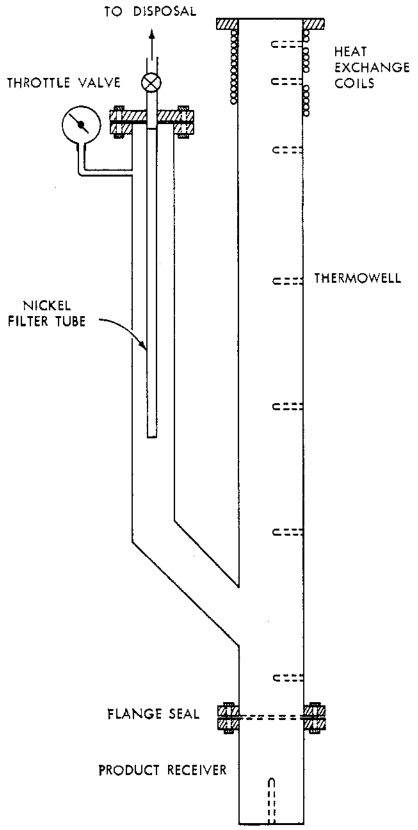

Figure 1.—Schematic diagram of open reactor column.

A diagram of the jet assembly is given in Figure 2. A 2-in. length of nickel pipe 1 in. in diameter which was welded to the upper flange member formed an annulus through which uranium hexafluoride vapor was introduced to the reactor column. The top of the annulus was sealed by a nickel disk, 0.5 in. in thickness, which was welded in place and machined internally on the upper side to form a tight seal with components of a commercial ultrahigh vacuum coupling.[6] The jet, through which hydrogen

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[1] Based upon work performed for the U. S. Atomic Energy Commission.

[2] To whom correspondence should be addressed.

[3] A. S. Wolf, J. C. Posey, and K. E. Rapp, *Inorg. Chem.*, **4**, 751 (1965).

[4] A plastic polymer of tetrafluoroethylene manufactured by du Pont de Nemours and Co.

[5] An electronically operated recording potentiometer manufactured by Leeds and Northrup.

[6] As manufactured by the Cajon Company, Cleveland, Ohio.

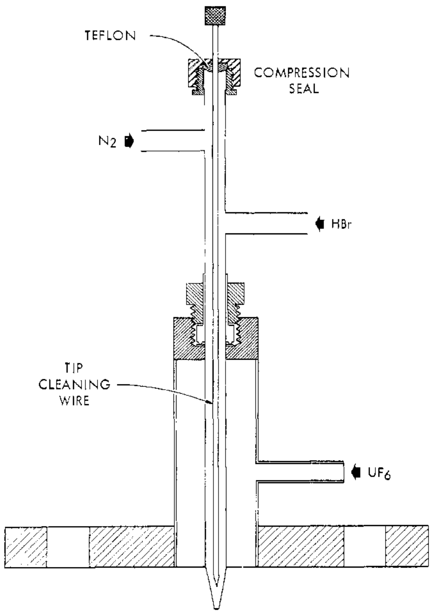

Figure 2.—Diagram of reactant gas jet assembly.

bromide and nitrogen could be introduced, was made of 0.25-in. nickel tubing. The end which extended into the reactor column was spun down to an orifice-like tip. A cleaning rod made of $^{1}/_{16}$-in. nickel weld rod, sharpened with a long taper at the lower end and fitted with a knurled knob at the upper end, was sealed into the top of the jet tube by means of a compression fitting with a Teflon gasket. This rod, usually held in the retracted position, could be lowered to free the jet of a plug developing as a result of solid reduction products forming at the jet tip. A small amount of heat was supplied to the jet assembly by means of an infrared lamp.

The metered supply of hydrogen bromide came from a 10-lb. commercial cylinder, marketed by the Matheson Co. as having a minimum purity of 99.8%. From the pressure regulating valve the gas was passed through an adjustable orifice; this produced a pressure drop which was reflected by the liquid level difference in a U-tube manometer made of Fluorothene[7] tubing and filled with a low-viscosity halocarbon oil. This flow system was calibrated before use by condensing and weighing the hydrogen bromide passed during finite time intervals and under various pressure differentials. The supply of uranium hexafluoride delivered to the reactor column came from a cylinder initially containing about 50 lb. of solid uranium hexafluoride. Being a typical sample of diffusion plant "tails," the only impurity was a minor amount of light gases. This cylinder was heated in a regulated air bath at a temperature of 70° and was connected to the reactor through a block valve, a throttle valve, and a calibrated capillary, all of which were contained in the heated air bath. A DBM[8] pressure transmitter sensed the pressure differential across the capillary and a PBM[8] pressure transmitter connected to the supply line downstream from the capillary measured the absolute pressure of uranium hexafluoride being supplied to the reactor. The disposal system consisted of five traps and a vacuum pump.

Two or three hours prior to starting operation, the column is heated to 65° while being evacuated to a pressure of $50\ \mu$. With the hydrogen bromide valve to the jet assembly closed, the hydrogen bromide cylinder valve is opened and the flow control valves are set to their predetermined positions. A low flow of dry nitrogen is opened to the jet, and, by closing the throttle valve at the top of the exhaust stack, the column pressure is allowed to rise to slightly above atmospheric pressure. With the uranium hexafluoride flow control valves preset and the slow flow of nitrogen being continued, the uranium hexafluoride valve to the jet assembly is opened; simultaneously the throttle valve to the disposal system is opened and adjusted to maintain the column pressure at 1 atm. When the pressures have become steady, usually within 5 min., hydrogen bromide is admitted to the jet and the nitrogen flow is discontinued. Occasionally, minor flow adjustments are necessary to maintain the 150% molar excess of uranium hexafluoride, and the temperature of the upper section of the column is observed so that water can be supplied to the heat exchanger when the temperature begins to approach 70°. Beyond this, the system requires very little attention.

During operation the trap nearest the reactor exhaust stack, immersed in ice water, collects most of the excess uranium hexafluoride. The second trap, immersed in a Dry Ice–trichloroethylene slush, retains most of the bromine and hydrogen fluoride and any uranium hexafluoride which passes the first trap. The third trap, at the temperature of liquid nitrogen, traps any bromine or hydrogen fluoride escaping the second trap. Although the reaction of the hydrogen bromide is normally quantitative, any hydrogen bromide not reacting completely is caught in this trap. As an extra precaution against trap failure, the evacuation pump is protected by a soda lime trap followed by another cold trap at liquid nitrogen temperature.

When the operation is to be discontinued, the hydrogen bromide cylinder valve is closed. The regulator pressure is allowed to diminish to 5 p.s.i.g., at which time the valve to the jet assembly is closed and nitrogen is admitted to the jet for about 5 min. The reactor is swept for approximately 30 min. with uranium hexafluoride to remove the gaseous products from the column. At this point the throttle valve from the exhaust stack is closed and the uranium hexafluoride pressure in the column is allowed to equilibrate with the supply cylinder before the supply is shut off at both the cylinder and jet assembly valves. Additional heat is then supplied to the column and the product receiver so that the temperature may rise to 200°, where it is maintained for 24 hr. During this period the column pressure rises to approximately 2.5 atm. The receiver is now cooled, the throttle valve to the disposal system is partially opened, and a slow nitrogen purge is started. While this is taking place, a polyethylene sleeve 6.25 in. in diameter and about 4 ft. long is slipped over the receiver and lower section of the column and is taped in place with masking tape. Two crescent wrenches, extra flange bolts, and two blank flange plates are put into the sleeve and the open end is taped shut with a tube to introduce nitrogen inserted at one corner. Air is purged from the sleeve while the column is rapidly evacuated at a pressure $<100\ \mu$. The column is brought to atmospheric pressure with nitrogen as the flange bolts are loosened. With the sleeve still closed and nitrogen passing through it, the flange bolts are removed and the receiver containing the product is lowered. Both the column and the receiver are closed by a blank flange plate tightened against a Teflon gasket. The sleeve is now removed and the receiver and wrenches are transferred to a drybox for sampling and subsequent handling operations.

In the analysis of uranium pentafluoride U(V) is hydrolyzed to U(IV) and U(VI) and is determined as tetravalent uranium equivalent and total uranium. A typical analysis for the product prepared by this procedure is as follows. *Anal.* Calcd.: U(IV), 35.73; total U, 71.47. Found: U(IV), 34.90; total U, 72.55. X-Ray analysis of the aged product indicated only polycrystalline α-uranium pentafluoride was present.

Clean-up of the gas metering systems only requires evacuation. The reaction column, after the receiver is removed and the bottom is sealed by the flange plate, is cleaned by room temperature exposure to fluorine gas at atmospheric pressure. When the reaction products of this treatment are evacuated the column is ready for reuse.

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(7) Solid polymer of chlorotrifluoroethylene made by Union Carbide Corporation for the U. S. Atomic Energy Commission.

(8) Indirect pressure sensing devices manufactured by the Taylor Instrument Co. The DBM transmitter measures the difference in pressure between two sensing legs. The PBM measures absolute pressure by relating line pressure to vacuum.

Several observations should be made at this point which have a bearing upon the success of the described process. A nitrogen flow through the hydrogen bromide jet is desirable if not necessary to prevent diffusion of uranium hexafluoride into the jet; reaction taking place within the jet tube when the hydrogen bromide is first admitted might plug the small opening of the jet with reaction product.

Varying the specific flow rates of the reactant gases so that the excess of uranium hexafluoride varies from 50 to 200% has little effect upon the quality of the unaged product; in all cases material sampled prior to the aging process is a gray to brown mixture, found by X-ray analysis to contain both α- and β-uranium pentafluoride as well as some diuranium enneafluoride. Since the gross uranium hexafluoride pressure was at all times well above the disproportionation pressure of both forms of uranium pentafluoride, it is concluded that in the immediate zone of reaction (a) the partial pressure of uranium hexafluoride is sharply reduced by both hydrogen bromide and the gaseous reaction products and (b) the reaction temperature is probably somewhat above 65°, the measured gas temperature approximately 1.5 in. from the jet tip. Although reaction would occur at a lower temperature, 65° is the minimum operating temperature which will ensure complete removal of the bromine as a vapor. Higher temperatures would merely emphasize a deficiency in the uranium hexafluoride overpressure.

The presence of other intermediate uranium fluorides in the unaged product is a shortcoming which this preparative method has in common with previously developed methods. However, the high surface area and small particle size produced by the relatively low temperature gas phase reaction favor complete reconversion of the material to α-uranium pentafluoride during the aging process. The tetravalent uranium equivalent was less than half the total uranium, probably because of adsorbed uranium hexafluoride. One expects this as a result of the short period of evacuation at room temperature employed before the product receiver was removed. Since some uranium hexafluoride pressure is necessary at all temperatures to prevent disproportionation, it is probably desirable not to remove the sorbed uranium hexafluoride too thoroughly if the product is to be stored for any length of time.

Both the product and the product receiver should be handled in a dry atmosphere at all times. The presence of any sorbed uranium hexafluoride merely enhances the susceptibility of the products to hydrolysis. If the receiver is exposed to moist air before reuse or if it is desirable to make a change in the isotopic concentration of the uranium hexafluoride feed, the receiver with its residual contents, when reinstalled at the bottom of the column, can be thoroughly decontaminated by exposure to fluorine at room temperature.

CONTRIBUTION FROM THE RESEARCH LABORATORY
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A Tridentate Ligand from Pyridine-2-aldehyde and Ammonia

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Received June 15, 1964

In the unsuccessful attempts to prepare an iron(II) complex of 2-pyridinalimine ($C_5H_4N{\cdot}CH{=}NH$) from pyridine-2-aldehyde, ammonia, and a ferrous salt, the formation of a strongly colored compound was observed in which apparently 1 mole of ammonia has reacted with 2 moles of the aldehyde. From a reaction mixture of ferrous chloride (1 mole), pyridine-2-aldehyde (4 moles), and ammonium bicarbonate (2 moles) in aqueous ethanol, sodium perchlorate precipitated a dark red, amorphous product. Analytical results are in agreement with the values calculated for bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]iron(II) perchlorate (I, R = OH). A well-crystallized, hexahydrated chloride was obtained by allowing pyridine-2-aldehyde to react with ferrous chloride and ammonium chloride in aqueous solution. Part of the pyridine aldehyde is thereby transformed into the hydrochloride. Finally, the same complex species is formed on reaction of a ferrous salt with the 2-pyridinalimine trimer described by Harries and Lénárt.[1]

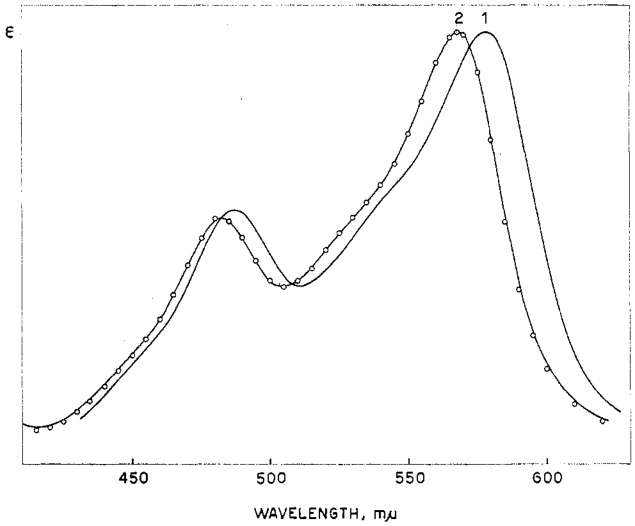
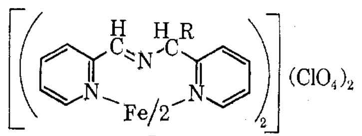


Figure 1.—Absorption spectra of: (1) bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]iron(II) chloride; and (2) bis[2-(2′-pyridylmethyleneaminomethyl)pyridine]iron(II) perchlorate (solid line refers to authentic sample (3A), points to product (3B) obtained by reduction of the hydroxymethyl derivative). Solvent water. Curves are drawn to equal height at the main absorption maximum. The numerical values of the molar absorbancy indices at these maxima are: 1, 1.05×10^4; 2, 1.1×10^4.



I

In solution and even in the solid state the new iron(II) complex slowly decomposes or changes otherwise, as shown by distinct changes of its absorption spectrum. This spectrum (λ_{max} 578 and 487 mμ) is very similar to that of the iron(II) complex of the tridentate ligand 2-(2′-pyridylmethyleneaminomethyl)pyridine (I, R = H) obtained by Lions and Martins[2] from pyridine-2-aldehyde and 2-aminomethylpyridine (see Figure 1). Spectroscopic evidence thus supports the proposed structure.

In order to provide chemical structural proof, an attempt was made to reduce the >CH·OH grouping to

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[1] C. Harries and G. H. Lénárt, *Ann. Chem.*, **410**, 115 (1915).

[2] F. Lions and K. V. Martins, *J. Am. Chem. Soc.*, **79**, 2733 (1957).