September, 1987] Bull. Chem. Soc. Jpn., 60, 3189—3193 (1987)

Preparation and Characterization of $U_2O_2F_7$

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(Received January 22, 1987)

Reaction of UO_2F_2 with UF_5 at 400 °C under UF_6-pressure of 3 atm followed by evaporation of excess UF_5 has yielded a greenish white residue. Its X-ray diffraction pattern and infrared spectrum are sufficiently unique to establish that this material is a true compound. Its chemical formula has been shown to be $U_2O_2F_7$, on the grounds of chemical analysis and thermal decomposition. The oxygen content was determined directly by means of ^{18}O isotopic dilution method based on the combustion of the samples with BrF_5.

In our article on the studies of the physical properties of liquid UF_5,[1] a brief mention was made of our encounter with a possibly new fluoride oxide of uranium which was definitely lower than hexavalent. This article describes the results of the closer investigation into this compound.

Preparation and Isolation

(1) Encounter with the New Compound.[1] UF_5 melts at 348 °C.[2] Physical properties of liquid UF_5 were measured with an alumina tube of high purity (>99.5%) as the container. Sufficient pressure of UF_6 (e.g., 3 atm at 400 °C) was maintained over the melt, to prevent the disproportionation of UF_5.[3]

Examination of the solidified UF_5 after measurements revealed that the bottom part of the sample was occasionally very hard and whitish in color, in contrast with the upper main mass which was easy to be raked out and saphire-blue in color. X-Ray diffraction pattern of this whitish material contained a series of characteristic reflections (Table 1) together with those assigned to α-UF_5.[3] The substance identifiable with these reflections as the fingerprint will be named tentatively the phase X.

The phase X is presumably insoluble in liquid UF_5. And its density is between that of liquid UF_5 (4.50 g cm^{-3}[1]) and U_2F_9 (7.60 g cm^{-3}, at room temperature[3]), because they were found in this order in the alumina container when they coexisted.

Volatility of UF_5 (vapor pressure: 65 mmHg (1 mmHg=133.322 Pa) at 400 °C[2]) gives a means to purify UF_5. An impure sample of UF_5 contained in an alumina tube was put into a bigger alumina tube and heated to 400 °C under UF_6-pressure of 3 atm. Evaporated UF_5 condensed on the upper (cooler) wall of the outer tube in the form of ice-blue needles. The residue in the inner tube was white with a tinge of green and its X-ray diffraction pattern contained no reflection other than those assigned to the phase X. Chemical analysis made on a small sample gave a value, 5.3_9, for the mean valence of uranium in that material.

Table 1. Comparsion of X-Ray Diffraction Patterns of the Phase X (This Article) and the Phase ϕ[11]

Phase X		Phase ϕ	
d/Å	Intensity/%	d/Å	Intensity/%
4.92	100	4.87	s
4.33	w	4.26	ww
3.97	w	3.91	ms
3.86	w	3.82	mw
3.80	15	3.73	ms
3.62	10	3.57	m
3.34	10	3.30	w
3.06	10	3.04	w
2.77	w	2.77	ww
2.70	10	2.69	w
2.612	10	2.60	w
2.520	w	2.50	w
2.473	30	2.46	m
2.102	20	2.09	s
2.088	20	2.02	mw
		1.99	mw
1.951	w	1.95	m
1.928	w		
1.916	w		
1.854	w		
1.809	w		
1.685	w		
1.652	10		
1.483	w		
1.448	w		

(2) Preparation. Since UF_5 is very hygroscopic, it was natural to assume that the phase X had its origin in the hydrolysis of UF_5, though the latter was handled always in a dry box. On exposure to moist air, α-UF_5 changed rapidly into a yellow-green mouldy mass, which proved to be amorphous by X-ray diffraction. A mixture of this intentionally hydrolyzed UF_5 and ordinary UF_5 was subjected to the isolation process described in the above, and the solid residue showed again the X-ray diffraction pattern characteristic of the phase X.

Though the above-stated procedure certainly gives a synthetic route to the phase X, it is impossible to incorporate oxygen in a quantitative manner. This

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difficulty has been overcome by replacement of hydrolyzed UF_5 with well-crystallized UO_2F_2. (The latter was prepared as follows. UF_6 was hydrolyzed by water in a Kel-F tube. The pasty product was dried under vacuum at 180 °C, transferred into an alumina tube and heated at 600 °C in an equimolar mixture of HF and O_2 at about 1 atm.[4] To our surprise, alumina was inert to this atmosphere.) A typical synthetic result was as follows; treatment of 1.0 g of UO_2F_2 and 1.6 g of α-UF_5 at 370 °C for 16 h yielded about 2 g of product free from α-UF_5 and UO_2F_2.

The phase *X* was very hygroscopic, too.

Identification

(1) X-Ray Powder Diffraction. All the uranium compounds appearing in this article are more or less sensitive to moisture, so we have designed an air-tight sample holder which can be handled in a dry box and mounted on the goniometer of an X-ray diffractometer. The windows of the holder are equipped with aluminum foils 30 μm in thickness; a pair of these foils reduces the intensity of Cu *Kα* X-ray to about one half.

Diffraction patterns of more than ten samples from different preparations are put in order as shown in the left column of Table 1. The values of *d* have been corrected with those of α-UF_5 as the internal standard. This pattern is unique; definitely different from those of UO_2F_2,[5] $U_3O_5F_8$,[6] α-UOF_4,[7] and β-UOF_4[8] and also dissimilar to those of Pa_2OF_8[9] and $NpOF_3$.[10]

A comparison of diffraction patterns (Table 1) shows a close similarity between the phase *X* and the phase *ϕ* reported by Rude et al.[11] Their work will be referred to later in the Discussion section.

(2) Infrared Spectrum. Infrared spectra of good quality were recorded by Jacob and his coworkers in their studies on some hygroscopic compounds of uranium.[7,12] They resorted to the Nujol method with CsI disks as the windows, using a vacuum kneader. Instead, we added CaH_2 powder into Nujol to prevent hydrolysis of samples[13] and could thus obtain spectra comparable to theirs.

The infrared spectrum of the phase *X* is shown in Fig. 1. It is definitely different from those of UO_2F_2,[14] α- and β-UF_5,[12] and UOF_4,[7] and could be used for identification purposes.

Determination of Oxygen

In the determination of chemical formula of uranium oxyfluorides, it has been a common practice that the uranium and fluorine content are obtained by actual analyses and the oxygen content by difference. Since the weight fraction of oxygen in those fluoride oxides is generally small (10% or less) the accuracy of the oxygen content thus obtained is open to question, though measured values of the valence of uranium serve as a check.

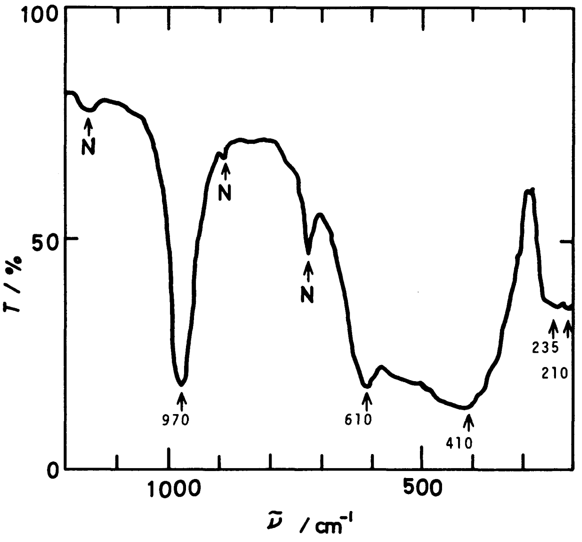

Fig. 1. Infrared spectrum of the phase *X*. (Absorption bands denoted by N are those due to Nujol.)

Jacob et al.[7] determined the oxygen content in UOF_4 by reacting the samples with carbon at 2000 °C and analyzing CO by infrared spectroscopy. On the other hand, Otey et al.[6] burned their sample of $U_3O_5F_8$ with ClF_3, put the gaseous product to gas chromatography and obtained the O/U ratio from the peaks of O_2, ClO_2F, and UF_6. At first we followed Otey's method, with BrF_5 replacing ClF_3. This modification was made, first because BrO_2F is far less stable than ClO_2F[15,16] and hence no oxygen-containing compound other than elemental oxygen would be formed; and secondly because a Br-compound has generally longer retention time than the corresponding Cl-compound, leading to better separation. This approach was, however, abandoned because the retention time of BrF_3, a by-product, was found nearly equal to that of UF_6. Thereupon, we made a shift to an ^{18}O isotopic dilution method, as described below.

An unknown sample and ^{18}O-labelled U_3O_8 (spike), each containing 5—10 mg of oxygen, were weighed in turn into a nickel crucible. The crucible was put into a monel reaction tube and the valve on the latter was closed. The reaction tube was taken out of the dry box and connected to a vacuum manifold. After evacuation, BrF_5 (pre-purified by distillation) was collected into the tube with liquid nitrogen to Br/U ratio of about 5. (By the way, IF_7 was found inadequate as the fluorinating agent; it seemed not to decompose water completely into elemental oxygen at room temperature. IF_7 was tried, because it was known to clean apparatus contaminated with uranium-bearing deposits at 20 °C or above.[17]) The tube was then held at 300 °C for about 1 h, to convert the sample and the spike together completely into a gaseous product.

With the tube immersed in liquid nitrogen, part of the elemental oxygen liberated was expanded into a pair of glass samplers through a liquid nitrogen trap, and subsequently analyzed for ^{18}O atom-fraction by mass spectrometry (Atlas, model CH 4). The ^{18}O atom-fraction in the spike (U_3O_8) was obtained in the same manner. Thus, oxygen content of the unknown sample was estimated by the conventional isotope dilution method.

The chemical form U_3O_8 was chosen as that of the spike, because it is a weighing form in gravimetry of uranium, in spite of the existence of some solid solution ranges.[3] Ammonium diuranate formed on introduction of UF_6 into aqueous ammonia (about 28 wt%) was filtered, dried at 130 °C and ignited at 800—900 °C in open atmosphere to constant weight. Next, a portion of thus prepared U_3O_8 was brought to contact with ^{18}O-enriched oxygen (0.2 atm) at 700 °C, with the gaseous phase renewed every 10—15 h. (The enriched oxygen used (The British Oxygen Co.) was found to be a synthetic mixture of nearly pure $^{18}O_2$ and $^{16}O_2$ in the ratio of 1:4. Since the ^{17}O atom-fraction of this gas was as small as 0.045 atom% and the natural abundance of ^{17}O is 0.0374 atom%, no correction was required for the contribution of $^{17}O_2$ to the MS peak, $m/z=34$.) The ^{18}O atom-fraction of the spike measured repeatedly over a period extending for a few months ranged at random between 13.86 to 14.06 atom% with the mean value at 14.01±0.03 atom%. This seemed to form a strong evidence for the absence of any exchange reaction between U_3O_8 and atmospheric oxygen at room temperature, as well as the absence of water adsorbed within the reaction system which should have interfered the analysis.

The accuracy of this analytical method was tested with the U_3O_8 sample of isotopically natural composition, which had been prepared as described in the foregoing paragraph. The mean value of six determinations of the oxygen content was 15.24±0.11 wt% (theor.: 15.20 wt%) and the O/U ratio was calculated to be 2.68±0.02 (theor.: 2.67) on the assumption that the sample contained no element other than uranium and oxygen.

It may be worthwhile to refer to the isotopic equilibrium in the oxygen gas evolved on combustion of U_3O_8. Equilibrium was always attained in the case of the spike only, but not in the case of the mixture of the spike and natural U_3O_8. The ratio of MS peaks, $m/z=32$, 34, and 36, was away from the binominal distribution, but closer to it than in the hypothetical case that oxygen was liberated separately from the enriched and natural U_3O_8 and then mixed together. Since no isotopic exchange was observed between $^{18}O_2$ and $^{16}O_2$ at 300 °C, it is safely presumed that some oxygen-bearing compound, such as U_3O_8, some fluoride oxide or OF_2, should have taken part in the exchange.

The analytical method was tested further with the crystallized UO_2F_2 mentioned before. Satisfactory results were obtained again, with the mean value of two determinations being 10.39±0.13 wt% (theor.: 10.39 wt%).

In the following a brief mention is to be made of some articles related to the analytical method developed in the present work. Trace of oxygen in metals was determined by ^{18}O isotopic dilution, with the oxygen extracted as CO and CO_2.[18] Oxygen contents in metal oxides were determined gasometrically, by burning the oxides with either BrF_3 or $KBrF_4$ and collecting elemental oxygen with a Toepler pump.[19,20]

Determination of Chemical Formula

(1) Chemical Analysis. Determination of U(IV) was made by oxidation with $K_2Cr_2O_7$ followed by back titration with Fe(II). The total uranium content was obtained as follows; the sample was dissolved in an alkaline H_2O_2 solution, evaporated to dryness as sulfate, passed through a Jones Reductor and after addition of $K_2Cr_2O_7$ back-titrated with Fe(II).

Fluorine was determined by the method of Combs and Grove.[21] The sample was brought to solution as in the total uranium analysis. Fluorine was precipitated by $SmCl_3$ at pH 3.0—3.5 and the excess Sm(III) was titrated with EDTA. Under carefully controlled conditions, no interference by uranium was observed; for example, a weighed sample of UF_6 was hydrolyzed in a NaOH solution and after neutralization with H_2SO_4 six aliquots were subjected to analysis, with the result of 32.53±0.09 wt% (theor.: 32.38 wt%).

Results of analysis of the phase *X* are summarized in Table 2. Main conclusions deduced from this table are as follows.

a) The mean valence of uranium calculated from data of U(IV) and Total U is 5.51±0.02, while that from data of Total U, O, and F is 5.47±0.07. These values are very close to $5\frac{1}{2}$.

b) The O/U ratio calculated from the data of Total U and O is equal to 1.04±0.02, a value very close to unity. The simplest formula in agreement with these two findings is $U_2O_2F_7$.

Table 2. Composition of the Phase *X* (wt%)

	Phase *X*	$U_2O_2F_7$ (Theoretical)
U (IV)	17.82±0.04(2)[a]	18.57
Total U	72.15±0.87(2)[a]	74.27
O	5.05±0.06(5)[a]	4.99
F	19.55±0.22(6)[a]	20.74
Total	96.75±0.90	100

a) Number of determinations.

(2) Thermal Decomposition. Composition of the fluoride oxide can be estimated by the weight loss on thermal decomposition, referring to the method reported by Wilson.[22,23] That is, the following experimental results can be explained by assuming the decomposition reaction:

$$2U_2O_2F_7=2UO_2F_2+UF_4+UF_6\uparrow$$

In a dry box, about 200 mg of the sample was weighed into a platinum crucible equipped with a lid and the crucible was put into a monel reaction tube. The tube was connected to a vacuum manifold and was heated for 24 h at 300 °C under continuous evacuation through a liquid nitrogen trap. The residue was whitish green and was composed of UO_2F_2 and UF_4 by X-ray analysis. The O/U and F/U ratio of the original sample calculated from the weight loss (30.3%) and the mean valence of uranium in the original sample (5.51) were 0.96 and 3.60, respectively, while those calculated from the weight loss and the valence in the residue (5.45) were 1.05 and 3.50, respectively. Though the relative errors of these ratios might be as large as 5%, this decomposition experiment was regarded as a corroboration of our conclusion based on chemical analyses.

$U_2O_2F_7$ does not decompose at 400 °C under UF_6 pressure of 3 atm, though it decomposes at 300 °C in vacuum, as detailed in the earlier section. It would be of value to measure its dissociation pressure at different temperatures, as in the work of Agron on intermediate fluorides of uranium.[3]

Discussion

The chemical formula $U_2O_2F_7$ can be found in the report by Rude et al. published in 1971.[11] They reacted UF_4 with ClO_3F or OF_2 at 200—300 °C, to produce UF_6. The solid residue was diversified in color, ranging from white to green. Its X-ray diffraction pattern contained a series of reflections, together with those of UO_2F_2 and/or UF_4. They named the substance identified with these reflections the phase ϕ. As shown in Table 1, there is certainly a close similarity between *their* phase ϕ and *our* phase X, though the synthetic routes are entirely different from each other.

They assigned the chemical formula $U_2O_2F_7$ to this phase ϕ; but without well-grounded evidence, as summarized in the following. First, their samples were more or less contaminated with UO_2F_2 and/or UF_4, because they had no means to isolate their phase ϕ. Secondly, their analytical data were too much scattered to allow any quantitative deduction (for example, their data for U(IV) content on seven preparations ranged from 9.7 to 28 wt%). So, we claim this work as the first confirmation of the compound, $U_2O_2F_7$.

Appendix

In conjunction with the present work, some other attempts to prepare fluoride oxides of uranium in lower oxidation states were made, but were terminated without great success, as described below.

(1) Reaction of UF_4 with Oxygen. This reaction has attracted much attention as a method for the production of UF_6 without the use of elemental fluorine.[3,24,25] The work of Kirslis et al.[26] has a distinctive feature, in that the reaction was carried out with alternating oxygen pressure and vacuum. A cloud of white particles was blown out of the reactor into a filter chamber. The chemical formula, U_2OF_8, was assigned to this white material, on the ground of chemical analysis (wt% Found U, 72±2; U(IV), 36±1; F, 21±2). Assignment of this formula is, however, not convincing, since straightforward calculation from their analytical data (mean valence of U: 5.00±0.04 and F/U: 3.65±0.36) gives a value, 0.67±0.18, for the O/U ratio. They claimed that thermal decomposition of the material at 300 °C yielded UF_6, UO_2F_2 and UF_4 in the proportion 1 : 1 : 2 in agreement with the formula, U_2OF_8, but no analytical data were shown. Its X-ray diffraction pattern was reported to be similar to that of U_4F_{17}.[3]

Our experimental procedure was nearly identical with Kirslis's. A platinum boat containing UF_4 was placed in a monel tubular reactor lined with a platinum plate. After evacuation and introduction of HF to about 0.5 atm, the reactor was heated to 500 °C. Then HF was replaced by oxygen at 1 atm, and the temperature was raised to, typically, 685 °C. As observed by Kirslis, the lower the temperature and the shorter the period of alternating evacuation and pressurization with O_2, the greater was the yield of the white material collected on a sintered nickel filter placed 30 cm downstream of the reactor. Out best result was as follows. Starting with 1.3_5 g of UF_4, the reaction was carried out for 150 min, with the cycle of 0.5 min for evacuation and 0.5 min for pressurization. The residue on the boat weighed 0.7 g and was composed mainly of UO_2F_2, together with some unreacted UF_4 (X-ray analysis). (A few thin leaves, transparent and amber-colored, were found attached to the rim of the boat. The X-ray diffraction pattern of this material had reflections *only* at d=5.20, 2.60, and 1.74 Å. These reflections correspond to those of UO_2F_2 with the hexagonal Miller indices, $h=k=0$ and $l=3n$ (n=1, 2, ···).[5]) Over the downstream half of the platinum plate was found about 0.2 g of UF_4. A cold trap at the farmost downstream collected 0.11 g of UF_6. About 0.1 g of the white material had deposited on the filter.

The X-ray diffraction pattern of the white material revealed that it was amorphous, excepting a trace of UO_2F_2 and/or UF_4. Its infrared spectrum as shown in Fig. 2 is unique. Values of the mean valence of uranium determined for three preparations were 5.1_4, 5.1_3, and 4.9_5. We have thus reconfirmed the main features of the experiments by Kirslis et al. And it was established that *our* $U_2O_2F_7$ is different from *their* U_2OF_8.

(2) Hot Filament Reduction of UF_6. In 1970 Schröder and Grewe[27] claimed the first synthesis of WF_5, by reducing WF_6 with a hot tungsten filament and collecting WF_5 on the wall of a cooled glass container. Later, Falconer et al.[28] synthesized some metal fluorides by use of a less

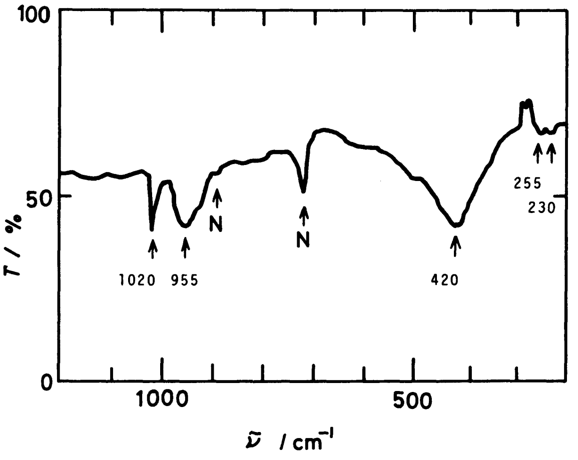

Fig. 2. Infrared spectrum of the white material deposited on the filter. (Absorption bands denoted by N are those due to Nujol.)

sophisticated apparatus.

After successfully reproducing the results of Falconer's on MoF_5, we tried reduction of UF_6 with a nickel filament. Three nickel wires, 0.5ϕ×1200 mm, were coiled to the length of 300 mm, connected in parallel, rinsed with HNO_3 and suspended in a Pyrex tube, 31ID×370 mm. After evacuation, UF_6 was introduced and purified until its vapor pressure was reduced to 25 mmHg or less at 0 °C. (The pressure was measured by a bellows gauge.[29]) With the tube immersed in ice water to the neck, the filaments were heated electrically to dull red (800 °C). The inner wall of the tube was gradually covered with a white material. After 3 h of lighting, 0.15 g of the white material was recovered, which proved to be β-UF_5 by X-ray analysis and determination of mean valence of uranium. No contamination with nickel fluoride was detected.

Next, we repeated the experiment with 80 mmHg of elemental oxygen added into the system, with the intention of preparing some fluoride oxide. But the product was again β-UF_5. Experiments with the nickel filaments covered with platinum black could not alter the result.

The authors thank Mr. Keiichi Hayashi, now with Sumitomo Atomic Industries, who took charge of the earlier stages of the determination of the oxygen content.

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